

Green Energy and Technology

For other titles published in this series, go to
<http://www.springer.com/series/8059>

Ibrahim Dincer · Adnan Midilli · Arif Hepbasli ·
T. Hikmet Karakoc
Editors

Global Warming: Engineering Solutions

 Springer

Editors

Ibrahim Dincer
University of Ontario
Institute of Technology (UOIT)
Fac. Engineering & Applied Science
2000 Simcoe Street N.
Oshawa ON L1H 7K4
Canada
ibrahim.dincer@uoit.ca

Adnan Midilli
Department of Mechanical Engineering
Nigde University
51200 Nigde
Turkey
amidilli@gmail.com

Arif Hepbasli
Department of Mechanical Engineering
Ege University
35100 Bornova, Izmir
Turkey
arif.hepbasli@ege.edu.tr

T. Hikmet Karakoc
Anadolu University
School of Civil Aviation
26470 Eskisehir
Turkey
hkarakoc@anadolu.edu.tr

ISSN 1865-3529 e-ISSN 1865-3537
ISBN 978-1-4419-1016-5 e-ISBN 978-1-4419-1017-2
DOI 10.1007/978-1-4419-1017-2
Springer New York Dordrecht Heidelberg London

Library of Congress Control Number: 2009930937

© Springer Science+Business Media, LLC 2010

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden. The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Global warming is considered an average increase in the Earth's temperature due to greenhouse effect as a result of both natural and human activities. In common usage, "global warming" often refers to the warming that can occur as a result of increased emissions of greenhouse gases from human activities, e.g., carbon dioxide, methane, water vapor, and fluorinated gases, which act like a greenhouse around the earth, trapping the heat from the sun into the earth's atmosphere and increasing the Earth's temperature.

Catastrophic events around the world have brought a desperate picture to forefront! The Global Conference on Global Warming 2008 (GCGW-08) was initiated to bring all disciplines together for local and global solutions to combat global warming. It is a multi-disciplinary global conference on global warming (and climate change), not only in engineering and science but also in all other disciplines (e.g., ecology, education, social sciences, economics, management, political sciences, and information technology). It covers a broad range of topics on energy and environment policies, energy resources, energy conversion technologies, energy management and conservation, energy security, renewables, green technologies, emission reduction and abatement, carbon tax, sustainable development, pollution control and measures, policy development, etc.

Intensifying global environmental problems require internationally coordinated responses, which must balance the goals of energy security, environmental protection, and economic growth. The adoption of a comprehensive approach to energy and environment issues and the integration of energy and environment policies have become central activities of several countries. National and global solutions to reduce pollutants and greenhouse gas emissions have implications for energy security, energy trade, economic growth, etc. To some extent the global climate change is still perceived by many as a debatable issue. For example, despite the policy measures taken to date, unless the rapid establishment and implementation of further effective policies and programs to reduce emissions are conducted, greenhouse gas emissions would continue increasing unless the right cure is underway. Of course, this requires the full range of possible areas for action and policy instruments.

This book is a unique collection of 45 selected papers out of the papers presented in the GCGW-08 in Istanbul, Turkey, on July 6–10, 2008, to cover a wide variety of topics from the main principles of thermodynamics and their role in design, analysis, and performance improvement of energy systems to the potential impact of global warming on human health and welfare.

Although the main focus of this book is engineering solutions to combat global warming, there is a diverse coverage from carbon sequestration to risk management, from sustainable construction to waste management, and many more to serve as a sustainable source of knowledge and information for researchers, scientists, engineers, practitioners, etc.

As mentioned above, global warming is one of the major concerns of the human beings in this century. A significant part of global warming comes from the human activities, such as consuming fossil energy sources, e.g., oil, coal, and natural gas. In the solution of global warming, engineering approaches play a key role. These approaches are linked to many areas including energy and environment policies, energy conversion technologies, energy management and conservation, energy saving, energy security, renewable and sustainable energy technologies, emission reduction, sustainable development, pollution control and measures, policy development, global energy stability and sustainability, carbon tax, and waste management. Innovative engineering solutions are needed to reduce the effects of global warming and also to obtain better efficiency, better cost effectiveness, better use of energy and resources, better energy security, better environment, and better sustainability. In this book, several engineering approaches and potential solutions from renewables to hydrogen, including data analysis, modeling, simulation, assessment, optimization studies, that reduce the effects of global warming are discussed in detail.

Incorporated through this book are many wide-ranging practical examples, case studies, and policy and strategy development which provide useful information for practical applications. Complete references are included with each chapter to direct the curious and interested reader to further information.

We hope this volume allows unique solutions for combating global warming to be more widely applied and the benefits of such efforts more broadly derived, so that the future can be made more efficient, clean, and sustainable.

Last, but not the least, we gratefully acknowledge the assistance provided by several individuals, including Dr. Can-Ozgur Colpan, Dr. Anand Joshi, Mr. M. Fatih Orhan, Mr. M. Tolga Balta, Dr. Nirmal Vijay Gnanapragasam in reviewing and revising several chapters, checking for consistency, and finalizing them for publication.

Ibrahim Dincer
Adnan Midilli
Arif Hepbasli
T. Hikmet Karakoc

Contents

1. Global Warming – Where Is the Cure?	1
2. On the Principles of Thermodynamics – Effects on the Environment, Global Warming, and Sustainability	47
3. Role of Renewable Energy in Sustainable Development.....	71
4. Residential Solar Power Generation Systems for Better Environment	89
5. Hydrogen Production from Ammonia as an Environmentally Benign Solution for Vehicles	109
6. Environmentally Benign Nuclear-Based Hydrogen Production	129
7. Environmental Benefits of Geothermal-Based Absorption Cooling Systems.....	147
8. Reducing Greenhouse Gas Emissions from a Landfill Site Using Various Thermal Systems	161
9. Partial Gasification for CO ₂ Emissions Reduction.....	179
10. A Strategic Program to Reduce Greenhouse Gas Emissions from Food Industry.....	197
11. Environmental and Economic Issues from Changing a Major Fuel Type as Energy Resource in an Industrial City in Korea	211
12. Emission Characteristics of Diesel Engine-Powered Cogeneration Systems	225
13. Effects of Fuel Consumption of Commercial Turbofans on Global Warming.....	241
14. Marnoch Engine Performance for Multiple Pressure Vessel Configurations	255
15. Exergy Analysis of Food Drying Processes	267
16. Carbon Sequestration: A Comparative Analysis	281
17. Coal-Based Hydrogen Production with CO ₂ Capture in the Aspect of Clean Coal Technologies	295
18. CO ₂ Absorption in a Mini-module Membrane Contactor	307
19. CO ₂ Hydrogenation to Methanol on Cu–ZrO ₂ Catalysts.....	315
20. CO ₂ and SO ₂ Capture Capability of Two Greek Limestones	329
21. Effect of Oxidative Medium on Removal of Sulfur and Mineral Matter from the Can Lignites	347
22. Biogenic Emission and Essential Oils of Some Eucalyptus Species: A Comparison Study	357
23. Embodied Carbon: The Concealed Impact of Residential Construction	367
24. Sustainable Construction Practices in Malaysia	385
25. Emission Market at the End of the Commitment Period	399
26. Game Analysis of Kyoto and Post-Kyoto Schemes	407

27. Enterprise Risk Management Perspective	423
28. Environmental Assessment of Solar Heating and Cooling Systems in Kuwait Climate	439
29. Steam Network Optimization by Utilizing Biomass and Solar Energy Sources in an Oil Refinery	455
30. Calculation of Global Solar Radiation Based on Cloud Data for Major Cities of South Korea	467
31. Relationship Between Air Pollutants and Some Meteorological Parameters in Erzurum, Turkey	485
32. Planning for the Impacts of the Caspian Sea Level Rise and Climate Change in the North of Iran	501
33. Impacts of Climate Change on Water Resources in Saudi Arabia	511
34. Warming Tendency in the Eastern Mediterranean Basin and Its Influence on West Nile Fever Outbreaks	525
35. Water Management Works in Târnava River Basin, Romania	535
36. North–South Gap in Wastewater Management: A Comparative Study for Germany and Jordan.....	545
37. A Pervaporation Application for Treating Methyl <i>tert</i> -Butyl Ether (MTBE)-Contaminated Water/Wastewater	555
38. Temperature Variations and Their Effects on Rainfall in Nigeria	565
39. Multimedia Pollutant Sources and Their Effects on the Environment and Waste Management Practice in Turkish Shipyards.....	579
40. Nitrous Oxide Emission from Agricultural Practices in Japan	591
41. Phenological Adaptation of Cereal Weeds to Climate Variations ...	601
42. Chemical Characteristics and Source Reconciliation of Organic Aerosols in Algiers City Area	609
43. Removal of Cu^{2+} and Ni^{2+} from Aqueous Solution by Algerian Clay Materials	621
44. Health Impacts of Heat Waves of 2007 in Hungary – Background and Experiences.....	629
45. Potential Impact of Climate Change on Pandemic Influenza Risk	643
Index	659

Contributors

Nazirah Zainul Abidin, University Science of Malaysia, Malaysia

Aysegul Abusoglu, University of Gaziantep, Turkey

Lena Ahmadi, K. N. Toosi University of Technology, Iran

Fuat Tolga Akanlar, Yıldız Technical University, Turkey

Hiroko Akiyama, National Institute for Agro-Environmental Sciences, Japan

Ahmat Aksakal, King Fahd University of Petroleum and Minerals, Saudi Arabia

Kamel K. Alzboon, Al-Balqa Applied University, Huson College, Jordan

Faisal M. Al Zawad, Presidency of Meteorology and Environment, Saudi Arabia

A. Özer Arnas, United States Military Academy at West Point, USA

Ferroudja Bali, Université des Sciences et de la Technologie, Algeria

Mustafa T. Balta, Ege University, Turkey

Matthias Barjenbruch, Technician University of Berlin, Germany

Panagiotis Basinas, Chemical Process Engineering Lab, Thessaloniki, Greece

Janos Bobvos, National Institute of Environmental Health, Hungary

Makhlouf Boufatit, USTHB, Algeria

Mustapha Bounechada, Université Ferhat Abbès, Algeria

Angelo Cecinato, Istituto sull'Inquinamento Atmosferico-C.N.R, Italy

Uğur Buğra Celebi, Yıldız Technical University, Turkey

Neslihan Colak, Ege University, Turkey

C. Ozgur Colpan, Carleton University, Canada

Can Coskun, Balıkesir University, Turkey

Daniela Curseu, University of Medicine and Pharmacy, Romania

Soraya Dib, USTHB, Algeria

Romney B. Duffey, Atomic Energy of Canada Limited, Canada

Nilufer Durmaz Hilmioglu, Kocaeli University, Turkey

Zafer Erbay, Ege University, Turkey

Mohamed Fenni, Université Ferhat Abbes, Algeria

Yousef Filizadeh, Shahed University, Iran

Yazid Foudil-Cherif, USTHB, Algeria

Adel A. Ghoneim, College of Technological Studies, Kuwait

Nirmal V. Gnanapragasam, University of Ontario Institute of Technology, Canada

John R. Grace, University of Ontario Institute of Technology, Canada

P. Grammelis, Centre for Research and Technology Hellas, Greece

Jale Gulen, Yildiz Technical University, Turkey

Feridun Hamdullahpur, Carleton University, Canada

Geoffrey P. Hammond, University of Bath, UK

Arif Hepbasli, Ege University, Turkey

Osita Ibe, University of Ibadan, Nigeria

Filiz İçier, Ege University, Turkey

Haruo Imai, Kyoto University, Japan

Ryosuke Ishii, Kyoto University, Japan

Homan Rajabi Islami, Islamic Azad University, Iran

Louise Jalowiecki-Duhamel, Unité de Catalyse et Chimie du Solide, France

Craig I. Jones, University of Bath, UK

Anand S. Joshi, University of Ontario Institute of Technology, Canada

- Ibrahim M. Kadad, College of Technological Studies, Kuwait
- S. P. Kaldis, Centre for Research and Technology Hellas, Greece
- Kandil M. Kandil, College of Technological Studies, Kuwait
- Mehmet Kanoglu, University of Gaziantep, Turkey
- T. Hikmet Karakoc, Anadolu University, Turkey
- Ali Khouider, USTHB, Algeria
- Aydin Kilic, University of Nigde, Turkey
- Christopher J. Koroneos, Aristotle University of Thessaloniki, Greece
- D. Koutsonikolas, Aristotle University of Thessaloniki, Greece
- Ebru Kuzgunkaya, Izmir Institute of Technology, Turkey
- Riad Ladji, Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques, Algeria
- Byeong-Kyu Lee, University of Ulsan, S. Korea
- Kwanho Lee, Ulsan College, S. Korea
- C. J. Lim, University of British Columbia, Canada
- I. Marnoch, Marnoch Thermal Power Inc., Canada
- Brahim Y. Meklati, USTHB, Algeria
- Adnan Midilli, Nigde University, Turkey
- Shin-Ichiro Mishima, National Institute for Agro-Environmental Sciences, Japan
- Adel M. Mohammedein, College of Technological Studies, Kuwait
- G. Naterer, University of Ontario Institute of Technology, Canada
- Kyoung Hwan Noh, University of Ulsan, S. Korea
- E. F. Nymphas, University of Ibadan, Nigeria
- Sevda Ocak, Ataturk University Environmental Problems Research Center, Canada

Zuhal Oktay, Balikesir University, Turkey

Mehmet F. Orhan, University of Ontario Institute of Technology, Canada

Anna Páldy, National Institute of Environmental Health, Hungary

M. Hassan Panjeshahi, Sharif University of Technology, Iran

G. Pantoleonos, Centre for Research and Technology Hellas, Greece

Hung-Suck Park, University of Ulsan, S. Korea

Sohee Park, University of Ulsan, S. Korea

Shlomit Paz, University of Haifa, Israel

Simon Perry, University of Manchester, UK

Monica Popa, University of Medicine and Pharmacy Cluj-Napoca, Romania

Ramona Ratiu, Dimitrie Cantemir University, Romania

Bale V. Reddy, University of Ontario Institute of Technology, Canada

Marc A. Rosen, University of Ontario Institute of Technology, Canada

Dimitrios C. Rovas, Aristotle University of Thessaloniki, Greece

G. P. Sakellariopoulos, Aristotle University of Thessaloniki, Greece

Dana Sirbu, University of Medicine and Pharmacy, Romania

George Skodras, Aristotle University of Thessaloniki, Greece

Adam Smoliński, Central Mining Institute, Poland

Victor Sorocovschi, Dimitrie Cantemir University, Romania

Ioan Stoian, IPA S.A. R&D Institute, Romania

Sema Tulbentci, Istanbul Technical University, Turkey

F. Sezer Turalioglu, Ataturk University, Turkey

Onder Turan, Anadolu University, Turkey

Nurten Vardar, Yıldız Technical University, Turkey

Tony Verrelli, Cleanfield Energy, Inc., Canada

Mihai Voda, Dimitrie Cantemir University, Romania

William Robert Wagar, University of Ontario Institute of Technology, Canada

J. Weston, Marnoch Thermal Power Inc., Canada

Kazuyuki Yagi, National Institute for Agro-Environmental Sciences, Japan

Noureddine Yassaa, USTHB, Algeria

Ahmet E. Yildirim, Sem Ltd, Turkey

Ayşe Kucuk Yilmaz, Anadolu University, Turkey

Hochun Yoo, University of Ulsan, S. Korea

Calin Zamfirescu, University of Ontario Institute of Technology, Canada

Kamran Zolfinejad, Guilan Department of Environment, Iran

Global Warming – Where Is the Cure?

Romney B. Duffey and Ibrahim Dincer

1.1 Introduction: The Health of the Planet

As the world proceeds into the 21st century, international dimensions of environmental problems have become more apparent and increasingly important. Globalization of the economy, emergence of worldwide communication and information networks, and rapid development of bio- and nanotechnologies all have important consequences for the environment. One may expect that by the middle of this century about 10 billion people will be placing stresses on the world's natural resources which will lead to further environmental problems (Dincer 2003). In fact, future environmental problems arise not only from the exhaustion of natural resources but also from how those resources are consumed. New technologies can and will lessen damaging environmental impacts if they are employed wisely, guided by the market system under some main pillars, such as better efficiency, better cost-effectiveness, better use of energy resources, better environment, better energy security, and better sustainable development.

Environmental impact is now certain to be one of the most important political issues in this century, but one that will not have the urgency (born of novelty) voiced in the late 1960s/early 1970s. Many nations have made much progress, but experience has brought recognition of numerous deficiencies dealing with environmental problems. As the complexity of many environmental problems becomes increasingly apparent, the focus may shift from identifying needs to identifying and applying new methods for solving problems and providing effective long-term care.

Intensifying global environmental problems require internationally coordinated responses, which must balance the goals of energy security, environmental protection, and economic growth. The adoption of a comprehensive approach to energy and environment issues and the integration of energy and environment policies have become central activities of several countries. National and global solutions to reduce pollutants and greenhouse gas emissions have implications for energy security, energy trade, economic growth, etc. The global climate

change issue poses for energy policy makers is the focus of continuing international debate. For example, despite the policy measures taken to date, unless the rapid establishment and implementation of further effective policies and programs to reduce emissions are conducted, greenhouse gas emissions would continue increasing unless the right cure is underway. Of course, this requires the full range of possible areas for action and policy instruments.

As a consequence we are faced with major decisions that potentially cover our entire social structure and well-being, including

- change in lifestyle and habits to become more conscious;
- environmentally benign technologies;
- global energy sustainability;
- economic competitiveness of industries and nations;
- energy technology dimensions;
- health and welfare of people;
- energy security nationally and internationally;
- rights and privileges of a few and of the many;
- allowable energy and greenhouse gas emissions;
- managing emissions and wastes;
- radical shift in use of energy resources;
- implementation of right energy strategies and policies; and
- many other ramifications of social and environmental importance.

Many countries (e.g., Canada, the USA, Japan, the European Union) have taken initiatives to develop energy–environment technologies, particularly for the integration of the existing energy and environment-related projects. This move is based on the understanding that energy and environmental problems represent two sides of the same coin, and technological breakthroughs are expected to provide means to overcome limits imposed by such problems and provide sustainable growth. The integration of the existing projects will make possible the incorporation of environmental viewpoint in the development of energy technologies and vice versa.

This chapter aims to bring a new dimension to energy policies and provides a kind of prescription for better policies and strategies to current energetic and environmental issues.

1.2 The Planetary Patient

Uncontrolled human activities since the industrial revolution have brought the planet up to a level that the amount of emissions and the magnitude of global environmental impact are indigestible. So, we have finally figured out that the planet has the symptoms of inadvertently catching a disease. This is a kind of disease with both high fever, referring to the increasing Earth's surface temperature (i.e., global warming) and diarrhea, referring to the wastes disposed into the planet. The question we can pose here is "Is it global warming and global warning?" If

one looks at what is happening around us, it confirms that it has gone beyond warning!

The symptoms have of course slowly become more apparent as a slight rise in the global atmospheric temperature. There is no agreement on the cause or the consequence. Some ascribe this rise as due to an addiction to uncontrolled energy use, and moreover carbon-based energy and the emissions of infrared absorbing gases. The so-called “climate change,” we are literally burning up a fever with a giant bonfire, a respirable disease of carbon-based fuels that we are literally steadily breathing out as an added atmospheric pollution, CO₂ and CH₄ burden. By having a measurable effect by altering global surface temperatures, it perhaps influences many to otherwise previously normal or accepted behaviors or lifestyles. Of course, like with any disease, the diagnosis depends highly on the experience of the physician, the exactness on the presence of recognizable symptoms, and the precise recommended medicine, surgery, or cure on who and which specialist one is consulting. But we need to beware of the false claims, wrong diagnoses, ineffective treatments, and “snake oil” that are being peddled as easier or cheaper alternatives to really effective cures. We now look at the actual clinical data available to date and show that this simple medical analogy helps us to understand and explain the large difference between the claims and the real cures for what may ail the planet.

The planet’s symptoms, given the uncertainty or lack of conclusive evidence, raise a fundamental question and a huge issue: given the patient’s apparent ills: should we be running a climate change experiment on the planet? Our answer to that question must also consider rejecting experimental therapies and unproven treatment regimes, dismissing plainly fake remedies, and deciding whether to seek lifestyle changes over emergency triage.

1.3 The Doctor

So we now have our planet as a severely infected patient and need to find the right doctor, a procedure which is not really an easy task. There are so many doctors, consultants, and specialists around in every discipline ranging from engineering to science, from sociology to economy, from geology to psychology, and all claim to be the best doctors. This is something creating a kind of dilemma on even whom to see and consult. So, this is not something we can check with friends or relatives to find out who is the best in the neighborhood. The smart idea here is to find a group of doctors comprising the engineers, scientists, economists, sociologists, policy and strategy makers and try to bring their professional opinions together.

Since economic wealth and personal health are both tied to energy and electricity use, the carbon fuel ladder to any country’s future is measured and predicted by how much is used per person, and that relates directly to how much income each person has. Wealthy countries are usually healthier and free of the diseases due to poverty. In a country using lots of carbon energy (e.g., the USA) income is about \$30,000 per person: for the carbon energy poor it is more like

\$1000. No wonder everyone wants more energy to drive forward and to improve: it is a matter of human well-being, human health, and social and economic development (Duffey and Miller, 2006).

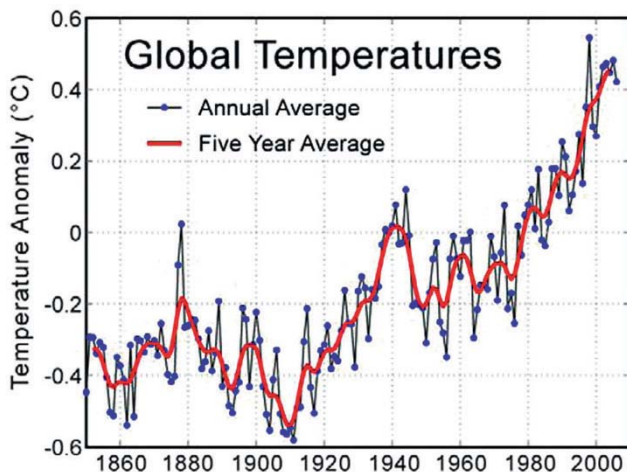


Fig. 1.1 Instrumental record of global average temperatures taken from Brohan et al. (2006) (as a record of surface temperatures collected from land-and ocean-based stations).

In fact, energy use could even be considered a right, just like breathing, and perhaps it is even unethical to deny or restrict energy use. Symptoms of malnutrition exist from those in energy poverty. As humans, who are we to deny anyone's ability or our fellow humans' desire to improve their personal health, to use light bulbs, build factories, computers, and have well-paying jobs? Even if it is causing some problems! So we cannot at all consciously restrict energy growth for those who now really need it, who also wish to share in the world's wealth, and improve their lives. We cannot divide the world into those who have the right to use energy and those who have not. But as with any doctor, the prescribing of any treatment regime must depend also on the chances of survival and success.

1.4 The Symptoms

In any illness, the doctor(s) must first look for the symptoms in order to make a diagnosis, test the vital signs and overall well-being, and ask the patient how they feel. It is well known that somehow the Earth's atmosphere is showing signs of a rising fever and this has even been the subject of movies (Gore, 2006) as well as extensive international study (e.g., IPCC, 2007). The average global temperature and indeed in some places the local temperatures are seemingly rising (see Fig. 1.1), some say by one or more degrees over the last century, as documented by several sources (e.g., IPCC, 2007). It is slow and almost imperceptible among other fluctuations, but it is there. It is easier to see in the history and records of land temperature readings taken regularly over the last 100 years using calibrated thermometers in

places like in Europe. Similar measurements all show that the last few years have been the warmest ever recorded in many places. The remaining clinical and genetic record is sketchy, derived using indirect measurements to forensically deduce (detective like) the global temperatures from ice core composition going back millions of years, tree ring growths covering thousands of years, and historical accounts for a few centuries. The reconstructed inferences and images of our past temperature (what are called surrogates because they are implied) tell us two things. First, the past is uncertain and had strongly varying temperatures too, due to natural causes; second the relationship between carbon dioxide in the atmosphere and temperature fluctuates, but implies a link or correlation—higher levels are associated with higher temperatures.

Now in any diagnosis we must also seek the presence or absence of multiple symptoms, so just one observation is not sufficient. There are other symptoms too that have been observed or implied all over the world as due to a rising fever. The geologists see that more obviously in colder Arctic, Antarctic, and mountainous regions, where shrinking sea ice, retreating glaciers, splitting ice shelves, and melting snow caps seem to happen in some regions. Perhaps as a result, sea levels are slowly rising. We could only be certain that the recent trends appear to be ominous. In addition, oceanographers report changes in global (corporal) circulation where in warmer regions near the equator, more hurricanes and changing sea currents might be occurring; geophysicists increasing acidity in the patient's water that is potentially harmful to the food chain; biologists adverse trends in species lifetime and habitat; meteorologists possible or potential changes in precipitation patterns; and zoologists alterations in species habitat and migration patterns. As for any disease, none of these symptoms are by themselves conclusive. As has been well argued by Singer and others (Singer, 2008) entirely natural variations can account for many of the symptoms, and some even seem to repeat. But that argument begs the uncertainty question: we cannot wait until we have complete certainty, or until the patient exhibits potentially fatal or life-threatening condition, but must take precautionary measures, remedies, and cures now if the risk of a worsening condition is significant. As always in science, medicine, and society, this treatment decision is a matter of informed judgment.

Taken together, the prognosis is indeed of a worsening condition if there is no treatment and no cure (IPCC, 2007), since global energy use and emissions will rise unabatedly and so will the resulting fever. As always, this prognosis is not exact but uncertain, the knowledge imperfect, the modeling approximate, the data imperfect, some signals conflicting, but the potential consequences of avoiding or delaying treatment are both dire and potentially irreversible. The patient feels and looks sick, and may be getting worse – but we are not yet sure exactly what to do.

1.5 The Cure

In the current circumstances what we need is the appropriate effective cure. If one looks at the dictionary, the short definition for “cure” is “successful remedial

treatment.” In our search for a cure we must distinguish between real cures and false claims. So the medical practice and analogy helps us again here.

- Cure: successful remedial treatment
- Snake oil: any of various concoctions of questionable value, sold as an all-purpose curative, especially by traveling hucksters

There is a need to distinguish successful cures from others that are not so effective, despite the claims. Specifically, “snake oil” was infamous in the US wild west during the 19th century, when doctors were few and illnesses were many in the developing states. They have clearly been defined too, in more recent times by Herbert (2006): “Products promoted for profit to the public without passing peer process are almost without exception ineffective ...”

We need to find the right doctor to get the right prescription for cure, and right implementation of the prescription will cure the problem. We find not one but many treatment options. The prescription may be as long as the following:

- changing lifestyle and habits
- making systems and applications more efficient, cost-efficient, and environmentally benign
- developing cleaner technologies
- using renewable and green energy
- implementing hydrogen and fuel cell technologies
- conserving energy
- diversifying energy options
- purchasing more efficient appliances
- giving priority to district energy systems and cogeneration
- providing proper education and training
- using more cost-effective energy systems and applications
- seeking alternative energy dimensions for transportation
- using sustainable fuels
- increasing public awareness
- taking necessary energy security measures
- monitoring and evaluating energy indicators
- implementing right energy strategies and policies (avoid side effects!)
- and many more socio-economic activities
- with a target to achieve some of the following main pillars:
 - better efficiency
 - better cost-effectiveness
 - better resources use
 - better design and analysis
 - better environment
 - better sustainability
 - better energy security

Of course, we should expect and will find many of these listed cures offered to us in varying amounts. Whom should we believe? What is real, tested, and actually works? We must be on our guard: and we will carefully reject cures that are not

supported by data or real clinical trials under known conditions, and reported by reputable means. We must be particularly wary of alternative treatments, regimes, and overclaiming, and those where easy money is to be made, or we are offered a panacea or cure-all. We have only one Earth: we had better treat it right and with due and diligent care. Let us look at the fragile situation through what is going on around us now as the disease progressively seems to be gaining hold. Figure 1.2 is an example, showing the latest size variation in the Arctic sea. It exhibits a steady average decline as a blue line since measurements were available.

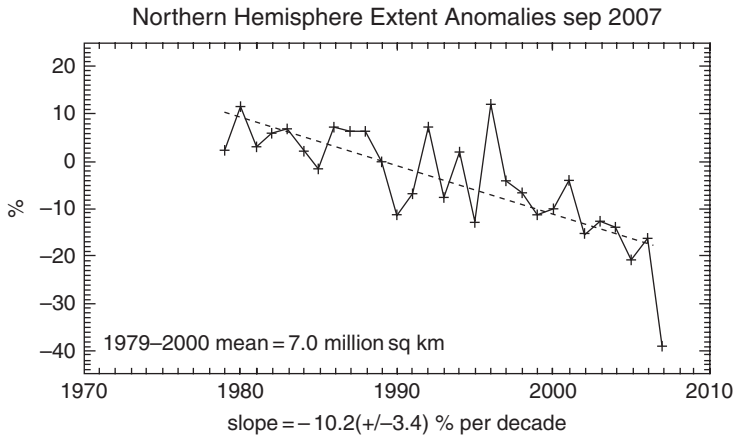


Fig. 1.2 The latest size variation in sea ice in the Arctic for 1977–2008, showing the decline as a *dotted line* since measurements were available (NASA, 2008 and NOAA, 2008).

Lastly, we cannot be sure that this type of temperature variation (Fig. 1.2) has not occurred sometime before man even appeared; perhaps it is an even natural pattern of the patient itself. We may never know, we may never be able to properly measure and analyze everything, and we may never be totally sure.

1.6 The Diagnosis of the Cause: Is It Stupidity of Humans?

Given the symptoms of an apparently rising temperature, we needed to find out what can additionally warm the atmosphere, apart from more sunlight and city streets, and despite the shading by trees and clouds. Thinking of the atmosphere not as what we just breathe but what also helps provide the weather conditions, it has long been known that there is also a corresponding rise in CO_2 gas in the atmosphere, which acts as an absorber of the radiative heat from the Earth itself. In fact, the term greenhouse gas arises from the action of water vapor and carbon dioxide resonantly absorbing the re-radiated heat in the infra-red spectrum from the Earth which the Earth has already absorbed the visible and ultraviolet light from the Sun, just as in a garden greenhouse. The clearest trend is the increases since the industrial revolution, or about 1790 onward, when carbon (coal) burning,

gasoline (petrol) use, and natural gas (methane) combustion have been essential in many sectors and drastic use. Although varying, there is a possible link between the increase in carbon dioxide emitted by humans activity and increasing temperatures. But the cause is clouded by the fact that only about half of the CO₂ we emit from our factories, power plants, and cars appears in the atmosphere. Half of it goes missing. We think the other half is absorbed by the oceans, lakes, and seas, which are full of dissolved gases anyway just like we see as bubbling bubbles rise up when we warm water in a saucepan, and in the growth of trees and shellfish.

Direct symptomatic measurements, taken daily, of the gases in the atmosphere have only been made in many places over the last 20–40 years, as pioneered by Charles Keeling (Keeling et al. 2005). Looking at this “breathalyzer test” for the atmosphere, the trend is an almost straight line increase with time, with a superimposed cycle though the year as seasons change. Current levels are some 380 ppm by volume, which is seemingly small. But more importantly the present concentration levels are higher than before 1790 (about 280 ppm), and higher today than ever before in the ice core history of about half a million years (Petit et al. 1999). We are indeed on an historic “high,” so just perhaps this is a cause of the symptoms!

Understanding the warming phenomena and modeling of the entire patients, including the atmosphere, industrial emissions, and the global circulations, are crucial. This is all too complex to be exact, but gives some feedback to the ideas and diagnosis that there is a link. It is clear that the same trends of increasing temperature with increasing gases in the atmosphere, of course, are subject to the same kind of uncertainties as the measurements prove themselves! So it does not hold that the models are exact or true, nor do they have to be: since the trends are correctly recovered this implies the link. Absence of evidence is not evidence of absence.

The initial and preliminary diagnosis is simple: emissions that are man-made and come from our industrial and transport activity are causing the increase. Not everyone agrees, nor do they need to, since we can now seek a second opinion from other specialists, which is natural if we are suffering from a potentially deadly or poorly diagnosed, controversial malady.

1.6.1 A second opinion confirms the fears

Specialists are experts who have become an authority in their area through experience, practice, and studies carried out. They may be highly specialized in certain diseases, or just especially knowledgeable about the particular topic. Generally, an expert, specialist, or consultant is someone who knows what it is they do not know, what does not work, and what cannot be occurring, as well as what might be happening and its cause. They are also independent, so they should not be unduly influenced by business, fiscal, and unscientific factors.

Nowadays, specialists and their tests can also often delicately distinguish genetic or in-built traits from acquired trends, the mental from the physical, and the curable from the treatable, and what might be a successful or unsuccessful and ineffective treatment. In our case this specialist role is performed by the UN’s Intergovernmental Panel on Climate Change (IPCC) which is a body of specialists

armed with the latest models, data, experience, and records that are globally available. This does not mean infallibility or that certainty is achieved: that can only be from data which as we know may never be fully available (i.e., from a postmortem only can we truly give the cause of death). Although its independence and integrity have been questioned, and even how they interpret and select the available symptoms challenged (see, e.g., Singer, 2008), the panel does provide detailed written records and reports as to how their opinion was derived. One should avoid that contingency and degree of certainty at least as far as the Earth is concerned.

Now medicine is an experimental science and the human body is an extremely complicated system. In conjunction with this, we can say that the planet is not an easy laboratory and no cadavers are available. But many IPCC specialists are involved and available, so the IPCC have produced extensive compendia, diagnoses, studies, and predictions (IPCC, 2007). As with all specialists, as more evidence is accumulated so the opinion becomes firmer. Presumably not easily convinced, and hopefully impartial and technical in their judgment, the latest report IPCC is not happy reading (IPCC, 2007). In the recent report, seven major measures are described that reflect actual changes in climate other than temperature, from warm spells to droughts to sea levels. They went further in their consultation, ascribing whether the symptoms were likely or not, whether human in cause, and a glimpse of the future prognosis. This summary of the latest IPCC is shown in Table 1.1. The analysis is typical of a critical standard whereby no one symptom is conclusive, but whether or not multiple items are likely present, may become more convincing. They are described as likely, and also likely to be human caused, where likely is about a 90% certainty, or odds of 10 to one of holding true in a bet. Moreover, not only do the historical symptoms suggest this human contribution but also dire prognosis of things are getting even worse. Still not everyone is convinced – the arguments include that perhaps the natural variations dominate the symptoms, and human activity is really not that significant (Singer, 2008). So, the question we now pose is, why such a dire worsening prognosis?

1.6.2 The prognosis about the future: carbon fuel dependency syndrome

The logic is simple and based on a lifestyle addiction or habit. Presuming the rise in emissions to be from energy use, which is linked directly to a nation's GDP (Duffey, 1999), then the burning of carbon-based fuels like coal, oil, and natural gas explains within a factor of 2 the rise in atmospheric amounts of CO₂. So increased energy use will and does cause worse symptoms, since such a large fraction ends up in the atmosphere and could and will raise the temperature. Since energy is used for making things like goods and chemicals and electricity, and this grows a nation's economy by providing jobs and products to sell, energy use is inextricably linked to economic growth if, any only if, carbon-based fuels are used without restricting the resulting CO₂ emissions. So unless we reduce emissions by reducing our carbon fuel use emissions, the temperature will presumably rise more. It is all in lock step: unless the habit changes, the symptoms will persist.

The global "habit" in this case is burning carbon-based fuels for energy, power, heating, and transportation as they are both easy to use and plentiful. The artificial

neural network (ANN) projection data of consumptions of world primary energy, fossil fuels, and green energy from 1965 to 2050 are displayed in Fig. 1.3. The past dependency on carbon-based fuels continues into the future, supplying over 90% of the demand. So carbon fuel use is a habit that is hard to kick without feeling major withdrawal symptoms and without a substitute helping out. It can be called carbon fuel dependency syndrome (CFDS) and acts like a drug.

Table 1.1 A summary of symptoms as identified by the IPCC.

Symptoms	Prior (1060+) symptoms	Human causation	Future (21st century) prognosis
Warmer and fewer cold days and nights over most land areas	Very likely	Likely	Virtually certain
Warmer and more frequent hot days and nights over most land areas	Very likely	Likely	Virtually certain
Warm spells/heat waves (with an increasing frequency in most land areas)	Likely	More likely than not	Very likely
Heavy precipitation events (with an increasing frequency in most land areas)	Likely	More likely than not	Very likely
Increased droughts affecting areas	Likely in many regions since 1970	More likely than not	Likely
Increased tropical cyclone activities	Likely in some regions since 1970	More likely than not	Likely
Increased incidence of extreme high sea level (with no tsunamis)	Likely	More likely than not	Likely

Source: IPCC (2007).

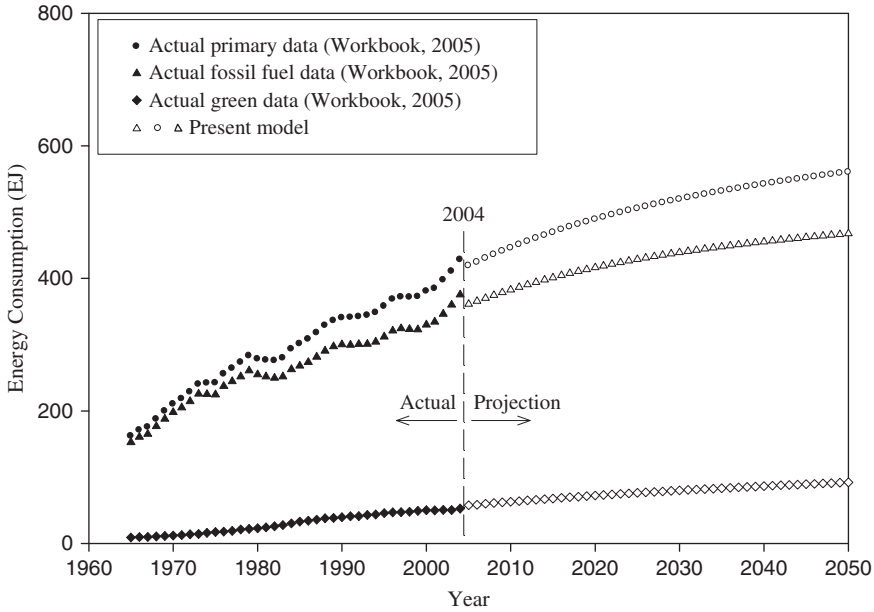


Fig. 1.3 Variation of actual and projected total world primary energy, fossil (carbon) fuel, and green energy consumption with time (adapted from Ermis et al., 2007).

Let us further elaborate on Fig. 1.3 as carried out by Ermis et al. (2007). The world primary energy consumption, fossil (carbon) fuel consumption, and green energy consumption exhibit a sigmoidal increase after 2004. World primary energy consumption is expected to reach 560 exajoules (EJ) by 2050, made up of 468 EJ of fossil fuel and 92 EJ of green energy. The dependency also grows as the population grows, and world population now exceeds 6 billion, doubling that of 40 years ago and is likely to double again by the middle of the 21st century. Even if birth rates decline so that world population becomes stable by 2050, the population will still be about 10 billion. Population, social equality, and wealth aspiration increases are all expected to lead to increasing price of fossil fuel resources with the shortfall of cheap conventional new supply with ever-increasing demand, as originally predicted by Hubbert (1956). The picture is even more complex today. In fact, there is a gap between theory and reality and changes depending on the phenomena. In regard to green energy, essentially wind power, such options will become increasingly needed to compensate for shortages of conventional resources. The ANN projection for world primary energy sources rises asymptotically to 590 EJ from 1984 to 2050 as follows, rounding off the numbers:

$$E_{wpc}(EJ) = 590 \left[1 + \exp \left[- \left(\frac{Y - 1984}{22} \right) \right] \right]^{-1} \text{ and } (R^2 = 0.999) \quad (1.1)$$

where E_{wpc} denotes world primary energy consumption in EJ. Other (Edmonds et al., 2007; IEA, 2005; IPCC, 2007) projections all show dependency increases depending on the scenario of about three to seven times by 2050 or so.

This increase indicates not only our dependence on the fossil fuels. If the increase of fossil fuel consumption continues in this manner, it is likely that the world will be affected by many negative symptoms and problems. Therefore, it is expected that the green (non-carbon) energy consumption will increase at the same trend as in Fig. 1.3. In the near future, green energy will likely become increasingly important to compensate for shortages of conventional energy resources.

Figure 1.4 shows the variations of the fossil fuel consumption ratio as a function of the green energy consumption ratio over time based on actual data (Workbook, 2005) and ANN projection data. As shown in the figure, the world fossil fuel consumption ratio was decreases with time while the world green energy consumption ratio increases. The world green energy consumption ratio was 5.58% and the world fossil fuel utilization ratio was 94.42% in 1965 based upon the actual data. The world green energy utilization ratio increased to 12.31% in 2004 while the fossil fuel consumption ratio decreased to 87.69% or at about 0.2% per year. Based on the projected data (see Ermis et al., 2007 for assumptions and their details) it is expected that the world green energy consumption ratio will reach 16.48% and the world fossil fuel consumption ratio will decrease to 83.69% in 2050 or a rate of ratio reduction of now only 0.1% a year. Thus, to increase the world green energy consumption ratio to the value needed for sustainable development (or a ~50% ratio reduction from c. 2010 values) and to reduce the harmful effects of fossil fuels, green energy substitution strategies must and should be put into practice at a rate of at least $(83.69-50)/(2050-2010) = 0.84\%$ a year, or five to ten times faster than the historic rate. The required dependency substitution or addiction reduction rate is then a 40-year average of $(590/2) \times 0.08 \sim 23$ EJ per year. The ANN projection of world green energy consumption is expected to play a key role in developing sustainable energy and global stability strategies in the future.

Just like cigarette smoking, the dependency or CFDS happened so easily because it made life easier and more pleasurable. It made money for the drug suppliers who made it; the governments who taxed it, the auto makers who made cars to use it; from the power plant owners who burnt it to sell power; to the consumer who felt better because of all the good things it made available, plus the money to spend from all the factory and office jobs created. Whole countries suddenly became immensely rich on selling carbon fuels around the world, from the UK to Saudi Arabia, from Columbia to Russia, from Norway to North America, from Australia to Iran, from Scotland to Morocco. Vast networks of pipelines grew up, connecting oil and gas supplies from those who made it or where it was found, to those who used it or needed energy for their factories and automobiles notably in Europe and the USA. We are all hooked on carbon. Even those without it want it, from China to South Africa, and it makes everyone happy. Except the Earth, which it appears to become sicker and sicker. Perhaps then, so we can all feel good, is not the best way forward to find a way treat the symptoms and not the cause? Then we can all feel better, even if the disease is not cured.

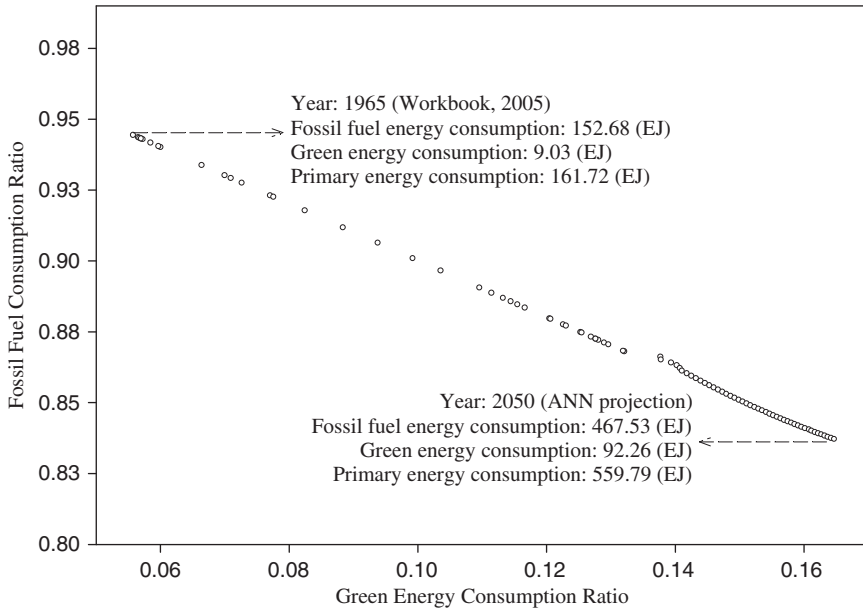


Fig. 1.4 The world fossil fuel consumption ratios as a function of the world green energy consumption ratios (adapted from Ermis et al., 2007).

1.6.3 Panaceas, painkillers, and procrastination

True to our medical analogy, there are many such “feel good” treatments available. It is obvious that we are clearly suffering typical global and human symptoms:

$$\text{Rising fever} + \text{Chemical dependency syndrome} + \text{Carbon fuel addiction} + \text{Poor diagnosis} + \text{Delays in treatment} = \text{Continuing problem} \quad (1.2)$$

We share the human desire to look for a “quick fix” solution so as a result we have a confusing menu of short-term panaceas and ineffective painkillers that treat symptoms:

- Kyoto Protocol aimed to reduce and carbon pricing mechanisms but which has actually not decreased emissions worldwide.
- Seeking alternative medicines and supplements – windmills, biofuels, and efficiency improvement which sound good to do even if they do not necessarily work well.
- Denial of problem – putting off real treatment until major surgery required, which is an effective means to avoid unpleasant truths.

- Need for “lifestyle” and feel-good cures – unqualified “offsets,” “carbon neutral,” and “allowances” that allow the energy rich to feel good with unsustainable lifestyle.
- Shortage of key/real specialists – living in an era with information pollution in world of unqualified knowledge and with many unqualified specialists we turn to instant judgments and views of self-anointed witch doctors, who have almost magical insights.
- Long waiting times – insufficient funding for real cures means that long-term treatment is hard to find even after waiting in line for emergency help.
- Unbalanced coverage – media looking for headlines, social issues, celebrities, and awards providing the sensational but not the solution.
- Business opportunities – out of such a complex disease there is money to be made from peddling cures in the rush to profit from the ailments of the masses.

1.6.4 How much green is green? or is green really green?

Not surprisingly, the motivation of making money is quite appealing. Somehow, almost inexplicably, just being re-packaged “green” is now quite literally and almost magically considered a fashionable cure. Available at any checkout stand or health store, popular health gurus have appeared in numerous “green guide” articles, with political maneuvering and calls for energy use reduction. We would all like such a simple cure, and feel good about it, but of course not only a change of diet is needed but also a change of habit.

We must also, as usual in medical situations, divide the world into those who can afford the treatment, and those who certainly cannot. Those still having inadequate calories in their energy diet are most of the world’s population, and a diet is not feasible as they simply want and still need more energy.

True to form, now on sale from many gurus are ideological and idealistic “cures” to reduce climate change impacts, industrial emissions, and damaging carbon fuel use for those affluent enough to consider and pay. Ideas and remedies are not only being proposed just by professional scientists and engineers but also by entrepreneurs and investors, and they are being pushed using media savvy techniques. Lectures, award winning documentaries, editorials, books, and consultancies are all now available that propose their own cures (Gore, 2007). Unfortunately, and as to be expected, much “snake oil” is now available. As usual this is apparently cheap, and cures all known ills without needing professional diagnosis, scientific testing, or a professionally written prescription. Unfortunately, selling the so-called “green” products is big business and leads to conspicuous consumption of “green” products, without any sense of the energy use or emissions impact. The list of cures becomes longer and longer and the packaging slicker and slicker – recent quotes from a sample of magazines on sale at local North American supermarkets include self-proclaimed energy reducing “Green Guides” and descriptions of the new concepts and/or misconcepts:

- “Green is glam”
- “Green is the new black”

- “Reduce the use of planet’s resources”
- “Green retail opportunity”
- “Green has become new fashion”
- “Next economy based on life values”
- “Making money by saving nature”
- “Green education”
- “Green justice”
- etc.

These are all quotes from recent articles and interviews with consumer, fashion and business experts in North America. Labels and products are now described and slanted as “Recycled,” “Organic,” “Reclaimed,” “Eco-,” and “Sustainable,” giving the implied and vague suggestion that they are somehow kinder and more natural ways of making, using, and selling consumer goods while somehow helping to save the planet. This is big business and the so-called “Green Market” is now estimated at more than \$250 B in North America. Confusing, yes; understandable, yes; global emissions reducing, no. Any increase in sales offsets any savings in emissions – as we shall see. Not everyone is taken in by the green re-packaging.

Thus credibility is like energy, easy to use, and very easy to lose. Energy, like medicines and medications, is a profitably traded global commodity but in liquid (oil and LNG), gas, and solid (coal) forms, as well as in the form of electricity over wires between neighboring states and nations. Just as with drug makers and oil companies, unless subsidized or domestically price controlled, what we must pay for energy is whatever the highest bidder will pay anywhere in the world, and we compete for the energy resources to grow global and national economies.

Emissions are global too: so what one country exhales another breathes the effects. Thus although we need globally applied solutions, we must have locally taken and highly personal medicines. Many political leaders now understand the health of the planet does indeed depend on this “low carbon” cure approach, and also on the curative policies and actions they must take. But they are misled by many of the cures that are now literally “on sale,” misled into believing, thinking, and supporting cures that are not.

1.6.5 Cure alls: the product range now on sale at your local store

Look carefully at the various cures we are all now offered, noting that many have not had real clinical testing or any peer review. We can make some real, painful, difficult, and technical judgments based on the actual clinical trials and the experience that we already have, and the prognosis that we can make. We can and must distinguish the local treatments of symptoms from the globally effective cures of cause. If we do not we may invest and pay for the wrong thing, in good faith and with good intentions. We need to consider rationally the claims made for, and look at the data for the effectiveness of the various cures and treatments. We may classify not conventionally but in medical terms as follows:

- a) Pain killers for local and political relief of our individual and collective efficiency of energy use, ignoring whether this really will decrease the energy

use symptoms compared to the reality. These include efficiency improvements and conservation measures that attack personal and business use, from insulating the home to more efficient equipment, which although being more expensive up front may ultimately pay off in reduced energy bills. The concern here is whether this actually reduces global energy use and emissions, or just slows down the growth.

- b) Palliatives or panaceas to calm fears by adopting “renewables,” meaning massively deploying sources of energy like wind power, where the hope is that the non-emitting power productions will displace or replace emitting sources (like gas, oil, and coal) and the concern is whether this actually reduces the symptoms, or simply defers real treatments or worse implies only one solution or treatment option is needed.
- c) Alternative medicines or curatives of “pricing,” “permitting,” or “trading” carbon emissions, which reduce emissions simply based on the idea that by pricing what was previously free the buyer or emitter will be discouraged from emitting, as it costs money for the ultimate consumer who ends up paying. The question here is simple – what is the incentive to actually reduce, and is it effective, or does this approach just “allow” emissions to occur, albeit at a price.
- d) Public universal or managed care, where indirectly there are subsidies or insurance payments to non-carbon energy sources with guaranteed prices and power sales – almost a no-risk cure that we can buy if everyone pays the same. But realistically we must consider how socialized practices will work in a capitalist, competitive world market. The issue is whether such public care is unduly expensive, dependent on easy but false pricing, and does not really make energy affordable for those who actually need it and is a disincentive to innovative cures.
- e) Health treatments or “feel good” remedies of reducing your personal consumption, so your individual contribution hopefully helps the collective good. But it may not make any actual difference to the global disease, so although the planet will not get better, one’s self-image is improved. Such approaches may be applicable to developed nations by substituting a specialized medication (like fluorescent lighting) but not for the energy needy, who require generic products of any type (say, just one or two light bulbs of any sort) and will apply whatever is not used or made available by others, especially if it is cheap and/or affordable (in this case implying a huge surge in electricity demand from the surplus manufacture of unwanted and cheaper bulbs)¹.
- f) Institutionalized exercises, proscribing existing known ineffective regimes, such as the Kyoto Protocol, using externally enforced therapeutic limits and bureaucratic measures. Here the value of the exercise regime appears to be in the exercise itself, but actually it may delay effective treatment and does not

¹ Also known as the “Law of Unintended Consequences,” when in this case meddling with markets, products, taxes, and incentives produces an unexpected but totally understandable and often opposite result.

affect a real cure. The concern is that such approaches produce artificial “consensus” rules designed not to offend, damage, or deny any one sector, country, political grouping, or business sector, in some way or manner.

- g) Experimental therapies, unproven and untried by true clinical trials, such as “intensity reductions” or “footprints,” and “offsets,” which do not produce emissions. We have made an apparent and willing effort by eliminating some past wasteful practices but we do not actually reduce emissions globally or in the full energy cycle. This therapy route should raise concerns with inadequate testing, unrealistic expectations, and unfulfilled hopes, while still actually enabling continued worsening symptoms and bad usage habits.
- h) Faith healing, where believing in a cure is seen as the answer, such as a return to the unattainable historic “global village,” the so-called ethical treatments and organic fuel use. These are usually based on dreams or beliefs that may not be directly or scientifically testable but they become almost dogma or accepted as truth, so the issue is that it is impossible to use rational approaches or change views since, by definition, all else is untrue or unacceptable.
- i) Holistic treatments, herbal remedies, or popular movements, where concern and sharing are emphasized, appeal is made to simplicity and “natural” medications but no actual cure is affected. The issue here is wasted resources, and lack of research and of objective data on effectiveness since results are highly subjective, reflect personal behavior(s) and norms, and perhaps induce placebo effects (a cure that is not). While not actually working on the larger problem and population, such treatments may negatively counter or interact with accepted or conventional approaches.

Given these care options, no wonder we all may be confused and overwhelmed, and we clearly need a second, truly independent and professional opinion and prognosis. Given the quantities offered of snake oil, instant cures, and palliatives that have not and do not work, we examine and show what can be done to affect the real cure. This means large doses of non-carbon-based energy (some say as large as 80%) (IPCC, 2007; G8, 2009) must be deployed, displacing and removing the dependency on carbon-based fuels, energy sources, and products. The candidate medicines are few, and the surgery is targeted and must be done with care: it entails changing habits, cutting out the old views, and implanting new ideals.

1.6.6 Truly disabling treatments: does efficiency improvement work?

It should be intuitively obvious that if we improve the efficiency of energy use – make or do more with or using less – that should reduce our demand and need for energy. If that were also economic that would be another incentive. So this sounds like a true “no brainer” – use less, pay less, and emit less as in, for example, the many articles and opinions on the role of efficiency, which exploits the apparent accounting merit of cost avoidance in the present versus capital investment for the future (Lovins, 2005, 2007, 2008). But despite major reductions in energy intensity and large improvements in and “buying” more snake oil end-use efficiency, totally unmentioned is the fact that locally, nationally, and globally both energy use and GHG emissions still rise, as we now show.

In fact efficiency standards have become mandatory for some appliances like refrigerators and indeed they do use much less energy as a result. If the increased initial cost if any can be paid back by reduced energy bills and costs, then the “payback time” to recoup the expenditure can be defined, and we can prove that real money savings can be achieved. So, we discuss the concept behind this below.

In fact, we can show this for light bulbs, where fluorescent lights use less power than incandescent or standard types (one uses a gas discharge, the other filament heating), depending on the rate of interest on the money used up front to buy the more expensive light. Older inefficient refrigerators are used for storing other goods, and so the use doubles.

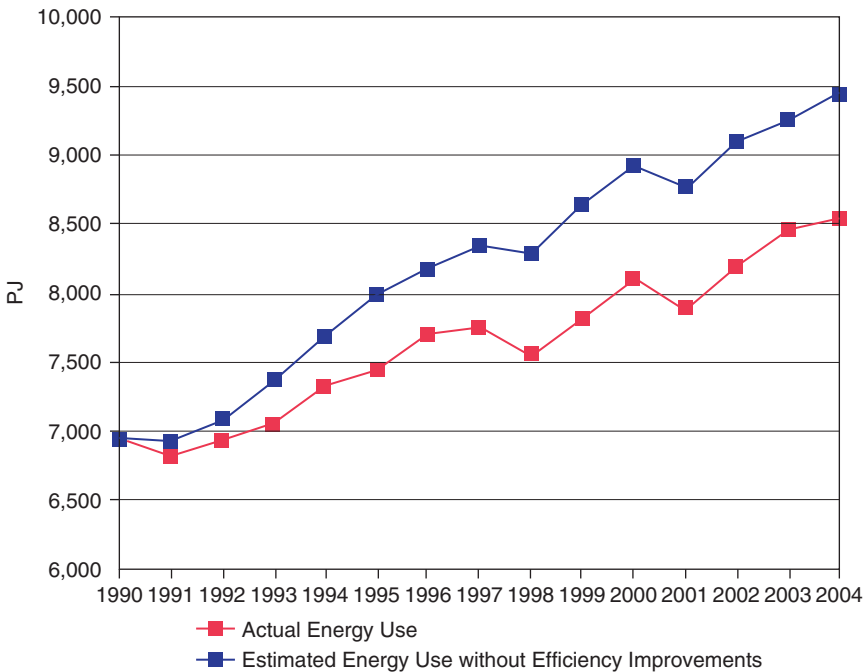


Fig. 1.5 Energy use growth in Canada from 1990, showing the impact with (grayline) and without (dark line) efficiency improvements (NRCan, 2008).

However, globally and especially nationally this has the opposite effect, in a perverse example of the law of unintended consequences. To illustrate this we show the data for Canada in Fig. 1.5 for the energy actually used compared to that estimated to be used without efficiency improvements. The rate of increase of energy use declines, but there is no real decrease in total amount used! The reasons are simple, and rather annoying.

First, and fundamentally, by making products cheaper by using less energy, more units are sold. So there is no incentive to actually reduce production com-

mercially, but to make more for the same or less energy costs since manufacturers want to sell more, not less.

Second, the energy not used in the particular process is now available for use in and by others, in other factories, businesses, and plants, and other countries, since a reduced demand has made that unused energy available in the market place, so the energy use simply moves elsewhere.

Third, in free market economies like Canada, business wants and needs to increase its market share, turnover, shareholder returns, and profits. So economic growth is king, and no business wants to actually sell less, so the pressure is to make and sell more at lower prices. Market efficiency and competitive pressures dominate and total consumption grows, and manufacturing facilities move to the location of lowest energy and labor costs (the classic example is the 50 years of migratory manufacturing locations for those essential items, the knife and fork) (Duffey 2008).

So, overall, energy use grows and never declines, as all the available data show, although individual businesses and factories may be much more efficient and hence competitive. It is good business to be frugal and cost sensitive, as many customers are also. So we see a paradox: efficiency is indeed good for business, but only if more products are sold.

1.7 Measuring the Cure: Efficiency Improvement

The measure of energy efficiency is the energy intensity or the amount used per unit produced. This can also be used as a social measure, as the amount used per person in any country. Reducing intensity sounds like a good idea: after all the so-called rich, industrialized nations have a high intensity and the energy-poor ones a lower value (MED, 2008). So if we reduce the energy intensity, nationally or at factories, we should help achieve efficiency, equity, and economy at one swoop. But, as we should have come to expect of course this naïve hope is not the case either.

Table 1.2 Potential for energy intensity reduction for New Zealand.

Sector	2030			
	Energy intensity reduction		Emission intensity reduction	
	Realizable potential (%)	Per year(%)	Realizable potential(%)	Per year(%)
Homes	29	1.1	19	0.8
Commercial buildings	25	1.0	17	0.7
Light industry	17	0.7	12	0.5
Heavy industry	35	1.4	33	1.3
Total non-transport energy	28	1.1	22	0.9

Source: MED (2008).

Here, let us look at an example from New Zealand on energy intensity reduction targets. MED (2008) in New Zealand indicate that there is substantial potential for the energy intensity and emissions intensity of the economy to reduce over time, although it varies by sector. A reduction in energy may reflect a change in the underlying composition of a sector (e.g., some types of business are by their nature more energy intensive) or an improvement in the energy efficiency within the sector. The most significant energy efficiency opportunities are when assets are replaced or upgraded. Some estimates of the realizable potential for energy intensity reduction in the intensity stationary energy demand sectors are shown in Table 1.2. However, demand for energy services does not always drop after an energy efficiency improvement. For example, after insulating a home, people may prefer to use the same amount of energy to keep their rooms warmer for comfort and health reasons instead of cutting their energy usage. This can be a good outcome.

MED (2008) also discuss the progress they have made as follows: Existing measures to encourage New Zealanders to use energy more efficiently in the stationary energy sector have centered around products, homes, buildings, and industry:

- EnergyWise home grants have helped retrofit insulation in about 25,000 pre-1977 houses occupied by low-income families. The project has had major health benefits for the families involved, particularly for people with asthma or other respiratory illnesses.
- A home energy rating scheme is under development to give home owners an incentive to make energy efficiency improvements and use renewable energy.
- The scheme will help ensure the value of improvements is recognized when homes are sold.
- The government's solar water heating finance assistance program encourages people to use solar water heating technology and helps strengthen New Zealand's solar water heating industry.
- A number of electricity efficiency initiatives including a compact fluorescent lamps campaign and pilot projects for water heating and the replacement of old, inefficient fridges are run. Such initiatives so far have already achieved savings of 208 GW h per annum at a cost of \$8.12 million, or a specific value \$39/MW h.
- The Department of Building and Housing is presently reviewing the Building Code to target significant energy efficiency improvements in houses and buildings.
- The joint New Zealand and Australia minimum energy performance standards and labeling program covering appliances and various types of machinery are underway. Endorsement labeling has also been introduced for highly efficient products.
- Energy audit grants and support to the country's 300 largest industrial energy consumers to identify and implement energy efficiency initiatives are provided. Savings reported by consumers in 2005/2006 were 2.2 PJ (MED, 2008).

- Some programs are piloting an electricity efficiency project in commercial lighting, in addition to pilot projects for motors and air compressors in industry.
- Some programs support the Energy Intensive Business program, which provides cash grants for demonstration projects for energy efficiency measures in target industries.
- The government has shown leadership in implementing energy efficiency measures in buildings, transport, and appliances.

All these initiatives aim to achieve reducing environmental impact (through reducing greenhouse gas emissions), saving energy and using it more efficiently, employing renewable, increasing the business activities (e.g., job creation), playing some key role, and leadership in international arena. Of course, it will take some time to see the outcomes of their initiatives.

Another example comes from the USA. The EIA (2008) states that the heroic reduction in energy intensity per gross domestic dollar produced shows a growing economy with less energy use (the ratio of energy to GDP \$), with a nearly 30% improvement. Energy use meanwhile has risen and will rise by over 50%. So for every percent improvement in intensity we have nearly 2% growth in energy use. It is working backward again – being such that efficiency improvement is overwhelmed by economic improvements. Needless to say, the emissions in the USA rose in lockstep with the energy use increase too. Furthermore, it clearly states that improved efficiency (technology) was responsible for about 60% of the observed decline in energy intensity, while it is now declining and more expensive to introduce. As a result of the continued improvements in the efficiency of end-use and electricity generation technologies, total energy intensity in the reference case is projected to decline at an average annual rate of 1.6% between 1999 and 2020. The projected decline in energy intensity (1.6%) is considerably less than that experienced during the 1970s and early 1980s, when energy intensity declined, on average, by 2.3% per year. Approximately 40% of that decline can be attributed to structural shifts in the economy – shifts to service industries and other less energy-intensive industries; however, the rest resulted from the use of more energy-efficient equipment. Although more advanced technologies may reduce energy consumption, in general they are more expensive when initially introduced. In order to penetrate into the market, advanced technologies must be purchased by consumers; however, many potential purchasers may not be willing to buy more expensive equipment that has a long period for recovering the additional cost through energy savings, and many may value other attributes over energy efficiency. In order to encourage more rapid penetration of new and clean technologies for reducing energy consumption and carbon dioxide emissions, it is really important to have right market policies and appropriate standards.

Based on the data should we argue that it is actually worse for the world to improve our wasteful ways of using energy? We are told otherwise, but it is apparently wrong. This perverse result is felt everywhere. In California, long cited as a leader in energy conservation and environmental concerns, we have the following statement of reality from the Governor Arnold Schwarzenegger's Office in

2007 (GovCa, 2008): “Because of California’s massive and growing economy, the state is the 12th largest emitter of carbon in the world despite leading the nation in energy efficiency standards and lead role in protecting its environment.”

In fact, California’s CO₂ emissions have increased by 10% over the time period 1990–2002, to some 500 Mt per year, according to the California Environmental Protection Agency 2007 report, which was released at the same time as the much vaunted Climate Action Plan. So the data say that a major effort by a major emitter has also resulted in a major failure.

In fact, many countries, states, and nations now fashionably have climate action plans (Canada, the UK, Quebec, etc.). Groupings of like-minded neighbors have gathered in the Regional Greenhouse Gas Initiative (RGGI) in the northeast USA, and European nations under the EU “umbrella,” with the intent to place some limit on their collective emissions and to be able to trade shortfalls and excesses between themselves (see the later discussion on setting the price of carbon).

It is now almost fashionable to blame China and other developing countries for their increased energy use and emissions rise – after all they now exceed those in the USA and are excluded from the Kyoto Protocol limits of achieving some percentage reduction below 1990 levels by 2010. They are accused of being inefficient and environmentally insensitive. But it is not their fault. Major exporting nations from Europe and North America have been busy selling emissions causing coal plants and automobiles to the expanding market and energy needs. These same nations have moved their manufacturing to China and started importing the goods from there. There is no requirement not to, and it is good business to expand sales. In fact, automakers reveal that more vehicles will go on roads, especially in China, India, Turkey, etc., than what they do in North America – so who is to blame for the spreading of the disease?

Dincer (2003) stated that the following basic steps are the key points in order to implement an efficient energy utilization strategy plan which we emphasize here:

1. **Defining the main goals:** It is a systematic way to identify the clear goals, leading to simple goal setting process. It is one of the crucial concerns and follows an organized framework to define goals, decide priorities, and identify the resources to meet those goals.
2. **Identifying the community goals:** It is significant step to identify priorities and links between energy, energy conservation, environment, and other primary local issues. Here, it is also important to identify the institutional and financial instruments.
3. **Environmental scan:** The main objective in this step is to develop a clear picture of the community to identify the critical energy-use areas, the size and shape of the resource-related problems facing the city and electrical and gas utilities the organizational mechanisms and the base data for evaluating the plan’s progress.
4. **Increase public awareness:** Governments can increase other customers’ awareness and acceptance of energy conservation programs by entering into performance contracts for government activities. They can also publicize the results of these programs and projects. In this regard, international workshops

to share experiences on the operation would help to overcome the initial barrier of unfamiliarity in countries.

5. **Information analysis:** It carries out a wide range of telephone and fax interviews with local and international financial institutions, project developers, bilateral aid agencies to capture new initiatives, lessons learned, and viewpoints on problems and potential solutions.
6. **Building community support:** It covers the participation and support of local industries and public communities, and the understanding of the nature of conflicts and barriers between given goals and local actors; improving information flows; activating education and advice surfaces; identifying institutional barriers; involving a broad spectrum of citizen and government agencies, referring to participation and support of local industrial and public communities.
7. **Analyzing information:** It includes defining available options and comparing the possible options against factors, e.g., activity/plan implementation costs, funding availability, utility capital deferral, potential for energy efficiency, compatibility with community goals, environmental benefits.
8. **Adopting policies and strategies:** Priority projects need to be identified through a number of approaches which are the best for the community. The decision process should evaluate the cost of the options in terms of savings in energy cost, generation of businesses and tax revenues, and the number of jobs created, as well as their contribution to energy sustainability and their benefit to other community and environmental goals.
9. **Developing the plan:** Once a draft plan is adopted, it is important for the community to review it and comment upon it. The public consultation process may vary, but a high level of agreement should be aimed.
10. **Implementing new action programs:** It is about to decide which programs to concentrate on, with long-term aims being preferred over short-term aims. The option that has the greatest impact should be focused on, and all details defined, no matter how difficult it seems. Financial resources need to be identified to implement the plans/programs.
11. **Evaluating the success:** It is the final stage for evaluating and assessing how well the plan performed, which helps to detect its strength and weaknesses and to determine who is benefitting from it.

These are self-evident steps in self-help, removing denial, defining the problem, taking expert advice, fighting the disease, taking the right medicine in the right doses; and at the same time attacking the root source of the addiction and illness, and measuring progress.

1.8. Advice from Advisors: Suffering from “Wedgemanian”

Almost every leading thinker and executive has an opinion they are prepared to share on what will happen. The truth is that given the global forces at work, many individuals are now exposed to and are catching other infectious, mental or disabling

diseases: fear, greed, dread, paralysis, helplessness, paranoia, guilt, and many similar syndromes. We may quote a few here that cut across the spectrum of opinions even as oil and gas prices were rising to record highs and producing record profits:

“But the point is, for the foreseeable future, energy demand will still be satisfied largely by hydrocarbons, with oil and gas leading the way,” according to the CEO of a leading global oil company (Pillari, 2006). This observation seems to cleverly combine realism with denial at the same time.

Even having to pay for emissions is seen as a business opportunity or a planned activity in the biggest oil businesses, since according to the previous chief executive of the same company: “We have worked for most of the last decade on the basis that one day carbon will be priced and that the application of technology which can reduce carbon will have a commercial value” (Lord Browne, 2005). So it is clear that there are plans to continue to expand carbon fuel use: after all the major suppliers do not want to sell less of their product or make less money.

The other extreme is those who see the end of the world, at least as one that encompasses humans in it. In viewing the world as a reactive, almost living organism it is realized that the matter of a radical cure is rather more urgent: “We face unrestrained heat... The immediate need is secure and safe sources of energy to keep the lights of civilization burning and for the preparation of our defences against rising sea level. There is no alternative but nuclear fission . . .” (Lovelock, 2006). This almost apocalyptic vision stands in stark contrast to the smooth and almost detached “business as usual forever” stance of many large energy corporations.

Needless to say there are those who seek a monopoly on curatives and have almost holistic and all encompassing remedies: “The marvelous truth about the environmental movement is that there is no hierarchy. We are all in this together” (Ref: Elizabeth May, in magazine interview 2007). However, this grouping includes self-styled “environmentalists” who have no time not only for the three previous views but inconsistently then deliberately exclude some known cures and remedies without any facts, and even regard some cures (like nuclear energy or centralized power plants) as unacceptable, an analogy to some sects that refuse forms of medical treatment on the basis of religious beliefs.

So here we have extreme views that encompass essentially everything from prescribing more of the same forever, a viewpoint which leads others to envisage a catastrophic end point unless drastic measures are taken, while still others desire the well-being that might arise if we all act in some collective, but idealistic, manner.

We should expect that the most sensible views should come from specialists, being those who have studied the technological and clinical data and evaluated objectively the possible prognosis and trends. Hence, it is clear that there are goals that could be set for emissions reduction to alleviate the symptoms, and a wide range of technologies and techniques are potentially available to attain that reduction over a given time frame. By defining “wedges” of possible reduction, a simple linearly increasing reduction is sought, by some combination of means. However this does not include any consideration of market forces, economics, costs,

and realities, so it is an idealist and overly simplistic view, almost as if more mental exercise alone is needed and the patient has an ideal response. It is a wish list that is well worth repeating in full as a measure of the possible measures, and because if we could get them all to act and add together it is theoretically a total and almost magical cure (NRTEE, 2007):

- Carbon capture and storage wedge.
- Carbon capture and storage (CCS) and energy efficiency (EE) overlap.
- The fuel switching wedge represents the contribution of switching from coal to oil products to natural gas to electricity; this portion also includes the contribution of renewables (wind, hydroelectricity, etc.) and nuclear power.
- The output wedge represents the GHG reductions due to lower physical output.

All these are to be coupled by the following:

- Implement a strong, clear, consistent, and certain GHG emission price signal across the entire economy.
- Institute a market-based policy that takes the form of an emission tax or a cap-and-trade system or a combination of the two.
- Develop complementary regulatory policies, in conjunction with the emission price signal, to address sectors of the economy that do not respond effectively to such price signal or where market failures exist.
- Establish a plan, in the earliest possible time frame, that leads to better coordination of complementary federal, provincial, and territorial GHG emission reduction policies aimed at common or shared targets, time frames, and actions.
- Apply GHG emission reduction policies that incorporate adaptive management practices and have built-in monitoring and assessment mechanisms to allow for regular reviews to ensure efficiency and effectiveness.

However, not only are they not linearly additive (as assumed) but also selective “wedgemanias” occurs, where some of the possible contributions are given totally unrealistic goals and some are excluded on arbitrary grounds.

In Fig. 1.6, we show an extreme recent example, whereby selecting many technologies the overall effect looks reasonable, whereas the curative contributions are in fact quite arbitrary and unsupported by any data. Undue reliance on large doses of unproven cures (e.g., carbon sequestration or capture, wave power, cogeneration, electricity intensity, wind power, ethanol, and “industrial efficiency”) means there are over 630 million tonnes (Mt) of unproven or at best questionable emission reductions in this example. That is about 60% of the claimed, assumed linearly extrapolated total, which also excludes any economic competitiveness analysis of any form.

This is not deceit, but purely wishful thinking, which then almost falls in the category of “faith healing,” or certainly in the rather dubious category of “cures that are not.” Some of the individual elements now certainly smell very much like real “snake oil,” defined as an attractive cure-all pedaled on the basis of claimed curative powers unsupported by facts. Many such cures may seem attractive to the

non-expert when reinforced by bogus claims of prior efficacy: there is indeed one born everyday.

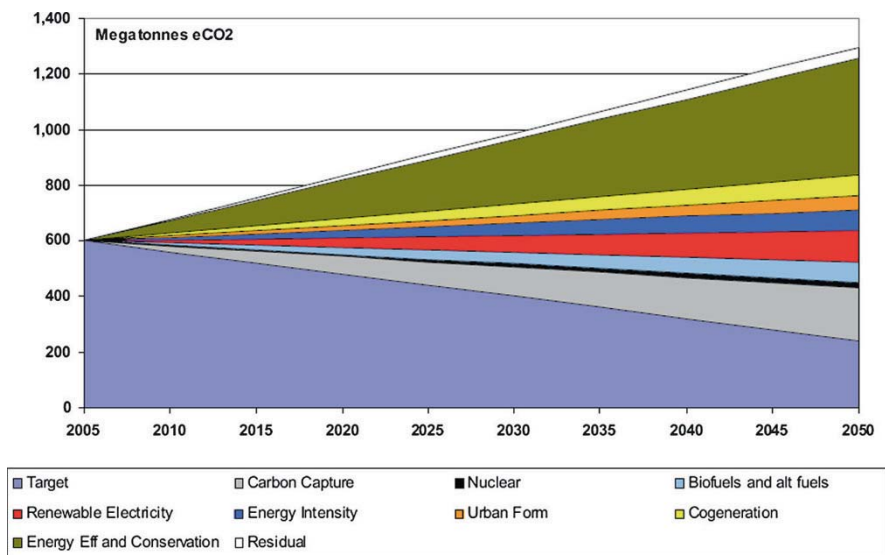


Fig. 1.6 The wedgemania selection for GHG reduction as proposed by NRTEE (2007).

1.9. A Plethora of Ineffective and Costly Therapies

In the recent popular book, the DVD, and movie “*An Inconvenient Truth*” (Gore, 2007) the original Socolow wedges are further simplified and consolidated to four groups (Pacala and Socolow, 2004). This grouping is given simply without explanation, and with no rationale given for the values or for the omissions in the proposed wedgemania cure. More importantly the claimed reductions do not agree with the data we have so far in the world, since the claimed efficiency gains do not produce any actual reduction, and wind and biofuels not really producing or displacing other needed sources at the scales claimed. So despite drawing public and media attention to the symptoms, the book, movie, and DVD fail to provide a real cure but rely on almost rah-rah messages that since we are all in this together, we can do it by appealing to a qualitative feel-good approach. This also really approached faith healing too (if only one believes then it must happen). But an objective evaluation of the claimed reductions shows that they are all questionable; these may actually increase the symptoms based on the data available today; and there exists the fatal neglect of the competitive nature of global energy markets. The question arises as, What then is the truth? What then is the inconvenient answer?

It is indeed too painful to tell the patient that the disease may be fatal; that the offered placebos are actually better than real medicine; and that the projections and prognosis are actually unsubstantiated guesses? Is there a confidence gap or credibility gulf that is too wide to cross? Are there not real cures that constitute a truly inconvenient answer? How can a layperson, the unqualified, and manipulated but very “concerned citizen” assess and be told what the uncomfortable reality is?

The medical analogy demands a process of consultations with experts and specialists who have knowledge from prior clinical cases or studies of the relevant and possible cures, and establish not only the cause but also the treatment plan. In a complete reverse of this sensible action plan, rather than consulting with qualified specialists, recently attempts have been made to include the “public” (meaning us) in the decision-making debate.

Furthermore, analogous to defining the right diet, one example of the consultation process to define a forward energy strategy is the UK Energy White Paper Consultation (DTI, 2007). This consultation, apparently required, includes many large reports on weighty topics such as the “Dynamics of GB Electricity Generation Investment – Prices, Security of Supply, CO₂ Emissions and Policy Options” and other seemingly academic and esoteric topics. The consultation reports are nominally intended to provide some kind of unbiased base position: it is like we are offering finding “the cure” as open to all those who think they may have an opinion about any cure, and may propose its possibility, but not necessarily has to possess or suggest one!! Since the sole qualifications for “consultation” comments are the ability to access the Internet and be able to read and type input, there is no fundamental discriminator on the quality of the advice, the presence or absence of “snake oil”, or the fiscal rewards of the consulting frenzy that surrounds such a process. All views offered apparently have the same weight: it is as if the patient is not only open for public inspection and diagnosis by quacks and charlatans but also for practice dissection by any volunteer from among the morbid audience. While consultations are in principle a very good thing, they are often now used as vehicles where set prior claims, cures, and opinions are regurgitated “for the record”. Consultations may also simply show that such a process was followed as a matter of good practice but not of good judgment.

Thus the recent UK DTI consultation had at least two beautiful examples of nonsense parading in the interest of public debate. First, a wide range of possible future scenarios are presented to cover the wide range of ignorance or vacillation about the future, and hence the large uncertainty about the possible outcomes of treatment. As shown in Fig. 1.7, the CO₂ emissions from the electricity sector in the UK in 2030 are projected to lie between 140 and 220 Mt from a base on 2007 of about 190 Mt depending on the assumptions made about the future. This possible range is therefore $[(220-140)/190] \times 100 = [80/190] \times 100 = 42\%$ or nearly

about a half, so almost any outcome is possible based on what is assumed. Almost any guess will do!

The second UK example arises from an assumption of excluding a particular treatment, in this case the withdrawal of nuclear energy. The result is an increase in emissions of some 30 Mt CO₂ by 2030. This disbenefit to the patient is treated dispassionately as a serious option, which is not only denial of care but in effect actually seriously considers the full withdrawal of treatment.

In summary we should not expect consultations to provide instant relief, additional wisdom about cures, or freedom of bias, and most importantly exhibit uniformity of expertise. Some of the specialists can be trusted; much of the advice cannot.

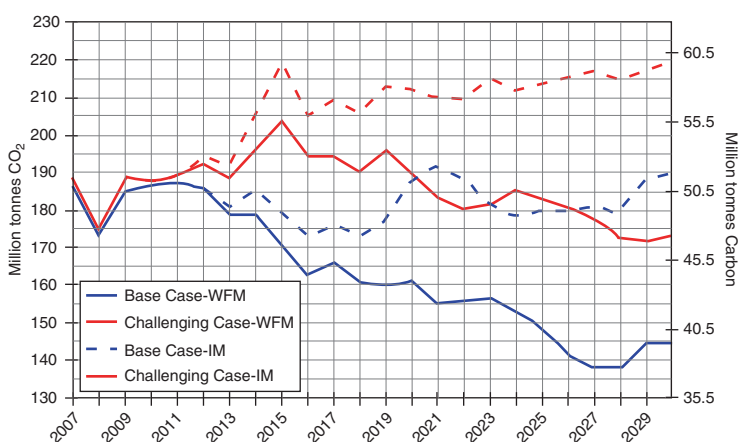


Fig. 1.7 Various cases for carbon and CO₂ emissions and their projections (DTI, 2007).

1.10. The Many Values of Carbon

Another popular remedy has been proposed. Instead of allowing CO₂ emissions to be free, we can put a value or a price on the emissions of carbon and other so-called “greenhouse gas.” In fact, the valuation of the costs of the impacts of climate change, and hence of the curative value, has been the subject of another extensive and multi-volume study by leading economics specialists (Stern, 2006). So once again we can turn to the experts for a second opinion.

“At 550 ppm CO₂, there is around a 50:50 chance of keeping increases below 3°C, but it is unlikely that increases would exceed 4°C. It is clear that stabilizing at 550 ppm or below involves strong action. For example, the power sector around the world will have to be at least 60% de-carbonized by 2050 and with a bigger

proportion de-carbonized in rich countries. What are the costs and benefits of taking action? The costs of removing most of that risk, getting to 550 (ppm CO₂) or below, are around 1% of GDP per year. The cost could be above or below 1% depending on policies, technological progress, and ambitions but would be in this region. This is equivalent to paying on average 1% more for what we buy – the price rise for carbon-intensive goods would be higher and for low carbon-intensive goods would be lower – it is like a one-off increase by 1% in the price level. That is manageable; we can grow and be green.”

So here we have a range of about 1% for the expected global socio-economic-techno-political cost of actually treating the symptoms. The value of carbon per emitted tonne is, however, different. Depending on the perspective, it ranges from the “true” economic or market value that is derivable to that applicable for political and social policy purposes. Hence we actually have a range of different values (Duffey and Miller, 2006):

- To stockholders and owners as the profit from sales
- To business as growth engine of the economy
- To power producers and users as a fuel
- To the world as potential climate change hazard
- To traders and emitters as an emissions right and cost
- To non-emitters as an avoidance credit/incentive
- To alternate technology developers and potential substitutes
- To governments in attaining policy, security, and taxes
- To the general public as part of daily living

Importantly, this last value to the global public is what they will actually pay for their diet. Depending on where they live, it will appear in what has to be paid for consumer products, energy bills, income and other taxes, personal and professional travel, and for alternatives to carbon fuels. Too much and it can damage personal and national economies; too little and it does not work effectively at the local and global levels.

We use energy everywhere, everyday, so we already implicitly value it. Thus as an example, the real value to any driver or family today is for the carbon energy used in transportation for goods, holidays, commuting, haulage, or just plain fun. So interestingly, we already value carbon since everyone who is an auto driver pays for gasoline at a filling station.

Assuming a present value for oil at \$50/bbl (and we can scale the results for any market price volatility range by using multiples or fractions of this number), this corresponds to \$120/t CO₂ based on the hydrocarbon content. At \$1/L at the gas pump, and anyone driving, say, 20,000 km per annum @ 8 km/L pays about \$2500 per annum in fuel costs. This corresponds to ~\$450/t CO₂ as the present transportation value of carbon emissions. This amount of driving also emits ~5t CO₂ per annum and the \$450/t is the implicit free market or economic value assigned to these presently nominally “free” or unconstrained GHG emissions.

As another real example of carbon value, let us look at what investors in a major oil company (BP, 2008) may expect from investing in energy stocks and shares. Now just 1 bbl oil equivalent at \$50/bbl has a carbon content of 115 kg C/bbl, which if burnt to produce energy also produces emissions of 422 kg

CO₂/bbl. This presumably typical oil and gas company makes money from the so-called “refining margin” of about ~ \$850/bbl. At the 2006 BP Annual General Meeting, and in the Financial and Operating Information for 2001–2005, it was reported that \$19 B was distributed to investors in 2005–2006 with a replacement cost/bbl in 2005 of ~\$48/bbl. With about 115 kgC/bbl, the profit per \$/kg C is 41.8¢/kg C or \$418/t C, which translates to a present carbon emissions value to investors of \$114/t CO₂, assuming no carbon is sequestered and all is used in combustion, oxidation, and/or transportation.

For the future investment return, this major international energy corporation at the 2006 Annual Meeting also promised a return in 2006–2008 of \$65 B value to stockholders in profits. In 2005 production from the companies refineries was stated as ~2.5 M bbl per day selling that at @ \$50/bbl produces an income stream from sales of \$45 B per annum. With this promised return of \$65 B over 3 years, or about ~\$22 B per annum, the profit per bbloe is given by:

$$\text{Profit per year/ Production per year in barrels (bbl)} = \$22\text{B}/(2500000 \times 365 \text{ bbl})$$

$$\text{or } \sim \$22 \text{ B} / 0.91 \text{ B bbl} = \$24 / \text{bbloe}$$

With each barrel having 422 kg CO₂ content when used, the Investors’ future carbon value as profit is now given by for each barrel:

$$\text{Profit per barrel/Produced CO}_2 \text{ per barrel} = \$24/0.442 \text{ t or } \sim \$54 / \text{t CO}_2 \text{ per annum}$$

As a gross profit margin over what is being paid at the pump, CO₂ profits are running at about $54/450 \times 100 \sim 12\%$. To attract investment or to be economically competitive without subsidy, any non-carbon alternate or carbon reduction scheme must have at least this substitute market investment value and return. Doubling of market prices, or any other variation, can be seen to yield even greater value.

1.10.1 The world value of carbon emissions

The world value of carbon emission can also be evaluated from the value of carbon energy to the world in providing economic growth. After all, this is how improvement in modern industrial society is measured and reported. The purely economic value of the carbon emissions and power source is reflected in producing financial wealth for every country (such as the national GDP) using carbon energy. Energy is greatest in developed (rich) nations and we observe a correlation between the growth in GDP to the growth in carbon energy use. This relationship also holds true at the global level. Hence the global growth in GHG concentration in the atmosphere over the last 30 years (measured as ppm CO₂ at Mauna Loa, Hawaii where 1 ppm CO₂ ~ 9.1012 t CO₂) is directly and linearly correlated to the GWP (measured in terra dollars, \$1012 US). We can compare the available GWP data with the actual CO₂ concentrations from Mauna Loa (Earthpolicy, 2008).

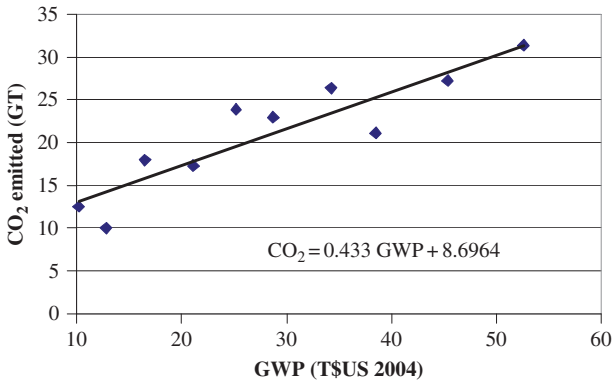


Fig. 1.8 The linear relationship between world economic growth and global emissions (Duffey and Miller, 2006).

To reduce the effect of the year-to-year noise in the atmospheric CO₂ concentrations, 5 year averages for GWP were plotted against the change in CO₂ measured over those 5 years. Rather than plotting ppm values of CO₂, the change was converted to billions of tonnes (Gt) of CO₂ released based on the 7.9 Gt of CO₂ required to cause a 1 ppm increase in the atmosphere accompanied by an equal release being absorbed in the oceans. So 1 ppm was taken to be equivalent to a total of 15.8 Gt of CO₂ released. It is reasonable to use 1950 as the base year since the CO₂ buildup prior to about 1950 was relatively small.

A linear fit of the data is shown in Fig. 1.8 as follows:

$$\text{CO}_2 \text{ (Gt)} = 0.433 \text{ GWP (t\$)} + 8.70$$

The data could well be interpreted as flattening over time – indicating diminishing energy intensity in the creation of value. But the average global economic value between 1950 and 2004 is a number worth remembering: 430 \$(US 2004)/t CO₂ which is equivalent to a global economic value of \$31 B of GWP per ppm CO₂. This global value per tonne of \$430/t CO₂ is remarkably and not coincidentally close to the personal economic value at the gas pump of \$450/t CO₂. The implication is obvious: what anyone pays for carbon used for energy is the same; your personal emissions appear and mirror the global ones; and hence personal value simply reflects the global value. The global symptoms (of rising temperature) are linked to the underlying cause of rising CO₂, which are linked to the basic disease of what everyone pays and uses for energy.

Of course, this is not the way carbon emissions are valued, when bought, sold, or traded, so what is the tradeable, fungible, real, or actual value of CO₂ in the marketplace today?

1.10.2 Valuing emissions: carbon trading business

Value can therefore be assigned from what emitters will actually pay to preserve or obtain the rights or credit of releasing GHGs. This value can be determined from a defined and hopefully market-driven “emissions trading” scheme, where the right to emit is established via some limit placed on the total allowed amount

(a so-called cap-and-trade system). Within the pre-determined GHG emissions amount, which is distributed between emitters and energy market sectors, credits can be traded and exchanged for a price determined by credit supply and emissions demand.

We might expect carbon emissions to be traded at values up to a significant fraction of the full economic value. Carbon market traders are already selling or managing carbon emission “credits,” “permits,” “allowances,” “offsets,” and “banks” at a price determined by supply and demand. All have the same purpose to set up a system of capping emissions at some pre-determined amount, and allowing those who emit less to take credit and also make some money from those who do not. The differential market price of the final product (electric power, automobile parts manufacturing, and oil refining costs) between those who have to pay and those who do not is meant to provide incentive not to emit.

Currently, as of the early phases of this market, it is estimated that about 100 Mt of carbon credits (Hasselknippe, 2004) are transacted in various markets worldwide. The World Bank report (IETA, 2005) stated:

“There are four active markets for GHG allowances as of May 2005 when we conducted this analysis: the EU ETS; the UK Emissions Trading System; the New South Wales trading system; and the Chicago Climate Exchange. Volumes exchanged on these allowance markets have increased dramatically compared with last year, and they are now comparable to the volumes exchanged through project-based transactions. Cumulative volume exchanged on these four markets from January 2004 to March 2005 is about 56MtCO₂e. Unlike project-based assets, allowances are homogeneous assets, and purchase contracts for allowances are fairly homogenous as well. As a result, the spread of prices for one tonne of CO₂ of emissions (an EUA) at any given point in time is small. In other words, one can speak of “the” price of EUAs traded between €7 and €9 in 2004, but their price has increased substantially in recent months, to reach more than €17 in March and April 2005”.

Of the four allowance markets listed above, the EU Emissions Trading Schemes (ETS) is the largest, with an estimated 39 Mt CO₂e exchanged since January 2004, the bulk transacted since January 2005. The EU Trading Scheme is something of a pioneer cure, due to the necessity to provide incentives for a number of countries to comply with an arbitrary cap. The ETS predictions have also been made in order to take account of the effect of demand on trading price (Nordhaus, 2005). The estimates ranged from \$20 to \$100/t CO₂ depending on the actual USA demand, which is presently zero. A useful conversion factor to bear in mind, since economic studies use different currencies, is that for 2006 currency conversion rates, \$100/t C = 20 €/t CO₂. Presently, for 2005–2006 the ETS trading value range is between (10 and 30 €/t CO₂ (Pointcarbon, 2008) or \$50 and \$150 /t CO₂ and fluctuating widely. This estimate is as close to an actual market value that is available but it is also artificial as being solely in the EU: it is not a global value depending on meeting the arbitrary EU Kyoto targets. We also note that the credits are a bargain as they are only some 30% of the total global and personal economic value. However it is also worth noting that emissions in the EU have not decreased with this scheme, as was the aim. As shown in Fig. 1.9, as for California, the claim of reducing effectiveness is false.

The increase shown in Fig. 1.9 is $3382 - 3335 \text{ Mt} = 47 \text{ Mt CO}_2$ or about 4 Mt CO_2 per year.

In fact the major emissions avoidance has been due to two other causes than the ETS: by the switching from coal-fired power plants to burning natural gas from the UK and Norway (now largely depleted and replaced by imports); and by the moving of manufacturing out of the EU itself, so these emissions now occur elsewhere (the so-called “leakage”). These real data say that this trading of emissions (the ETS) actually allows emissions to continue and even increase, albeit at a price. There is no evidence of an actual cure due to trading in the available data.

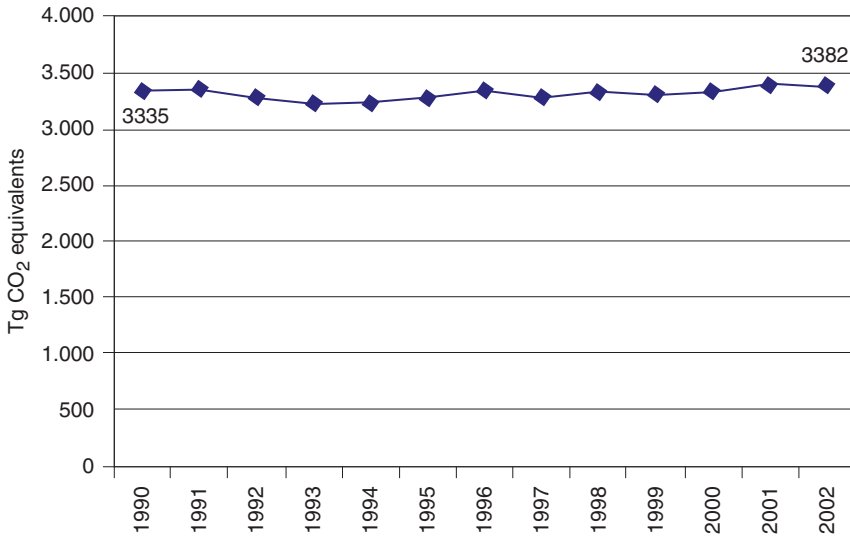


Fig. 1.9 The actual emissions history for the EU shows no actual reduction but a slight growth (European Environment Agency, 2004).

1.11 Feeling Good: Lifestyle Changes and Spa Treatments

There is a serious socio-political aspect to the search for an effective cure. There is inequality. Not everyone in the world is contributing equally to the symptoms, since wealth, emissions, and energy use are not distributed uniformly among human kind. Now it is common to define the world into the “haves” – those with developed or developing industrial economies – and the rest who do not. This separation can be based on energy use, gross domestic product or individual income, lifestyle and expectancy: those with the most. The more affluent, prosperous, higher income, more industrialized, technologically advanced, higher educated, and capitalist have possess and emit more than those with less. They enjoy an easier ‘lifestyle,’ because they can afford the best, providing the best generally means more GHG emissions per person, roughly in proportion to income.

It has always been possible for the more affluent and industrially afflicted countries (let us abbreviate them as the MAFFIA) to affect lifestyles that are fashionable. In the past, when medicines were not as effective, antibiotics unknown, diseases often not diagnosable, and surgery quite primitive, people would take “the cure” at spas and natural springs. Such treatments still exist today for those who can afford the luxury and cost and can include personalized regimes of diets, massage, and exercise as well as non-traditional therapeutic and herbal medications. The whole idea is if you feel good then that is better for you, and that pampering and personal care contribute to your well-being. It may be true that self-image and self-esteem, as well as personal habits and lifestyle may improve. So it is with the global symptoms: if the individual can believe that some spa-like treatment, alternative treatment or pronouncement will benefit society, so one can feel better about that. Examples are many, including

- riding a bicycle rather than driving a car, so the ~5 Mt CO₂ per year is partly reduced;
- purchasing “offsets” that theoretically reduce emissions somewhere and sometime due to emissions now;
- paying a price for “carbon,” as a tax or as a right to emit;
- investing in alternative energy (wind power) or “green” power, supposedly to distinguish between energy and electricity sources;
- buying power from non-emitting sources only, if available;
- driving a hybrid vehicle;
- installing solar water heaters;
- investing in so-called ethical, organic, green products, and companies;
- advising others to reduce energy use, particularly via celebrity web sites, articles, or interviews;
- exhorting a return to past rural societies;
- condemning modern industries, politicians, or corporations for wasteful or perceived emitting activities

Based on selected elements from this listing, we have spa-like treatment therapies, which are available to those who can afford them or those seeking alternative approaches. The advantage is that even if they do not work, they will not cause any additional harm or at worse not aggravate the symptoms. Recent examples are the Climate Action Plans from California, and from Quebec, which are announced as curative paths that are attractive and effective. In the latter (Gouvernement de Québec, 2006), with the cover adorned with a cyclist, the list is simple and covers innovative technology, energy efficiency, carbon fuel replacements (ethanol?), voluntary industrial reductions, incineration and biogas capture, and agricultural biomass (due to strong rural lobby). One item of “government leadership” was credited 0.2 Mt per annum and “public awareness” another 0.1 Mt per annum (see Table 1.3).

Without specifics, but based on incentives for avoidance, the Quebec treatment plan costs about \$200 M in carbon-related taxes plus \$328 M for other measures, with total program of about \$1.2 B. The plans stated objective is to avoid ~10 Mt per annum CO₂ in 6 years leading simply to a carbon emissions avoidance value range if fully achieved of

- High range $\sim \$1.2 \text{ B}/(10 \text{ Mt} \times 6) = \$20/\text{t CO}_2$
- Low range $\sim \$200 \text{ M}/(4.8 \text{ Mt} \times 6) = \$7/\text{t CO}_2$

As we shall show later this is actually a small amount, compared to the economic value and therefore fails a crucial test of effectiveness. It also turns out that the cost was apparently covered by equivalent federal government transfer payments (i.e., national not local taxes) amounting to some \$1B made a few months before the provincial elections. In a much heralded plan announced by their governor (GovCa, 2008) a similar but more complete list for California consisted of enforceable requirements, mainly from state agencies:

- AB – Global Warming Solutions Act
- SB1368 – Regulation of greenhouse gas emissions from local serving entities
- SB107 – Electricity generation from renewable energy resources
- AB1007 – Increased use of alternative fuels
- SB1 – Solar energy generation and energy conservation
- Executive Order S-20-06: Greenhouse gas emission reductions, market-based mechanisms
- Executive Order S-01-07: Low Carbon Fuel Standard

We simply note this list includes no measures that have been proven to be effective in actually reducing emissions. In particular, California itself states the classic Green Conundrum:

“Because of California’s massive and growing economy, the state is the 12th largest emitter of carbon in the world despite leading the nation in energy efficiency standards and lead role in protecting its environment” (GovCa, 2008). So the fact is that, despite having the reputation for curative properties, over the 12 years 1990–2012, emissions have actually risen.

The treatment record includes exporting manufacturing to other countries (e.g., China and Mexico), having LNG plants that cannot be easily licensed in State built in Mexico, importing hydroelectricity from British Columbia and gas from Alaska and Alberta, and not allowing any new nuclear plants. So accounting for the needed imported power from coal plants in Navajo Territory and other out-of-state sources, the admitted increase in emissions is about 50 Mt CO₂ or about $(50/(450 \times 12)) \times 100 \sim 1\%$ per year, which is mirroring the economic growth rate.

Perhaps the most encouraging aspect of all these alternative treatments is that they now have political and public visibility: the problem is recognised. But the measures and plans avoid unpopular or difficult surgery, such as mandatory reductions of emissions by industry, large taxes on carbon fuel use, closing major emitters, reducing automobile use by taxation, not using coal- or gas-fired power plants, and automobile driving and commuting restrictions. The plan also includes reducing the intent of autoemissions by some 50%, which is causing disputes over both the legality and possibility. We may simply note that previous mandatory standards for autoemissions reduction in California have not been achieved, so this is also an unproven cure. As we will demonstrate, this reduction goal for automobiles is one which is in fact attainable, at a known cost, with old technology cure that is available today but that requires new thinking.

Table 1.3 The assumed contributions to GHG reduction in the Quebec Plan.

Sector	GHG Emission Reduction by 2012
Energy and transport (including technological innovation, energy efficiency, carbon substitution, and transit of people and merchandise)	4.8 Mt CO ₂ e
Industrial (voluntary measures and regulation of halogens)	1.6 Mt CO ₂ e
Waste (regulations on incineration and biogas capture)	3.0 Mt CO ₂ e
Agriculture (biogas)	0.3 Mt CO ₂ e
Government leadership	0.2 Mt CO ₂ e
Public awareness	0.1 Mt CO ₂ e
Total	10.0 Mt CO ₂ e

Source: (Gouvernement de Québec, 2006).

1.12 Assessing the Alternative or Substitution Value

This value can be estimated based on alternate energy technology options that reduce emissions but with added development, deployment, and market costs that vary from technology to technology and from sector to sector. Thus, in principle, it is possible to consider the value of emissions reduction versus emissions avoidance approaches (e.g., switching to hydrogen as an energy carrier). As usual it is not so simple to apply a value which is a composite based on relative health, emissions, land use, fuel supply, social and political aspects to arrive at relative rankings for different substitute energy sources, emissions reduction technologies, and GHG sinks in a portfolio of options.

Let us first look at the simplest case of power generation. Different sources and means produce differing amounts of emissions over their full “life cycle,” meaning from mining the raw materials, the construction and the operation, and finally the disposal and decommissioning. For any given source of power, there is a GHG emissions amount per kW h.

To evaluate the relative emissions value of any two options, we can make a calculation as follows:

$$\text{Differential Value of Avoidance (\$)} = [\Delta g \text{ CO}_2/\text{kW h}] \times [\Delta \text{kW h}] \times [\Delta \$/\text{g CO}_2]$$

where $\Delta g \text{ CO}_2/\text{kW h}$ is the difference between the emissions for any two sources, $\Delta \text{kW h}$ is the difference in the amount of power generated, and $\Delta \$/\text{g CO}_2$ is the difference in the generating cost for any two sources.

The typical relative CO₂ emission values shown in Table 1.4 are for a variety of modern electric power units and a variety of studies to illustrate the order of magnitudes. For any given carbon value, for any given generation source, it is even more straightforward. For, say, generation of $\sim 8 \text{ TW h}$ of electricity each

year by a 1000 MW nuclear power plant avoids ~5 Mt/per annum. For emissions credits or trading at, say \$30/t, then the avoided emissions value is ~\$150 M/per annum.

We may also translate these emissions differences into generating costs impacts, that is the price actually paid by a consumer (cf. gasoline). Avoiding a value of \$150 M/year with a 1000 MW(e) plant generating ~8 TW h/year, the added value of emissions avoidance or conversely the benefit per unit electricity generated is 1.9 c/kW h, which is worth about a 30% increase in generating cost in the emitting plant or a credit for the non-emitting plant.

This type of analysis can be applied to any alternative technology or new treatment method that reduces emissions. For any energy unit utilized or generated, intuitively the formula can be modified to read:

$$\text{Differential Value of Avoidance (\$)} = [\Delta g \text{ CO}_2/\text{unit}] \times [\Delta \text{unit}] \times [\Delta \$/\text{g CO}_2]$$

If the cost of avoidance exceeds the benefit (a cost-to-benefit ratio of >1), then the approach, whatever it is, is less effective economically than if this same ratio is <1. Such analyses may be carried out and applied at the global level, if we can translate the difference into what is an allowable economic growth benefit. Since we have the value the world places today on emissions to provide global improvement, which is \$31 B/ppm per year, we may use the same value for the assumed reductions of 250 ppm. Hence we have

$$\text{Value of emissions avoidance} = 250 \text{ ppm} \times \$31 \text{ B GWP/ppm} \\ \sim \$7,750,000,000,000 \text{ per annum}$$

For providing the nuclear plants needed for the avoidance, say ~4000 nuclear new power plants at a cost ranging from \$2 to 4G/plant for 1 GW(e) per annum, the total investment cost is

$$\text{Cost of new nuclear reactors} = 4000 \times \$2\text{--}4,000,000,000 = \$8 \text{ to } 16,000,000,000,000$$

Table 1.4 Typical life cycle emissions for power generation from differing sources (g/kW h).

Electric energy technology	Switzerland 2000	Canada 2000	IAEA 2000	France (production only)
Natural gas	605		696	500
Coal	1071	974	978	
Solar panels	114–189		97	
Nuclear	16	3–15	21	0
Oil	856	778	811	701
Wind	36		36	
Hydro	4	15	16–23	

Source: Modified from EIA (2008).

This amount is almost exactly the same or at most twice as the annual global economic benefit. But the new plants will operate for 30–60 years and would be built over a similar time frame, so the value or benefit-to-cost ratio is crudely about 15 to 30 times disregarding any other income. Even if the cost amounts change by large factors and even if we load on all of the infrastructure and investment charges, this beneficial cost ratio is affordable and easily pays for itself with a global payback time of a few (1–5) years.

So we now have a rationale for a radical, affordable, implementable, cost-effective, environmentally beneficial, and global remedy. This is the hydrogen cure, the future dream of an emissions free energy world, reliable, abundant, and sustainable, with a healthy and long-lived planet. This real cure invokes massive substitution by nuclear power and hydrogen to tackle the disease, providing a real but inconvenient answer, which attacks the symptoms and uses carefully selective and targeted elective surgery to excise the remaining malignancy without removing whole human capabilities and aspirations.

1.13 The Hydrogen Cure

The whole hydrogen cure will have to be in carefully prescribed stages – first clinically introducing the short-term means (hybrid automobiles and nuclear electric power plants), with the compatible proven medicines (fuel cells and wind power), then modifying the long-term behavior by dietary habits and selective elective surgery (hydrogen pipelines, trains, ships, aircraft, heating, etc.). The cure will take faith in the leadership of professionals to undertake the right procedure, and full knowledge that the planetary convalescence may take sometime.

Much environmental impact is associated with energy-resource utilization. Ideally, a society seeking sustainable development utilizes only energy resources that release no or minimal emissions to the environment and thus cause no or little environmental impact. However, since all energy resources may somehow lead to some environmental impact, increased efficiency can somewhat alleviate the concerns regarding environmental emissions and their negative impacts. For the same services or products, less resource utilization and pollution is normally associated with increased efficiency.

Sustainability often leads local and national authorities to incorporate environmental considerations into energy planning. The need to satisfy basic human needs and aspirations, combined with increasing world population, will make the need for successful implementation of sustainable development increasingly apparent. Various hydrogen energy-related criteria that are essential to achieving sustainable development in a society follow (Dincer, 2007)

- information about and public awareness of the benefits of sustainability investments;
- environmental and sustainability education and training;
- appropriate energy and exergy strategies for better efficiency;
- promoting environmentally benign technologies;

- diversifying sustainable energy sources;
- clean hydrogen production technologies;
- development of sustainable hydrogen economy infrastructure;
- commercially viable and reliable hydrogen energy systems, including fuel cells;
- availability and utilization of renewable energy resources;
- use of cleaner technologies for production, transportation, distribution, storage, and use;
- a reasonable supply of financing and incentives;
- academia–industry–government partnership programs;
- policy development for sustainable energy programs;
- appropriate monitoring and evaluation tools; and
- road maps for future implementation.

Furthermore, environmental concerns are significantly linked to sustainable development. Activities that continually degrade the environment are not sustainable. For example, the cumulative impact on the environment of such activities often leads over time to a variety of health, ecological, and other problems.

Clearly, a strong relation exists between efficiency and environmental impact since, for the same services or products, less resource utilization and pollution is normally associated with increased efficiency. Note that improved energy efficiency leads to reduced energy losses. Most efficiency improvements produce direct environmental benefits in two ways: (i) Operating energy input requirements are reduced per unit output and pollutants generated are correspondingly reduced. (ii) Consideration of the entire life cycle for energy resources and technologies suggests that improved efficiency reduces environmental impact during most stages of the life cycle. That is why assessing the future hydrogen technologies such as fuel cells over their entire life cycle is essential to obtain correct information on energy consumption and emissions during various life cycle stages, to determine competitive advantages over conventional technologies, and to develop future scenarios for better sustainability.

It is obvious that utilization of hydrogen energy systems can help reduce environmental damage and achieve sustainability. Such systems essentially do not consume fuel, contribute to global warming, or generate substantial waste as long as hydrogen is produced through clean and renewable energy resources. In this respect, hydrogen and fuel cell technologies can provide more efficient, effective, environmentally benign, and sustainable alternatives to conventional energy technologies, particularly fossil-fuel-driven ones.

Hydrogen energy systems have a crucial role to play in meeting future energy needs in both rural and urban areas. The development and utilization of such technologies should be given a high priority, especially in the light of increased awareness of the adverse environmental impacts and political consequences of fossil-based generation. The need for sustainable energy development is increasing rapidly in the world. In fact, widespread use of these systems is important for achieving sustainability in the energy sectors in both developing and industrialized

countries. These systems are a key component of sustainable development for four main reasons:

- They have numerous advantages, such as energy efficiency and compatibility with renewable energy sources and carriers for future energy security, economic growth, and sustainable development.
- They generally cause much less environmental impact than other conventional energy sources and technologies. The variety of hydrogen and fuel cell technologies provide a flexible array of options for their use in various applications.
- Hydrogen cannot be depleted since the basic source is water. If used carefully in appropriate applications, it can provide a fully reliable and sustainable supply of energy almost indefinitely. In contrast, fossil fuel and uranium resources are diminished by extraction and consumption. Furthermore, while it is possible to produce hydrogen from water, current world's production of hydrogen is based on hydrocarbons and not on water. That is, 78% of the world's production of hydrogen is based on petroleum and natural gas (Muradov, 2009).
- These technologies favor system decentralization and local and individual solutions that are somewhat independent of the national network, thus enhancing the flexibility of the system and providing economic and environmental benefits to small isolated populations. Also, the small scale of the equipment often reduces the time required from initial design to operation, providing greater adaptability in responding to unpredictable growth and/or changes in energy demand.

It is also important to note that if we produce hydrogen through conventional technologies using fossil fuels, this will not make hydrogen inherently clean in that they may cause some burden on the environment in terms of pollutant emissions, solid wastes, resource extraction, or other environmental disruptions. Nevertheless, the overall use of these technologies almost certainly can provide a cleaner and more sustainable energy system than increased controls on conventional energy systems. This is in fact clearly shown in the case studies.

Before closing here, it is better to reflect some views from Hennicke and Fischdick (2006) that for many people, even among politicians, at a first glance, a "hydrogen economy" seems to be the solution and a vision to fulfill these principles. Several reasons are that hydrogen

- can be converted from all traditional primary energy sources (coal, natural gas, biomass) and, by electricity, from all renewable energy sources (via electrolysis) and from nuclear (via electrolysis or high-temperature cracking);
- can be used in stationary and mobile applications without damaging emissions especially by using fuel cells;
- could be made available everywhere and could substitute oil and gas and could be burned without changing the climate.

Therefore, few people doubt whether hydrogen will play an important role in sustainable energy systems. But the crucial questions to answer are, Where do we get

hydrogen from? How much hydrogen do we need, at what time, at what costs, and instead of which alternatives? These questions have to be answered before putting large sums of capital into the start up of a “hydrogen economy”. Hydrogen is only a secondary energy source (a “storage carrier”) and must be produced from a primary energy source. Because of physical reasons there will always be losses from these conversion processes and therefore in any case the costs of hydrogen must be higher than the costs of the energy used to produce hydrogen. This simple physical reason makes the decision on priorities and timescales for the introduction of hydrogen extremely complex. It is the same simple methodology leading to a higher CO₂-mitigation effect while using the input energy carrier for the production of hydrogen directly.

The scientific and technical challenges for the hydrogen economy may be given as follows (e.g., Edwards et al., 2006):

- Lowering the cost of hydrogen production to a level comparable to the energy cost of petrol.
- Development of a CO₂-free route for the mass production of sustainable hydrogen at a competitive cost.
- Development of a safe and efficient national infrastructure for hydrogen delivery and distribution.
- Development of viable hydrogen storage systems for both vehicular and stationary applications.
- Dramatic reduction in costs and significant improvement in the durability of fuel cell systems.

The pathway for the transition from current energy economies to hydrogen economy has some scientific, technological, and economical drawbacks. The most significant milestones for the hydrogen pathway must be mainly based on the intensification of research and innovation programs. Figure 1.10 shows some research and development priority areas.

It should be noted that universities play an important role in providing the sustainable development of hydrogen and fuel cells through some partnership programs with the relevant industry and government organizations. The output of research conducted in universities is open to other researchers. Hence, being aware of the previous studies and getting benefit of them, new methodologies are developed for better design, analysis, and operation of these technologies. Some challenges to the universities in this issue may be summarized as follows:

- funding challenges;
- coordination of research efforts within and between academic/research institutions; and
- collaboration between researchers and governmental institutions.

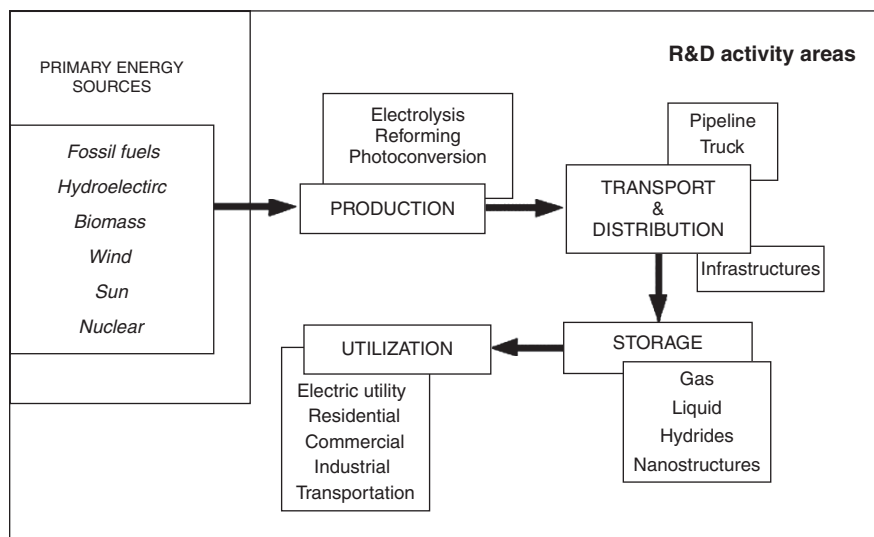


Fig. 1.10 Major R&D activity areas for the pathway to hydrogen economy (Conte et al., 2001).

1.14 Conclusions

What we conclude is simple! Although the early warning symptoms of climate change and global warming are present, they are not conclusive as to the diagnosis of the viral cause. Nevertheless, the prognosis from specialists is that the most likely cause (carbon dioxide and other emissions from human activity) means that the symptoms will get worse, unless a cure is implemented. Some are in denial, and the evidence is all questionable; opinions are varied even among trusted consultants and specialists.

We can avoid treatment, but at the cost of potentially irreversible damage. We can take early treatment and action as a matter of prudence but at a potential global economic and social cost. There is no “magic bullet” or panacea available, despite the claims for reducing carbon fuel addiction, increasing efficiency, reducing energy consumption, pricing carbon and non-carbon power sources. We are addicted to energy use, as it yields wealth and prosperity. There are many vested interests, in selling unproven treatments, in feeding the carbon addiction, in supplying alternative remedies, and in making money. As humans we cannot experiment on the only planet that we have – prudence demands we adopt and elect for early and effective treatment. Such moral and social imperative means we must not only look at what is being sold to us but what may affect a real cure.

We know now, based on data and reality, that on their own efficiency improvements, conservation, alternate energy sources, renewable and nuclear energy, carbon dioxide capture and sequestration, carbon pricing or “cap and trading” schemes, portfolio standards, using more natural gas, switching to hybrid cars

without green electricity, hydrogen power, all will not work except as a full spectrum, as a truly multi-vitamin energy pill.

Some medicines and treatments may be unpleasant to take: let us hope we have the fortitude to take the full spectrum of cures and a large although unpleasant dose of hydrogen, as quickly as we can.

References

- BP (2008). Climate Change, British Petroleum, at www.bp.com.
- Brohan, P, Kennedy, JJ, Haris, I, Tett, SFB, Jones, PD (2006). "Uncertainty estimates in regional and global observed temperature changes: a new dataset from 1850". *Journal of Geophysical Research* 111: D12106. DOI:10.1029/2005JD006548.
- Conte, M, Iacobazzi, A, Ronchetti, M, Vellone, R (2001). "Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives", *Journal of Power Sources* 100, 171–187.
- Dincer, I (2003). "On energy conservation policies and implementation practices", *International Journal of Energy Research* 27(7), 687–702.
- Dincer, I (2007). "Environmental and sustainability aspects of hydrogen and fuel cell systems", *International Journal of Energy Research* 31(1), 29–55, 2007.
- DTI (2007). UK Energy White Paper Consultation available at www.dti.gov.uk, May 2007.
- Duffey, RB (1999). "Vision of Energy Supply in the 21st Century: Managing the Global Bonfire", Presented at Climate Change & Energy Options Symposium Canadian Nuclear Society, Ottawa, 17–19 November.
- Duffey, RB and Miller, AI (2006). "The Value of Non-Carbon Power and Emissions Avoidance", Presented at the 2006 IEEE Power Engineering Society General Meeting, Montreal, Canada.
- Duffey, RB (2008). "Nuclear production of hydrogen: When worlds collide", *International Journal of Energy Research* – Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/er.1428.
- Earthpolicy (2008) available at http://www.earthpolicy.org/Indicators/Econ/Econ_data.htm.
- Edmonds, JA, Wise, MA, Dooley, JJ, Kim, SH, Smith, SJ, Runci, PJ, Clarke, LE, Malone, EL, Stokes, GM (2007). Global Energy Technology Strategy, Phase 2 findings from an international public-private sponsored research program, Battelle, May.
- Edwards, PP, Kuznetsov, V, David, WIF, Brandon, N (2006). "Hydrogen and fuel cells: towards a sustainable energy future". Mini Energy Project, Foresight.
- EIA (2008). Energy Information Administration, US Government. <http://www.eia.doe.gov/>.
- Ermis, K, Midilli, A, Dincer, I, Rosen, MA (2007). "Artificial neural network analysis of world green energy consumption", *Energy Policy* 35(3), 1731–1743.
- European Environment Agency (2004). Annual European Community Greenhouse Gas Inventory 1990–2002 and Inventory Report, Submission to the UNFCCC Secretariat, Project Managers André Jol, and Andreas Barkman.
- G8 (2009). Joint Statement by the G8 Energy Ministers and the European Energy Commissioner, Energy Ministers Meeting, May 24, Rome, Italy.
- Gore, A (2006). *An Inconvenient Truth*, Rodale, New York and www.algore.com, accessed on 07/09/2007.
- Gouvernement de Québec (2006). Plan d'Action 2006–2012, "Le Québec et les Changements Climatiques: Un Défi pour l'Avenir".
- GovCa (Government of California) (2008). Office of the Governor, State of California, at www.gov.ca.gov.
- Hasselknippe, H (2004). Climate Change & Business, Auckland, PointCarbon, November.
- Hennicke, P, Fischdick, M (2006). "Towards sustainable energy systems: the related role of hydrogen", *Energy Policy* 34, 1260–1270.
- Herbert, V (2006). "Unproven (questionable) dietary and nutritional methods in cancer prevention and treatment", *Cancer* 58 (8 suppl), 1930–1941.

- Hubbert, M King (1956). "Nuclear Energy and the Fossil Fuels", Presented before the Spring Meeting of the Southern District Division of Production, American Petroleum Institute, Texas, 7–9 March. Publication No. 95, Shell Development Company, Exploration and Production Research Division, Houston, Texas, June 1956.
- International Energy Agency (IEA) (2005). *Projected Costs of Generating Electricity*, 2005 Update, NEA-OECD, Paris, France, p. 178.
- International Emissions Trading Association (IETA) (2005). "State and Trends of the Carbon Market", World Bank Washington, DC, May.
- IPCC (2007). "Climate Change 2007: The Physical Science Basis: Summary for Policymakers", Approved at the 10th session of the IPCC Working Group I, Paris, February 2007 and Climate Change: Synthesis Report Summary for Policymakers, IPCC Plenary XXVII, Valencia, Spain, 12–17 November. Available www.ipcc.ch.
- Keeling, CD, Piper, SC, Bacastow, RB, Wahlen, M, Whorf, TP, Heimann, M, Meijer, HA (2005). "Atmospheric CO₂ and 13CO₂ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications", in *A History of Atmospheric CO₂ and its effects on Plants, Animals, and Ecosystems*, editors, Ehleringer, JR, Cerling, TE, Dearing, MD, Springer Verlag, New York, pp. 83–113.
- Lord Browne (2005). "BP Group Chief Executive", Dewhurst Lecture, Speech to the World Petroleum Congress, Johannesburg, 29 September. Available: <http://www.bp.com>
- Lovelock, J (2006). quoted from "The Revenge of Gaia".
- Lovins, AB (2005). "Energy End-Use Efficiency", Commissioned by InterAcademy Council (IAC), Amsterdam, www.interacademycouncil.net, as part of its 2005–06 study on Transitions to Sustainable Energy Systems, Rocky Mountain Institute, available: www.rmi.org; plus the many references to Lovins work therein.
- Lovins, AB (2007). "Public Lectures 1-5 in Advanced Energy Efficiency", Stanford University, available www.rmi.org.
- Lovins, AB (2008). "Profitable, Business-Led Solutions to the Climate, Oil, and Nuclear Proliferation Problems", Berlin Conference on the Human Dimensions of Global Environmental Change (by video), 23 February 2008, available: www.rmi.org.
- MED (2008). "Using Energy More Efficiently", Draft New Zealand Energy Strategy to 2050, Ministry of Economic Development, at http://www.med.govt.nz/templates/MultipageDocumentPage_25256.aspx.
- Muradov, NZ (2009). *Production of Hydrogen from hydrocarbons, Included in Hydrogen Fuel: Production, Transport and Storage*, edited by R. B. Gupta, CRC Press, Boca Raton, FL p. 35.
- NASA (2008). www.nasa.gov.
- NOAA (2008). www.noaa.gov.
- Nordhaus, WD (2005). "Life After Kyoto: Alternative Approaches to Global Warming Policies", Yale University, December.
- NRCAN (2008). "Climate Change Impacts and Adaptation Program, the Natural Resources of Canada", available: <http://www.nrcan-rncan.gc.ca/com/subsuj/envenv-eng.php>.
- NRTEE (2007). "Advice on a Long-term Strategy on Energy and Climate Change", The National Round Table on the Environment and the Economy, accessed at <http://www.nrtee-trnee.ca/eng/publications/wedge-advisory-note/ecc-wedge-advisory-note-eng.pdf>. and "Getting to 2050: Canada's transition to a low emissions future", ISBN 978-1-894737-14-2, Ottawa, Ontario, www.nrtee-trnee.ca, Section 2.1.5 and Fig. 7.
- Pacala, S, Socolow, R (2004). "Toward a Hydrogen Economy", *Science* at www.sciencemag.org v.305, 968–972.
- Petit, JR et al. (1999). *Nature* v.399 (6735), pp. 429–436.
- Pillari, R (2006). "Energy for a Sustainable and Secure Future", 26 January 2006, Washington DC, President & CEO, BP America.
- Pointcarbon (2008). <http://www.pointcarbon.com>.

Stern, N (2006). "The Economics of Climate Change", Speaking Notes, Stern Report, UK.

Singer, SF (ed.) (2008). "Nature, not Human Activity, Rules the Climate: Summary for Policymakers of the Report of the Nongovernmental International Panel on Climate Change", Science and Environmental Policy Project, Heartland Institute, Chicago, Illinois, U.S.A., available online at: www.heartland.org.

Workbook, (2005). BP Statistical Review of World Energy 2005. Available online at <http://www.bp.com/statisticalreview>.

On the Principles of Thermodynamics – Effects on the Environment, Global Warming, and Sustainability

A. Özer Arnas

2.1 Introduction

Precise thermodynamics education is a requirement to discuss issues that one faces in global warming, energy conversion, and other energy-related topics that affect sustainability of the environment in the global sense. For this reason, learning, understanding, and meaningful and relevant application of topics in thermodynamics are required. To accomplish this, educating students at the undergraduate and graduate levels in classical, statistical, and non-equilibrium thermodynamics becomes important. Here a short synopsis of fundamentals of classical thermodynamics is discussed with the intent of bringing clarity to the laws of thermodynamics and their application in design of experiments, applications in other fields such as heat transfer, and physical interpretation of the mathematical relations that are so useful in explaining why certain things happen in thermodynamics and nature. Nature is the ultimate customer.

For all scientist and engineers, the courses that end in –ics must be studied and understood well with their correct and precise application, such as mathematics, physics, chemical kinetics, mechanics, and the like. Of course, thermodynamics is one portion of mechanics that is very important in the education of all engineers but particularly mechanical and chemical engineers. It relates natural phenomena to some order and disorder. From a thermal energy point of view, therefore, thermodynamics is the science that dictates what happens in nature and what not and why. Thus to better understand nature, the implications of energy usage on the environment, and sustainability of what we enjoy today, we need to study precise thermodynamics.

2.2 Definitions

Definitions in thermodynamics must be precise to make everything that follows correct. Thus, in nature, there are only three types of systems. The closed system is one for which the mass within the boundaries remains a constant, such as a tank or a piston-cylinder arrangement. The filling/emptying system is one that a tank with a valve characterizes where mass can either enter or leave the tank. Both

cannot occur simultaneously. If a system has mass entering and leaving the boundaries, then it is called open.

There are only eight thermodynamic properties. The measurable ones are pressure, p , volume, V , and temperature, T . As a consequence of the first law of thermodynamics, internal energy, U , is introduced followed by the second law of thermodynamics and the introduction of entropy, S . Then three convenience properties are defined in terms of the five above: enthalpy $H = U + pV$, the Gibbs' function $G = H - TS$, and the Helmholtz potential $F = U - TS$. The rest should be called physical properties of a system such as the mass m .

In thermodynamics, equilibrium is required to solve a problem. By definition, when two systems reach the same temperature T , they are called to be in thermal equilibrium. When they reach the same pressure p , they have mechanical equilibrium, and when they have the same electrochemical potential μ_i , they have chemical equilibrium. When all three happen simultaneously, then thermodynamic equilibrium exists.

One of the more important statements in thermodynamics is the state principle. This principle is important not only in thermodynamic analyses but in applied areas like heat transfer. This principle states that any two independent and intensive thermodynamic properties would define any of the others and fix a thermodynamic state, and the situation is unique no matter which choice is made. A lack of understanding of this principle may lead to published work which has no meaning at all, Chawla (1978). Thus once a thermodynamic state is defined then a characteristic line that connects any two such states is called a thermodynamic process. A sequence of thermodynamic processes ending up at the initial thermodynamic state is called a thermodynamic cycle.

2.3 Conservation Equations

These equations that apply may be obtained using the Reynolds' Transport Theorem. Its use is common to all of these conservation laws and will be done systematically for each one of them. Considering at time t , $B_{\text{system}}(t) = B_{\text{CV}}(t)$ and at time $t + \Delta t$, $B_{\text{system}}(t + \Delta t) = [B_{\text{CV}}(t + \Delta t) + B_{\text{out}} - B_{\text{in}}]$, where the amount of B that exited the control volume is given as $B_{\text{out}} = b(m_{\text{out}}) = b[(\rho)(\vec{V}_{\text{out}})(A_{\text{out}})(\Delta t)]$ and $B_{\text{in}} =$

$b(m_{\text{in}}) = b[(\rho)(\vec{V}_{\text{in}})(A_{\text{in}})(\Delta t)]$ is the amount of B that entered the control volume. Subtracting the first term from the second and dividing by Δt results in

$$\frac{B_{\text{system}}(t + \Delta t) - B_{\text{system}}(t)}{\Delta t} = \frac{B_{\text{CV}}(t + \Delta t) - B_{\text{CV}}(t)}{\Delta t} + \frac{b[(\rho)(\vec{V}_{\text{out}})(A_{\text{out}})(\Delta t)] - b[(\rho)(\vec{V}_{\text{in}})(A_{\text{in}})(\Delta t)]}{\Delta t}.$$

Taking the limit of this equation as Δt approaches 0 yields the simplified equation

$$\frac{dB_{\text{sys}}}{dt} = \frac{dB_{\text{CV}}}{dt} + b\rho \left[\vec{V}_{\text{out}} A_{\text{out}} - \vec{V}_{\text{in}} A_{\text{in}} \right].$$

Rewriting the outflow and inflow terms

$$\text{for the entire control surface in this equation gives } \frac{dB_{\text{sys}}}{dt} = \frac{dB_{\text{CV}}}{dt} + \int_{\text{CS}} \rho b \vec{V} \cdot \vec{n} dA$$

where the dot product, $(\vec{V} \cdot \vec{n})$, is defined as $(V n \cos \theta)$, where θ is the angle between

$\vec{V}$ to $\vec{n}$. The total amount of extensive property B , ($B = m b$), in the control volume is determined by integrating over the entire control volume as $B_{cv} = \int_{cv} \rho b dV$.

Upon substitution and combination, the Reynolds' Transport Theorem is obtained

as $\frac{dB_{sys}}{dt} = \frac{d}{dt} \int_{cv} \rho b dV + \int_{cs} \rho b (\vec{V} \cdot \vec{n}) dA$ where the left-hand term is the time rate of change of extensive property (B) in the system, the first term on the right-hand side of the equation is the time rate of change of intensive property (b) in the control volume, and the second term on the right-hand side of the equation is the net flow of intensive property (b) across the control surface. A positive value indicates that net flow across the control surface is out of the control volume while a negative value indicates that net flow across the control surface is into the control volume.

There are two conservation equations, that of mass and energy – the first law of thermodynamics. For the case of conservation of mass,

Closed system: $m = \text{constant.}$

Open system: $\sum_{in} \dot{m} = \sum_{out} \dot{m}$

Filling system: $m_{initial} + \sum_{in} m = m_{final}$

Emptying system: $m_{initial} - \sum_{out} m = m_{final}.$

Applying the Reynolds' Transport Theorem to the first law of thermody-

namics, the result becomes $\frac{dE_{system}}{dt} = \frac{d}{dt} \int_{cv} \rho e dV + \int_{cs} \rho e (\vec{V} \cdot \vec{n}) dA$. This state-

ment is very similar to money and banking; the difference is that nature does not permit overdraw of funds, namely one cannot use what is not there, whereas the bank just charges us money for overdraft. At steady state, therefore, $\delta Q - \delta W = dU$. For a cycle, $\oint \delta Q = \oint \delta W$ resulting in the fact

that $\oint dU = \oint d(\text{property}) = 0$. This is a very important result which will be used later. Application of the above theorem to various systems in nature results in the first law of thermodynamics as

Closed system: $Q_{ie} - W_{ie} = U_e - U_i$

Open system: $\dot{Q}_{ie} - \dot{W}_{ie} = \sum_e \dot{m} \left(h + \frac{\vec{V}^2}{2} + gz \right) - \sum_i \dot{m} \left(h + \frac{\vec{V}^2}{2} + gz \right)$

Filling system: $Q_{ie} - W_{ie} = m_2 u_2 - \sum_i m \left(h + \frac{\vec{V}^2}{2} + gz \right) - m_1 u_1$

Emptying system:

$$Q_{ie} - W_{ie} = \sum \frac{m}{c} \left(h + \frac{\vec{v}^2}{2} + gz \right) + m_2 u_2 - m_1 u_1$$

2.4 Sign Convention in Thermodynamics

We cannot overemphasize the importance of this since most, if not all, textbooks do not strictly follow the convention. What convention is followed is not important, but the consistent use of it is. For example, Callen (1960) says that all energy in is positive and all energy out is negative, and in that text this is followed consistently whereas most commonly used undergraduate and graduate textbooks do not, as is shown in the bibliography and references of Arnas et al. (2003). Precision is very important, as is mentioned in Obert (1960). In most textbooks, all energy transfer due to a difference of temperature only called heat in is positive and heat out is negative, and all energy transfers due to a potential difference other than temperature called work in is negative and work out is positive giving us HIP to WIN. In all that we will do, this convention will be followed due to its universal and more common usage. For the equivalence of heat to absolute temperature, consider a Carnot cycle, Fig. 2.1. It is made of two reversible adiabatic lines and two reversible, constant temperature heat reservoirs. If the working fluid is considered to be an ideal gas, for simplicity of algebra, then the energy added at T_H is given by, for an ideal gas, $\left(Q_{bc} = \frac{m\mathfrak{R}}{M} T_H \ln \frac{V_c}{V_b} \right)$.

Similarly for the process (d-a), $\left(Q_{da} = \frac{m\mathfrak{R}}{M} T_L \ln \frac{V_a}{V_d} \right)$; thus the ratio becomes

$$\left[\frac{Q_{da}}{Q_{bc}} = \frac{T_L}{T_H} \left(\frac{\ln \frac{V_a}{V_d}}{\ln \frac{V_c}{V_b}} \right) \right]. \text{ Since the process (a-b) is reversible and adiabatic, then}$$

$$[-m c_v dT = p dV] = \left[\frac{m\mathfrak{R}}{M} T \frac{dV}{V} \right]. \text{ This integrates to give for process (a-b) the}$$

$$\text{result of } \left\{ -\frac{M}{\mathfrak{R}} \int_{T_L}^{T_H} c_v \frac{dT}{T} = \ln \frac{V_b}{V_a} \right\}. \text{ For the process (c-d), a similar result is ob-}$$

$$\text{tained as } \left\{ -\frac{M}{\mathfrak{R}} \int_{T_H}^{T_L} c_v \frac{dT}{T} = \ln \frac{V_d}{V_c} \right\}. \text{ Therefore, since the limits of integration are}$$

$$\text{reversed, the equivalence gives } \left\{ \ln \frac{V_a}{V_b} = \ln \frac{V_d}{V_c} \right\} \text{ or } \{-[\ln V_c - \ln V_b]\} = [\ln V_a - \ln$$

$V_d]$ resulting in $\left(\ln \frac{V_c}{V_b}\right) / \left(\ln \frac{V_a}{V_d}\right) = -1$. This upon substitution yields the expected

result of $\left(\frac{-Q_L}{Q_H} = \frac{T_L}{T_H}\right)$. This relation permits one to substitute temperatures for

heat quantities in the determination of Carnot performance criteria which quickly give extremum values for the actual efficiencies for engines, η , as well as coefficient of performances for refrigerators, β , and heat pumps, γ . It must be remembered that one of the heat quantities is negative, out of a system, as it should be since the ratio of absolute temperatures is always positive. With reference to Arnas et al., (2003), we can examine the various details of this result particularly with respect to engine efficiency and refrigerator and heat pump coefficient of performances. For this demonstration, we will use the sign convention of Callen (1960) that all energy transfers into a system are positive and all out of the system are negative.

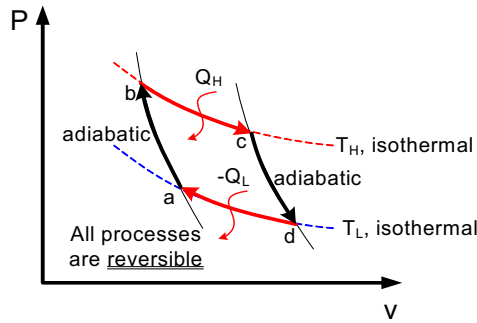


Fig. 2.1 The Carnot cycle.

2.5 Performance Characteristics of Devices

Consider a heat engine that receives energy (Q_H) from a reservoir at (T_H) and produces work ($-W_{\text{net}}$) while rejecting energy ($-Q_L$) to a reservoir at (T_L). Since the performance of any device is measured by the ratio of the net useful effect to the

total cost to obtain that effect, then $\eta = \left(\frac{-W_{\text{net}}}{Q_H}\right)$. Also we have $\Sigma E_{\text{in}} = \Sigma E_{\text{out}}$

giving $Q_H = [-W_{\text{net}} + (-Q_L)]$. Solving for ($-W_{\text{net}}$) and substituting into the effi-

ciency equation, the result becomes $\eta = \left(\frac{Q_H + Q_L}{Q_H}\right) = \left(1 + \frac{Q_L}{Q_H}\right)$. Using the equi-

valence equation, the efficiency of a Carnot engine reduces to $\eta = \left(1 - \frac{T_L}{T_H}\right)$.

For a refrigerator, the net effect is the cooling that we get, (Q_L) , from a cold reservoir at (T_L) . The work required to pump this energy is (W_{net}) , and the energy given off to the environment at a temperature (T_H) is $(-Q_H)$. Therefore, the performance parameter, coefficient of performance for a refrigerator becomes

$$\beta = \left(\frac{Q_L}{W_{\text{net}}} \right) = \left[\frac{Q_L}{-Q_H + (-Q_L)} \right] = \frac{1}{\left(-\frac{Q_H}{Q_L} - 1 \right)} \text{ which reduces to } \beta = \left(\frac{T_L}{T_H - T_L} \right) \text{ for}$$

a Carnot refrigerator.

For a heat pump, the net effect is the heating that we get, $(-Q_H)$ into a reservoir at a temperature of (T_H) . The work required to pump this energy is (W_{net}) , and the energy that is taken out of the environment at a temperature (T_L) is (Q_L) . Therefore, the coefficient of performance for a heat pump becomes

$$\gamma = \left(\frac{-Q_H}{W_{\text{net}}} \right) = \left[\frac{-Q_H}{-Q_H + (-Q_L)} \right] = \frac{1}{\left(1 + \frac{Q_L}{Q_H} \right)} \text{ which reduces to } \gamma = \left(\frac{T_H}{T_H - T_L} \right) \text{ for a}$$

Carnot heat pump. It is also easy to prove that $\{\gamma = (1 + \beta)\}$ using the results obtained above.

2.6 Second Law of Thermodynamics

The second law of thermodynamics denies a system the possibility of utilizing energy in a particular or arbitrary way. There are two basic definitions of the second law which were stated at different times by different people, historically speaking.

2.6.1 Kelvin–Planck statement

It is impossible to construct an engine which is operating in a cycle that will produce no effect other than the extraction of energy from a reservoir and the performance of an equivalent amount of work. Thus an efficiency of 100% is not a possibility.

2.6.2 Clausius statement

It is impossible to construct a device which while operating in a cycle will produce no effect other than the transfer of energy from a colder to a hotter body. Thus a refrigeration unit requires energy input as work; otherwise it cannot function. These two statements are equivalent and the assumption of the validity of one leads to the situation given by the other. Consider that the Kelvin–Planck statement is valid. If one now constructs a refrigerator running with the work of the engine and extracting energy $[-Q_c]$ from the cold reservoir, then the engine–refrigerator system is one which absorbs energy from a cold reservoir and transfers it to the hot reservoir without any external work, a situation which the Clausius statement refutes. If this were possible, the energy in the oceans at a low and

cold temperature could be utilized to run all kinds of equipment without any external work; an impossible situation known to all.

If now the Clausius statement is considered to be valid, then the refrigerator functions without any external work. At the same time, an engine placed between the same two reservoirs produces work. The refrigerator–engine system leads to a situation where an amount of energy is absorbed from a hot reservoir and an equivalent amount of work is performed, a situation that the Kelvin–Planck statement refutes. If this were valid, all the fuel consumed in the engine of a car would be used in the form of work without any losses whatsoever another impossible situation that is well known to all. All physical systems must function in such a way as not to violate either one of these statements. Otherwise a perpetual motion machine of the second kind will result.

2.7 The Carnot Principle

This is one of the fundamental principles of thermodynamics. It says that there is no heat engine operating between two given reservoirs that can be more efficient than a Carnot heat engine operating between the same two reservoirs. To prove this statement, assume that the reverse is true, Fig. 2.2. Then since the Carnot engine is reversible, it can be reversed to operate as a refrigerator. Therefore, if the engine E is more efficient than the Carnot engine CE, the result becomes ($\eta_E > \eta_{CE}$).

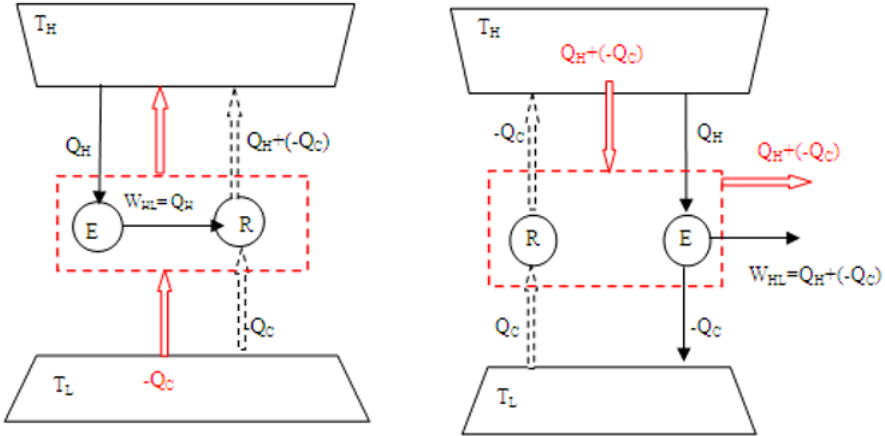


Fig. 2.2 The graphical explanation of the Kelvin–Planck and Clausius statements of the second law.

This can also be written as $\left(\frac{W}{Q_H} > \frac{W}{Q_C} \right)$ giving as the final result ($Q_C > Q_H$). If this is the case, then there is a net flow of energy in the form of

heat from the cold to the hot reservoir without any consumption of work or other external effects. Such a result is impossible since it leads to the contradiction of the Clausius statement of the second law of thermodynamics. Thus the original assumption was wrong which says that the efficiency of an engine cannot be larger than that of a Carnot engine operating between the same two reservoirs.

A corollary to the Carnot principle is that all Carnot engines operating between the same two temperature reservoirs T_H and T_L have the same efficiency. The proof of this statement follows from the above. Assume that the first one is more efficient than the other. A contradiction will be observed. Then assume the other way around. The same contradiction will be obtained. The only possibility remaining, therefore, is naturally the equivalence of the two efficiencies.

2.8 Entropy

Entropy is a thermodynamic property which comes about as a result of the second law of thermodynamics. To demonstrate its existence, following Zemansky (1943) and Mooney (1953), consider a reversible process from an initial state i to a final state f and use the first law to give $[Q_{if} - W_{if} = (U_f - U_i)]$, Fig. 2.3. From i and f draw two reversible adiabatic lines. Then construct a reversible isotherm ($a-b$) so that the area above and below the isotherm and between the original process ($i-f$) and the adiabatic lines is equal. Thus we obtain that $(W_{if} = W_{iabf})$. Therefore, now the heat terms give $(Q_{if} = Q_{iabf})$ since $(U_f - U_i)$ does not change because of the general character of a thermodynamic property. Also Q_{ia} and Q_{bf} are equal to zero since they are adiabatic processes resulting in $(W_{if}) = (W_{iabf}) = (W_{ia} + W_{ab} + W_{bf})$. Therefore, the result becomes $[Q_{ab} - W_{if} = (U_f - U_i)]$ giving the final result that $(Q_{ab} = Q_{if})$. In general, therefore, an arbitrary reversible process can always be replaced by a zigzag path between the same state points consisting of a reversible adiabatic line, a reversible isotherm, and another reversible adiabatic line, such that $\{Q_{\text{original process}} = Q_{\text{isotherm}}\}$, now the heat terms give $(Q_{if} = Q_{iabf})$ since $(U_f - U_i)$ does not change because of the general character of a thermodynamic property. Now, to reach the definition of thermodynamic quantity entropy, consider a smooth reversible cycle as shown in Fig. 2.4. On it inscribe reversible adiabatic lines of thickness Δ . For each slice or arc, which is a reversible process, inscribe an isotherm so that the condition given above is satisfied. The cycles thus formed are all Carnot cycles with the characteristic relationship obtained between heat transfer and absolute temperature

ratios. Thus for the first cycle drawn, $\left\{ \frac{Q_{H_1}}{-Q_{L_1}} = \frac{T_{H_1}}{T_{L_1}} \right\}$ or $\left\{ \frac{Q_{H_1}}{T_{H_1}} + \frac{Q_{L_1}}{T_{L_1}} = 0 \right\}$. In a

similar fashion, for the second cycle we have $\left\{ \frac{Q_{H_2}}{T_{H_2}} + \frac{Q_{L_2}}{T_{L_2}} = 0 \right\}$. Adding these

two results and generalizing for the sum of all such cycles, then $\left\{ \sum_i \frac{Q_i}{T_i} = 0 \right\}$. In the limit as $\Delta \rightarrow 0$, the adiabatic lines come closer thus making the heat quantities infinitesimal resulting in $\left\{ \oint_{\text{rev}} \frac{\delta Q}{T} = 0 \right\}$ which is the important Clausius theorem.

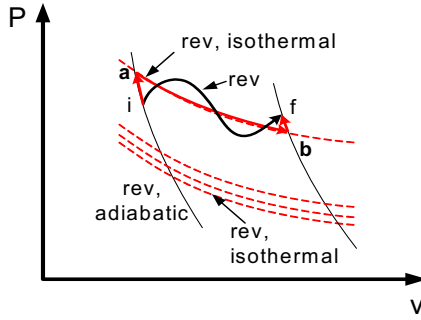


Fig. 2.3 Development of the Carnot cycle.

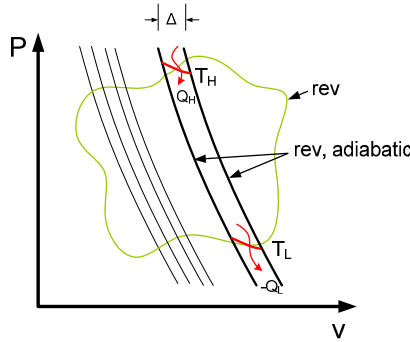


Fig. 2.4 Development of Clausius' statement and entropy.

Now consider two reversible processes R_1 and R_2 starting from the initial state i and ending at the final state f , Fig. 2.5. Since they are reversible, it is possible to change the sense of R_2 . Since R_1 and R_2 now form a reversible cycle, then

$$\left\{ \oint_{R_1 R_2} \frac{\delta Q}{T} = 0 \right\} \text{ and } \left\{ \int_{i_{R_1}}^f \frac{\delta Q}{T} + \int_{f_{R_2}}^i \frac{\delta Q}{T} = 0 \right\}. \text{ This results in the most general relation for}$$

the integral in a reversible process $\left\{ \int_{i_{R_1}}^f \frac{\delta Q}{T} \right\} = \left\{ \int_{i_{R_2}}^f \frac{\delta Q}{T} \right\} = \dots = \left\{ \int_{i_R}^f \frac{\delta Q}{T} \right\}$ which says

that if a reversible path is chosen, the path itself is not important so long as the process starts at i and ends at f . The quantity is, therefore, given by the end states and not the path. As is the case in the first law of thermodynamics, $\left[\oint \delta Q - \oint \delta W = \oint dU\right]$ and $\left(\oint dU = 0\right)$ since internal energy is a thermodynamic property, then $\left\{\oint_{\text{rev}} \frac{\delta Q}{T} = 0\right\}$ is a thermodynamic property and is called entropy, S .

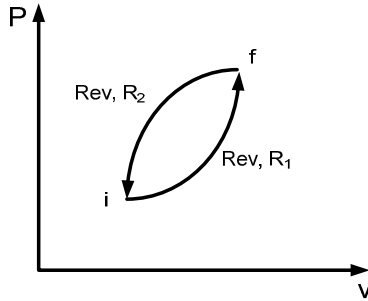


Fig. 2.5 A reversible cycle.

Therefore, $\left\{\int_{i_{\text{REV}}}^f dS = (S_f - S_i)\right\}$ or for an infinitesimal process,

$\left\{\frac{\delta Q_{\text{rev}}}{T} = dS\right\}$ that forms the mathematical formulation of the second law of ther-

modynamics. It is, therefore, seen that there is a similarity between the two laws of thermodynamics and their definition of internal energy and entropy. To further extend this discussion to the inequality of Clausius, consider the fact that all heat engines operating between a given high temperature source, T_H , and a lower temperature sink of T_L , none can have a higher efficiency than the Carnot engine.

Thus using the figure above, but this time having the process at T_H to be irrevers-

ible, then the result obtained is $\left(1 + \frac{Q_{L\text{REV}}}{Q_{H\text{IRREV}}}\right) \leq \left(1 + \frac{Q_L}{Q_H}\right)_{\text{REV}}$. Using the fact that

$\left\{ \frac{-Q_L}{Q_H} = \frac{T_L}{T_H} \right\}$ is for reversible energy transfers, then $\left(1 - \frac{Q_{L,REV}}{Q_{H,IRREV}} \right) \leq \left(1 - \frac{T_L}{T_H} \right)$.

Transposing and keeping in mind that there is a negative sign, the result becomes $\left(\frac{\delta Q_{L,REV}}{T_L} \right) \geq \left(\frac{\delta Q_{H,IRREV}}{T_H} \right)$. Using the definition of entropy as given above,

$$dS \geq \left(\frac{\delta Q_{H,IRREV}}{T_H} \right) \text{ or } \oint dS \geq \oint \left(\frac{\delta Q}{T} \right)_{IRREV}, \text{ which states that in all real processes}$$

entropy increases and the equality is only for the reversible process. This further reduces the result to what is expected, the inequality of Clausius, the fact that $\oint \left(\frac{\delta Q}{T} \right)_{IRREV} \leq 0$.

If the entropy changes of the system are added to the entropy changes occurring in the surroundings as a result of the changes in the system, the sum represents the total changes of the system and the surroundings and is called the entropy change of the universe or entropy generation, σ . For a reversible process, let δQ_{rev} amount of energy be absorbed by the system. Then $\left(dS_{system} = \frac{\delta Q_{rev}}{T} \right) > 0$ since it has been put into the system. Since this energy has to be given up by the surroundings, then $\left(dS_{surroundings} = \frac{\delta Q_{rev}}{T} \right) < 0$. As a result, the entropy generation is $(dS_{universe} = d\sigma = 0)$. Thus, when a reversible process is performed, the entropy of the universe remains unchanged.

The second law representation of the systems that we are interested in is as follows:

Closed system:
$$\Delta \sigma = m(s_2 - s_1) - \sum_j \left(\frac{Q_j}{T_j} \right)_{12}$$

Open system:
$$\Delta \sigma = \sum_e (\dot{m} s) - \sum_i (\dot{m} s) - \sum_j \left(\frac{\dot{Q}_j}{T_j} \right)_{ie}$$

Filling system:
$$\Delta\sigma = m_2s_2 - \sum_i(ms) - m_1s_1 - \sum_j\left(\frac{Q_j}{T_j}\right)ie$$

Emptying system:
$$\Delta\sigma = \sum_e(ms) + m_2s_2 - m_1s_1 - \sum_j\left(\frac{Q_j}{T_j}\right)ie$$

The product of the environment temperature T_0 with $\Delta\sigma$ is called the irreversibility, I_{ie} , of the process. Therefore, either entropy generation or irreversibility can be used to discuss the given situation. It is not important which choice is made. It is this irreversibility that gives rise to pollution and degradation of the environment leading to unsustainability of the present quality of life in nature.

2.9 Exergy

Exergy or available energy is the capacity to perform useful work with a given amount of energy. This can also be considered as the taxation of energy by nature. What nature is saying that although we may have an amount of energy that we should be able to use, the portion of that energy between the lowest available temperature T_0 [K] and 0[K] is the amount that is taken out by nature before any useful work can be obtained, $(T_0\Delta S)$. Unlike the government's share of our income as taxes, this amount is not negotiable. Therefore, this amount goes back to nature, unfortunately in the form of pollution. This result also states that if we want to produce useful products, such as electricity or transportation, we agree to pollute the environment.

Thus to be conscious of our responsibilities to our and future generations, better conversion technologies and conservation seem to be the only immediate solutions since any power generation MUST produce pollution of some sort that we may not be able to accept. Intelligent use of resources, therefore, must happen; otherwise the consequences are not very desirable.

The exergy formulation for the systems that we are interested in are as follows:

Closed system:

$$A_{12} = \sum_j Q_j \left(1 - \frac{T_0}{T_j}\right) + (U_1 - U_2) + p_0(V_1 - V_2) - T_0(S_1 - S_2) - T_0\Delta\sigma$$

Open system:

$$A_{ie} = \sum_j \dot{Q}_j \left(1 - \frac{T_0}{T_j}\right) + \sum_i \dot{m} \left[(h - T_0s) + \frac{\bar{V}^2}{2} + gz \right] - \sum_e \dot{m} \left[(h - T_0s) + \frac{\bar{V}^2}{2} + gz \right] - T_0\Delta\sigma$$

Filling system:

$$A_{fe} = \sum_j Q_j \left(1 - \frac{T_0}{T_j} \right) + \sum_i m_i \left[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz \right] + m_1(u_1 + p_0 v_1 - T_0 s_1) - m_2(u_2 + p_0 v_2 - T_0 s_2) - T_0 \Delta \sigma$$

Emptying system:

$$A_{fe} = \sum_j Q_j \left(1 - \frac{T_0}{T_j} \right) - \sum_e m_e \left[(h - T_0 s) + \frac{\bar{V}^2}{2} + gz \right] + m_1(u_1 + p_0 v_1 - T_0 s_1) - m_2(u_2 + p_0 v_2 - T_0 s_2) - T_0 \Delta \sigma$$

Use of these equations will give us the availability of energy, or exergy, for maximum obtainable work in any given system.

2.10 Non-measurable Thermodynamic Properties

The classical method of eliminating non-measurable thermodynamic properties is successive use of the Maxwell relations. However, this method is very time consuming at times since one does not know exactly in which direction the elimination must take place. Sometimes, due to this uncertainty, it does not work. There is a method, however, called the method of Jacobians which accomplish the same result in a very systematic way without any guess work, Somerton and Arnas (1985). Although the method was first introduced 50 years prior to this, the only text known that discusses these is that of Callen (1960).

This methodology has been used extensively to explain certain thermodynamic phenomena, to design experiments, and to eliminate the non-measurable thermodynamic properties, Arnas (2000). The measurable thermodynamic properties are p , T , V . Also the specific heats at constant pressure and volume, respectively, $c_p = T \left(\frac{\partial s}{\partial T} \right)_p$ and $c_v = T \left(\frac{\partial s}{\partial T} \right)_v$, the coefficient of thermal expansion,

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p, \text{ and the isothermal compressibility, } \kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \text{ of substances,}$$

can be measured. Using these parameters and since thermodynamic properties are mathematically well-behaved functions, namely the order of differentiation does not make any difference, i.e., $\left[\frac{\partial}{\partial X} \left(\frac{\partial Z}{\partial Y} \right) \right] = \left[\frac{\partial}{\partial Y} \left(\frac{\partial Z}{\partial X} \right) \right]$, the elimination of the non-measurable properties becomes simple.

In general, the Maxwell relations are obtained from $\{dZ = M dX + N dY\}$ as $\left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial N}{\partial X} \right)_Y$. Since $U = U(S, V)$ then $dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$. Comparing this equation to the Gibbs' equation, $\{dU = T dS - p dV\}$, it is seen that

$\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -p$. Additionally, using the above property, we can get the equality $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$.

Similar equalities can be obtained using the other Gibbs equations that relate other properties, i.e., enthalpy, $H = H(S, p)$ and $\{dH = T dS + V dp\}$, the Gibbs function $G = G(T, p)$ and $\{dG = -S dT + V dp\}$, and the Helmholtz potential $F = F(T, V)$ and $\{dF = -S dT - p dV\}$. These are also useful in the elimination of some of the non-measurable terms and thermodynamic properties.

In Somerton and Arnas (1985), the theory as well as the use of the method is given. For the general equation of $\{dZ = M dY + N dX\}$, the Jacobian formulation can be written as $\{[Z, \xi] = M[Y, \xi] + N[X, \xi]\}$, where ξ is any other thermodynamic property. Also, the equalities $[Z, Z] \equiv 0$, $[Z, \xi] = -[\xi, Z]$, and $\left(\frac{\partial(X, Y)}{\partial(X, Y)}\right) = 1$ are very useful. From fundamentals of mathematics we have

$\frac{\partial Y}{\partial X} = \left(\frac{\partial Y}{\partial \xi}\right)\left(\frac{\partial \xi}{\partial X}\right)$. Using the first law of thermodynamics for a cycle, we get $\oint \delta Q = \oint \delta W$ since $\oint dU = 0$. In Gibbs form, $\{dU = T dS - p dV\}$ giving for a cycle $\int T ds = \int p dV$ which in Jacobian form becomes $[T, S] = [p, V]$. The systematic use of these will permit one to convert nonmeasurable terms into measurable ones including $p, V, T, c_p, c_v, \alpha$, and κ_T .

The general methodology, therefore, is

1. Write down the given in terms of Jacobians.
2. Reduce by Maxwell equations using the various Gibbs equations.
3. Use the definition of c_p, c_v, α , and κ_T to further reduce the given equation.
4. If everything is done correctly, the result should only contain $p, v, T, c_p, c_v, \alpha$, and κ_T . If not, an error has been made; you need to go back and redo everything.

If this methodology is not used, then one goes around and around until a solution is obtained and one does not know if the route taken is the correct one. The advantage of the method of Jacobians is that the result shows if a mistake has been made.

The examples given in Somerton and Arnas (1985) are for learning the methodology. We will also look at other relations and get the physical significance of some other important thermodynamic phenomena, for example, throttling,

$\mu = \left(\frac{\partial T}{\partial p} \right)_h = \left\{ \frac{1}{c_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] \right\}$, and the speed of sound in any medium,

$$c^2 = \left(\frac{\partial p}{\partial \rho} \right)_s = \left[\frac{\partial p}{\partial \left(\frac{1}{v} \right)} \right]_s = \left\{ - \left(\frac{c_p}{c_v} \right) v^2 \left(\frac{\partial p}{\partial v} \right)_T \right\}.$$

As an example, start with $c_v = T \left(\frac{\partial s}{\partial T} \right)_v$. Therefore, following the methodology given,

$$\text{STEP 1:} \quad \left(\frac{\partial s}{\partial T} \right)_v \equiv \frac{\partial(s, v)}{\partial(T, v)} \left(\frac{\partial(p, T)}{\partial(p, T)} \right) = - \left[\frac{\partial(s, v)}{\partial(p, T)} \right] \bigg/ \left[\frac{\partial(v, T)}{\partial(p, T)} \right]$$

STEP 2: However, the denominator is by definition $\{-v\kappa_T\}$. Therefore,

$$\begin{aligned} \left(\frac{\partial s}{\partial T} \right)_v &= \frac{1}{v\kappa_T} \left[\frac{\partial(s, v)}{\partial(p, T)} \right] = \frac{1}{v\kappa_T} \left[\left(\frac{\partial s}{\partial p} \right)_T \left(\frac{\partial s}{\partial T} \right)_p \right. \\ &\quad \left. - \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \right] \\ \left(\frac{\partial s}{\partial T} \right)_v &= \frac{1}{v\kappa_T} \left[\left(\frac{\partial s}{\partial p} \right)_T \left(\frac{\partial v}{\partial T} \right)_p - \left(\frac{\partial s}{\partial T} \right)_p \left(\frac{\partial v}{\partial p} \right)_T \right] \end{aligned}$$

Using the Maxwell relation, $\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p$, which comes from the Gibbs form of the Gibbs' function equation, and the definitions of c_p , α , and κ_T ,

$$\frac{c_v}{T} = \frac{1}{v\kappa_T} \left[-(\alpha^2 v^2) + \frac{c_p}{T} (v\kappa_T) \right]. \quad \text{Rearranging,} \quad \left[(c_p - c_v) = T v \frac{\alpha^2}{\kappa_T} \right]. \quad \text{For an}$$

ideal gas, this general result reduces to $(c_p - c_v) = \frac{\Re}{M}$, where $\Re$ is the Universal gas constant and M is the molecular mass of the ideal gas, a well-known relationship. It is also possible to show that for an incompressible substance, i.e., liquid water, $(c_p - c_v) = 0$ which says that for those we must just use $\underline{c}$ as the specific heat without any subscripts. For those substances for which we have tables, enthalpies must be used and not $\Delta h = c\Delta T$, another common mistake in literature, Çengel and Boles (2008). In analyzing other derivatives of interest, these methodologies become very useful as well when we go through those quantities, for

example, $\left(\frac{\partial U}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial p}\right)_T$, and their values for an ideal gas. In Arnas (2000) these along with other characteristics are further studied. The slope of various functions on the Mollier, an (h-s) diagram, i.e. $\left(\frac{\partial h}{\partial s}\right)_T = \left\{ T - v \left(\frac{\partial T}{\partial v} \right)_p \right\}$, $\left(\frac{\partial h}{\partial s}\right)_p$, $\left(\frac{\partial h}{\partial s}\right)_v$, and other thermodynamic diagrams, such as the (p-h) for refrigerants, i.e., $\left(\frac{\partial p}{\partial h}\right)_s = \left\{ - \frac{\left(\frac{c_p}{c_v}\right)}{p} \left(\frac{\partial p}{\partial v}\right)_T \right\}$, is also explained to clarify the physics involved; for an ideal gas, this reduces to $\left(\frac{\partial p}{\partial h}\right)_s = \frac{\left(\frac{c_p}{c_v}\right)}{v}$.

To obtain pressure-temperature relation for an ideal gas under reversible adiabatic conditions, we start with $\left(\frac{\partial p}{\partial T}\right)_s = \left[\frac{p, s}{T, s} \right] = - \left[\frac{s, p}{T, s} \right]$. Substituting for the numerator and the denominator from Jacobian properties, then we get

$\left(\frac{\partial p}{\partial T}\right)_s = \frac{-\frac{c_p}{T} [T, p]}{[p, v]} = \frac{c_p}{T} \left(\frac{\partial T}{\partial v}\right)_p$, which is a general result. Using the ideal gas equation, the partial derivative on the right can be evaluated. Using the difference between the two specific heats for an ideal gas, as was shown above, the result becomes $\left(\frac{\partial p}{\partial T}\right)_s = \frac{p c_p}{T \left(\frac{\mathfrak{R}}{M}\right)} = \frac{p}{T} \left(\frac{k}{k-1}\right)$ where k is the ratio of the specific heats,

$\left(k = \frac{c_p}{c_v}\right)$. Therefore, $\left(\frac{dp/p}{dT/T}\right) = \frac{k}{k-1}$ which upon integration gives the well-

known result $\left[T = p^{\frac{k-1}{k}}\right]$. This result is only valid if we have an ideal gas which

undergoes a reversible and adiabatic, constant entropy, process. Again, this fact is not trivial and must be kept in mind before this result can be used. Similar results

can be obtained for $\left(\frac{\partial v}{\partial T}\right)_s = -\frac{c_v}{T} \left(\frac{\partial T}{\partial p}\right)_v$, in general, and when applied to an ideal

gas would give $\left(\frac{dv/v}{dT/T}\right) = -\left(\frac{1}{k-1}\right)$ or $[T = v^{1-k}]$. For $\left(\frac{\partial p}{\partial v}\right)_s$ we get the result, in general, $\left(\frac{\partial p}{\partial v}\right)_s = k\left(\frac{\partial p}{\partial v}\right)_T$. This equals for an ideal gas $\left(\frac{dp/p}{dv/v}\right) = -k$ giving $[p = v^{-k}]$.

The total intent in all this was to verify the physics of the situation using mathematics. Mathematics is just a tool to totally explain these physical phenomena that characterize nature. Nature is what physics is; mathematics is the explanation mechanism and nothing more.

2.11 Design of Experiments

In engineering, experimental verification of analysis or computational results is extremely important. For that, it is necessary to design experiments. Experiments can only be designed for those parameters for which we can make measurements. As was discussed before, the measurable parameters in thermodynamics are p , T , V , c_p , c_v , α , and κ_T . Therefore, the designed experiment can only involve these parameters.

As an example of this important issue, consider the Clausius' equation which is $\left(\frac{dp}{dT}\right)_{\text{saturation}} = \left\{\frac{Q_{12}}{T(v_2 - v_1)}\right\}$. By considering the T - s diagram, it is obvious that the heat transferred is equal to $Q_{12} = T(s_2 - s_1)$. From the Gibbs' equation for enthalpy, $\{dh = T ds + v dp\}$, and since at saturation the pressure and temperature are constants, then $\{dh = T ds\}$ giving $[(h_2 - h_1) = T(s_2 - s_1)]$. Upon substitution, $\left(\frac{dp}{dT}\right)_{\text{saturation}} = \left\{\frac{(h_2 - h_1)}{T(v_2 - v_1)}\right\}$, where 2 refers to the saturated vapor state, g, and 1 to the saturated liquid state, f. Therefore, the Clausius equation becomes $\left(\frac{dp}{dT}\right)_{\text{saturation}} = \frac{h_{fg}}{Tv_{fg}}$.

Clapeyron modified this equation by making certain assumptions. The first assumption is that $v_g \gg v_f$ which is an acceptable one since the vapor specific volume is much greater numerically than the liquid specific volume, as can be seen in the Steam Tables, Çengel and Boles (2008). The second assumption is that of an ideal gas for the vapor, i.e., $v_g \cong v = \left(\frac{\Re}{M}\right)\left(\frac{T}{p}\right)$ which, upon substitution,

makes the Clausius equation $\left(\frac{dp}{dT}\right)_{\text{saturation}} = \left(\frac{h_{\text{fg}}}{\left[\frac{\mathfrak{R}}{M}\right]}\right)\left(\frac{p}{T^2}\right)$. Collecting like terms,

this equation reduces to $\left[\frac{\left(\frac{dp}{p}\right)}{\left(\frac{dT}{T^2}\right)}\right] = \left[\frac{h_{\text{fg}}}{\left[\frac{\mathfrak{R}}{M}\right]}\right]$. Considering that h_{fg} is a constant, an

assumption that needs to be verified for the design of the experiment, and integrating and simplifying, the Clausius–Clapeyron equation is obtained as

$$\left[\frac{d(\ln p)}{d\left(\frac{1}{T}\right)}\right] = -\left[\frac{h_{\text{fg}}}{\left[\frac{\mathfrak{R}}{M}\right]}\right], \text{ which is only valid if } v_g \gg v_f \text{ and we have an ideal gas for}$$

constant h_{fg} . All of these three assumptions must be satisfied before the results of the experiment can have any significance. Therefore in the design of the experiment we must consider these facts very carefully.

In designing an experiment, the first assumption for the Clausius–Clapeyron equation is satisfied when one looks at the Steam Tables, Çengel and Boles (2008), to compare the numerical values of the specific volume as a vapor and a liquid. The second assumption, an ideal gas, requires some more discussion. When we look at the compressibility diagram for substances, we see that the compressibility for all substances approach unity, meaning they approach the characteristics of an ideal gas, as the reduced pressure of the substance approaches zero,

i.e., $Z \Rightarrow 1$ as $p_{\text{reduced}} = \frac{P}{P_{\text{critical}}} \Rightarrow 0$. This result signifies that the experiment

must take place at low real pressures, i.e., below atmospheric, since the critical pressure for steam is 22.09 MPa to make sure that we are approaching zero for the reduced pressure to guarantee ideal gas situation. Finally, constant h_{fg} assumption requires that the measurements must take place at a pressure an increment above and an increment below the saturation pressure under investigation. By taking this increment small and splitting it up for as many precise measurements as possible, all that is needed to do is to plot $(\ln p)$ versus $\left(\frac{1}{T}\right)$ using the absolute temperature.

The slope of the line is negative, as the Clausius–Clapeyron equation requires, and will give the value h_{fg} once the molecular mass of water is used. Other fluids can also be used in this experiment; the only requirement is to make sure that $Z \Rightarrow 1$

and $p_{\text{reduced}} = \frac{P}{P_{\text{critical}}} \Rightarrow 0$ for the liquid that is used.

For the speed of sound or the Joule-Thomson coefficient similar experiments can be designed, constructed, and experimental results can be obtained once their measurable forms are derived, as was done above. This methodology is good for any quantity for which an experiment is to be designed; the important thing to keep in mind is the assumptions under which the result is obtained. If any one of the assumptions is not met, then the experiment will not give the expected results.

This, of course, is not different from any scientific/engineering analysis or experiment. The results obtained are only as good as the assumptions made and the results are only valid under those assumptions. This may sound trivial but we will show that it is a mistake made quite commonly by researchers and/or authors of textbooks.

2.12 Errors Made in Literature

When one studies the literature carefully, one does find fundamental errors made due to the fact that simple understanding of thermodynamics is lacking. As we have already discussed very early on the state principle and the fact that any two independent intensive thermodynamic properties are sufficient to define a thermodynamic state, it is really of no consequence which two are selected since the final result has to be unique.

Chawla (1978) selects three different combinations of properties to determine the speed of sound. In the first case, the variables selected are the velocity, the pressure, and the enthalpy. The result for the speed of sound turns out to be

$$c^2 = \frac{1}{\left(\frac{\partial \rho}{\partial p}\right)_h + \frac{1}{\rho} \left(\frac{\partial \rho}{\partial h}\right)_p} \text{ where } \rho \text{ is the density, inverse of } v. \text{ The second case is}$$

for the velocity, density, and pressure. This time the result obtained be-

$$\text{comes } c^2 = \frac{-\rho \left(\frac{\partial h}{\partial \rho}\right)_p}{\rho \left(\frac{\partial h}{\partial p}\right)_\rho - 1}. \text{ The third case is for the velocity, pressure and temper-}$$

$$\text{ature. The result obtained is } c^2 = \frac{1}{\left\{ \frac{\left[-\left(\frac{\partial \rho}{\partial T}\right)_p \right]}{\rho c_p} \right\} \left[\rho \left(\frac{\partial h}{\partial p}\right)_T - 1 \right] + \left(\frac{\partial \rho}{\partial p}\right)_T}.$$

However, from the definition of the speed of sound, $c^2 = \left(\frac{\partial p}{\partial \rho}\right)_s$ and using the

methodology given above, it is indeed very simple to show that the analytical result is $c^2 = -v^2 \left(\frac{\partial p}{\partial v} \right)_s = -v^2 \left[\frac{p,s}{v,s} \right] = -v^2 \left(\frac{c_p}{c_v} \right) \left(\frac{\partial p}{\partial v} \right)_T$.

No matter which two properties along with the velocity are chosen, this is the result that must be obtained. Results are obtained in terms of non-measurable properties which are consequently solved numerically, Chawla (1978). Since the series variation of these properties do not have the same character, numerical truncation errors result in different forms for the answers. The author then tries to justify why they are different. However, we have seen that the result has got to be unique, the state principle, and it is demonstrated once again by Arnas (2000). All three results above are analytically the same, as it should be. Numerically, they are not! Therefore, a fundamental understanding of thermodynamics is very important to explain physical phenomena.

2.13 Shortcomings of textbooks

Apart from the shortcomings of books on thermodynamics, and there are many, similar shortcomings exist in other textbooks because of lack of being precise that discuss, for example, heat transfer which is an applied course heavily dependent on thermodynamic principles. The student is learning from the textbooks; therefore, they trust the contents as they must. However, if the topics are not precisely covered, then they learn the wrong material.

As an example, we will consider condensation phenomena since it is an important process in thermodynamics, as we have discussed above in the case of the Clausius–Clapeyron equation and the steam experiment, and since we must design condensers for technological purposes, using heat transfer. When one considers the condensation phenomenon as discussed in textbooks, also as was done by Arnas et al. (2004), there are many assumptions that are made to be able to analyze the physical situation. Unfortunately in all of these, the assumptions that are made are not justified for the final result. The final result is the same in all of the references, the only thing different are the symbols used. However, the student does not know if a given situation actually satisfies all the assumptions made. Therefore, for all situations, the only design equation is the one found in the texts and that one is used blindly. It is indeed possible to find situations where anyone of these conditions is not met which would make the equation useless. In Arnas et al. (2004) not only is the result obtained very rigorously and in a very clear and analytical fashion, the conditions under which the result is valid are also very clearly given so that the user, the student, the researcher, or the design engineer is able to ascertain if the problem actually fits the final design equation for convection in condensation.

In another study by Arnas et al. (1980), it was shown that the two-phase flow design equations are not usable under all conditions since they tend to decrease the entropy generation for certain combinations of flow rates and geometries, a condition that violates the second law of thermodynamics. Naturally,

under those conditions the equations cannot be used for design purposes and other correlations must be searched.

What has been attempted here is to show the importance of correct use of precise thermodynamics in teaching of thermodynamics as well as in all other fields of science and technology. If it is not used precisely, errors are made that could affect the designed equipment or lead to disastrous situations in extreme cases. In engineering we cannot make mistakes since, unlike the doctor, we do not kill one person at a time! Our failures are watched and seen by the whole world, for example the Space Shuttle disaster. We must teach well, in a correct way, and precisely and demand of our students at all levels the same precision in their work, Arnas (2005). Only in that fashion can we be sure that the next generation of engineers/scientists understands the critical ramifications of what is at stake. This is more important than anything else that we can teach our students, their understanding and appreciation of the importance of their precise work.

2.14 Conclusions

In this chapter, the precise teaching of thermodynamics has been emphasized since these topics are used in other fields of science and technology. The textbooks must be correct giving the precise description of systems, equations, and conclusions. Otherwise the students learn the wrong information and apply it in the same fashion. It has also been shown that methodologies exist for physical interpretation of mathematical expressions in thermodynamics by eliminating nonmeasurable quantities such as entropy, designing thermodynamic experiments, and investigating various applications in other fields of science and technology that use thermodynamic principles. The emphasis has been on correct and precise work, a quality that we must impose on our students. This type of instruction would ultimately affect students who are aware of the nature, the effect of everyday usage of energy on the environment, and what needs to be done within the restrictions of nature to be sustainable at least at the levels that we enjoy today. Of course, these must be done in all aspects of education not only in the education of engineers, in general, and thermodynamics education, in particular. Success in this will make life better now and forever.

The previous pages have emphasized undergraduate work. It is indeed very important to extend this into statistical and non-equilibrium thermodynamics for graduate students. The challenges of energy use, pollution, and sustainability all depend on clear, precise, and correct study of these and appropriate applications. It can and should be pursued very aggressively throughout.

Acknowledgment

The view expressed herein are those of the author and do not purport to reflect the position of the United States Military Academy, the Department of the Army, or the Department of Defense.

Nomenclature

A	Area (m^2)
B	Any extensive thermodynamic property
b	Any intensive thermodynamic property, $b=B/m$
c	Specific heat ($\text{kJ}/(\text{kg}\cdot\text{K})$); also speed of sound (m/s)
E	Energy (kJ)
e	specific energy (kJ/kg)
F	Helmholtz potential (kJ)
G	Gibbs free energy (kJ)
H	Enthalpy (kJ)
h	Specific enthalpy (kJ/kg)
k	Ratio of specific heats, $k=(c_p/c_v)$
M	Molecular mass (kmol); also arbitrary function
m	Mass (kg)
$\dot{m}$	Mass flow rate (kg/s)
N	Arbitrary function
n	Unit vector
p	Pressure (kPa)
Q	Heat (kJ)
$\mathfrak{R}$	Universal gas constant ($\text{kJ}/(\text{kmol}\cdot\text{K})$)
S	Entropy (kJ/K)
s	Specific entropy ($\text{kJ}/(\text{kg}\cdot\text{K})$)
T	Temperature (K)
t	Time (s)
U	Internal energy (kJ)
u	Specific internal energy (kJ/kg)
V	Volume (m^3)
v	Specific volume (m^3/kg)
$\vec{V}$	Velocity (m/s)
W	Work (kJ)
X	Arbitrary function
Y	Arbitrary function
Z	Arbitrary function; also compressibility factor (-)
z	Elevation (m)

Greek symbols

α	Coefficient of thermal expansion ($1/\text{K}$)
β	Coefficient of performance for a refrigerator
γ	Coefficient of performance for a heat pump
Δ	Difference
δ	Increment
η	Efficiency for an engine
Θ	Angle ($^\circ$)
κ_T	Isothermal compressibility ($1/\text{kPa}$)
μ	Joule–Thomson coefficient (K/kPa)
ξ	Arbitrary thermodynamics property
ρ	Density (kg/m^3)
σ	Entropy generation (kJ/K)

Subscripts

E	Engine
CE	Carnot engine
CV	Control volume
f	Liquid phase
fg	Phase change from liquid to vapor
g	Vapor phase

H	High
L	Low
v	Volume
p	Pressure
o	Atmospheric

References

- Arnas, AÖ (2000) On the Physical Interpretation of the Mathematics of Thermodynamics. *International Journal of Thermal Sciences* 39: 551–555.
- Arnas, AÖ (2005) Education, Energy, Exergy, Environment – Teaching Teachers to Teach Thermodynamics, Proceedings, Second International Exergy, Energy and Environment Symposium-IEEEES2, Kos, Greece, #167.
- Arnas, AÖ, Hendrikson, HAM, van Koppen, CWJ (1980) Thermodynamic Explanation of Some Numerical Difficulties in Multiphase Flow Analyses, Proceedings, European Two-Phase Flow Group Meeting, Glasgow, Scotland, F4.
- Arnas, AÖ, Boettner, DD, Bailey, MB (2003) On the Sign Convention in Thermodynamics-An Asset or an Evil, Proceedings, ASME-IMECE2003, IMECE2003-41048. Also, Boettner, DD, Bailey, MB, Arnas, AÖ (2006) On the Consistent Use of Sign Convention in Thermodynamics, *International Journal of Mechanical Engineering Education* 34/4: 330–348.
- Arnas, AÖ, Boettner, DD, Benson, MJ, van Poppel, BP (2004) On the Teaching of Condensation Heat Transfer, Proceedings, ASME-IMECE2004, IMECE2004-50277.
- Callen, HB (1960) *Thermodynamics*, Wiley.
- Çengel, YA, Boles, ME (2008) *Thermodynamics—An Engineering Approach*, 6th Edition, McGraw-Hill.
- Chawla, TC (1978) On Equivalency of the Various Expressions for Speed of Wave Propagation for Compressible Liquid Flows with Heat Transfer, *International Journal of Heat and Mass Transfer* 21: 1431–1435.
- Mooney, DA (1953) *Mechanical Engineering Thermodynamics*, Prentice-Hall.
- Obert, EF (1960) *Concepts of Thermodynamics*, Wiley.
- Somerton, CW, Arnas, AÖ (1985) On the Use of Jacobians to Reduce Thermodynamic Derivatives, *International Journal of Mechanical Engineering Education* 13–1: 9–18.
- Zemansky, MW (1943) *Heat and Thermodynamics*, Wiley.

Role of Renewable Energy in Sustainable Development

Anand S. Joshi, Ibrahim Dincer and Bale V. Reddy

3.1 Introduction

The conversion of energy is directly related to the pollution in terms of greenhouse gas emission caused by the power plants. The major greenhouse gases like carbon dioxide and carbon monoxide are causing global warming to the environment and hence there is a need to find out alternatives to produce energy in an environmentally benign way. The photovoltaic technology, amongst the others, is one that can be a novel alternative to this problem. The renewable energy sources such as hydro, solar, biomass, wind, geothermal, tidal, wave, ocean thermal are beneficial for electricity production as they cause less greenhouse gas emission into the atmosphere. Some of the renewable technologies like geothermal can be beneficial as it has an ability to provide power continuously whereas some (solar, wind) can provide it continuously by using a storage device like battery. Hydro uses the immense potential energy from water to produce electricity but the social impact is also large as it requires displacement of people to build a dam or retaining wall. The solar energy technology is acceptable in this regard and beneficial for rural development. The solar energy applications in photovoltaic can be beneficial wherever the electrical energy is needed. Based on the requirement of electrical energy various systems came into existence. The photovoltaic technology is pollution free and it uses solar energy that is freely and immensely available. Another advantage with the PV technology is that it causes less harm to the environment in terms of greenhouse gas emission during the operation and hence is environment friendly. The intermittency of solar radiation can be a limitation to the technology as it cannot supply electricity continuously during the off sunshine periods, but this problem can be encountered by using battery storage. However, there is a need to understand the application of this technology to make it feasible for its users. For example, to water a field, a farmer can use a solar water pumping system during day time and get benefited by the technology as he does not have to worry about the unwanted load shedding or power failure or to pay bills for the electrical

power consumptions. Another example could be solar street lighting; the electricity converted by PV panels during the sunshine hours can be stored in a battery and can be utilized to power the street lights in the off sunshine periods.

In this chapter, we aim to discuss and compare the non-conventional (renewable) energy sources for electricity generation and their role in sustainable development. The impact of electricity generation on environment by the various renewable sources namely hydro, solar, biomass, wind, geothermal in terms of greenhouse gas emission is also discussed. Solar energy application in photovoltaic technology is discussed for different types of photovoltaic systems and their various applications other than electricity production. An analysis is performed based on exergy efficiency for photovoltaic systems. The sustainability index is also studied as a key parameter with the exergy efficiency for better sustainability of the system.

3.2 Environmental Impact

In this section the environmental impact of the above-said non-conventional (renewable) sources of energy would be discussed in terms of equivalent carbon dioxide emission into the atmosphere. Figure 3.1 shows the equivalent CO₂ emission for different energy sources for direct and indirect carbon dioxide emissions. The former is used for the emission during the operation whereas the latter is responsible for CO₂ emission other than the operation, say, during the installation of a system.

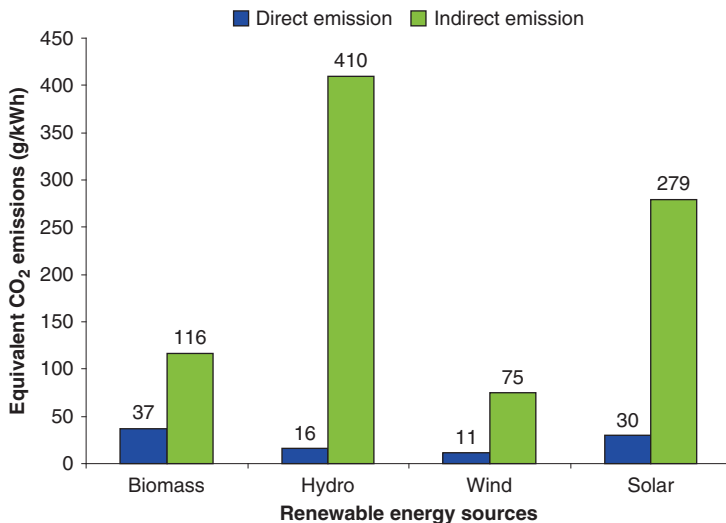


Fig. 3.1 Worldwide CO₂ emission into the atmosphere from various energy sources (data from IAEA, 2001).

It can be seen that the direct emissions per kWh electricity generation from the wind, biomass, hydro, and solar are 37, 16, 11, and 30 g/kWh and indirect emissions are 116, 410, 75, and 279 g/kWh, respectively. Some of the renewable technologies, i.e., hydro and wind, are competitive with conventional technologies as they have better efficiencies. Table 3.1 shows that the conventional technologies like coal and gas are more economical for per kWh electricity generation but they pollute the environment more. However, the price of per kWh electricity generation for coal and gas is lower than the renewable energy sources which is also given in Table 3.1.

Table 3.1 Mean price, efficiency of electricity generation, and average greenhouse gas emissions expressed as CO₂ equivalent for individual energy generation technologies.

Energy Sources	US\$/kWh	Efficiency (%)	gCO ₂ /kWh
Photovoltaic	0.24	4–22%	90
Wind	0.07	24–54%	25
Hydro	0.05	>90%	41
Geothermal	0.07	10–20%	170
Coal	0.042	32–45%	1004
Gas	0.048	45–53%	543

Source: Evans et al. (2009).

On the other hand the renewable energy sources are either cost-effective (for example, wind, biomass, and geothermal) or less polluting the environment. Further, the electricity generation efficiency of the different technologies is given in the same table and it is clear that some renewable sources (for example, wind and hydro), which possess better efficiency, are competitive with the conventional technology (coal, gas, etc.).

The greenhouse gases are responsible for global warming and climate change. Other than CO₂ some other pollutants like SO_x, NO_x, and CFCs, etc., also affect the environment adversely. Some other environmental problems are acid rains, ozone layer depletion, etc. Former is caused due to SO_x and NO_x whereas latter is due to CFCs, CO, and the unbent hydrocarbon from the exhaust of rockets.

Table 3.2 Sustainability indicators for some renewable energy sources.

	Photovoltaic	Wind	Hydro	Geothermal
Price	4	3	1	2
CO ₂ emission	3	1	2	4
Availability and limitations	4	2	1	3
Efficiency	4	2	1	3
Land use	1	3	4	2
Water consumption	2	1	3	4
Social Impact	2	1	4	3
Total	20	13	16	21

Source: Evans et al. (2009).

Evans et al. (2009) have given some sustainability indicators for some renewable technologies; each technology was ranked from 1 to 4 according to the corresponding indicator as shown in Table 3.2, with 1 being the best technology for that indicator. The average and range were considered together, where values were quantifiable, as there was often significant overlap between values.

Some impact categories, such as availability and limitations as well as social impacts that are unable to be quantified, were assessed qualitatively. In case of limitations, hydro was chosen as the least limited, due to its ability to provide base load power, number of suitable sites worldwide, and flexibility of operation. Wind was considered the second best for similar reasons. Geothermal is slightly more limited worldwide, with less suitable locations. Solar is considered the most limited, since excess power during daylight hours is not yet able to be stored enough to provide adequate power during off sunshine periods (nights and on cloudy days). As far as social impacts were concerned, wind was allocated the least negative social impacts, due to its benign nature. Solar was second, as careful management during manufacture and proper site selection mitigate its potential negative impacts, and geothermal was third due to increased seismic activity and pollution potential. Hydro had the largest impact, primarily due to the large number of people and animals displaced during dam inundation. The ranking in Table 3.2 suggests electricity production from wind is the most sustainable followed by hydropower and then solar and geothermal were found to rank the lowest from the four non-combustion renewable energy technologies (Evans et al., 2009). This ranking was provided for the global international conditions, while each technology can be significantly geographically affected. For a certain geographical location, some of the listed sustainability indicators may become more important than others.

3.3 Electricity Generation from Renewables

There are many conventional and non-conventional ways by which electricity can be produced. One of the conventional ways is to produce electricity by using fossil fuels. Coal-based power plants are the mostly used method to produce electricity. They are also referred to as thermal power plants. Though the energy produced by a thermal power plant is more economical as compared to non-conventional sources, it also causes greenhouse gas emission at a higher rate and hence called “dirty.” On the contrary the photovoltaic system causes no harm to the environment as it uses solar energy which is also called “clean energy” but the electricity produced by it is not economical as the photovoltaic material used to produce solar cells are costly and for off sunshine period the energy needs to be stored in a storage device like battery. In this section we will discuss both the non-conventional and conventional sources for electricity generation.

3.3.1 Hydro

Hydro-based power plants use the potential energy of water to generate electricity. Water of a river is allowed to keep its level up with the help of a retaining wall or

dam across the width of the river and on the other side of the wall/dam the water turbines are installed. The potential energy of water is then used to run turbines and then turbines run generators and produce electricity. The electricity is then supplied to the grid from where it is distributed to its users. Pelton wheel and Francis turbines are generally used for high water heads and the Kaplan turbines can be used for low water heads. Mini hydel power stations can also be built to fulfill the electrical demand of a community living near small rivers and where water head is not enough for big hydro power plants. Hydro power plants are more eco-friendly than the thermal power plants as they produce less harm to the atmosphere but they require community relocation for those who live near the river and hence sometimes face substantial public resistance.

3.3.2 Solar

The solar energy can be utilized either to convert the light into electricity through photovoltaic system or for heat generation. The estimated potential of the direct capture of solar energy for the above-said systems is enormous. After reflection by the atmosphere, Earth's surface receives around 3.9×10^{24} MJ incident solar energy per year which is almost 10,000 times more than current global energy consumption. Thus, the harvesting of less than 1% of photonic energy would serve all human energy needs (Markandya and Wilkinson, 2007). Photovoltaic systems, as discussed above, are a novel approach to the electricity generation as it uses solar energy which is freely available. Though the intermittent nature of solar radiation limits the use of this technology up to some extent, still for off sunshine periods the stored energy in a battery bank can be used. Photovoltaic systems can be used not only as stand-alone systems but also as connected to grid systems to supply continuous electricity throughout a day. The efficiency of the solar cell can range from 12–15 % typically for the silicon solar cell. However, it is as high as 25–30% for GaAs solar cells. The cost of the former is less as compared to the latter and the latter is used mostly for space applications. The efficiency of the photovoltaic system can also be calculated by taking the product of the efficiencies of its various components like solar cell, module, battery, etc. From a health perspective, the potential benefits of solar energy applications seem very desirable.

3.3.3 Biomass

Biomass can also be used as an alternative as it has a large stored potential of renewable energy, which can be utilized to produce power by combustion or by thermo-chemical or biochemical conversion to liquid (ethanol, methanol) or gaseous fuels (methane, hydrogen) (Sorensen, 2004). However, the inherent inefficiency of photosynthesis, which captures only a small percentage of solar energy reaching the Earth's surface, limits its usefulness as a major energy source (Miyamoto, 1997). Some high-yielding crops, for example, South American sugar cane, are already being used successfully as fuel sources mainly for transport. Bioelectricity can be an important option in supporting electricity needs particularly of rural populations in lower income countries. Furthermore, the production

of electricity using biomass has some health consequences but is still well below those from coal, oil, and natural gas.

3.3.4 Wind

Wind mills and horizontal-axis and vertical-axis turbines are used to convert the kinetic energy of the wind into electricity. It is one of the more cost-effective forms of renewable energy with today's technology. The electricity produced by wind energy can be supplied to grid. The technology is beneficial for the locations where the wind velocity is high, for example, the coastal and sub-coastal areas. For a better functioning of a wind energy system the knowledge of the natural geographical variation in wind speed is important so as to smooth out fluctuations. Similar to the limitations of solar energy, wind energy generation is also affected by the intermittent nature of wind speed.

3.3.5 Geothermal

Geothermal energy is limited to appropriate geographical sites or locations where the resource is present; however, there are many such sites worldwide, spread over 24 countries with an operating potential of 57 TWh/year (Bertani, 2005). Geothermal is attractive for its ability to provide base load power 24 h a day. Extraction rates for power production will always be higher than refresh rates. ReInjection helps restore the balance and significantly prolongs the life of the geothermal well. Geothermal emissions are most significantly impacted by technology choices. Waste gases are over 90% CO₂ by weight (Hammons, 2004), so if directly released, emissions will be high.

3.3.6 Others

Some other renewable sources can be tidal, wave, and ocean thermal technologies that can produce electricity or can help reduce the electrical load of a power plant. Tidal energy utilizes the power of tide to produce electricity whereas wave energy systems use the waves formed in an ocean or sea. Oscillators are placed in the sea and they oscillate when waves come in contact with them. This oscillatory motion is utilized to generate electricity. The ocean thermal technology uses the temperature difference between the upper and the deep lower level of ocean water. This thermal difference is utilized to generate electricity. In the next section the photovoltaic systems are discussed based on their applications.

3.4 Photovoltaic Systems

Photovoltaic is a novel technology that helps reduce the carbon dioxide emission into the atmosphere as it uses solar energy which is free from pollutions. Solar energy can be utilized into two ways:

- (i) photovoltaic and
- (ii) solar thermal applications.

The photovoltaic systems can be classified according to their use and applications. These systems can broadly be classified into two types: (1) photovoltaic (PV) systems

and (2) photovoltaic thermal (PV/T) systems. The first type can further be classified into space applications, stand-alone PV systems, grid-connected PV systems, photovoltaic hydrogen production systems, and miscellaneous small-scale applications whereas the second type can further be classified as PV/T air collector and PV/T water collector systems and others. Further, the stand-alone PV applications can be classified into two, agricultural water pumping and community or rural electrification. The PV/T air collectors can be used for agricultural greenhouse drying and space or room heating applications whereas the water collectors can be used for domestic and industrial water heating, water distillation (hybrid solar stills), space heating, etc. Some other miscellaneous applications of the PV and PV/T systems are also described later in this section. Now we will refer to each application one by one.

3.4.1 Photovoltaic (PV) applications

The photovoltaic applications can be beneficial wherever the electrical energy is needed. The photovoltaic technology has always had an upper edge on other technologies as it is pollution free and it uses solar energy that is freely and immensely available. Here, in this section, we are discussing various photovoltaic applications based on their performance in terms of efficiency.

3.4.1.1 Space applications

Probably this was the very first application of photovoltaic that it was started in 1958 and used in space craft and satellites. The efficiency of the PV panels was 6%. The lightweight PV panels were used to power the space craft/shuttle for their electrical demands in space. In space PV cell technology, GaAs-based cells are now mature and space qualified. High-efficiency thin Si cells give good and impressive performances when price, weight, maturity, and efficiency are balanced. The efficiency of Si cells, high-efficiency Si cells, double junction, triple junction, and quadruple junction solar cells are 13.5%, 16%, 22%, 25%, and 28%, respectively (Habraken, 2001).

3.4.1.2 Stand-alone systems

The prime objective of stand-alone system was to support the farmers for their electrical demand for agricultural water pumping and for community and rural electrification. The community schools, hospitals and other government buildings were also benefited with this technology. Figure 3.2 shows a solar water pumping system as an example of stand-alone system. The farmers require water to irrigate their fields and the stand-alone photovoltaic systems can be used for that. The DC water pump uses electricity generated by the photovoltaic panels and then pumps water from a well to the fields.

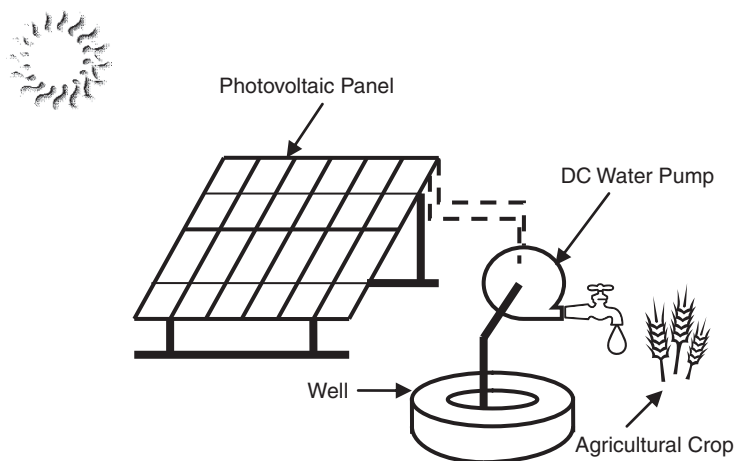


Fig. 3.2 Schematic diagram of an agricultural solar water pumping stand-alone system as an example of PV application.

3.4.1.3 Grid-connected PV systems

Attempts have already been made to connect a series of PV panels to generate a higher amount of electricity that can directly be given to the grid. To analyze the performance of a grid-connected PV system, certain parameters are important; they are yields (reference, array, and final), losses (array capture and system losses), PV and inverter efficiencies, and performance ratio. Based on above-said parameters Mondol et al. (2006) have examined the performance of a 13 kWp grid-connected photovoltaic system in Northern Ireland and found that the monthly average daily PV, system, and inverter efficiencies varied from 4.5 to 9.2%, 3.6%, to 7.8%, and 50% to 87%, respectively. The annual average PV, system, and inverter efficiencies were 7.6, 6.4, and 75%, respectively. The monthly average daily DC and AC performance ratios ranged from 0.35 to 0.74 and 0.29 to 0.66, respectively. The annual average monthly AC performance ratios for the 3 years were 0.60, 0.61, and 0.62, respectively.

3.4.1.4 Hydrogen production

PV panels can be utilized to produce hydrogen by electrolysis of water using the electricity produced by it. It needs higher and extensive research in this area as the hydrogen produced by this technology is not cost-effective as the PV technology is costly. The end product of the electrolysis was also oxygen. The electrolysis of distilled water using electricity produced by the PV panel takes place in electrolyzer unit and produces hydrogen and oxygen as the end product. Yilanci et al. (2009) have defined the performance of a solar-based hydrogen production system based on energy and exergy analysis of PV, charge regulators, inverter, and electrolyzer. They calculated the exergy efficiency of PV panel as (minimum–maximum) 9.8–11.5%, charge regulator as 85–90%, inverter efficiency as 85–90%

and the electrolyzer efficiency as 52% and energy efficiency of PV panel as (minimum–maximum) 11.2–12.4%, charge regulator as 85–90%, inverter efficiency as 85–90%, and the electrolyzer efficiency as 56%. Based on the exergy and energy efficiencies of each component one can calculate the overall exergy and energy efficiencies of the system by taking the product of respective efficiencies of each components. The exergy efficiency of the system is calculated as (minimum–maximum) 3.68–4.32% and the energy efficiency as (minimum–maximum) 4.53–5.02%.

3.4.1.5 Other applications

Another application of the PV technology is to use the PV panels on the rooftop of cars to harvest the solar energy and utilize the electricity produced to charge the batteries which further runs an electrical motor to power the car (Gaddy, 2003). This technology is still under development and can result in future generation automobiles. The street lights, traffic signals, solar lanterns, calculators, watches, dc fans, dc motors, inverters, etc., are some other applications of PV technology.

3.4.2 Photovoltaic thermal (PV/T) applications

The PV/T systems came into existence with an idea to utilize the thermal energy of the sun along with the electricity. Use of thermal energy also improves the energy and exergy efficiency and helps to maintain a good electrical efficiency of the PV system throughout its operation. The thermal energy available on the PV surface can be utilized for low potential works such as water and air heating. Further, the hot water/air can be utilized for various applications, for example, to heat up living space, greenhouse, solar dryers, solar stills, etc. In the next section we will discuss about the PV/T air and water collectors and their applications. Some potential applications of the technology are also discussed in brief at the end of this section.

3.4.2.1 PV/T air collector

A photovoltaic thermal air collector utilizes solar energy for both electricity generation and thermal application. A greenhouse dryer is used to dry the agricultural products using solar energy so that it can be stored for longer duration. If a PV/T air collector is attached to the dryer, this would add more thermal energy to it and the drying process would be faster. The greenhouse drying can be done for both natural and forced mode of air circulation.

Another application of this technology is to heat the living space. The space heating application further involves two types and they are transparent PV panels mounted on the roof of a building and PV panels installed on the ground and coupled with a living space. The former is an example of natural mode of heating a building as the transparent PV modules allow solar radiations to get inside the

building and heat the living space whereas the latter is an example of forced mode as it uses a blower or a small fan to circulate the room air to come in contact with the collector and get heated. A PV/T air heater can be coupled with a building or living space as well. Charalambous et al. (2007) suggested that the building integrated PV/T collectors are most suited for low climatic conditions to lower the temperature of the PVs and supply the hot air for space heating. The greenhouse technology is also benefited with the use of the PV applications in order to maintain controlled environment in terms of temperature and humidity. Greenhouse may use a transparent photovoltaic panel mounted on the roof for its electrical demand to run electrical motors, fans, and blowers to maintain the desirable environment suitable for the crop production. Transparent panel also allows solar radiation to pass through it and heat the greenhouse environment.

3.4.2.2 PV/T Water Collector

Similar to the air collectors, water collectors are used to heat up the water for various domestic and industrial applications. The domestic water heater generally uses flat plate collectors in parallel connection and runs automatically with the thermo-siphon action whereas the industrial water heater uses a number of flat plate collectors in series and the thermo-siphon action does not work in this case and hence it uses a photovoltaic-driven water pump to maintain flow of water inside the water collector. A schematic diagram of a PV/T water collector is shown in Fig. 3.3. A DC water pump is used to circulate water as the two flat plate collectors are connected in series.

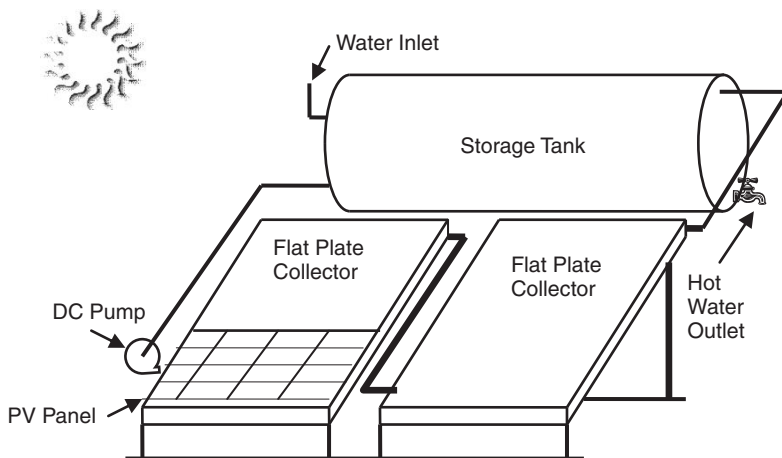


Fig. 3.3 Schematic diagram of a hybrid photovoltaic solar water heater as an example of PV/T application.

Another application of PV/T water collector is solar stills. Solar stills are used to purify or distill water and it is beneficial for the areas where brackish water has salinity of more than 10,000 ppm. This distilled water can be used in

various industries like battery industry, hydrogen production industry, etc. Solar stills are coupled with the photovoltaic water collector and use thermal energy to heat water and electricity to circulate water through a water pump. This system is known as hybrid solar still and gives a reasonably higher thermal efficiency.

3.4.2.3 Other applications

Fish growing (aqua culture) requires a specific environment in terms of water temperature. A PV/T water collector coupled with a greenhouse water pond can be beneficial for the growth of sweet water fish. In order to maintain the desired temperature of water in the pond, the PV-operated water collectors can be used. To circulate water in the flat plate collector a photovoltaic water pump can be used. The other applications of PV/T systems can be in wine distilleries, medicine industries, dairy industries, etc., wherever active distillation is required.

3.5 Case Study

An example of solar technology is adopted to demonstrate the link between sustainability and efficiency. An effective way to maintain a good electrical efficiency by removing heat from the solar panels and to have a better overall efficiency of a photovoltaic system is to utilize both the technologies simultaneously. This kind of system is known as hybrid photovoltaic/thermal (PV/T) system and can be beneficial for low-temperature thermal applications like water heating, air heating, agricultural crop drying, solar greenhouses, space heating, etc., along with electricity generation that can further be beneficial for rural electrification and agricultural applications like solar water pumping, etc. In this case study we are giving a simple demonstration on how both the technologies together give better efficiency which directly relates to better sustainability.

Based on the first law of thermodynamics, the energy efficiency of a PV/T system can be defined as a ratio of total energy (electrical and thermal) produced by PV/T system to the total solar energy falling on the photovoltaic surface and can be given as

$$\eta = \frac{En}{S_T A} = \frac{V_{oc} I_{sc} + \dot{Q}}{S_T A} \quad (3.1)$$

where $\dot{Q} = h_{ca} A (T_{cell} - T_{amb})$, and $h_{ca} = 5.7 + 3.8v$.

Here, h_{ca} , A , T_{cell} , T_{amb} , I_{sc} , and V_{oc} are the convective heat transfer coefficient from photovoltaic cell to ambient, area of the photovoltaic surface, cell temperature, ambient temperature, short circuit current, and open circuit voltage, respectively. The convective (and radiative) heat transfer coefficient from photovoltaic cell to ambient can be calculated by considering wind velocity (v), density of the air, and the surrounding (ambient) conditions (Tiwari, 2002).

The exergy efficiency is based on second law of thermodynamics that gives not only a quantitative assessment of energy but also the qualitative. A comparison of PV and PV/T system is also presented in the form of a case study later in this section.

The exergy efficiency of a photovoltaic system can be given as

$$\psi = \frac{\dot{E}x}{\dot{E}x_{\text{solar}}} \quad (3.2)$$

where $\dot{E}x$ is the exergy of the PV system which is mainly electrical power output of the system. Since the thermal energy gained by the system during the operation is not desirable in case of PV system, this becomes a heat loss to the system and hence needs to be subtracted from the former in order to calculate the exergy of a PV system. $\dot{E}x_{\text{solar}}$ is the exergy rate from the solar irradiance in W/m^2 which can be given as (Joshi et al., 2008, 2009)

$$\dot{E}x_{\text{solar}} = \left(1 - \frac{T_{\text{amb}}}{T_{\text{sun}}}\right) S_{\text{T}} A \quad (3.3)$$

An expression for the exergy of PV can be given as

$$\dot{E}x = V_{\text{m}} I_{\text{m}} - \left(1 - \frac{T_{\text{amb}}}{T_{\text{cell}}}\right) \dot{Q} \quad (3.4)$$

Here, I_{m} and V_{m} are the actual current and voltage.

Unlike PV systems, PV/T system uses the thermal energy available on the PV panel and this time the thermal energy gain can be utilized as a useful energy and hence, the exergy of the PV/T system becomes the sum of the electrical exergy and thermal exergy of the system and the exergy efficiency can be defined as

$$\psi = \frac{\dot{E}x}{\dot{E}x_{\text{solar}}} = \frac{\dot{E}x_{\text{e}} + \dot{E}x_{\text{th}}}{\dot{E}x_{\text{solar}}} \quad (3.5)$$

An expression for exergy of the PV/T system can be given as

$$\dot{E}x = V_{\text{m}} I_{\text{m}} + \left(1 - \frac{T_{\text{amb}}}{T_{\text{cell}}}\right) \dot{Q} \quad (3.6)$$

The relation between exergy efficiency and the sustainability index (SI) can be given as (Rosen et al., 2008)

$$\psi = 1 - D_{\text{p}} \quad (3.7)$$

where D_{p} is the depletion factor/number defined by Connelly and Koshland (1997) which can be given as

$$D_{\text{p}} = \frac{\dot{E}x_{\text{D}}}{\dot{E}x_{\text{in}}} \quad (3.8)$$

$$SI = \frac{1}{D_{\text{p}}} \quad (3.9)$$

3.6 Results and Discussion

We now apply the model presented above to some actual data (Joshi et al., 2008) sets as obtained through experiments in New Delhi, India, which is located at

77°12' E longitude and 28°35' N latitude. The test was performed from 9:00 a.m. to 4:00 p.m. on March 27, 2006, and the data measured included total solar irradiation, voltage, open-circuit voltage, current, short-circuit current, cell temperature, ambient temperature, and velocity of the air just above the photovoltaic surface. The data for hourly total solar radiation and the wind velocity are measured for different places on the photovoltaic surface and an average value for both is used to calculate energy and exergy of the photovoltaic system. The uncertainty analysis of measured global radiation is done and the internal estimate of uncertainty is evaluated following (Joshi, 2006) and it is found that the value for uncertainty for the measured global radiation is 2.23% (Joshi, 2006). The system includes two modules in series, and the area of one solar cell is 0.0139 m². Number of solar cells in the two modules was 72. Therefore, the efficiency analysis of a PV system for its performance assessment is done here based on some experimental data as explained above.

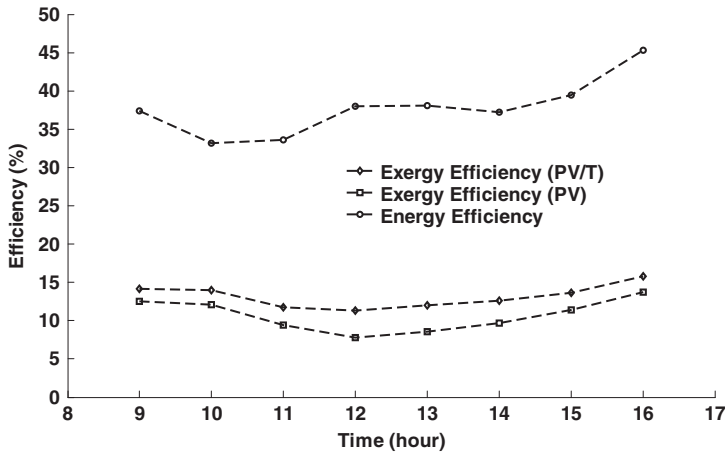


Fig. 3.4 Energy and exergy efficiencies of PV and PV/T systems.

Using Eqs. (3.1–3.6) and experimental data from Joshi et al. (2008), energy and exergy efficiencies are calculated and shown in Fig. 3.4. It is clear from the figure that the energy efficiency (33–45%) is higher than that of the exergy efficiency (11–16%) of PV/T system and (7.8–13.8%) of PV system. Maximum exergy efficiency for PV/T (16%) and PV (13.8%) can also be seen at 4 p.m. whereas a minimum exergy efficiency for PV/T (11%) and PV (7.8%) is at 12 p.m. In the present study, natural air is used to derive the heat from photovoltaic surface. However, if air is supplied beneath the photovoltaic surface by a forced mode, e.g., by putting a fan beneath the photovoltaic panel, as done by Joshi (2006), more thermal energy can be removed in a better as well as convenient way. In that case a higher energy and exergy efficiency can be achieved.

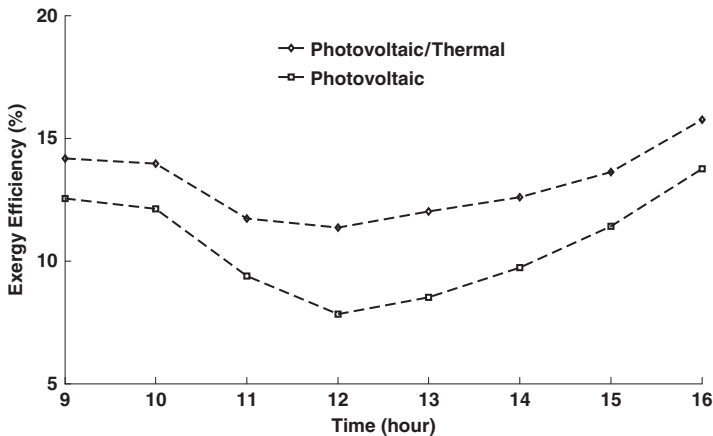


Fig. 3.5 Comparison of exergy efficiency of PV and PV/T systems.

Figure 3.5 shows the comparison of exergy efficiencies of both PV and PV/T systems. Comparing both the curves one can see that the exergy efficiency of PV/T is on an average 20% more than that of PV. Carbon dioxide, a major greenhouse gas, is responsible for the global warming hence there is a need to understand the ways by which we can reduce the greenhouse gas emission. One solution to this problem can be adopting non-conventional energy sources wherever applicable, for example, for water heating one can use solar energy which is more eco-friendly as compared to using an electrical water heater that runs on electricity produced by conventional sources. Another example could be solar pumping, farmers irrigate their field in day time and they can use solar water pumping instead of using an oil-based generator to produce electricity and use it to run the water pump. The non-conventional energy sources often called as renewable energy sources are environmentally benign as they emit less greenhouse gases into the atmosphere as compared to conventional ones. Though the non-renewable or conventional sources of energy like coal, oil, and natural gas are more economical than the renewable sources, they pollute the environment at a much faster rate. Coal-based electricity generation causes highest greenhouse gas emission amongst all conventional and non-conventional sources during the operation and the installation of the power plant.

In renewable energy sources solar energy sometimes is more attractive than the others as it can be used not only for small-scale applications like stand-alone systems but also for large-scale applications like grid connections. The hybrid technology can be a good alternative to reduce the greenhouse gas emissions and improve the electricity generation by coupling two technologies. This not only can give better reliability and sustainability of the system performance but also can help reduce the greenhouse gas emission into the atmosphere. Solar photovoltaic can be beneficial not only for electricity generation but also for thermal applications as it can be used for a variety of applications ranging from stand-alone systems to grid-connected systems.

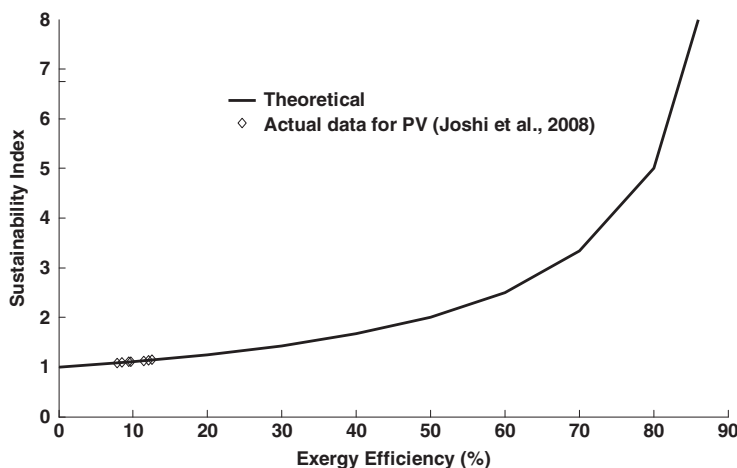


Fig. 3.6 Variation of sustainability index (SI) with exergy efficiency.

The sustainability index for the PV system has been calculated using Eqs. (3.7–3.9) and is shown in Fig. 3.6. A theoretical calculation is also done to show the variation of the sustainability index with exergy efficiency and shown in the same figure. The exergy efficiency of the PV system varies between 7.8 and 12.5% for the typical day of March 27, 2006, at New Delhi and the sustainability index (SI) varies between 1.08 and 1.14. It is clear from the graph that sustainability index (SI) increases with increase in exergy efficiency.

Sustainability index for PV/T system is also calculated and it varies between 1.13 and 1.19 for exergy efficiency ranging from 11.3 to 15.4%, respectively.

3.7 Conclusions

From this study we can extract the following remarks:

- Renewable energy sources emit less greenhouse gases into the atmosphere and hence are beneficial for electricity production in an eco-friendly manner.
- Photovoltaic technology can be beneficial for electricity production as it uses solar energy which is freely available and pollution free and it can be applied for various purposes like solar drying, greenhouses, space, air and water heating applications, solar stills, etc., along with electricity production.
- The exergy efficiency of PV/T system (minimum–maximum, 11.3–15.7%) is more than the exergy efficiency of PV system (minimum–maximum, 7.83–12.53%) as the former uses thermal energy also.
- The sustainability index (SI) increases from 1.08 to 1.14, with the increase in the exergy efficiency of PV system from 7.83 to 12.53%.

Acknowledgment

The authors acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada in Canada.

Nomenclature

A	Area (m^2)
D_p	Depletion factor
$\dot{E}x$	Exergy (W)
$\dot{E}x_D$	Exergy destruction (W)
$\dot{E}x_{in}$	Exergy input (W)
$\dot{E}x_{solar}$	Exergy of solar irradiance (W)
h_{ca}	Convective and radiative heat transfer coefficient from solar cell to ambient air ($\text{W}/\text{m}^2\text{K}$)
I_m	Current at maximum power generation (A)
I_{sc}	Short circuit current (A)
PV	Photovoltaic
PV/T	Photovoltaic/thermal
$\dot{Q}$	Available thermal energy (W)
SI	Sustainability index
S_T	Hourly measured total solar irradiation (W/m^2)
T_{amb}	Ambient air temperature ($^{\circ}\text{C}$)
T_{cell}	Photovoltaic cell temperature ($^{\circ}\text{C}$)
T_{sun}	Sun temperature (5777 K)
v	Wind velocity just above photovoltaic surface (m/s)
V_m	Voltage at maximum (actual) power generation (V)
V_{oc}	Open-circuit voltage (V)
ψ	Exergy efficiency
η	Energy efficiency
Subscripts	
e	Electrical
th	Thermal

References

- Bertani, R (2005) World geothermal power generation in the period 2001–2005. *Geothermics*, 34:651–690.
- Charalambous, PG, Maidment, GG, Kalogirou, SA, Yiakoumetti, K (2007) Photovoltaic thermal (PV/T) collectors: A Review. *Applied Thermal Engineering* 27: 275–286.
- Connolly, L, Koshland, CP (1997) Two aspects of consumption: using an exergy-based measure of degradation to advance the theory and implementation of industrial ecology. *Resources, Conservation and Recycling* 19:199–217.
- Evans, A, Strezov, V, Evans, TJ (2009) Assessment of sustainability indicators for renewable energy technologies. *Renewable and Sustainable Energy Reviews* 13:1082–1088.

- Gaddy, E (2003) Photovoltaics for hybrid automobiles. 3rd World Conference on Photovoltaic Energy Conversion. May 11–18, Osaka, Japan, 2827–2832.
- Habraken, S, Defise, JM, Collette, JP, Rochus, P, D'Odemont, PA, Hogge, M (2001) Space solar arrays and concentrators. *Asia Astronautica* 48 (5–12): 421–429.
- Hammons, TJ (2004) Geothermal power generation worldwide: Global perspective, technology, field experience, and research and development. *Electrical Power Compon Syst* 32: 529–553.
- International Atomic Energy Agency (2001) Sustainable Development and Nuclear Power. Vienna: IAEA, 2001.
- Joshi, AS (2006) Evaluation of Cloudiness/Haziness Factor and its Application for Photovoltaic Thermal (PV/T) System for Indian Climatic Conditions. Doctoral Thesis, IIT Delhi, New Delhi, India.
- Joshi, AS, Dincer, I, Reddy, BV (2008) Energetic and exergetic analyses of a photovoltaic system. Proceedings of the Canadian Society for Mechanical Engineering Forum 2008 Conference, Paper Number 1569103179, June 5–8, 2008, Ottawa, Canada.
- Joshi, AS, Dincer, I, Reddy, BV (2009) Performance analysis of photovoltaic systems: A review. *Renewable and Sustainable Energy Reviews* 13:1884–1897.
- Markandya, A, Wilkinson, P (2007) Electricity generation and health. *The Lancet* 370(9591): 979–990.
- Miyamoto, K ed. (1997) Renewable biological systems for alternative sustainable energy production (FAO Agricultural Services Bulletin—128). Rome: Food and Agriculture Organization of the United Nations.
- Mondol, JD, Yohanis, Y, Smyth, M, Norton, B (2006) Long term performance analysis of a grid connected photovoltaic system in Northern Ireland. *Energy Conversion and Management* 47:2925–2947.
- Rosen, MA, Dincer, I, Kanoglu, M (2008) Role of exergy in increasing efficiency and sustainability and reducing environmental impact. *Energy Policy* 36:128–137.
- Sorensen, B (2004) Renewable Energy 3rd Edition. Elsevier Academic Press, Burlington, MA.
- Tiwari, GN (2002) Solar Energy: Fundamentals, Design, Modeling and Applications. Narosa Publishing House, New Delhi and CRC Press, Washington.
- Yilanci, A, Dincer, I, Ozturk, HK (2009) A review on solar-hydrogen/fuel cell hybrid energy systems for stationary applications. *Progress in Energy and Combustion Science* 35(3):231–244.

Residential Solar Power Generation Systems for Better Environment

Calin Zamfirescu, Ibrahim Dincer, Tony Verrelli and William Robert Wagar

4.1 Introduction

The decline of the world's fossil energy supply, the increase in energy consumption, and the continuous trend of global warming caused by greenhouse gas emissions enforce innovation and research efforts toward the implementation of a global economy based on renewable energy. As mentioned in many sources (e.g., Baneman, 2008), with the increasing price of fossil fuels and augmenting taxes placed by governments on emissions, renewable energies will become progressively competitive.

This kind of energy comes from three “fundamental” sources, namely solar, gravitation combined with the movement of the planet, and geothermal heat stored or produced in the earth's crust (see Scheffler, 2001).

Produced by solar irradiation that hits the terrestrial atmospheric shell with an insolation (INcident SOLar radiATION energy flux) $I_{sc}=1367 \text{ W/m}^2$, solar energy is the most important of all renewable sources (see Duffie and Beckman, 2006). Kalogirou (2004) noted that 30 minutes of solar radiation falling on earth is equal to the world energy demand for 1 year. An overwhelming majority of the physical and chemical reactions encountered by air-breathing organisms on the earth's surface, including photosynthesis and water and air circulation in the atmosphere, are a direct or indirect result of solar radiation. Fossil fuels (oil, coal, natural gas, etc.) were originally produced by photosynthesis and solar heating (see also Kreith and Kreider, 1978).

Solar energy can be used for various purposes among which power generation looks the most attractive because it provides the ability to supply an increasingly important part of the world energy demand. Solar energy can be converted to electricity in two ways: either by using photovoltaics or by solar-driven heat engines coupled to electric generators. According to Baneman (2008) more than 70% of the world's solar energy is generated through Rankine cycle systems in California's Mojave desert.

Solar-driven heat engine systems represent a technology in continuous development, especially since the 1970s world energy crisis. Among various implementations of these systems, the one based on parabolic trough solar collectors has already become a mature technology, commercialized since the mid-1980s throughout the world. Among companies that commercialize solar trough technology, we note here Luz International Ltd, California (Baneman, 2008) and Turboden Ltd, Italy (Turboden, 2008).

The aim of this chapter is to document the development status of solar power (and heat) systems that can be used for residential applications and to show that these systems represent a promising option toward reducing greenhouse gas emissions and global warming. In the first part of the chapter, the impact of solar energy on the environment and sustainable development is analyzed based on a formerly proposed fossil fuel and solar energy utilization indicator and the assumed amount of investments in three scenarios. Subsequently, various small- (individual) to large-scale solar systems with relevance to residential power (and heat) generation are presented together with their specific components. A case study showing a preliminary design of a low-power solar-driven ammonia-water Rankine generator for power and heat is exemplified together with its analysis, modeling, and results. The chapter ends with concluding remarks and perspectives.

4.2 Solar Energy and the Environment

The attributes of solar energy technologies (e.g., modularity, flexibility, low operating costs) differ considerably from those for traditional, fossil fuel-based energy technologies. Solar energy technologies can provide cost-effective and environmentally beneficial alternatives to conventional power systems. Some of the benefits that make solar energy systems attractive follow (e.g., Dincer, 2000 and McGowan, 1990):

- Relatively independent of rising oil and other fossil fuel costs.
- Implementation is relatively straightforward.
- Normally minimize environmental degradation and widespread use would reduce pollution levels.
- Market demand is expected to increase significantly.

There are three main points that make solar technology sustainable:

- Their comparable environmental impact is minor and the variety of solar technologies provides a flexible array of options.
- They cannot be depleted. If used appropriately, solar energy resources are reliable and sustainable.
- They favor system decentralization which enhances the flexibility of the system, and small-scale equipment reduces the initial design time allowing more adaptation and growth.

Solar energy resources do have some characteristics that lead to problems, but they are often solvable technical and economic challenges: generally diffuse, not

fully accessible, sometimes intermittent, and regionally variable. The potential for overall benefits is often overlooked for solar energy technologies. They are often assessed as less cost-effective than traditional technology; however, as commented by Dincer and Rosen (2005) comprehensive assessments show many more benefits to using solar energy technology. Short lead times, incremental capacity addition, and flexibility allow solar technology to be very beneficial in present and future applications.

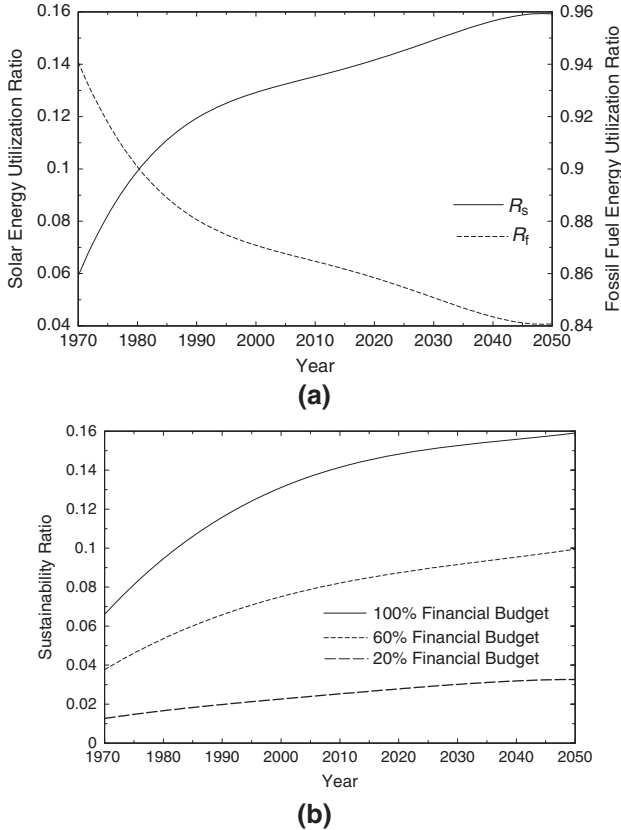


Fig 4.1 Energy utilization ratio comparison (a) and solar sustainability ratio (b) based on data from Dincer and Rosen (2005).

The following parameters are introduced by Dincer and Rosen (2005) to demonstrate solar energy technology's contribution to decreases in fossil fuel utilization and to correlate the sustainability of solar (and other renewable) technology with associated investment. The fossil fuel utilization ratio is defined below:

$$R_f = E_f / E_p \quad (4.1)$$

where E_f is the energy associated with the fuel consumption and E_p is the primary energy consumption.

Based on Midilli et al. (2006), the solar energy utilization ratio is shown in terms of the fossil fuel utilization ratio, namely $R_s = 1 - R_f$. Figure 4.1(a) presents the increase in solar energy utilization over a period of time with the decrease in fossil fuel utilization. Figure 4.1(b) shows the solar energy sustainability ratio over a period of time for three financial scenarios as proposed in Dincer and Rosen (2005), namely 20, 60, and 100% of the green energy financial investment for future years affecting the sustainability of solar technology development and implementation. The utilization of fossil fuels decreases in favor of solar energy. Furthermore, the sustainability of solar (and renewable) systems increases with investment input. An increased sustainability of energy systems is translated to a reduced impact on global warming.

4.3 Solar Power Generation Systems

In this section, the main kinds of established solar power systems, including small-(individual) and large-scale residential power generation are classified as shown in Figure 4.2 and analyzed in terms of their overall and component performance. A typical solar-driven heat engine system for residential power (and heat) generation consists of a solar concentrating collector that drives a heat engine (e.g., a Rankine cycle). The heat engine produces shaft work at an expander that in turn drives an electrical generator; additionally, the rejected heat may serve a useful purpose (e.g., water heating). Such a system can be connected to the grid or can work independently with energy storage in various ways, as will be discussed in the next section of this chapter.

Even though they are conceptually similar, large-scale solar systems differ from small-scale systems through the fact that they use a central power plant. In large systems, a field of collectors is used to capture the solar energy, which is transmitted by means of a heat transfer fluid to a standard power plant. In small-scale systems every individual unit is equipped with a low-power heat engine, usually placed in the focal point of a solar concentrator, close to the solar receiver.

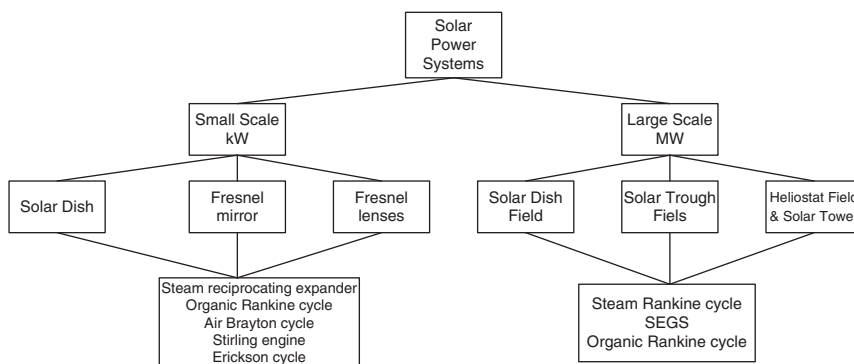


Fig 4.2 Types of solar power generation systems.

Small-scale systems are mainly based on paraboloidal dish solar concentrating collectors. As its name suggests, a solar concentrating collector's role is to concentrate the solar radiation on a small spot. This is done with the purpose of reducing the exposure of the heated surface to the environment and thus to avoid heat losses. A concentrating solar collector has two main parts, that is, a solar concentrator and a solar receiver. The solar concentrator receives solar radiation under an aperture of area A_a and focalizes the incident radiation on a small spot. The solar receiver (or absorber) is placed at the focus of the concentrator and has a small aperture area A_{ab} . The characteristic parameter of concentrating solar collector is the concentration ratio $C=A_a/A_{ab}$.

Apart from dish concentrator (of paraboloidal surface) another established option is the Fresnel mirror formed from an assembly of plane or curved surface mirrors suspended by a frame structure. The individual mirrors point toward a single focal point where the solar receiver is placed. For tracing the sun, the whole assembly rotates around the azimuth and zenith angles. A similar option is represented by Fresnel lenses which use light refraction phenomenon to focalize the incident radiation.

Based on Jaffe and Poon (1981) and Jaffe (1989) there are, discussed here, a number of small-scale designs introduced to use parabolic dish concentrators for solar thermal power systems:

- The OMNIUM-G concentrator has a 6 m diameter paneled dish which provided 7–12 kW to a Rankine engine under $I_T=1 \text{ kW/m}^2$ insolation.
- The Test Bed concentrator had an 11 m paneled dish and provided 76 kW to its heat engine under the same conditions.
- Lajet designed a concentrator consisting of 24, 1.5 m diameter dishes. This system delivered 33 kW to a Brayton engine under $I_T=1 \text{ kW/m}^2$ insolation.
- The Advanco concentrator provided 74 kW to its Stirling engine using a 10.6 m diameter paneled dish under the same insolation conditions.
- Again, normalized to 1 kW/m^2 insolation, General Electric's Parabolic Dish Concentrator 1 used a 12 m paneled dish to provide 72.5 kW to a heat engine.
- Power Kinetics had a 9 m square-shaped paneled concentrator that delivered 28 kW to a boiler under $0.88\text{--}0.94 \text{ kW/m}^2$ insolation.
- The Acurex Parabolic Dish Concentrator 2 used an 11 m paneled dish and was shown to have an optical efficiency of 0.88 even at concentration ratios as high as 1300.
- Boeing decided to create reflector panels and test them using the Test Bed concentrator. These panels were $0.6 \times 0.7 \text{ m}$ and provided an optical efficiency of 0.8 up to concentration ratios of 3000.
- By comparison, the ENTECH Fresnel Concentrator Lens Panel had dimensions of $0.67 \times 1.2 \text{ m}$ and could only provide an optical efficiency of 0.68 at a concentration ratio of 1500.

Currently, the largest single-dish power system is Australia's "Big Dish," which produces 50 kW_e feeding a 500°C boiler with an aperture of 400 m² and can operate at peak efficiencies up to 29%.

Although paraboloid dish collectors have been around as long as trough collectors, there is a cost and technological gap which needs to be closed in order to exploit their high efficiencies. By innovative design, analyzing performance–cost trade-offs and introducing technologies such as direct steam generation or organic Rankine cycles, the gap can be tightened allowing for low-cost, high-efficiency, large-scale, and residential applications to be viable.

The cost of a solar dish power generator is tightly correlated to the optical performance of the solar concentrator. The performance factors of a dish system can be greatly degraded with changes in geometry, and therefore, accuracy and rigidity are important for their design.

Based on Jaffe and Poon (1981) one can extract that for an optical efficiency of 0.90–0.93, concentration ratio of 2000–5000, intercept factor of 0.98, and a life-time of 30 years, a low-cost price estimate is \$200–350/m². Note that all cost estimates in this chapter are reported for 2008 monetary value.

Another estimate can be made based on the Acurex concentrator – described by Overly and Bedard (1981) – with optical efficiency of 0.86 and concentration ratio of 1900. This estimate of \$330/m² involves the assumption of a large dish system with production quantities of 100,000 units per year.

Back silvered glass is standard for the mirror component of the design and have about 94% reflectivity. The reflector can be a single layer which is more efficient and more expensive, or it can be broken into components, which is cheaper but less efficient. Another interesting option is the stretched membrane mirror. Manufacturing stretched membrane mirrors involves a vacuum process, as well as non-uniform loading. Stretched membrane technology was initially used to create highly effective, low-cost heliostats. Singular element stretched membrane mirrors have demonstrated optical efficiencies of 0.915. Although the performance of stretched membrane mirrors is lower than that of the best glass–metal mirrors, stretched membrane mirrors cost much less. Stretched membrane mirrors are often made in facets, in which, several smaller elements are connected to form a larger element. The smaller elements are generally produced in sizes of 3–4 m diameter, which is the approximate size of the projected residential solar dish unit presented in the case study below (see, e.g., Alpert and Houser, 1988).

The dish support can be a solid metal structure or a truss structure which may include tension cables for additional support. The receiver support can be central or extended structures; however, shading and distortion influence the effectiveness of the support. The foundation is often a concrete ring for azimuth rotation.

Two methods of tracking control are used where in the first, sensors provide optical feedback to allow for variable tracking, and in the second, the system is pre-programmed to follow the sun. For non-reactive tracking, there are two more options whereby polar tracking allows a single axis motion over the course of a day and adjusts a second axis daily or weekly, and azimuth tracking allows for constant two-axis tracking (see Jaffe, 1983a). Hydraulic-drive tracking systems are simpler while electric-drive tracking systems are cheaper.

For low-power generation systems specific to solar dish systems, Rankine cycles operated with organic fluids (e.g., toluene), known also as Organic Rankine Cycles (ORC), are believed to be the most effective. This fact is due to the gas

dynamic characteristics of organic fluids that are suitable for development of cost-effective turboexpanders.

Steam cannot be used in low-power applications (below MW) with regular steam turbines. To use steam in low-power Rankine cycles, a special steam expander (e.g., reciprocating or pulse turbines) must be considered. Ammonia water is another working fluid worth being considered. It should be mentioned that if ammonia, ammonia water, or organic fluids are used in the Rankine cycle, then low-cost refrigeration compressors of scroll or screw type can be used as expanders. This feature increases the marketability of independent low-power solar-driven generators. An example of ammonia-water Rankine generator that is able to match the temperature profiles at both source and sink has been developed by Zamfirecu and Dincer (2008a,b). Due to the feature of ammonia-water solution to vary its temperature at vapour-liquid phase change, the temperature differences at sink and source can be minimized for better energy and exergy efficiency.

Solar-driven Rankine cycle systems compete with other solar thermal energy conversion alternatives, each of them having notable drawbacks and advantages. A review by Kongtragool and Wongwises (2003) shows that the solar power systems based on Stirling engines operate at very high pressures, of the order of 200 bar and temperatures in the range of 700–800°C working with helium or hydrogen. These gases leak easily, which raises maintenance problems. Additionally, hydrogen is highly flammable which imposes severe safety issues; however, Stirling systems are very compact and reach high efficiency around 40% (of the engine). As reported by Kongtragool and Wongwises (2003) an efficiency of 22% was obtained for a dish-Stirling system operating for 10 h/day. Another system, known as SAIC/STM SunDish obtained a peak efficiency of 26% for 23 kW. One of the main drawbacks of using Stirling engines in solar applications is related to the long warm-up time needed, which is in contradiction with the reality of solar energy's fluctuating nature.

Open-air Brayton cycle engines mounted at the dish focal point were also used in some applications (see e.g., Jaffe, 1983a). They operate efficiently at higher receiver temperatures than usual for Stirling and Rankine cycles, that is, over 1000°C where Brayton engines may attain over 26% efficiency. At lower temperatures, the system efficiency drops under 20%.

Modern large-scale solar technology came about in the 1980s when nine substantial power generating stations totaling 354 MW power generating capacity were built in California's Mojave desert. These systems are based on parabolic trough collectors which are considered to be the most proven of all solar technologies. These plants make use of linear parabolic reflectors that concentrate the solar energy on lengths of tubing. Within the tubing, heat is collected and transferred to steam, which is then passed through a steam Rankine cycle. In the summer months, trough plants can operate from 10 to 12 h/day solely on solar energy.

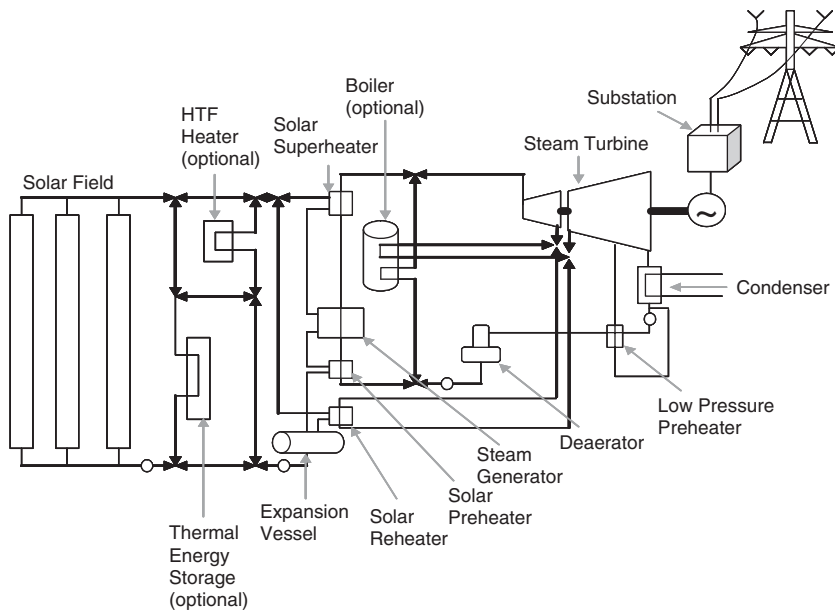


Fig 4.3 Schematic of 30 MW hybrid solar trough power plant (modified from Kearney and Miller, 1988).

To date, most of the large-scale solar plants are hybridized with a fossil fuel (gas/coal) burning system to keep the flow of power relatively constant. Notable examples of solar power plant technology obtain a Power Output per Unit of Receiver Area ranging from 120 to 175 (W/m^2) and an average operating temperature of 360°C . The Luz LS-3 is regarded as the most advanced trough technology presently available. The performance factors of several systems are presented in Table 4.1.

A significant example of large-scale solar trough power plant is illustrated in Fig. 4.3 and refers to the 30 MW plant VI referenced in Kearney and Miller (1988) which serves as a benchmark for solar technology with a net efficiency of 10.7% and a capital cost of \$150 million. The plant is hybridized with 25% of its energy coming from natural gas in low solar radiation periods. By comparison, an 80 MW Integrated Solar Combined Cycle System with the constant addition of fossil fuel assistance would cost \$3850/kW, with an efficiency of 13.5%. In the future, with advancing technology, economy of scale, and by adding thermal storage capacity, tilted collectors, and direct steam generation, efficiencies are predicted to increase by 30%, and cost reductions of 30%/kW are predicted by 2030. Additionally, operation and maintenance costs are expected to decrease by 25%.

The second representative large-scale power plant is based on solar tower technology. The solar tower is in fact a large size Fresnel lens assembly that focus the solar radiation on a central receiver placed on a tower at certain height. Being of large size, these systems are suitable for using thermal storage of solar radiation in molten salts (see Ortega et al., 2008).

Table 4.1 Solar collector characteristics.

Collector	Acurex 3001	M.A.N. M480	Luz LS-1	Luz LS-2	Luz LS-2	Luz LS-3
Year	1981	1984	1984	1985	1988	1989
Area (m ²)	34	80	128	235	235	545
Aperture (m)	1.8	2.4	2.5	5	5	5.7
Length (m)	20	38	50	48	48	99
Collector diameter (m)	0.051	0.058	0.042	0.07	0.07	0.07
Concentration ratio	36:1	41:1	61:1	71:1	71:1	82:1
Optical efficiency	0.77	0.77	0.734	0.737	0.764	0.8
Receiver absorptivity	0.96	0.96	0.94	0.94	0.99	0.96
Mirror reflectivity	0.93	0.93	0.94	0.94	0.94	0.94
Receiver emittance	0.27	0.17	0.3	0.24	0.19	0.19
@Temperature, °C			300	300	350	350
Operating temperature, °C	295	307	307	349	390	390

Source: Compiled from Mackay and Probert (1998), Winter et al. (1990).

Luzzi and Lovegrove (1997) opined that among all solar energy conversion systems, solar dish fields with centralized power generation are believed to be the most viable solution for the future and provide the highest efficiency of all. Australian National University consecrated large efforts in the development of solar dish heat engines. They demonstrated a 28 dish field system having the peak solar power of 2 MW_e and supplemented with 4 MW_e gas-fired plant. Steam at 50 MPa and 500°C is generated by each solar dish for an equivalent electrical power of 50 kW corresponding to an insolation of 950 W/m² (see Kaneff, 1999).

Table 4.2 Summary of performance of large-scale systems.

Technology	Parabolic trough + oil	Solar tower system	Solar dish field
Mean net efficiency	14	13.8	19
Specific power generation (kWh/m ² – yr)	308	316.5	340
Levelized capital costs (\$/kWh – yr)	2.39	4.22	2–4
Operation and maintenance (c\$/kWh)	4.96	6.05	4–6
Levelized electricity cost (\$/kWh _e)	0.248–0.295	0.24–0.31	0.2–0.4

Source: Compiled from Ortega et al. (2008) and Lovegrove et al. (2007).

Another option, proposed by Luzzi and Lovegrove (1996) at the Australian National University, consists of using ammonia as an energy transfer and chemical energy storage medium. In this case, the receiver of each solar dish unit has a chemical reactor for ammonia decomposition. This reaction is endothermic, and

the reverse reaction, ammonia synthesis is exothermic according to $\text{NH}_3 + 66.5 \text{ kJ/mol} \leftrightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2$.

The decomposition products, hydrogen and nitrogen, are stored under pressure in a specially devised vessel. For power generation, the hydrogen and nitrogen are combined in a synthesis reactor and deliver the associated heat of formation. Two options were proposed for power generation. One involves driving a typical Rankine cycle with the reaction heat. The other involves using a Brayton cycle, where the produced ammonia is expanded for power generation. Two other thermochemical storage options were considered: the sulfur trioxide $2\text{SO}_3 + 196.4 \text{ kJ/mol} \leftrightarrow 2\text{SO}_2 + \text{O}_2$ and the ammonium hydrogen sulfate $\text{NH}_4\text{HSO}_4 + 132 \text{ kJ/mol} \leftrightarrow \text{NH}_3 + \text{H}_2\text{SO}_4$

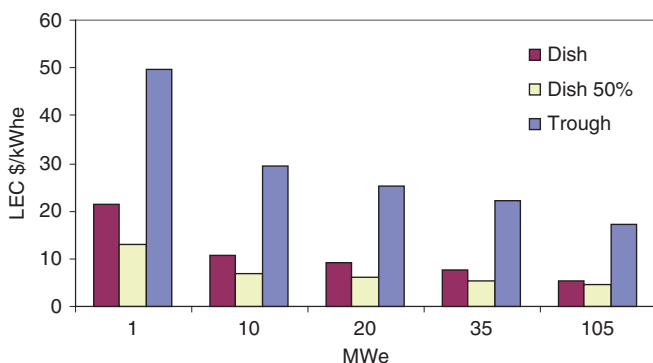


Fig 4.4 Levelized electricity cost (LEC) for large-scale solar systems; compiled based on data from Kaneff (1999) and Price (2003).

Solar generators imply very reduced maintenance costs. Thus, the cost of generated electricity is levelized based on the investment cost, maintenance cost, and lifetime of the system. The following formula applies for calculating the levelized electricity cost

$$\text{LEC} = (\text{CC} + \text{MC}) / (\text{LT} \eta_s I_T) \quad (4.2)$$

In Table 4.2, we present a comparison between the three kinds of large-scale solar power generation systems discussed above in terms of efficiency and costs. An additional comparison is presented in Fig. 4.4 where, based on data from Kaneff (1999) and Price (2003), we correlated the levelized energy cost (LEC) of solar power systems for paraboloidal dish fields and for parabolic trough systems. In the case of dish systems two scenarios were considered, namely systems relying 100% on solar energy and hybrid systems that use 50% fossil energy. Dish-based systems are more cost competitive than parabolic trough, mainly due to their better performance. As expected, the LEC decreased with the installed performance. It is worth noting that the same trend is expected for individual dish system units, namely their associated LEC decreases with production size.

One important aspect involves the CO₂ mitigation expected from the foreseen solar energy expansion. Based on data from Brackmann (2008), which predicted the trend of expansion of solar energy utilization in future years, we obtained the plots presented in Fig. 4.5. Figure 4.5a shows the estimated CO₂ saved per year from using solar energy power generation instead of fossil fuel. Figure 4.5b shows the predicted investment evolution from present to the year 2025.

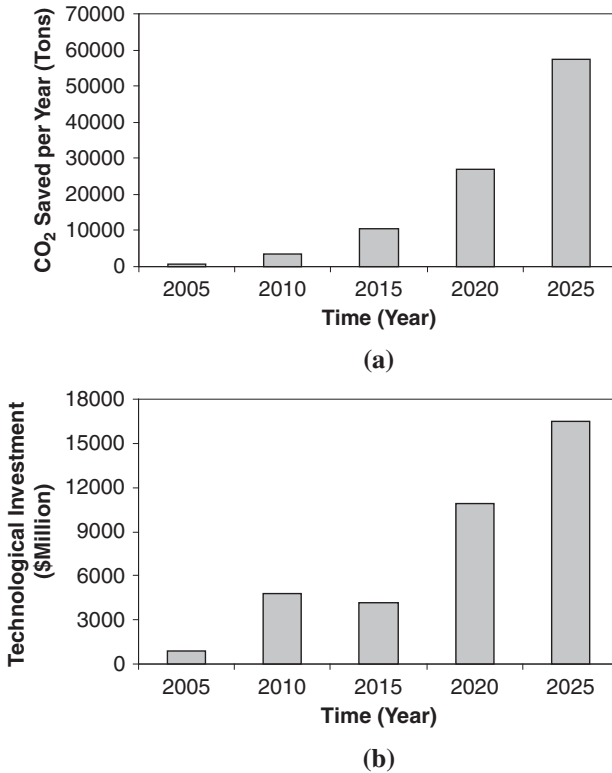


Fig 4.5 Predicted CO₂ mitigation induced by solar power (a) and associated investment costs (b).

4.4 Parabolic Solar Dish System

In what follows, we illustrate the benefits of solar power generation on sustainability, on reducing greenhouse gas emission and on reducing global warming by a case study. The study refers to a residential (single) unit for solar power conversion based on a paraboloidal mirror that is illustrated in Fig. 4.6. The solar dish concentrates the insolation on a glazed tube receiver that plays the role of desorber for an ammonia-water Rankine cycle. For expansion and work production, a scroll machine is capable of operating in a two-phase regime. The rejected heat of the

heat engine may not in principle be “thrown out” in the environment, but rather is used for cogeneration through water heating.

Based on the insolation I_T we summarize in Table 4.3 the relationships for relevant efficiencies (see also the Nomenclature). In the definition of efficiency for the system with cogeneration we assumed that the rejected heat to the cold reservoir, $\dot{Q}_0$, is a useful heat (e.g., for water heating).

Table 4.3 Definition of the parameters used for system modeling.

Parameter	Definition
Optical efficiency	$\eta_{\text{opt}} = \frac{I_c A_{\text{ab}}}{I_T A_a}$
Thermal efficiency	$\eta_{\text{th}} = \frac{\dot{Q}_{\text{ab}}}{I_c A_{\text{ab}}}$
Solar collector	$\eta_{\text{coll}} = \eta_{\text{opt}} \eta_{\text{th}}$
Heat engine	$\eta_{\text{pc}} = \frac{\dot{W}}{\dot{Q}_{\text{ab}}}$
System without cogeneration	$\eta_s = \frac{\dot{W}}{I_T A_a}$
System with cogeneration	$\eta_s = \frac{\dot{W} + \dot{Q}_0}{I_T A_a}$

The first step in solar energy system modeling and its design calculations is to determine the solar collector geometry and characteristics for maximum performance. This, in fact, is to maximize the collector efficiency. The derivation of the collector’s efficiency results from the energy balance stating

$$I_T A_a = I_c A_{\text{ab}} + \dot{Q}_{\text{loss}} \quad (4.3)$$

where $\dot{Q}_{\text{loss}} = UA_{\text{ab}}(T_{\text{ab}} - T_0)$ represents the heat losses expressed in a linearized way. Dividing Eq. (4.3) with $I_T A_a$, extracting η_{opt} as a common factor on the LHS, and identifying the concentration ratio one obtains

$$\eta_{\text{coll}} = \Omega \gamma (1 - F_{\text{coll}} / C \gamma) \quad (4.4)$$

where we denoted with $F_{\text{coll}} = U(T_{\text{ab}} - T_0) / (I_T \zeta \rho \tau \alpha)$ the collector factor depending on the solar absorber temperature (assumed at the average), the insolation and optical properties which are accounted for through the optical factor

$\Omega = \zeta \rho \tau \alpha$ including the shading and light blocking factor ζ , reflectivity ρ , transmissivity of receiver's glazing τ , and absorptivity α of the receiver's surface.

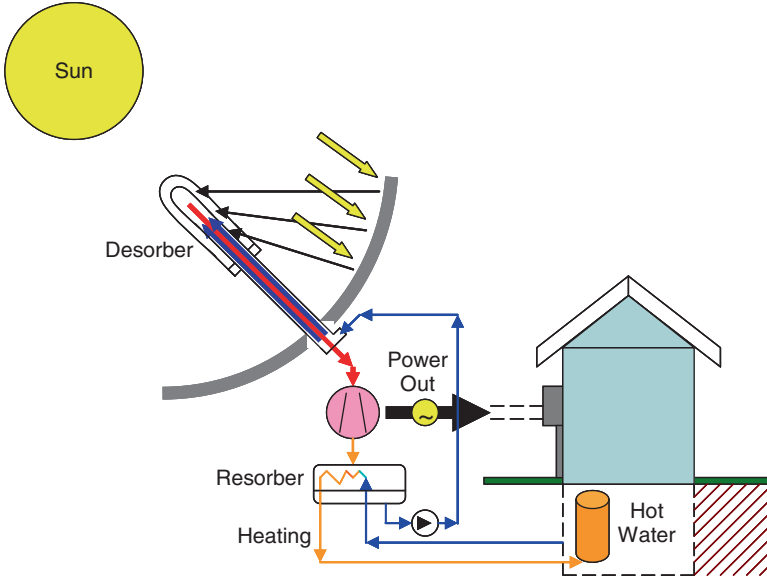


Fig 4.6 Typical residential solar-driven heat engine system.

In Eq. (4.4), the intercept factor $\gamma = \eta_{\text{opt}} / \zeta \rho \tau \alpha$ which represents the ratio between solar energy flux absorbed by the receiver and the concentrated energy flux focalized on it is introduced. The intercept factor is an important parameter of the optical system that depends on the concentration ratio, the rim angle ϕ (i.e., the angle between the focal axis and a ray connecting the rim with the focal point), and the angular optical errors δ (expressed in mrad). The optical error is due to the conjugated effect of mirror specularity, mirror slope errors, pointing error, and sun-shaped non-uniformities. Among several correlations for γ summarized in Jaffe (1983b), we selected the one of Duff and Lamieiro (1974) that gives less than 10% estimation error.

For the solar concentrator we introduce the optical efficiency defined by $\eta_{\text{opt}} = \Omega \gamma$ and thermal efficiency defined by $\eta_{\text{th}} = 1 - F_{\text{coll}} / C \gamma$. From Eq. (3.4) and the definitions of optical and thermal efficiencies it results the following expression $\eta_{\text{coll}} / \Omega = f(C, \phi, \delta, F_{\text{coll}})$, which can be maximized with respect to the concentration ratio C , and rim angle ϕ for fixed angular error δ and collector factor F_{coll} . This optimization is demonstrated in the next section. Its physical interpretation is explained by the trade-off between the need of a larger spot for capturing all concentrated light and a smaller absorber area for minimizing the heat losses.

In Duffie and Beckman (2006), the receiver's heat losses through radiation can be expressed as, $\epsilon_{\text{ab}} \sigma A_{\text{ab}} (T_{\text{ab}}^4 - T_0^4) = A_{\text{ab}} [\sigma (T_{\text{ab}}^2 + T_0^2) (T_{\text{ab}} + T_0) (T_{\text{ab}} - T_0)]$, or if one may assume an average temperature difference between the absorber and envi-

ronment as, $A_{ab}(4\sigma T^3)(T_{ab} - T_0)$; this last expression identifies an equivalent radiation heat transfer coefficient $h_{rad} = 4\sigma T^3$. Considering the other heat losses, U is

$$U = h_{rad} + h_{cnv} + h_{ins} A_{ins} / A_{ab} . \quad (4.5)$$

Here, an important observation regards the trade-off between the collector and the heat engine efficiencies: high receiver temperature means bad collector efficiency and good engine efficiency, and vice versa. This trade-off is a fundamental thermodynamic problem, as pointed out by Bejan et al. (1981). In this respect, the stagnation temperature $T_{ab,max}$ defined as the solar receiver temperature for which all incident radiation is dissipated into the ambient as heat loss (this is the ideal maximum collector temperature). If the heat engine is Carnot, Bejan et al. (1981) demonstrate that the optimal collector temperature that maximizes the work output is $T_{ab,max}^{0.5}$.

We developed a numerical model for our heat engine that runs on a peculiar kind of Rankine cycle that, as mentioned above, uses ammonia-water as working fluid. Furthermore, the heated fluid is expanded just after the boiling is initiated using a scroll expander that operates completely in two phase. A detailed analysis of the cycle including its modeling and optimization is presented in Zamfirescu and Dincer (2008a, b) and omitted here for brevity. We used the model for optimization of the receiver temperature, which is the similar to the optimization of F_{coll} for maximum system efficiency.

4.5 Results and Discussion

We started our numerical analysis with a two-step optimization process of the solar collector for conditions assumed in our case study. In this respect, we estimated a range for the collector factor based on typical values of heat transfer coefficient at the receiver, typical insolation, receiver temperature, and optical properties. We concluded that $F_{coll}=50-100$ covers the values of practical interest for our case study. Furthermore, typical values of the rim angle for paraboloidal dishes are in the range $30-75^\circ$, and typical optical error in the range $5-20$ mrad; for smaller angular error, the cost of the optical system increases dramatically. For the optical factor, we assumed a constant value $\Omega = 0.9$.

The first step in the optimization is illustrated in Fig. 4.7(a) which shows the variation of the collector efficiency for a fixed collector factor and rim angle. There is always an optimum concentration ratio that maximizes the collector efficiency. This optimization has been repeated for four values of the angular optical error. One may observe that the collector efficiency is very sensitive to the optical system quality, and it is worth mentioning that this is a cost-sensitive aspect. The second step in optimization implies to compute the maximum collector efficiency (as obtained for every optimal concentration ratio) for a range of rim angles. The results are reported on the right side of Fig. 4.7(b) and demonstrate that there is an

optimal rim angle that maximizes the collector's performance. This angle is quite insensitive to the optical surface properties, and moreover we observed by repeating the computations for several values of the collector factor that the efficiency is insensitive to F_{coll} as well. The optimal value of the rim angle is around 62.5°C . This is an important result, meaning that the parabolic dish can be constructed with a rim angle of 60° for most of situations.

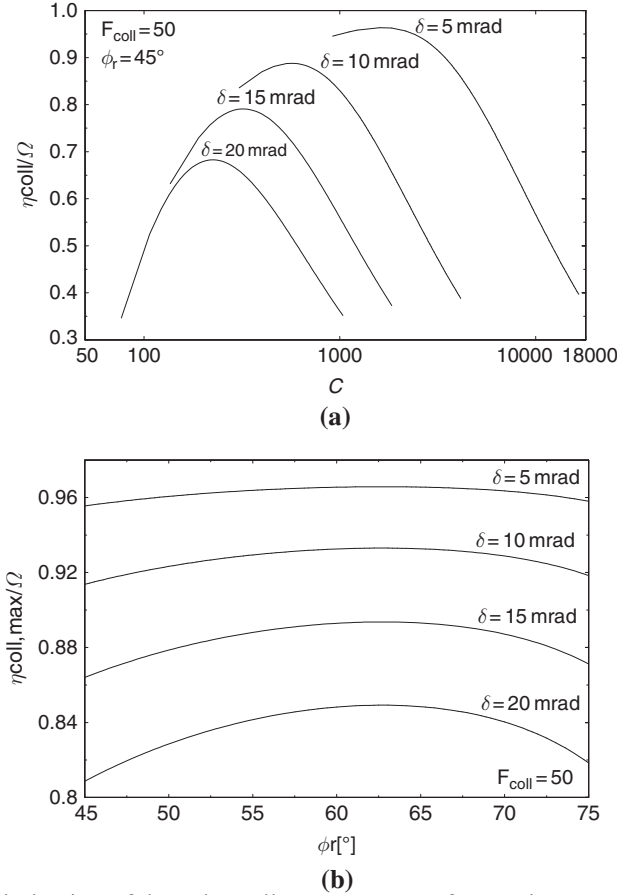


Fig. 4.7 Optimization of the solar collector geometry for maximum performance: influence of concentration ratio (a) and of rim angle (b).

The maximum values of the collector efficiency, obtained by optimization with respect to C and ϕ , are computed for a range of collector factor F_{coll} , and the results of this process are reported in Fig. 4.8(a). As expected the collector efficiency decreases with F_{coll} , that is, it decreases with the increase of the receiver temperature. Larger receiver temperature means large F_{coll} and large heat losses. Alternatively, large F_{coll} means higher insolation for fixed T_{ab} , which, in turn, also means higher

heat losses. On the same plot from Fig. 4.8(b), we presented the variation of the heat engine efficiency with the heat source temperature (expressed also through the collector factor). Doing so, we got the opportunity to multiply the collector and heat engine efficiency and to get the system efficiency (without cogeneration) in the right side plot of the same figure.

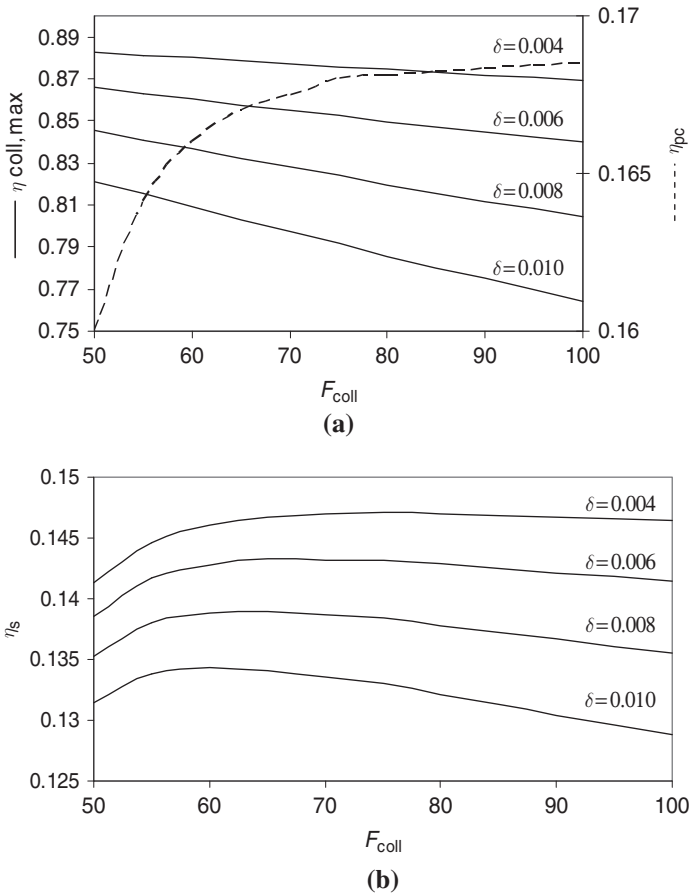


Fig. 4.8 Optimization of the system operation parameters for maximum performance: collector and power cycle efficiency (a) and system efficiency (b).

4.6 Conclusions

This chapter presents a review and analysis of solar-driven heat engines for power generation with relevance to residential applications. The impact of solar systems on sustainable development is quantified based on fossil fuel vs solar energy utilization factors predicted over the next decades and by sustainability factor as introduced also in other works, e.g., by Dincer and Rosen (2005). The established large-scale and small-scale systems are presented and analyzed based on their

performance parameters. A case study is presented illustrating the benefits of solar system in CO₂ mitigation and reducing global warming by relating to renewable sources rather than fossil fuels.

The optimization of the solar-driven heat engine is important for obtaining a low-levelized electricity cost and augmented CO₂ mitigation through solar power generation. With this fact in mind we developed here a model for a solar heat engine and optimization and identified the important optimization parameters which are the quality of the optical system expressed in terms of angular error δ , the concentration ratio C , the rim angle ϕ , the collector temperature corroborated with the insulation, as expressed by the collector factor F_{coll} . The system can be optimized sequentially for each of the three relevant parameters C, f, F_{coll} for a given angular error δ . The optimal rim angle is robust having a value of $\sim 62.5^\circ$, independently on operating conditions. The system efficiency varies largely with optical system quality, and this will obviously influence the levelized electricity cost and the CO₂ mitigation ability.

Acknowledgments

The authors acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada, the Ontario Centres of Excellence, and the Cleanfield Energy Inc.

Nomenclature

A	area, m ²
C	concentration ratio
CC	capital cost, \$/m ²
E	energy, J
I	solar radiation flux, W/m ²
LEC	levelized electricity cost, \$/kWh
LT	lifetime, years
MC	maintenance costs, \$/m ²
$\dot{Q}$	heat flux, W
R	energy utilization factor
T	temperature, K
U	heat transfer coefficient, W/m ² K
$\dot{W}$	power output (electrical), W
Greek letters	
α	absorptivity
γ	intercept factor
δ	angular optical error, rad
ε	emissivity
ξ	shading coefficient
η	efficiency
ρ	reflectivity

ϕ	focal angle
σ	Stefan–Boltzmann constant, $\text{W/m}^2\text{K}^4$
τ	transmissivity
Ω	optical factor
Subscripts	
0	dead state (environment)
a	concentrator's aperture
ab	absorber (solar receiver)
cnv	convection
coll	collector
f	fuel
ins	insulation
hr	heat recovery
loss	heat losses into ambient
max	maximum
opt	optical
p	primary
pc	power conversion
rad	radiation
s	system
sc	solar constant
T	total (beam + diffuse)

References

- Alpert, DJ and Houser, RM (1988) Optical Evaluation of Prototype Stretched-Membrane Mirror Modules for Solar Central Receivers. 4th International Symposium on Research, Development, and Applications of Solar Thermal Technology, Santa Fe, NM 13 June.
- Baneman, J (2008) Status report on solar trough power plants. Pilkington. Internet source <http://www.solarpaces.org/Library/docs/PiStaRep.pdf> (accessed at May 1, 2008).
- Bejan, A, Kearney, DW, and Kreith, F (1981) Second law analysis and synthesis of solar collector systems. *Journal of Solar Energy Engineering* 103:23–30.
- Brackmann G (2008) Concentrated solar thermal power now! Internet source www.greenpeace.org/raw/content/international/press/reports/Concentrated-Solar-Thermal-Power.pdf (accessed on May 26, 2008).
- Dincer, I (2000) Renewable energy and sustainable development: a crucial review. *Renewable and Sustainable Energy Reviews* 4:157–175.
- Dincer, I and Rosen, M (2005) Thermodynamic aspects of renewables and sustainable development. *Renewable and Sustainable Energy Reviews* 9:169–189.
- Duff, WS and Lameiro, GF (1974) A performance comparison method for solar concentrators. ASME paper 74-WA/Sol-4, New York.
- Duffie, JA and Beckman, WA (2006) *Solar engineering of thermal processes*, 3rd edn., John Wiley and Sons, Hoboken, NJ, pp. 908.
- Jaffe, LD (1983a) Dish concentrators for solar thermal energy. *Journal of energy* 7:304–312.
- Jaffe, LD (1983b) Optimization of dish solar collectors. *Journal of Energy* 7:684–694.
- Jaffe, LD (1989) Test results on parabolic dish concentrators for solar thermal power systems. *Solar Energy* 42:173–187.

- Jaffe, LD and Poon, PT (1981) Secondary and Compound Concentrators for Distributed Point Focusing Solar Thermal Power Systems. Proceedings of the Intersociety Energy Conversion Engineering Conference, Atlanta, Ga., 1752–1758.
- Kalogirou, SA (2004) Solar thermal collectors and applications. *Progress in Energy and Combustion Science* 30:231–295.
- Kaneff, S (1999) Viable distributed dish/central plant solar power: status, new developments, potential. *Journal of Physics IV*, 9:195–200.
- Kearney, D and Miller, C (1988) Solar Electric Generating System VI – Technical Evaluation of Project Feasibility, LUZ Partnership Management, Inc.: January 15, 1988.
- Kongtragool, B and Wongwises, S (2003) A review of solar-powered Stirling engines and low temperature differential Stirling engines. *Renewable and Sustainable Energy Reviews*, 7:131–154.
- Kreith, F and Kreider, JF (1978) Principles of solar engineering. Mc-Graw-Hill NY, p. 778.
- Lovegrove, K, Zawadski, A, and Conventry, J (2007) Paraboloidal Dish Solar for Multi-Megawatt Power Generation. Presented at Solar World Congress, Beijing, September 18–22.
- Luzzi, A and Lovegrove, K (1997) A solar thermochemical power plant using ammonia as an attractive option for greenhouse-gas abatement. *Energy* 22:317–325.
- Mackay, RM and Probert, SD (1998) Likely market-penetration of renewable-energy technologies. *Applied Energy* 59:1–38.
- McGowan, JG (1990) Large-scale solar/wind electrical production systems – predictions for the 21st century. In: Tester JW, Wood DO, Ferrari NA, editors. *Energy and the Environment in the 21st Century*. Massachusetts, p. 1026.
- Midilli, A, Dincer, I, and Ay, M (2006) Green energy strategies for sustainable development. *Energy Policy* 34:3623–3633.
- Ortega, JI, Burgaleta, JI, and Téllez, FM (2008) Central receiver system (CRS) solar power plant using molten salt as heat transfer fluid. Internet source. http://www.sener.es/EPORTAL_DOCS/GENERAL/FILE-cwa0fcc36424ab41b7bf04/SO-LARTRES.pdf (accessed on May 1, 2008).
- Overly, P and Bedard, R (1981) Acurex Parabolic Dish Concentrator PDC2. Parabolic Dish Solar Thermal Power Annual Program Review Proceedings, Atlanta, Ga. Paper 5105–118.
- Price, H (2003) Assessment of Parabolic Trough and Power Tower Solar Technology Cost and Performance Forecasts. Technical report NREL/SR-550-34440, p. 344.
- Scheffler, M (2001) Investigation of the Feasibility of a Parabolic Trough Driven Solar Energy Storage System Using Ammonia. Diploma thesis, Stuttgart University.
- Turboden (2008) High efficiency Rankine cycle for renewable energy and heat recovery. Internet source http://www.turboden.it/en/applications_detail.asp?titolo=Solar (accessed on May 24, 2008).
- Winter, CJ, Sizmann, R, and Vant-Hull, L (1990) Solar Power Plants – Fundamentals, Technology, Systems, Economics. Springer-Verlag, Berlin, p. 437.
- Zamfirescu, C and Dincer, I (2008a) Thermodynamic analysis of a novel ammonia-water Rankine cycle. Proceedings of the 2nd International Conference on Energy Sustainability ES-2008, August 10–14, Jacksonville, Florida, USA, paper 54344.
- Zamfirescu, C and Dincer, I (2008b) Thermodynamic analysis of a novel ammonia-water tri-lateral Rankine cycle, *Thermochimica Acta* 477:7–15.

Hydrogen Production from Ammonia as an Environmentally Benign Solution for Vehicles

Calin Zamfirescu and Ibrahim Dincer

5.1 Introduction

Since historical times mankind is dependent on the use of fossil fuels. The exploitation and use of fossil fuel grew exponentially in the last two centuries when world experienced the industrial development. This period was characterized by extensive combustion of petroleum, natural gas, coal and as a consequence there are produced visible unbalances in the natural environment, especially due to the associated CO₂ emissions.

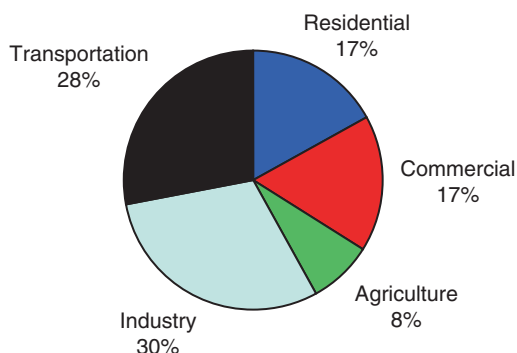


Fig. 5.1 Distribution of CO₂ emissions from various sectors in North America (data from PEW Center, 2008)

In the march toward a non-polluting economy that relates mostly on renewable resources, there is a need of transitional solutions, like finding alternative synthetic fuels for clean (zero-emission) vehicles. The transportation sector is responsible for 28% of the total CO₂ emission in North America and this situation is about the same for other industrialized countries. The distribution of CO₂ emissions from various sectors is illustrated in Fig. 5.1.

For reducing the CO₂ emissions from transportation sector and the associated global warming impact, a broadly accepted solution suggests using fossil fuels and renewable energy sources to produce hydrogen as an ideal synthetic and clean fuel (see Veziroglu, 2007 and Dincer, 2007). However, in order to make the hydrogen-based economy a reality, there is a need of major investments for the development of competitive production, distribution, and especially hydrogen storage technologies, which in the present are not satisfactory enough. The barrier to be overcome is represented by the development of the hydrogen distribution infrastructure that implies complicated safety issues because hydrogen is volatile and has a low flash point, presents high explosion danger, and its flame is invisible.

Ammonia, NH₃, known mainly as nitrogen source for agriculture and refrigerant has high content of hydrogen atoms per unit of volume. Because of this reason, as reviewed by Bomelburg (1982), ammonia has been used occasionally in the past as a hydrogen source for internal combustion engines and fuel cells. There are 108 kg H₂/m³ embedded in liquid ammonia at 20°C and 8.6 bar. The most advanced storage methods in metal hydrides reach about 25 kg H₂/m³; this storage density is ~3 times lower than that in NH₃.

The toxicity of NH₃ is a challenge in its serious consideration for use as hydrogen source on a global scale. However, this issue has largely been addressed for ammonia handling, storage, and use in various forms (i.e., gaseous, liquid, and solid), especially in agriculture, chemical, and refrigeration.

As suggested by Christensen et al. (2006) a way to cope with the ammonia toxicity is by adsorbing it in porous metal ammine complexes, e.g., hexaamminemagnesium chloride, Mg(NH₃)₆Cl₂. To do this NH₃ is passed over an anhydrous magnesium chloride (MgCl₂) powder at room temperature. The absorption and desorption of ammonia in and from MgCl₂ are reversible. The ammine can store 0.09 kg H₂/kg and 100 kg H₂/m³.

Despite its toxicity, NH₃ is still one of the most attractive ways to store and distribute H₂ due to the following facts:

- It can be thermally cracked into hydrogen and nitrogen using low energy, i.e., ~12% from the higher heating value (HHV) to produce hydrogen for fuel cells and internal combustion engines.
- The distribution infrastructure already exists for ammonia (see Christensen et al., 2006) to deliver it in amounts larger than 100 million tons yearly or more.
- It is also an excellent working fluid for thermodynamic cycles. Such cycles, operating for cooling, heating, power, or any combination of those can be coupled with internal combustion engines. Recently, Zamfirescu and Dincer (2008a–c) and Zamfirescu and Dincer (2009) have analyzed the possibility to use the onboard ammonia as refrigerant while it is consumed as fuel for vehicle propulsion.
- It is a NO_x reduction agent.
- It is still safer than pure hydrogen and various other hydrogen sources like methanol, ethanol, methane, gasoline due to the following properties:
 - If escapes into the atmosphere it dissipates rapidly because its density is lighter than that of air.

- It is self-alarming: any leakage can be detected by nose in concentrations as low as 5 ppm.
- It has a narrow flammability range and therefore, it is generally considered non-flammable and presenting no explosion danger when properly transported; this fact is evident from the data listed in Table 5.1 which were compiled from various sources (indicated below the table).

Table 5.1 Some features of ammonia as compared to other conventional fuels.

Property	Gasoline	Diesel	Natural gas	H ₂	NH ₃
Flammability limit, volumes % in air	1.4–7.6	0.6–5.5	5–15	4–75	16–25
Auto-ignition temperature, °C	300	230	450	571	651
Peak flame temperature, °C	1,977	2,053	1,884	2,000	1,850

Source: From Brandhorst et al. (2007), McFarlan (2007), Olson (2007), Lide (1991)

Hydrogen can easily be obtained from ammonia via thermal cracking, which is a kind of well-known technology, even though there is still room for further development. The main challenge is to device the reforming unit sufficiently compact and yet capable of decomposing the ammonia at a rate in accordance with the consumption. Such units are currently in development and there are several promising results published in the open literature (Ganley et al., 2004, Sørensen et al., 2005).

Ammonia can be produced either from fossil fuels of all kinds (coal, natural gas, petroleum, naphtha, etc.), from any renewable energy source (e.g., solar, wind, hydro, geothermal, ocean thermal energy conversion) or from heat waste or electricity (e.g., nuclear) using water, biomass, or organic/city waste and air as primary.

Using ammonia as a hydrogen source is a fully recyclable solution because, at production place, ammonia is synthesized basically from water and nitrogen, substances available everywhere in the environment, and at the consumption point (on vehicles), after decomposition followed by hydrogen combustion, the same amounts of water and nitrogen are returned back into the environment. It may be argued that due to its qualities ammonia provides both a short- and long-term solution to the hydrogen economy. There are former studies and occasional implementations regarding the use of ammonia as hydrogen source either for internal combustion engines (e.g., Starkman et al., 1967, Kroch 1945, Holbroock, 2007, Stockes, 2007) or for fuel cells (e.g., Cairns, 1968, Kordesh et al., 2007, Maffei et al., 2007 Xie et al., 2007).

In the first part of this chapter the use of ammonia as hydrogen source is analyzed and the advantages of such a alternative to hydrogen economy are discussed. Hydrogen stored in the form of ammonia is compared with other conventional fuels as well as with pure hydrogen from the point of energy storage density per unit of volume and of mass, and the cost per unit of storage tank volume. In the subsequent section the possibility of using ammonia on vehicles simultaneously as hydrogen source, as working fluid (for engine heat recovery and work

conversion), and refrigerant (for engine/fuel cell system cooling or air conditioning) is proposed. The cooling effect is quantified in terms of refrigeration power vs. generated power. We further study some more technical parameters, namely driving range, tank compactness, and cost associated with 100 km driving range for the hydrogen from ammonia alternative.

5.2 Hydrogen Production from Ammonia

The common approach to hydrogen economy is illustrated in Fig. 5.2 and consists of the following steps: production of hydrogen from primary energy sources at some locations, hydrogen distribution (infrastructure not yet developed), and hydrogen delivery on vehicles where it is used for power generation/propulsion. Our aim here is to assess the total cost of hydrogen per unit mass at the utilization point (i.e., on the vehicle) for two alternative layouts of the hydrogen transportation economy. The first layout was just introduced and illustrated in Fig. 5.2. The second layout refers to the hydrogen from ammonia option and will be introduced later.

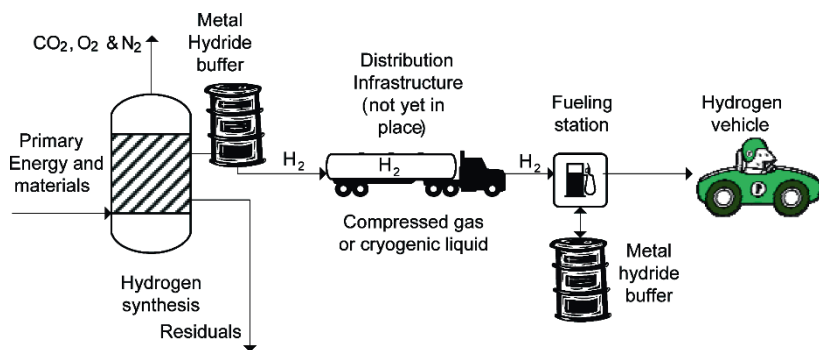


Fig 5.2 The layout of hydrogen economy for transportation.

For a preliminary analysis, let us assume that hydrogen is produced from liquid water, either by electrolysis or by thermo-chemical splitting. The corresponding reaction and the associated (ideal) reaction heat are



Here, in the ideal situation for every kmol of produced hydrogen one needs $\Delta H_{\text{H}_2\text{O}} = 286 \text{ MJ/kmol H}_2$ of energy to split the water molecule. Obviously, the real energy needed to drive this process is larger than the theoretical one due to the imperfections. After produced, the hydrogen has to be stored in buffers at the production place, and then charged on vehicles specialized for pressurized or cryogenic hydrogen transport, then is distributed to fueling stations, and finally delivered to the consumers vehicles. Along this complex chain the cost of hydrogen

will increase with amounts proportional to the energy specific to each phase. We will later study the distribution costs and discuss the total cost of hydrogen delivery.

We now introduce the second alternative where, instead of hydrogen, ammonia is produced at a synthesis plant then buffered locally, then distributed to fueling stations, and charged on vehicles where it is reformed to hydrogen by thermal cracking of the ammonia molecule. This scenario is illustrated in Fig. 5.3. Only ~12% from ammonia's HHV is needed for reforming. There is enough heat on board of a vehicle: the most advanced H_2 ICEs have efficiency of 50–60% and the most advanced fuel cell systems of 60–70%; the rest of the hydrogen energy is dissipated as heat. Thus, the onboard reforming process is “for free”. Exception may make only PEM fuel cell system for which the heat being rejected at low temperature is unsuitable for ammonia cracking. In this case, which is not analyzed now, a small part of the produced hydrogen can be combusted for generating the reformation heat.

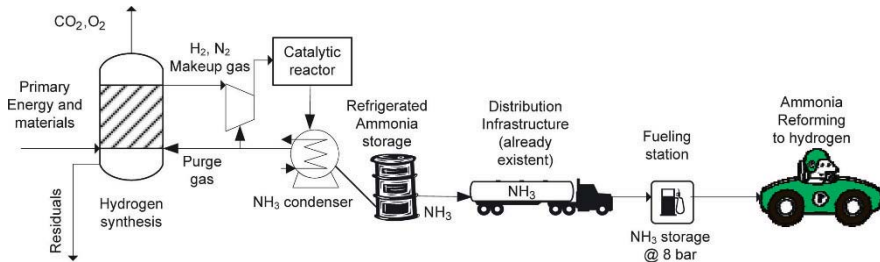


Fig. 5.3 The layout of hydrogen from ammonia economy for transportation.

Furthermore, ammonia is industrially produced from hydrogen and nitrogen via the well-established Haber–Boch process. Hydrogen can be obtained from water (gasification, thermochemical water splitting, or electrolysis) according to the reaction (5.1), while the nitrogen comes from the atmospheric air. In order to obtain an ammonia quantity corresponding to 1 mole of hydrogen, the following reactions have to be considered (ideal case)



Thus the energy needed to produce 1 mole of hydrogen embedded in ammonia is 286–30.7 MJ or $\Delta H_{NH_3} = 255.3 \text{ MJ/kmol } H_2$. Therefore, on a mass basis the cost of NH_3 over the cost of H_2 can be estimated as proportional to the energy for their synthesis as

$$\frac{c_{NH_3}}{c_H} = \frac{3}{\mu_{NH}} \frac{\Delta H_{NH_3}}{\Delta H_{H_2O}} = 0.157 \quad (5.3)$$

According to Eq. (5.3) the ideal cost of ammonia represents less than 16% from the cost of hydrogen per unit of mass. From the stoichiometry one has that 1 kg of ammonia contains $3/17 = 0.175$ kg of hydrogen. As mentioned above, this quantity of hydrogen can be released by NH_3 cracking at no cost on board of vehicles, using the heat generated locally. Therefore, producing hydrogen from ammonia becomes attractive if

$$\frac{c_{\text{NH}_3}}{c_{\text{H}}} < 0.175 \quad (5.4)$$

Note that from Eqs. (5.3) and (5.4) it appears that, on an ideal basis, producing locally hydrogen from ammonia is more efficient than producing and on board using pure hydrogen.

Up to this moment the irreversibilities of the chemical reactions and the fuel production and distribution costs were not considered in the analysis. One can of course expect that due to the irreversibilities of the production process, the cost of ammonia is higher than that of the hydrogen from which is synthesized. However, if one considers the distribution and storage costs the picture may reverse. Therefore, to complete this analysis, the market prices of ammonia and hydrogen at production site and the costs of their distribution and storage were investigated to derive the total well-to-wheel cost of the two considered scenarios.

Hydrogen, as state above, is the most difficult to store in a compact form. Therefore the distribution and storage-related costs will impact mostly on the total costs. Depending on the production method the hydrogen cost varies from $\sim \$1/\text{kg}$ at coal gasification to $\sim \$9.50/\text{kg}$ using solar energy for electricity generation that in turn is used for water electrolysis (see NRC-NAE, 2004).

After production, hydrogen is stored at the manufacturer location for certain period prior delivery. The hydrogen storage is costly, because the hydrogen molecule is small and leakage cannot be avoided. The best option to store hydrogen at the production facility location (and at the distribution pump) is in metal hydrides. As reviewed in Schlappbach et al. (2001), metal hydrides tanks may operate at pressures of 15–20 bar and store up to 25–30 $\text{kg H}_2/\text{m}^3$. In order to completely release the hydrogen from the tank, some amount of heat is needed.

It must be noted that metal hydrides do not appear as a feasible solution for transportation of hydrogen. For 1 kg of hydrogen, the metal hydride tank will have about 160 kg. For transportation, hydrogen must be either compressed to extremely high pressures (~ 300 – 800 bar) or cooled for liquefaction at cryogenic temperatures. According to NRC-NAE (2004), liquefaction adds at least 30% to the hydrogen price per kg, and in top of this one must add the energy consumed to keep the storage tank at cryogenic temperatures during the storage time. If the transportation takes 1–3 days, the minimum cost penalty for hydrogen storage on transport vehicle (cistern) is CN \$ 0.3/kg for compressed H_2 and CN\$ 0.7/kg for liquefied H_2 , where CN\$ stands for Canadian dollars.

If one assumes, for example, that the hydrogen transport is made in pressurized containers at 345 bar the transported energy content is $8 \text{ GJ}/\text{m}^3$, i.e., four times smaller than for gasoline case ($32 \text{ GJ}/\text{m}^3$). In NRC-NAE (2004) it is shown that if a pipeline is to be developed to distribute hydrogen at such high pressure the tubes' thickness must be more than 50% thicker with respect to natural gas pipes.

At distribution points (fuel stations) the hydrogen may be stored also in metal hydrides. Additional costs are associated with leakages during hydrogen delivery to consumers. The high explosion risk of hydrogen will raise the price even more because of the safety measures. It is shown in NRC-NAE (2004) that due to these factors, the estimated minimum cost of hydrogen distribution is more than \$1/kg H₂. Further, one realizes that storage of hydrogen on vehicles (that is made either in compressed gas or in cryogenic liquid) implies additional costs due to leakages or continuous running of the cryogenic plant to maintain the hydrogen in liquid phase.

Thus, if one considers the production, storage, and distribution costs the minimum expected hydrogen price at delivery point should be more than CN \$2.5/kg, if produced from coal, and ~CN \$11/kg from electrolysis driven by solar energy. The goal of DOE (2008) for 2015 is to achieve \$2–3/kg H₂ delivered, untaxed and regardless of the production method. As a matter of fact, the North American selling price of hydrogen in 2002 varied, according to IG (2008), from 7.4 to \$11.3 /kg.

Ammonia is facile to store and it has a distribution network on roads, rail, ships, and pipeline already in place. The production of ammonia from fossil fuels has a common route with hydrogen production, because it involves gasification to produce syngas, gas cleaning, and CO₂ removal. In addition, the following steps are necessary for ammonia synthesis: compression of the reactants, catalytic conversion, and ammonia separation through condensation.

A highly energy consuming component of the ammonia production process is represented by the makeup gas compression which is needed to facilitate the synthesis. This apparent drawback is compensated by a very efficient synthesis process that is possible at high pressure. Moreover, ammonia synthesis is an exothermic process and modern technologies use work and heat recovery to reduce the production costs.

The minimum cost for ammonia production per unit of energy is obtained for the case of natural gas feedstock: the technical limit is 28 GJ natural gas for production of 22.5 GJ in the form of ammonia. The maximum energetic cost is obtained with coal as feedstock: ~65 GJ coal per 22.5 GJ of ammonia product. For other methods of production except solar the cost falls in between the two extremes. The actual cost of North American coal is in average ~CN \$1.5/GJ and that of natural gas is ~CN \$10/GJ. These figures give an estimate of ammonia price range at the production place, which is CN \$5.25–CN \$20.0/GJ or about CN \$0.10–0.38 per NH₃ kg.

The North African price is currently the lowest \$0.15/kg; other costs are \$0.2/kg in Trinidad Tobago (based on \$9/GJ natural gas feedstock), \$0.25/kg in Ukraine, \$0.3/kg in the USA; ammonia cost at Terra Industries in 2007 was \$0.35/kg. Ammonia price in the USA in 2007 varied between \$0.2 and \$0.4 per kg.

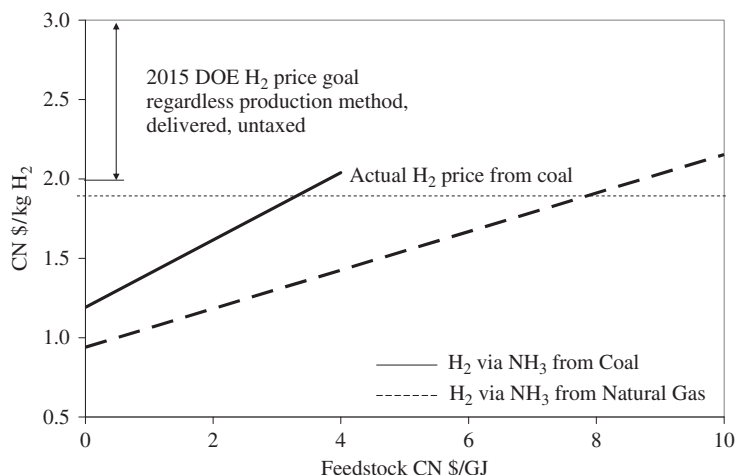


Fig. 5.4 Cost correlation for hydrogen obtained from ammonia at distribution points.

We used here the data from Waitzman (1979) to correlate the ammonia production price with the feedstock price in \$/GJ and eventually obtained the plot from Fig. 5.4. The cost of ammonia has been upgraded with the transportation costs. Since infrastructure development is not needed for ammonia distribution (e.g., a large pipeline network exists in the USA to transport ammonia at a cost of \$0.1 hydrogen equivalent per 1,000 km) the ammonia transportation costs were assimilated to the ones of gasoline. We used the data from NRC-NAE (2004) where it was shown that gasoline distribution costs represent 10–15% of the hydrogen distribution costs per kg of hydrogen equivalent. Finally, the cost of ammonia including transportation has been multiplied with $17/3=5.67$ to obtain the cost per kg of hydrogen stored in ammonia as shown in Fig. 5.4.

Figure 5.4 shows that if ammonia is produced from coal (currently at about ~\$1/GJ) hydrogen from ammonia is cost competitive with hydrogen transported in pure state. Furthermore, if ammonia is produced from natural gas, the hydrogen through ammonia alternative remains economically viable; it is better than hydrogen from coal solution up to natural gas prices of \$8/GJ. It should be kept in mind that as the feedstock cost increases, the hydrogen production costs does increase, too.

Since ammonia is produced from hydrogen, it is interesting to estimate and compare the amount of CO₂ emission at NH₃ and respectively the H₂ production. We assume here the natural gas as feedstock. Modern ammonia synthesis systems that use extensive heat recovery need ~30 GJ equivalent natural gas to produce 1 tonne of NH₃ (see Spath and Mann, 2001). Through stoichiometry one may deduce that ~1.32 kg of CO₂ is generated in order to produce 1 kg of NH₃; this is equivalent to ~8 kg CO₂ generated for 1 kg H₂ in the form of NH₃ which is similar to the amount of CO₂ released during H₂ production from natural gas. This

figure puts in evidence the technical, economical, and ecological values of NH_3 as a hydrogen source.

Moreover, ammonia can be synthesized at any location of the oil or natural gas extraction wells and the resulting CO_2 is re-injected back into the ground for sequestration. Ammonia can then be easily transported via pipelines, auto-cisterns, railway cars, and ships and delivered to consumption points where it can be used as a hydrogen source, chemical, fertilizer, fuel, working fluid, refrigerant, etc.

5.3 Energetic and Cost Parameters

In Table 5.2 we compare ammonia as hydrogen source with other fuels (gasoline, compressed natural gas [CNG]) and pure hydrogen based on the following energetic and economic indicators: specific energy per mass and per volume, respectively, and gravimetric, volumetric and, respectively energetic costs. Gasoline, stored in non-pressurized tank in liquid phase with a density of 736 kg/m^3 , is listed in Table 5.2 as a reference fuel.

Compressed natural gas (CNG) also represents an interesting path toward hydrogen economy. Usually, CNG, which is formed mainly from CH_4 , is combusted directly in internal combustion engines. The combustion products are cleaner than the gasoline products: lower CO_2 emissions and no SO_x emissions. We take here the opportunity to comment on a recently promoted solution by Wesley (2008) that is suitable for future CH_4 zero-emission transportation. That is to decompose methane into carbon and hydrogen according to the following reaction:



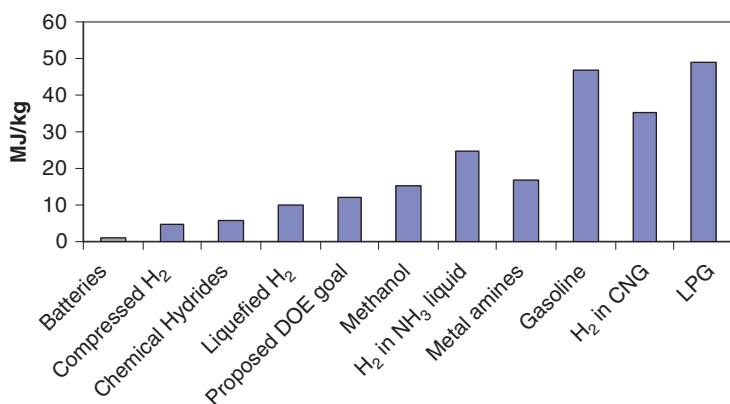
Table 5.2 Comparison of ammonia as hydrogen source with other options.

Fuel/storage	P (bar)	ρ (kg/m^3)	HHV (MJ/kg)	HHV''' (GJ/m^3)	c (CNS/kg)	C''' (CNS/m^3)	c/HHV (CNS/GJ)
Gasoline/liquid	1	736	46.7	34.4	1.36	1,000	29.1
Hydrogen/ CH_4 pressurized tank	250	188	35.5	6.6	1.20	226	33.8
Hydrogen/metal hydrides	14	25	142	3.6	4.00	100	28.2
Hydrogen/ NH_3 pressurized tank	10	603	25.0	15.1	0.30	181	12.0

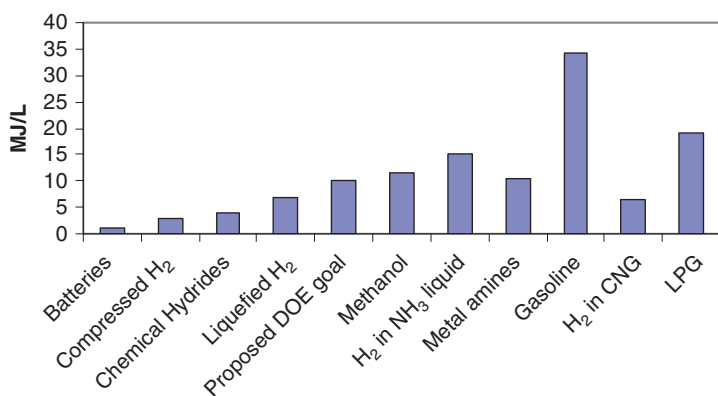
In such supposed layout, the carbon is recycled in the form of nanotubes or carbon fibers. Carbon can be collected on vehicles after decomposition and delivered to fueling stations where it is combined with hydrogen from water to form synthetic CH_4 according to the following reactions



Here, the ideal (neglecting the reaction irreversibilities) energetic cost to produce synthetic methane is thus 211 MJ for 1 kmol of H_2 equivalent. Based on stoichiometry and the energy of formation, it results that, on per mass basis, the cost of methane is 0.185 which differs from the cost of hydrogen for equivalent energy content. On the other hand, since 16 kg of CH_4 contains 4 kg of H_2 , it results that in order to be competitive the methane costs must be 0.25 which differ from hydrogen cost on a per mass basis. Since $0.185 < 0.25$ it results that, on an ideal basis, using CH_4 as hydrogen source for zero-emission engines is feasible. Compared to ammonia as a hydrogen source, one must observe that CH_4 decomposition needs about 22% from its HHV for decomposition vs. 12% in the case of NH_3 . Further comparison of CH_4 with NH_3 can be made regarding the onboard storage.



(a)



(b)

Fig. 5.5 Comparison of specific energy densities (a) and volumetric energy densities (b) of various fuels and NH_3 .

Typically, CNG is stored under 250–350 bar pressure on special “integrated storage systems” on vehicles. This system consists of a number of tubular tanks interconnected to each other and embedded in safety foam to minimize the damage of a possible tank fracture during a crash that can produce serious damage because CH_4 is toxic, flammable, has explosion danger, and greenhouse gas effect.

The current cost of natural gas in Ontario is ~CN \$0.3 for a standard cubic meter, i.e., ~CN \$0.45/kg. However, the compression work is significant and this raises the CNG price about three times. Current price for CNG in Ontario is around CN \$1.2/kg. The HHV of hydrogen-stored CH_4 can be estimated taking in to account that 4 kg of methane contains 1 kg of H_2 . Because of its gaseous phase the energy density in the CNG tank is low (i.e., 6.6 GJ/m³) and this fact leads to an expensive specific energy (i.e., \$33.8/GJ). Since this estimation is based on CNG price, more cost is expected if synthetic CH_4 is used as a hydrogen source.

Ammonia, if used as a hydrogen source appears more attractive than CH_4 in several aspects (see Table 5.2): it stores more hydrogen energy per tank volume, energy cost is about three times less, despite of its toxicity it presents less danger because ammonia is not flammable and does not present explosion risk.

In Fig. 5.5 we compare the gravimetric and volumetric energy content of various fuels and ammonia, where ammonia is viewed as a hydrogen source. As it is made clear by the figure, ammonia is the best hydrogen source among those considered for analysis. Note that in Fig. 5.5 the gasoline and LPG (liquefied petroleum gas – propane) are indicated for comparison purpose only – they are treated as fuels and not H_2 sources.

5.4 Onboard Refrigeration with Ammonia

The presence of ammonia on board offers the opportunity to use it as a refrigerant for engine cooling. Moreover, ammonia can be used as working agent to recover engine heat and convert it into some additional shaft work. Optionally, the refrigeration effect of ammonia, i.e., its high latent heat of vaporization, can be used to produce some air conditioning on board.

The cooling effect of ammonia is equivalent to the heat needed to raise its temperature plus, if it applies, the heat needed to decompose it (partially or totally) to produce hydrogen. Expressed in terms of enthalpy this heat is

$$\Delta h_{\text{c},\text{NH}_3}(T) = h(T) - h'(T_0) + x_d \eta_d \Delta h_d(T) \quad (5.7)$$

where T represents the temperature at which NH_3 is usually decomposed, x_d represents the fraction in which the ammonia stream is dissociated into H_2 and N_2 (if this applies), η_d is the efficiency of the decomposition unit, which based on the results by Yin et al. (2004) is assumed here to be 0.9, and Δh_d represents the dissociation heat at T . Note that in some applications, for instance, fueling internal combustion engines, there is no need to completely decompose ammonia into

hydrogen, because these systems may operate with a mixture of ammonia and hydrogen. The decomposition takes place according to the following reaction:



The heat of this endothermic reaction has been calculated here as a function of the temperature based on Shomate equation as implemented by the NIST (2008). Recent developed technologies operate reaction (5.8) at temperatures in the range of 300–700°C, respectively.

In order to quantify the cooling effect of ammonia in relative terms we introduce here a cooling effectiveness, defined through the heat given by Eq. (5.7) and the lower heating value (LHV) of ammonia:

$$\varepsilon_{c,\text{NH}}(T) = \Delta h_{c,\text{NH}}(T) / \text{LHV} \quad (5.9)$$

The results of applying Eq. (5.9) for a range of ammonia reforming temperatures and various decomposition fractions are presented in Fig. 5.6. The thermodynamic data for plotting Fig. 5.6, as well as throughout this chapter, are calculated using the FluidProp software developed by Colonna and Van der Stelt (2004).

The case $x_d=0\%$ represents the hypothetic situation where ammonia is only preheated prior to oxidation and one assumes that no decomposition occurs. This case is illustrated for reference, because in reality, at temperatures over 300°C some ammonia decomposes spontaneously, even without the presence of catalysts. The case for which $x_d=5\%$ is applicable to some internal combustion engines, where as discussed above, a small fraction of ammonia is usually decomposed to produce hydrogen that boosts the combustion process. The extreme situation when $x_d=100\%$ is applicable to some fuel cell systems that are supplied with pure hydrogen produced from ammonia.

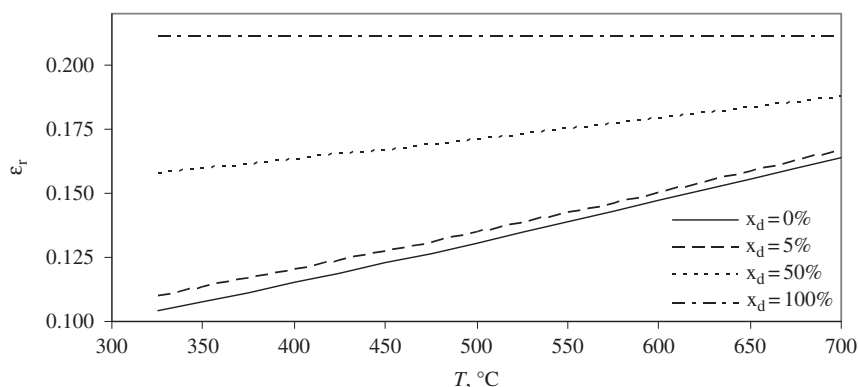


Fig. 5.6 Cooling effect of NH_3 vs. the decomposition temperature and for several decomposition fractions.

The results in the above figure show that the maximum achievable engine cooling with ammonia represents slightly over 20% of the LHV. Thus, in power systems

using hydrogen than ammonia, the usual water-cooling system may be downsized with up to 20%. Optionally, a part of this cooling may satisfy some air-conditioning needs on the vehicle.

With reference to Fig. 5.7, one assumes that the saturated liquid is extracted from the thermally insulated fuel tank. The liquid stream can be throttled such that the fuel evaporation is conducted at the desired temperature (e.g., 5–10°C will suffice either for engine cooling or for obtaining some air-conditioning). After throttling, the fluid passes through a heat recovery heat exchanger where the engine coolant is cooled with ammonia. If air-conditioning is desired, the heat recovery will take place in two steps: first the air and subsequently the engine's coolant are cooled with ammonia.

In order to give a numerical example, let us assume the temperature in the fuel tank to be 25°C, the evaporation temperature to be 5°C, and the ammonia temperature at the evaporator to be 15°C (superheated vapor). With these figures, the cooling effect is quantified at 6.3% of the LHV of ammonia. This means that for a medium size car equipped with 70 kW engine while the engine runs on H_2 than ammonia at full load the obtained refrigeration effect to be used in the form of air-conditioning amounts to ~4.4 kW. In top of this, up to 15% LHV meaning 10.3 kW is available for engine-cooling purpose. Alternatively, ~15 kW can be made available for engine cooling only.

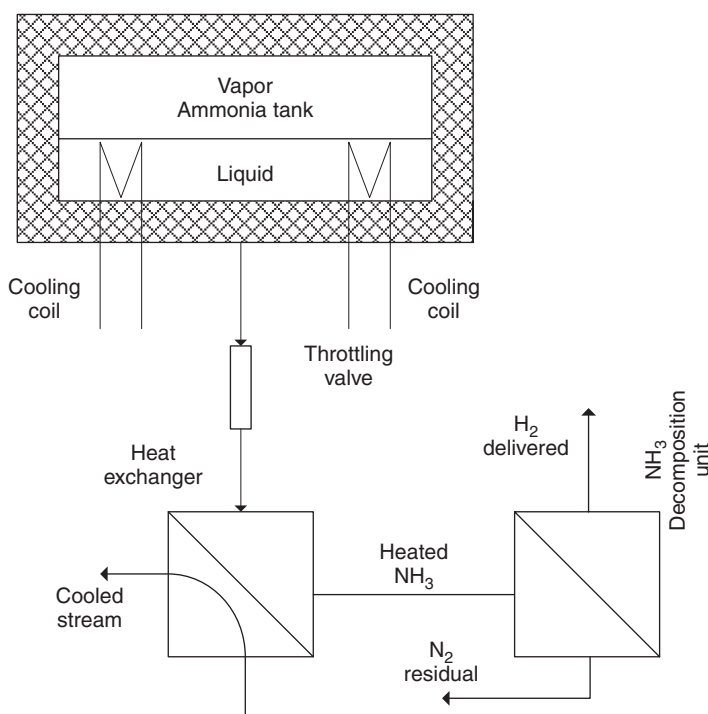


Fig. 5.7 Cooling with ammonia prior its use as fuel on a vehicle.

One important remark is that while leaving the tank the liquid takes-out its flow enthalpy. This enthalpy is replaced by evaporation of the corresponding quantity of liquid in a manner that the temperature and pressure in the tank could be maintained constant. A coil can be immersed into the liquid through which air and coolant circulate. The coolant is subject to cooling while ammonia is consumed from the tank, and this cooling effect can be exploited for any useful need on board. The equation $h'(T)\dot{m}_{\text{NH}_3} = \dot{m}_{\text{air}}(h_{\text{in}} - h_{\text{out}})$ represents the energy balance for the cooling coil, where the LHS is the enthalpy of the leaving liquid and RHS is the enthalpy change of the coolant (e.g., air).

The improvement of engine efficiency due to the associated cooling effect of ammonia can be quantified based on the typical coefficient of performance (COP) of the vehicular cooling systems. The gain in work at the engine shaft due to the available cooling from ammonia (i.e., the one that comes from fan, pump, and compressor power savings) is

$$w_{\text{NH}_3} = \Delta h_{\text{c,NH}_3} / \text{COP} \quad (5.10)$$

and induces an engine performance improvement that can be quantified by the effectiveness introduced below

$$\varepsilon_{\text{r,NH}_3} = \frac{w_{\text{NH}_3}}{\text{LHV}} = \frac{\varepsilon_{\text{c,NH}_3}}{\text{COP}} \quad (5.11)$$

For an assumed (typical) COP of 2 (COP of the engine-cooling system and air-conditioning system at an average), the maximum gain in efficiency is about 10%. It is to be remarked that the simplicity of this cooling system (that consists only of one or two heat exchangers and one throttling valve) lowers both the initial, operation, and maintenance costs by eliminating or downsizing the conventional mechanical cooling system (that comprises the compressor, condenser, water pump, fan, and radiator).

5.5 Driving Range and Its Cost

It is interesting to investigate the driving range as a function of the system effectiveness. In this respect we assume system effectiveness and a performance indicator of the powertrain given in terms of shaft torque energy for each kilometers of driving. We consider here a reasonable value for this indicator of 1 MJ/km and take three illustrative values for system effectiveness defined as

$$\varepsilon_{\text{f}} = \eta + \varepsilon_{\text{r,NH}_3} \quad (5.12)$$

Figure 5.8 compares some performance indicators for hydrogen from ammonia solution, pure hydrogen, and more conventional fuels. To calculate the data shown in Fig. 5.8 we assumed that gasoline, CNG, and LPG vehicles run with 28% efficiency. For methanol we assumed a fuel cell system with 40% efficiency. For hydrogen a PEM fuel cell system has been considered, and an efficiency of 50%. For

H₂ from NH₃ case the power system is not specified; thus we only considered two efficiencies (35, 45, and 55%) that are specific for fuel cell systems and ICEs.

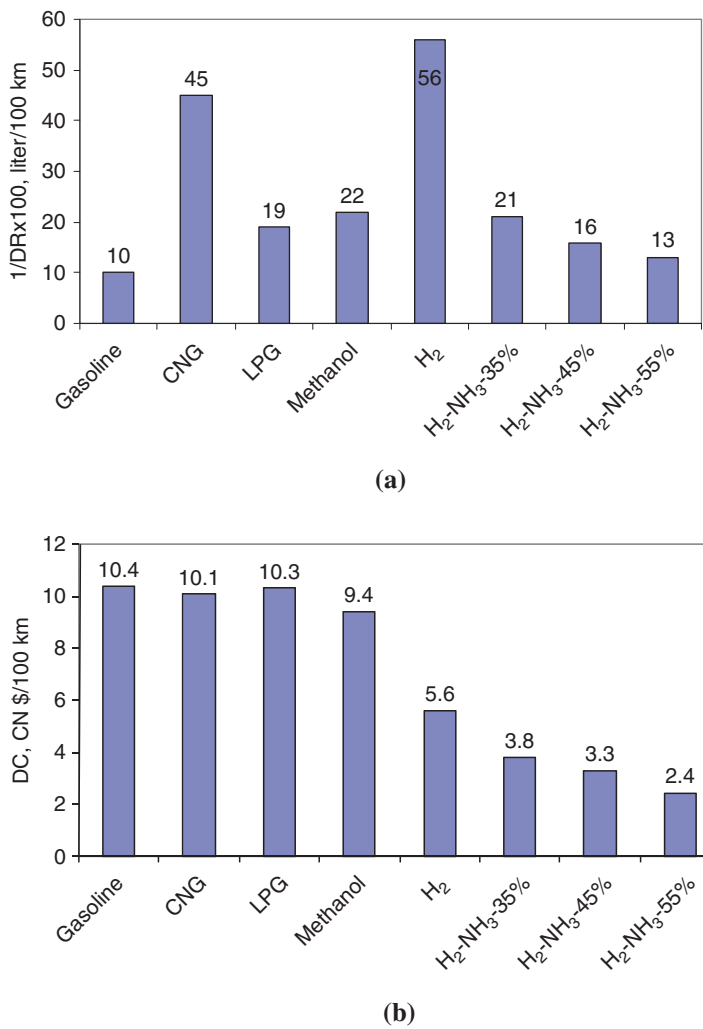


Fig. 5.8 Comparative performance analysis of several power systems for vehicles; fuel tank compactness (a) and specific driving cost (b).

The results in the above figure show that the driving range of gasoline vehicles is the largest, but the associated cost is the highest among all options considered here. The hydrogen tank is the least compact. However, the driving cost of hydrogen vehicle is at half with respect to all common fuels. Regarding the hydrogen from ammonia alternative, the fuel tank is reasonably compact, and the specific

driving cost is the lowest. If the considered specific cost of ammonia would be 25% higher, i.e., CN \$ 0.4/kg, still the cost of driving of “hydrogen from ammonia” vehicle with 35% efficiency is lower than that of hydrogen vehicle at 50%.

Table 5.3 Conversion of a H₂ICE Ford Focus to NH₃ fuel.

Parameter	Unit	H ₂	NH ₃
Storage tank volume	Liter	217	76
Storage pressure	Bar	345	10
Energy on board	MJ	710	1025
Cost of full tank	CN \$	25	14
Driving range	km	298	430
Driving cost	CN \$/100 km	8.4	3.2
Tank compactness	Liter/100 km	73	18

Several automakers have developed the prototypes of hydrogen-fueled vehicles in recent years. Here, for analysis purposes, we select a Ford Focus (2008) H₂ICE prototype. In Table 5.3 we list the performance parameters of the actual prototype and some calculation results for the same prototype when converted to NH₃ fuel. In calculation it has been assumed that the cost of ammonia is \$0.30/kg and the powertrain performance is characterized by 1.19 MJ/km shaft power. This figure has been deduced from the published data by automaker (Ford Focus, 2008) and is based on stated 50% efficiency, 710 MJ stored in the full tank, and 298 km driving range. The efficiency of the ammonia engine has been taken the same as the hydrogen engine. In fact, ammonia can be decomposed on board at no additional cost (only using the heat rejected by the ICE) and the engine is fuelled with pure hydrogen.

As can be observed, the driving range of the NH₃ vehicle is much higher and hence more economical as shown by a driving cost of \$3.2/100 km as compared to \$8.4/100 km of H₂ICE. Moreover, the tank compactness of the ammonia car is about four times better.

5.6 Conclusions

Here, we have discussed the use of ammonia as a sustainable H₂ source. We have also proposed the option of using ammonia simultaneously as a refrigerant for cooling purposes on vehicles. This effect was quantified in terms of refrigeration power vs. engine's power. A performance investigation was performed for comparison of the proposed systems with other alternatives through energy efficiencies and effectiveness, along with a study of some additional parameters, such as driving range and cost associated with 100 km driving. Here are some concluding remarks:

- Ammonia as source of hydrogen leads to the lowest costs in terms of CN \$ per GJ stored on board.
- Among the considered alternative “H₂ from NH₃” is the cheapest fuel per 100 km driving range.

- There is an advantage of by-product refrigeration, ~20% from LHV, which reduces the costs.

Some additional advantages of NH_3 are commercial availability, global distribution network, handling experience, mature storage, and safety technologies.

Acknowledgment

The authors acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada in Canada.

Nomenclature

c	unit price, CN \$/kg
COP	coefficient of performance
DC	driving cost, CN \$/100 km
DR	specific driving range, km/l
h	specific enthalpy, kJ/kg
HHV	higher heating value, MJ/kg
LHV	lower heating value, MJ/kg
T	temperature, °C
w	specific work, kJ/kg
x	dissociated NH_3 fraction
Greek symbols	
ϵ	effectiveness (dimensionless)
η	efficiency, %
μ	molar mass, kg/kmol
ρ	density, kg/m ³
Superscripts	
'	liquid
'''	per unit of volume
Subscripts	
c	cooling effect
d	dissociation
r	refrigeration effect
w	work recovered

References

- Blarigan, BV (2000) Advanced Internal Combustion Engine Research. Proceedings of the DOE Hydrogen Program Review, NREL/CP-570-28890.
- Bomelburg, HJ (1982) Use of ammonia in energy-related applications. Plant/Operations Progress 1:175–180.
- Brandhorst, H, Tartachuk, B, Cahlea, D, Barron, T, Baltazar-Lopez, M (2007) Ammonia transformation and utilization. Proceedings of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. Published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.

- Cairns EJ, Simons EL, Tevebauch AD (1968) Ammonia-oxygen fuel cell. *Nature* 217:780–781.
- Christensen, CH, Johannessen, T, Sorensen, RZ, Norskov, JK (2006) Towards an ammonia-mediated hydrogen economy? *Catalysis Today* 111:140–144.
- Colonna, P, a Van der Stelt, TP (2004) FluidProp: a program for the estimation of thermo physical properties of fluids, Energy Technology Section, Delft University of Technology, The Netherlands. Published online at www.FluidProp.com.
- Dincer, I (2007) Environmental and sustainability aspects of hydrogen and fuel cell systems, *International Journal of Energy Research* 31:29–55.
- Dincer, I, Zamfirescu, C (2009) Methods and apparatus for using ammonia as sustainable fuel, refrigerant and NOx reduction agent. US Patent 61/064,133.
- DOE (2008) DOE Announces New Hydrogen Cost Goal. Published online at http://www1.eere.energy.gov/hydrogenandfuelcells/news_cost_goal.html (accessed on April 1, 2008).
- Ford Focus (2008) H₂ICE Ford Focus. Internet source http://media.ford.com/article_display.cfm?article_id=16375 (accessed on February 4, 2008).
- Ganley, JC, Seebauer, EG, Masel, RI (2004) Development of a microreactor for the production of hydrogen from ammonia. *Journal of Power Sources* 137:53–61.
- Holbroock J (2007) Wrap-up/Ammonia and the clean energy portfolio. Proceedings of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.
- IG (2008) Hydrogen. The innovation group. Published online at <http://www.the-innovation-group.com/ChemProfiles/Hydrogen.htm> (accessed on April 1, 2008).
- Kordesh, K, Aronsson, RR, Kalal, P, Hacker, V, Faleschini, G (2007) Hydrogen from cracked ammonia for alkaline fuel cell – rechargeable battery and ICE vehicles. Proceeding of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. Published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.
- Kroch, E (1945) Ammonia – a fuel for motor buses. *Journal of the Institute of Petroleum* 31:213–223.
- Lide, DR (1991) CRC Handbook of Chemistry and Physics, 72nd edition, CRC Press, Boca Raton, Florida.
- Maffei, N, Pelletier, L, Charland, JP, McFarlan, A (2007) A Direct Ammonia Fuel Cell Using Barium Cerate Proton Conducting Electrolyte Doped With Gadolinium and Praseodymium. *Fuel Cells* 4:323–328.
- McFarlan, A (2007) Development of Direct Ammonia Fuel Cells for Efficient Stationary CHP Applications. Proceedings of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. Published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.
- NIST (2008) Chemistry Webbook. Published online at <http://webbook.nist.gov/chemistry/> (accessed on February 24, 2008).
- NRC-NAE (2004) The hydrogen economy – opportunities, costs, barriers and R&D needs. National Research Council and National Academy of Engineering. The National Academic Press. Washington DC, p. 256.
- Olson, N (2007) BioAmmonia – A comparison with other biofuels. Proceedings of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. Published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.
- PEW Center (2008), The Distribution of CHG Emissions by Sector. PEW center on global climate change. Published online at http://www.pewclimate.org/global-warming-basics/facts_and_figures/us.emissions/usghgemsector.cfm (accessed on May 27, 2008).

- Sørensen, RZ, Nielsen, LJE, Jensen, S, Hansen, O, Johannessen, T, Quaade, U, Christensen, CH (2005) Catalytic ammonia decomposition: miniaturized production of CO_x-free hydrogen for fuel cells. *Catalysis Communications* 6:229–232.
- Spath, PL a Mann, MK (2001) Life cycle assessment of hydrogen production via natural gas steam reforming. National Renewable Energy Laboratory p. 33.
- Starkman, ES, Newhall, HK, Sutton, R, Maguire, T, Farbar, L (1967) Ammonia as a spark ignition engine fuel: theory and application. SAE Transactions paper 660155, pp. 765–784.
- Stockes, K (2007) Ammonia construction record and comments on ammonia fuel. Proc. Of the Ammonia – Sustainable, Emission Free Fuel Conference, October 15–16, San Francisco, CA, Iowa Energy Center. Published online at <http://www.energy.iastate.edu/Renewable/ammonia/ammonia/ammoniaMtg07.htm>.
- Thomas, G, Parks, G (2008) Potential Roles of Ammonia in a Hydrogen Economy. published online at http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf (accessed on April 2, 2008).
- Veziroglu, TN (2007) 21st Century's energy: hydrogen energy system. *International Scientific Journal for Alternative Energy and Ecology* 4:29–39.
- Waitzman, DA (1979) Ammonia from coal: a technical/economic review. Process technology and flow sheets. V. Cavaseno Eds., Chemical Engineering, McGraw-Hill Publishing Co., NY, pp 63–65.
- Wesley, C (2008) Separating carbon from natural gas and reusing it to make carbon fiber. *Canadian Business*, March 17:64–64.
- Xie K, Ma Q, Jiang Y, Gao J, Liu X, Meng G (2007) An ammonia fuelled SOFC with a Ce_{0.9}Nd_{0.1}O_{3-δ} thin electrolyte prepared with a suspension spray. *Journal of Power Sources* 170:38–41.
- Yin, SF, Xu, BQ, Zhou, XP, Au, CT (2004) A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications. *Applied Catalysis A: General* 277:1–9.
- Zamfirescu, C, Dincer, I (2008a) Environmentally-benign hydrogen production from ammonia for vehicles. *Proceedings of Global Conference on Global Warming, Istanbul* July 6–10 paper 626.
- Zamfirescu, C, Dincer, I (2008b) Using ammonia as a sustainable fuel, *Journal of Power Sources* 185:459–465.
- Zamfirescu, C, Dincer, I (2008c) Ammonia as a green fuel for transportation. *Proceedings of ASME, Energy Sustainability Conference*, August 10–14, Jacksonville, FL, paper 54329.
- Zamfirescu, C, Dincer, I (2009) Ammonia as a green fuel and hydrogen source for vehicular applications. *Fuel Processing Technology*. 90:729–737.

Environmentally Benign Nuclear-Based Hydrogen Production

Mehmet F. Orhan, Ibrahim Dincer and Marc A. Rosen

6.1 Introduction

Energy is a mainstay of an industrial society. It is, therefore, not surprising that many important organizations have attempted to analyze the future need for energy and the availability of various energy sources. Energy consumption growth is closely linked to population growth, although changes in life styles and efficiency improvement have a substantial influence on the per capita annual consumption. The structure of population and the share between urban and rural populations also affect energy demand (Torjman and Shaaban, 1998).

As a result of the worldwide increasing consumption of energy due to an increasing population and rising living standards in less industrialized countries, the world faces the problem of depleting energy resources and the impairing impact of present energy consumption patterns on the global climate as well as on humanity and the environment (Verfondern and Nishihara, 2005).

The risk of global climate change is of great concern to policy makers and to the public. The relation between the energy generation sector and environmental pollution is being carefully considered in industrialized countries. Before executing any power generation project, extensive and comprehensive studies are performed concerning the impact of such a project on the environment. Measures for decreasing climate change and environmental pollution are considered.

Beyond fossil fuels, the mismatch between energy consumption and energy production becomes more obvious. Nuclear facilities produce energy at a constant rate, while renewable energy facilities produce energy at a variable rate. Neither type of production matches demand. Because of day–night and seasonal variations of sunlight, the typical capacity factor of solar devices is 18%. (The capacity factor is the actual energy output in a year divided by the potential energy output if the device were operated at full capacity for the entire period.) The capacity factor for wind is about 35%. For renewable energy sources, the mismatch between generation and demand is so large that it has been estimated that if as little

as 15% of the electricity were produced by solar or wind, there would be limited economic incentive to obtain more energy from such sources, even if they are free. This is because backup power production facilities must be built to meet demand when these renewable energy sources are not available (Forsberg, 2005).

Research and development of clean, economic, stable, safe, and abundant energy should be promoted from the viewpoint of technology as a potential measure to mitigate global warming as well as for developing large and stable energy supplies. We have various alternative energy options to fossil fuels: solar, geothermal, hydropower, nuclear energy, etc. While available natural energy is limited due to its stability, quality, quantity, and density, it is certain that nuclear energy has the potential to contribute a significant share of energy supply and utilization. Nuclear energy has been almost exclusively utilized for electric power generation, but the direct utilization of nuclear thermal energy can be used to increase energy efficiency and thereby facilitate energy savings in the near future. Hydrogen production is one of the key technologies for direct utilization of nuclear thermal energy (Ponomarev-Stepnoi, 2004).

Hydrogen has ideal characteristics as secondary energy carrier. It can be stored, transported with lower loss compared with electricity, and used as fuel. If necessary, the chemical energy of hydrogen can be converted into electrical energy by means of fuel cells and other devices. Since it can be produced from water and, after oxidation, it returns to water, hydrogen is "clean" from the viewpoint of environmental effects. Therefore, the realization of a "hydrogen energy system" where hydrogen and electricity serve as complementary secondary energy carriers has been considered for a long time (Onuki et al., 2005).

Two candidates for large-scale production of hydrogen in the near future are nuclear-assisted thermochemical water splitting and natural gas steam reforming. They may both serve as hydrogen-producing technologies in the transition to a hydrogen-fuelled future. It is therefore interesting to investigate their relative environmental performances to gain a better understanding of the possible roads to a hydrogen society. Most of the hydrogen produced worldwide today is from fossil fuels, primarily through steam reforming of natural gas. Fossil fuels can also be subjected to several other reactions (gasification of coal, catalytic decomposition, partial oxidation, etc.) to obtain hydrogen. Unfortunately, this fossil fuel based hydrogen is not environmentally benign and does not contribute toward reducing greenhouse gas emissions. Hydrogen has to be extracted from water, using non-fossil fuels, in order to avoid the pollution problems and resource limitations of the fossil fuel-based production technologies.

The nuclear energy-driven thermochemical cycle is one of the potential water-splitting processes for producing hydrogen that has good potential for the future. The electrolysis of water is a well-known technology, but subject to lower overall efficiencies due to the inherent inefficiency of the conversion of thermal energy to electrical energy in thermal power stations. This inefficiency can be avoided through thermochemical cycles that consist of a sequence of chemical reactions yielding a net reaction of decomposition of water (Utgikar and Ward, 2006). In this chapter we describe nuclear-based hydrogen production technologies and discussed the role of the Cu-Cl cycle for thermochemical water decom-

position, potentially driven by waste/process heat from a nuclear power generation station, in reducing GHG emissions.

6.2 Energy Sources for Nuclear-Based Hydrogen Production

6.2.1 High-temperature gas-cooled reactor (HTGR)

Hydrogen production using thermochemical cycles has been studied in the last four decades. The thermal energy source for these processes has been high-temperature gas-cooled reactors (HTGR), which have been and/or are being developed. The maximum operating temperature of these cycles has been limited to about 800°C, which is the available temperature level of gas-cooled nuclear reactors. The high-temperature gas-cooled reactor (HTGR) is one of the most suitable nuclear reactors for producing the secondary energy carrier hydrogen owing to its capability of producing high-temperature heat at close to 1000°C, which assures an efficient energy conversion.

6.2.2 Advanced gas reactor (AGR)

The AGR is a commercial thermal reactor that has been built in the UK for electricity production in 1550 MWth units, with 14 units still in operation. The AGR core consists of uranium oxide fuel pellets in stainless steel cladding within graphite blocks. The graphite acts as a moderator and carbon dioxide is the coolant. The achievable temperature of the coolant at the reactor exit during normal operation is around 650°C. The carbon dioxide circulates through the core at 4.3 MPa. For future design and implementation, there is the potential to increase the operating pressure of the AGR in order to couple it to a direct cycle supercritical CO₂ power conversion system. The temperature of the reactor coolant for a future design can be driven up to 750°C with new designs and analysis. This combination can enable high-efficiency, economic hydrogen production through steam electrolysis at medium temperatures.

6.2.3 Advanced high-temperature reactor (AHTR)

The molten-salt-cooled advanced high-temperature reactor (AHTR) is a new reactor concept designed to provide very high-temperature (750–1000°C) heat to enable efficient low-cost thermochemical production of H₂ or production of electricity (Forsberg et al., 2003). The AHTR uses the solid coated-particle fuel in a graphite matrix like the MHR, but a molten-fluoride-salt as coolant. It combines the high-temperature fuel from the HTGR with a denser coolant for the molten salt reactor. The proposed design temperature of the coolant at the reactor exit is 1000°C. The graphite blocks are compatible with fluoride salts as coolant. The reactor concept is designed for atmospheric pressure operation. This design uses Ni-based high-temperature alloys that have been similarly adopted for molten

salts. The reactor is proposed to be built in large sizes (2000 MWth) with passive safety systems for decay heat removal.

6.2.4 Modular helium reactor (MHR)

The MHR is a thermal reactor that can be used both for hydrogen and electricity production in modules of 600 MWth. Its core consists of prismatic blocks of graphite that allow coolant flow and contains ceramic fuel. The temperature of the coolant, He gas, at the reactor exit is currently designed to achieve temperatures around 850°C. It is proposed to achieve 1000°C in the future within a new design, based on the same reactor concepts, called the very high-temperature reactor. The operating pressure of the MHR is 7 MPa. The core design can provide passive safety by achieving high temperatures during transients and by large thermal inertia.

6.3 Hydrogen Production Systems

To produce hydrogen, the hydrogen bonds in hydrocarbons or water must be broken and hydrogen must be separated from the reaction mixture. The most efficient method for meeting increasing energy needs could be to convert nuclear power into electricity and hydrogen, thus providing effective and universal energy carriers. Nuclear power plants produce heat that can be used directly or converted into electricity for the production of hydrogen. Four classes of H₂ production options are under development (e.g., Forsberg, 2007):

- electrolysis (electricity + H₂O [liquid] → H₂ + O₂);
- high-temperature electrolysis (electricity + H₂O [steam] → H₂ + O₂);
- hybrid cycles (electricity + heat + H₂O → [cyclic chemical reactions] → H₂ + O₂);
- thermochemical cycles (heat + H₂O → [cyclic chemical reactions] → H₂ + O₂).

The near-term option is electrolysis. The longer term options involve using heat to convert water to hydrogen and oxygen. Because heat is less expensive than electricity (because the cost is avoided of converting heat to electricity with associated losses), these advanced processes have the long-term potential of lower production costs (Forsberg, 2007).

Estimates from Japan are that the cost of nuclear thermochemical H₂ production could be as low as 60% of that for nuclear H₂ production by the electrolysis of water (Forsberg et al., 2003). At the most fundamental level, thermochemical H₂ production involves the conversion of thermal energy to chemical energy (H₂) while electrolysis involves the conversion of thermal energy to electricity and subsequent conversion of electricity to chemical energy.

Nuclear energy provides a source of heat to produce H₂. Multiple processes are being investigated to produce H₂ from water and heat. If nuclear energy is to be used for H₂ production, the nuclear reactor must deliver the heat at conditions

that match the requirements imposed by the H₂ production process. At this stage of development, it is unclear which chemical processes will be the most economic; thus the major candidate technologies were examined to determine if they impose similar requirements on the reactor (Forsberg, 2003).

Methods for obtaining hydrogen using carbon compounds as the raw material will probably be the main methods in the near future. However, the raw materials and ecological limitations of steam conversion of methane are stimulating the development of processes to produce hydrogen from water. The most interesting of these methods in the context of nuclear power are electrolysis and thermochemical and thermoelectrochemical cycles. Figure 6.1 presents an overview of nuclear-based hydrogen production technologies. The main processes for hydrogen production include steam reforming of natural gas, catalytic decomposition of natural gas, partial oxidation of heavy oil, coal gasification, water electrolysis, thermochemical cycles, and photo-chemical, electrochemical, and biological processes. The first four processes are based on fossil fuels.

6.3.1 Steam conversion of methane

Large amounts of hydrogen and hydrogen-containing products are now produced primarily by steam conversion of the methane in natural gas. Steam and heat at 750–850°C are required to separate hydrogen from the carbon base in methane; this is what happens on catalytic surfaces in chemical steam reformers. The first step of the reaction splits methane and water vapor into hydrogen and carbon monoxide (the synthesis gas). Next the “shift reaction” converts carbon monoxide and water into carbon dioxide and hydrogen. This reaction occurs at 200–250°C. For the endothermic process, about half of the initial gas is consumed. A model of this system can consist of a nuclear part, which generates the synthesis gas and a process part, where the input gas is used to produce the final product. Figure 6.2 shows the principle of steam methane reforming, and based on this figure its chemical formula is expressed as $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{CO}_2 - 185 \text{ kJ/mol}$. The heat of reaction is 185 kJ/mol, the heat for 1 mol hydrogen is 46.25 kJ/mol, and this reaction is endothermic (Chikazawa et al., 2005).

6.3.2 Thermochemical and thermoelectrochemical cycles

High temperatures (above 2500°C) are required for direct thermal decomposition of water into hydrogen and oxygen. However, water can be decomposed thermally at lower temperatures using a sequence of chemical reactions which perform the following functions: binding water, splitting hydrogen and oxygen from the water, and recovering the reagents. Figures 6.3 and 6.4 show, respectively, the schematics for thermochemical processes that do not require electricity input and electrothermochemical processes that require electricity input in addition to thermal energy input (Yildiz et al., 2006).

The thermochemical process for producing hydrogen with an efficiency of up to 50% employs a sequence of chemical reactions and requires heat at a tem-

perature of about 1000°C. A high-temperature reactor serves as the heat source for thermochemical decomposition of water. Electrolysis and plasma can be used, together with heat, for splitting off hydrogen at individual stages of such processes. Many combinations of chemical reactions, where water is split into hydrogen and oxygen in a closed cycle with heat and electricity being absorbed, have been studied. Some examples are as follows as:

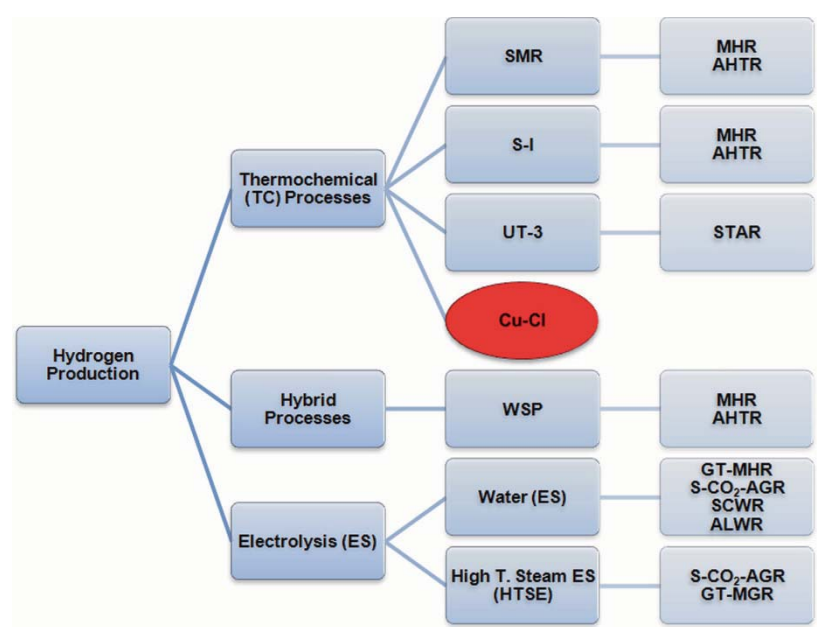


Fig. 6.1 Technology options for nuclear hydrogen production (modified from Yildiz and Kazimi, 2006).

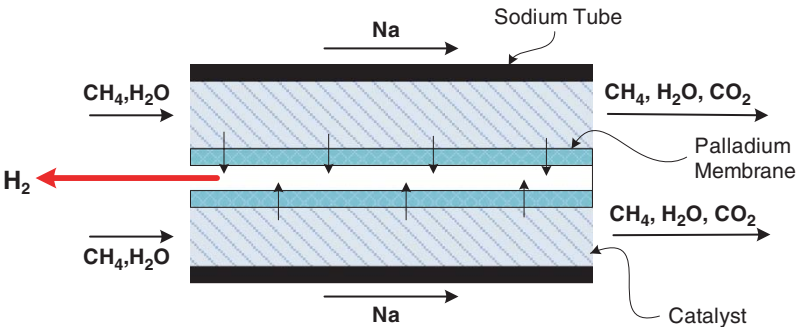


Fig. 6.2 Principle of membrane reformer (adapted from Chikazawa et al., 2005).

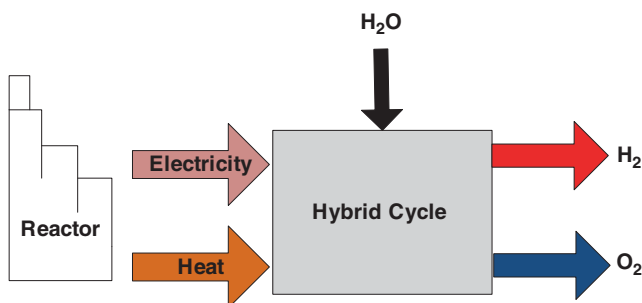


Fig. 6.3 Simple coupling of an electrothermochemical water-splitting process, a nuclear reactor, and a power conversion system for hydrogen production.

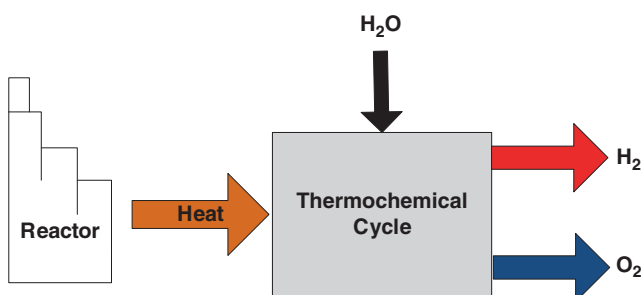


Fig. 6.4 Simple coupling of a thermochemical water-splitting process and a nuclear reactor for hydrogen production.

6.3.2.1 Iodine–sulfur cycle

The IS process consists of the following three chemical reactions:

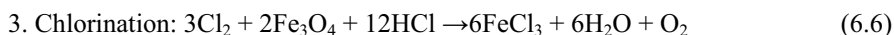
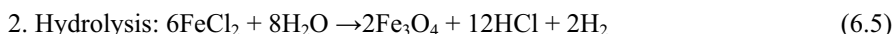


The principles for the IS process are illustrated in Fig. 6.5. The so-called Bunsen reaction, Eq. (6.1), is an exothermic sulfur dioxide (SO₂) gas absorbing reaction, which proceeds spontaneously in the liquid phase at 20–100°C. Gaseous sulfur dioxide reacts with iodine and water producing an aqueous solution of hydriodic acid and sulfuric acid. The two kinds of acids are separated by liquid–liquid phase separation in the presence of excess iodine. The hydrogen iodide (HI) decomposition reaction, Eq. (6.2), produces hydrogen with a low endothermic heat of reaction at 300–500°C in the gas phase. It can also be carried out in the liquid phase. The sulfuric acid (H₂SO₄) decomposition reaction, Eq. (6.3), is an endothermic oxygen-producing reaction, which proceeds in two stages. First, gaseous H₂SO₄ decomposes spontaneously into H₂O and SO₃ at 400–500°C and then SO₃ decom-

poses into SO_2 and O_2 at about 800°C in the presence of a solid catalyst. By carrying out these three reactions sequentially, the net result is that water is decomposed into hydrogen and oxygen (Xinxin and Kaoru, 2005).

6.3.2.2 ISPRA mark 9 cycle

The ISPRA Mark 9 thermochemical cycle (shown in Fig. 6.6), one of the several proposed thermochemical cycles reported in the literature, is a three-step cycle involving iron chlorides as shown below:



The hydrolysis reaction is conducted at 650°C , which is the highest temperature in the cycle. The decomposition of Fe (III) chloride is conducted at 430°C and the chlorination at 150°C (Utgikar and Ward, 2006).

6.3.2.3 Hybrid sulfur cycle

In the Hybrid sulfur cycle (see Fig. 6.7), developed by Westinghouse, H_2SO_4 is decomposed into SO_2 at high temperature, and the SO_2 is converted back into H_2SO_4 in a PEM electrolyzer at 80°C . Overall only water and energy are consumed, and H_2 and O_2 are produced (Sivasubramanian et al., 2007).

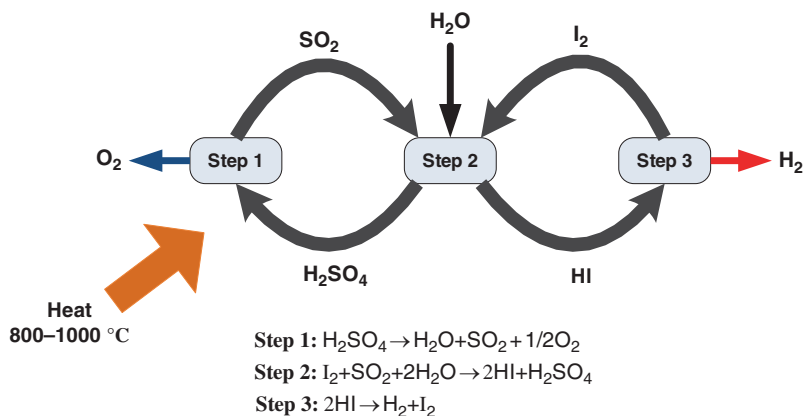


Fig. 6.5 Iodine-sulfur process for thermochemical production of H_2 (adapted from Xinxin and Kaoru, 2005).

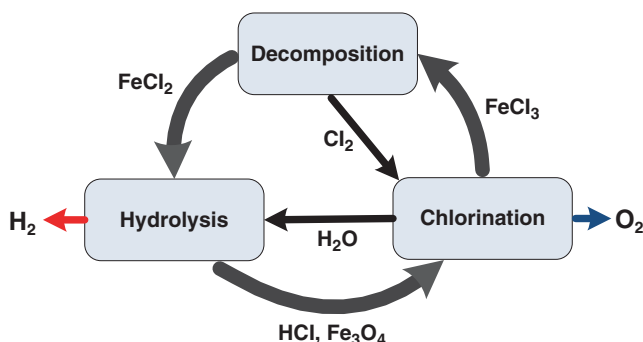


Fig. 6.6 Flow diagram for the ISPRA Mark 9 hydrogen production process (adapted from Utgikar and Ward, 2006).

6.3.2.4 Ca–Br cycle

In the calcium–bromine cycle, as illustrated in Fig. 6.8, CaO and CaBr₂ are recycled in high-temperature, solid–gas, fixed bed reactors, and HBr is converted into Br₂ in a PEM electrolyzer at 80°C. Overall only water and energy are consumed, and H₂ and O₂ are produced.

6.3.2.5 Copper–chlorine cycle

Most thermochemical cycles require process heat at high temperatures, exceeding 850–900°C. However, existing nuclear power plants in the USA and elsewhere are typically water-cooled plants operating at 250–500°C. Recently, Atomic Energy of Canada Limited and Argonne National Laboratory in the USA have been developing low-temperature cycles, designed to accommodate heat sources around 500–550°C. Such cycles can be more readily integrated with nuclear reactors. For this temperature range, the copper–chlorine (Cu–Cl) cycle is one of the most promising. Several Cu–Cl cycles have been examined in the laboratory and various alternative configurations identified. Proof-of-principle experiments that demonstrate the feasibility of the processes have been undertaken and a preliminary assessment of the cycle efficiency has demonstrated its potential.

A conceptual layout of a Cu–Cl pilot plant is illustrated in Fig. 6.9. Thermochemical water decomposition, potentially driven by nuclear heat with a copper–chlorine cycle, would split water into hydrogen and oxygen through intermediate Cu and Cl compounds. This cycle consists of three thermal reactions and one electrochemical reaction. The cycle involves five steps: (1) the HCl(g) production step using such equipment as a fluidized bed, (2) the oxygen production step, (3) the copper (Cu) production step, (4) the drying step, and (5) the hydrogen production step. A chemical reaction takes place in each step, except the drying step. The chemical reactions form a closed internal loop that re-cycles all of the copper–chlorine compounds on a continuous basis, without emitting any greenhouse gases externally to the atmosphere. The five steps of the copper–chlorine cycle are described in Table 6.1. The Cu–Cl cycle is one of the most promising ways to produce hydrogen efficiently, without emitting greenhouse gases into the atmosphere.

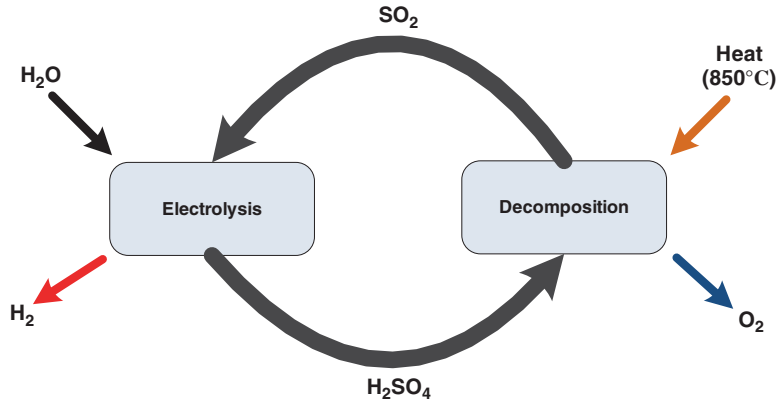


Fig. 6.7 A schematic of the hybrid sulfur cycle (adapted from Sivasubramanian et al., 2007).

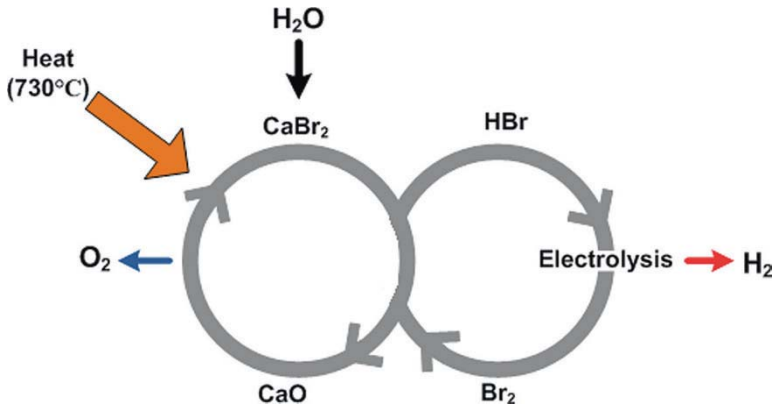


Fig. 6.8 A schematic of the modified Ca–Br cycle (adapted from Sivasubramanian et al., 2007).

Table 6.1 Key steps of Cu–Cl cycle with their corresponding reaction (adapted from Lewis et al., 2003).

Step	Reaction	Temperature range (°C)	Pressure (kPa)	Feed/output (note: Q-thermal energy, V-electrical energy)	
1	$2CuCl_2(s)+H_2O(g)\rightarrow CuO\cdot CuCl_2(s)+2HCl(g)$	400	101	Feed:	$CuCl_2(s)+H_2O+Q$
				Output:	$CuO\cdot CuCl_2(s)+HCl(g)$
2	$CuO\cdot CuCl_2(s)\rightarrow 2CuCl(l)+1/2O_2(g)$	500	101	Feed:	$CuO\cdot CuCl_2(s)+Q$
				Output:	Molten CuCl salt + O_2
3	$4CuCl(s)+H_2O\rightarrow 2CuCl_2(aq)+2Cu(s)$	25–80	101	Feed:	CuCl and H_2O+V
				Output:	Cu and slurry
4	$CuCl_2(aq)\rightarrow CuCl_2(s)$	>100	101	Feed:	$CuCl_2(aq)+Q$
				Output:	$CuCl_2+H_2O$ vapors
5	$2Cu(s)+2HCl(g)\rightarrow 2CuCl(l)+H_2(g)$	430–475	101	Feed:	Cu + HCl
				Output:	$H_2+CuCl(l)$ salt+Q

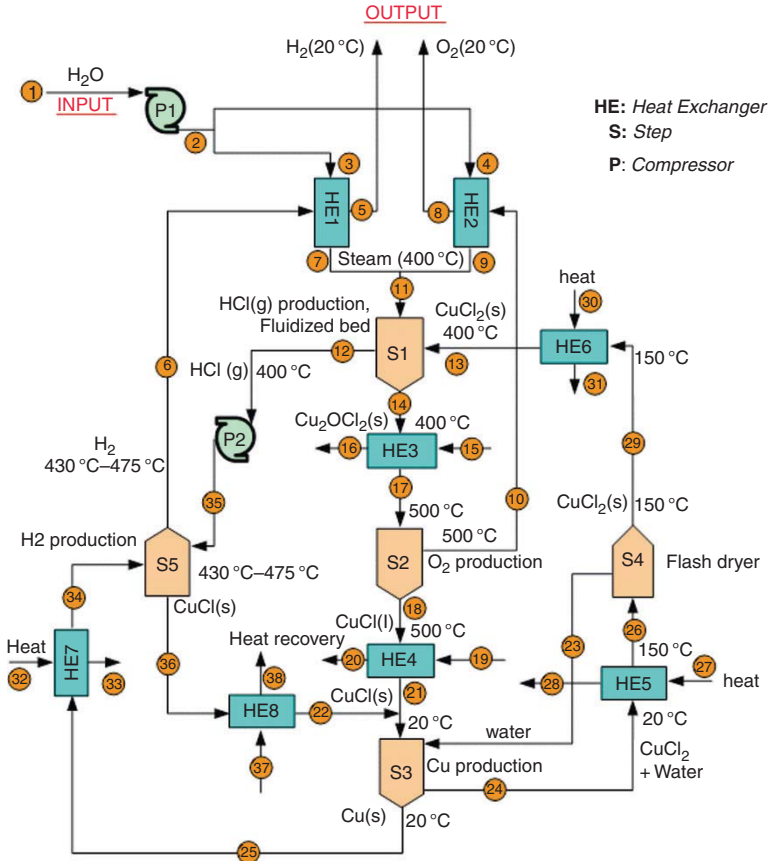


Fig. 6.9 Conceptual layout of a thermochemical Cu–Cl hydrogen production cycle.

The heat transfer for a chemical process involving no work interaction W is determined from the energy balance $\dot{E}_{\text{in}} - \dot{E}_{\text{out}} = \Delta \dot{E}_{\text{system}}$ applied to a system with $W = 0$. For a steady-state reaction process, the energy balance reduces to

$$Q = H_P - H_R = \sum n_P (h_f + h - h)_{\text{P}} - \sum n_R (h_f + h - h)_{\text{R}} \quad (6.8)$$

The variations of the reaction heats for steps involving a chemical reaction (steps 1, 2, 3, and 5) with the temperatures of the reactions are illustrated in Fig. 6.10. As explained earlier, all steps are endothermic except the fifth. The reaction in fifth step, in which hydrogen production occurs, is exothermic and the heat produced is seen in Fig. 6.10 to be rejected from the system. As reaction temperature increases,

the reaction heat for steps 1, 3, and 5 decreases while that for step 2 increases. In all cases, the relations are nearly linear.

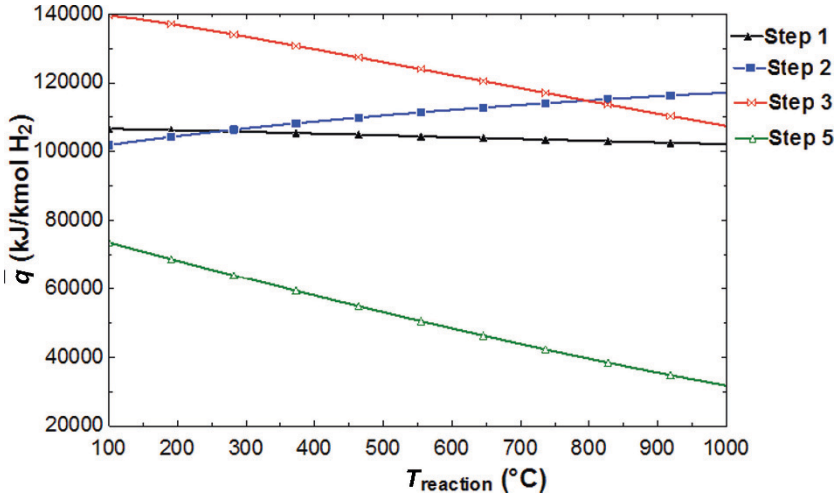


Fig. 6.10 Variation of reaction heat with reaction temperature for several steps in the Cu–Cl cycle.

An exergy balance can be used in formulating an exergy efficiency for the reacting system (for each step of Cu–Cl cycle, individually); at steady state, the rate at which exergy enters the reacting system equals the rate at which exergy exits plus the rate at which exergy is destroyed within the system. It is assumed that the reactor is well insulated, so that there is no exergy transfer accompanying heat transfer. There is also no work $\dot{W}_{cv}$. Accordingly, exergy exits only with the reaction products. An exergy efficiency can be written as

$$\eta_{ex} = \frac{\overline{ex}_{out}}{\overline{ex}_{in}} \quad (6.9)$$

where $\overline{ex}_{in}$ is the exergy that enters with the reactants plus heat, in the case of endothermic reaction, and $\overline{ex}_{out}$ is the exergy that exits the system with the products plus heat, in the case of exothermic reaction. Using the exergy balance for the reacting system, the exergy efficiency expression can be written alternatively as

$$\eta_{ex} = 1 - \frac{\overline{ex}_{destroyed}}{\overline{ex}_{in}} \quad (6.10)$$

Using Eq. (6.10) the exergy efficiency of each step of the Cu–Cl cycle is given in Table 6.2, based on the specified state. These efficiencies may change by changing the state (i.e., temperature, pressure) of the reaction/process. As illustrated in Table 6.2, the efficiency of each step seems to be high, however, the overall efficiency of the cycle is not that high, at below 50%.

Table 6.2 Exergy efficiencies of the steps associated with Cu–Cl cycle at specified temperature and pressure.

Step	Name	Reaction heat (kJ/kmol H ₂)	Temp. (°C)	Pres. (kPa)	η_{ex} (%)
1	Fluidized bed	105,266	400	101.325	76
2	O ₂ production step	110,523	500	101.325	96
3	Cu production step	140,450	45	101.325	99
4	Evaporator	18,346	150	101.325	67
5	H ₂ production step	–55,493	450	101.325	99

As mentioned earlier, we are analyzing a hypothetical Cu–Cl plant and that has not been built yet. Thus, many parameters such as quantity, capacity, and material of equipment (pumps, heat exchangers, compressors, fluidized bed, evaporator, etc.) that we need for these analyses are unknown. Therefore, for simplicity, in overall efficiency calculations we consider only the five main steps of the Cu–Cl cycle and assume that there are no heat losses in these steps, individually. However, overall we assume a total heat loss (Q_{loss}) from the Cu–Cl cycle as a percentage of total heat (Q_{in}) that enters the cycle.

The overall energy efficiency of the Cu–Cl cycle, η_{overall} , can be described as the fraction of energy supplied that can be recovered from the energy content of H₂ based on its lower heating value:

$$\eta_{\text{overall}} = \frac{\overline{LHV}_{\text{H}_2}}{\overline{Q}_{\text{in}} + \overline{Q}_{\text{loss}}} \quad (6.11)$$

where $\overline{LHV}_{\text{H}_2}$ is the lower heating value per kmole of hydrogen and $\overline{Q}_{\text{in}}$ is the total energy demand by the process to produce a unit amount of product hydrogen. This total energy demand of the Cu–Cl cycle is the summation of the reaction heats of the five main steps described above. Note that in this summation of reaction heats, the exothermic reaction heat (i.e., fifth step) is taken as negative, assuming this heat can be used for other endothermic reactions. The lower heating value of hydrogen is given as 242,400 kJ/kmol H₂. As explained earlier energy loss from the cycle (Q_{loss}) cannot be calculated, so in this study we presume Q_{loss} as a percentage of Q_{in} . Using these assumptions and Eq. (6.11), we obtain Fig. 6.11 showing the relation between energy efficiency (η) and the cycle

temperature (T_{cycle}). In this figure, curves (a), (b), and (c) are obtained assuming Q_{loss} is equal to 20, 30, and 40% of Q_{in} , respectively.

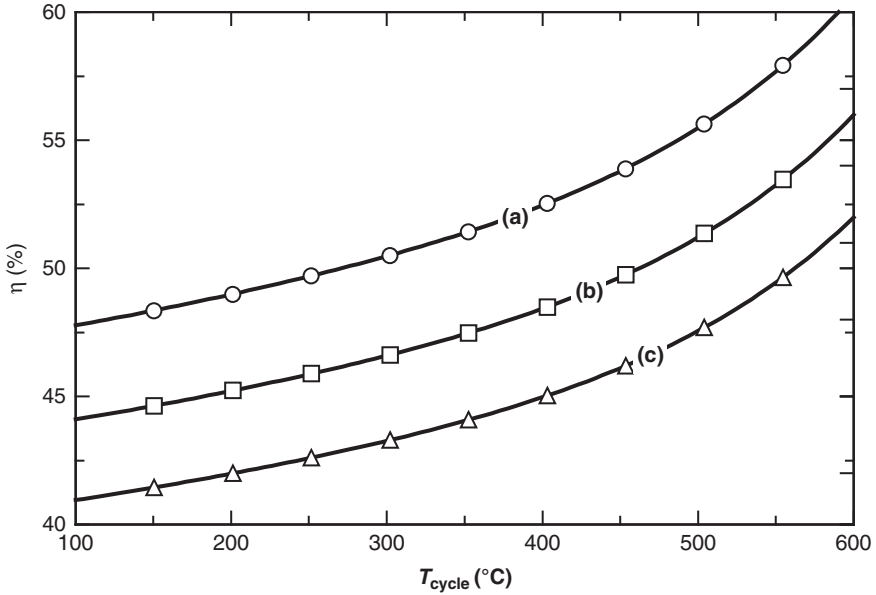


Fig. 6.11 Variation of overall energy efficiency of the Cu–Cl cycle with the cycle temperature based on three different assumptions: (a) $Q_{\text{loss}}=0.2Q_{\text{in}}$, (b) $Q_{\text{loss}}=0.3Q_{\text{in}}$, (c) $Q_{\text{loss}}=0.4Q_{\text{in}}$.

The overall exergy efficiency of the Cu–Cl cycle, $\eta_{\text{ex, overall}}$, can be described as the fraction of exergy supplied that can be recovered from the exergy content of hydrogen:

$$\eta_{\text{ex, overall}} = \frac{\overline{ex}_{\text{H}_2}}{(\overline{Q}_{\text{in}} + \overline{Q}_{\text{loss}}) * (1 - \frac{T_0}{T_{\text{cycle}}})} \quad (6.12)$$

where $\overline{ex}_{\text{H}_2}$ is the specific exergy content of the hydrogen produced, taken to be 236,098 kJ/kmol (Ertesvag, 2007). Figure 6.12 shows the relation between overall exergy efficiency of the Cu–Cl cycle with its temperature. In this figure, curves (a), (b), and (c) are obtained assuming Q_{loss} is equal to 40, 30, and 20% of Q_{in} , respectively.

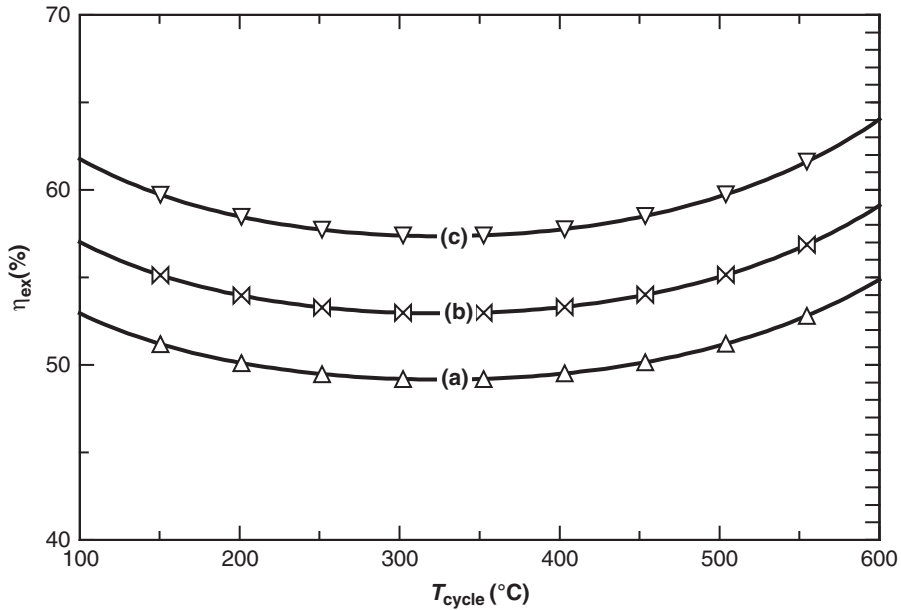


Fig. 6.12 Relation between overall exergy efficiency and temperature of the Cu–Cl cycle. (a) $Q_{\text{loss}}=0.4Q_{\text{in}}$, (b) $Q_{\text{loss}}=0.3Q_{\text{in}}$, (c) $Q_{\text{loss}}=0.2Q_{\text{in}}$.

6.4 Concluding Remarks

This chapter describes nuclear-based energy sources and technologies such as thermochemical cycles for hydrogen production. The efficiency analysis reported in this chapter for a Cu–Cl thermochemical water decomposition cycle for hydrogen production has allowed several findings. For each of the steps in the cycle, the variations of reaction heat with parameters like process temperature have been quantified and characterized. Also exergetic efficiency of each step has been obtained based on a specified state for each step. In particular, a parametric study is reported of how the reaction heat in each chemical reaction, overall energy, and exergy efficiencies of the Cu–Cl cycle vary with the cycle temperature. This information should assist efforts to understand the thermodynamic losses in the cycle and to improve efficiency. It can be concluded that advanced hydrogen production processes show great potential for future applications.

Acknowledgment

The authors acknowledge the support provided by the Ontario Research Excellence Fund.

Nomenclature

E	Energy, kJ
Ex	Exergy, kJ
$\overline{ex}$	Specific molar exergy, kJ/kmol
H	Enthalpy, kJ
h	Specific enthalpy, kJ/kg
$\overline{h}$	Specific molar enthalpy, kJ/kmol
h^{-0}	Specific molar enthalpy at reference state, kJ/kmol
h_f^{-0}	Specific molar enthalpy of formation, kJ/kmol
n	Number of moles per cycle, kmol/kmol H_2
Q	Heat, kJ
$\overline{q}$	Specific molar reaction heat, kJ/kmol
T_{cycle}	Cycle temperature, °C
T_0	Reference-environment temperature, °C
Greek Letters	
η_e	Energy efficiency
η_{ex}	Exergy efficiency

References

- Chikazawa, Y, Konomura, M, Uchida, S, Sato, H (2005) A feasibility study of a steam methane reforming hydrogen production plant with a sodium-cooled fast reactor. *Nuclear Technology* 152: 266–272.
- Ertesvag, IS (2007) Sensitivity of chemical exergy for atmospheric gases and gaseous fuels to variations in ambient conditions. *Energy Conversion and Management* 48: 1983–1995.
- Forsberg, CW (2003) Hydrogen, nuclear energy, and the advanced high-temperature reactor. *International Journal of Hydrogen Energy* 28: 1073–1081.
- Forsberg, C (2005) Futures for hydrogen produced using nuclear energy. *Progress in Nuclear Energy* 47: 484–495.
- Forsberg, CW (2007) Future hydrogen markets for large-scale hydrogen production systems. *International Journal of Hydrogen Energy* 32: 431–439.
- Forsberg, CW, Peterson PF, Pickard, PS (2003) Molten salt-cooled advanced high temperature reactor for production of hydrogen and electricity. *Nuclear Technology* 144: 289–302.
- Lewis, MA, Serban, M, Basco, JK (2003) Hydrogen production at <550°C using a low temperature thermochemical cycle. *Proc. Nuclear Production of Hydrogen: Second Information Exchange Meeting*, pp. 145–156, Argonne, Illinois, U.S., 2–3 October 2003.
- Onuki, K, Inagaki, Y, Hino, R, Tachibana, Y (2005) Research and development on nuclear hydrogen production using HTGR at JAERI. *Progress in Nuclear Energy* 47: 496–503.
- Ponomarev-Stepnoi, NN (2004) Nuclear-hydrogen power. *Atomic Energy* 96: 375–385.
- Sivasubramanian, PK, Ramasamy, RP, Freire, FJ, Holland, CE, Weidner, JW (2007) Electrochemical hydrogen production from thermochemical cycles using a proton exchange membrane electrolyzer. *International Journal of Hydrogen Energy* 32: 463–468.
- Torjman, M, Shaaban, H (1998) Nuclear energy as a primary source for a clean hydrogen energy system. *Energy Conversion and Management* 39: 27–32.

- Utgikar, V, Ward, B (2006) Life cycle assessment of ISPRA Mark 9 thermochemical cycle for nuclear hydrogen production. *Journal of Chemical Technology and Biotechnology* 81: 1753–1759.
- Verfondern, K, Nishihara, T (2005) Safety aspects of the combined HTTR/steam reforming complex for nuclear hydrogen production. *Progress in Nuclear Energy* 47: 527–534.
- Xinxin, W, Kaoru, O (2005) Thermochemical water splitting for hydrogen production utilizing nuclear heat from an HTGR. *Tsinghua Science and Technology* 10: 270–276.
- Yildiz, B, Hohnholt, KJ, Kazimi, MS (2006) Hydrogen production using high-temperature steam electrolysis supported by advanced gas reactors with supercritical CO₂ cycles. *Nuclear Technology* 155: 1–21.
- Yildiz, B, Kazimi, MS (2006) Efficiency of hydrogen production systems using alternative nuclear energy technologies. *International Journal of Hydrogen Energy* 31: 77–92.

Environmental Benefits of Geothermal-Based Absorption Cooling Systems

Can Coskun, Zuhul Oktay and Ibrahim Dincer

7.1 Introduction

Environmental problems have become more apparent through a continuously growing range of pollutants, hazards, and ecosystem degradation over wider areas. Although the most significant air pollution problems were acid precipitation, stratospheric ozone depletion, and global climate change, the focus has been on global warming due to drastic increase in greenhouse gas emissions and their immediate results through catastrophic climate changes/events.

Recently, a variety of potential solutions to the current environmental problems associated with the greenhouse gas emissions has evolved. In this regard, energy systems (heat pumps, refrigeration systems, etc.) have received much attention. Absorption Cooling Systems (ACSs) have been gaining some popularity as they operate on environment friendly refrigerants conforming Montreal and Kyoto Protocols. These systems also utilize geothermal, biomass, solar energy, and waste heat as less expensive alternative energy source. Therefore, much research has been devoted to the improvement of ACSs (e.g., Misra et al., 2006; Sun 1998; Sozen 2001; and Saravanan et al., 1998). The main advantage of ACSs lies under the possibility of being powered directly by thermal energy at moderate temperature levels. Thus, it is a good alternative to utilize the waste or inexpensive heat in the cooling (Bassols et al., 2002). Utilization of ACSs becomes suitable in the case of inexpensive heat energy source over 70°C. Therefore, geothermal energy has a wide range of application potential for cooling. ACS provides reliable and quiet cooling using thermal energy. The most widely used ACS is the ammonia–water system, in which ammonia and water serve as the refrigerant and transport medium, respectively. The other ACSs include water–lithium chloride and water–lithium bromide systems, where water serves as the refrigerant.

Turkey's primary energy consumption is about 64 MTOE in 2003, mostly provided by fossil fuels (74.7%). Renewables collectively provide 25.3% of the primary energy, in the form of hydro (14.6%), combustible renewable and waste (9%), geothermal (1.2%), and the other renewables (0.5%). Although Turkey is ranked as seventh in the world for its geothermal energy potential, it utilizes only about 4% of this potential effectively (Akpınar et al., 2008).

Eight geothermal district heating systems (GDHSs) in Turkey appear to be suitable for absorption cooling according to district heating supply or wellhead temperature (Oktay et al., 2007a): Balçova–İzmir GDHS (85°C), Sandıklı–Afyon GDHS (70°C), Diyarın–Ağrı GDHS (78°C), Bigadiç–Balıkesir GDHS (75°C), Gönen–Balıkesir GDHS (80°C), Kızılcahamam–Ankara GDHS (80°C), Kozaklı–Nevşehir GDHS (90°C), and Salihli–Manisa GDHS (94°C).

In this chapter a new geothermal energy-assisted ACS concept is developed to study how it will help reduce energy consumptions and greenhouse gas emissions to combat the global warming. The first part of this study includes a feasibility study of incorporating an ACS into a geothermal district heating system (so-called: the Bigadic geothermal district heating system). In the second part, a study is conducted to analyze the cooling potential of the water–lithium bromide ACS for a building in the summer months, in addition to the geothermal district heating system which normally provides the necessary heating requirement. For both cooling and heating cases, comparisons are made with the cases using conventional fossil-fuel based energy sources to investigate how geothermal energy as a renewable and sustainable option will help reduce greenhouse gas emissions, particularly CO₂. While the geothermal fluid temperature entering the residence's main heat exchangers is in the range of 343–349 K, the supply temperature for the generator of ACS results in 345 K. Some parametric studies are conducted with a large amount of actual data to reflect the reality in the best possible way.

7.2 The Bigadic Geothermal District Heating System

The Bigadic Geothermal District Heating System (GDHS) has the longest geothermal pipeline in Turkey (considered world's third longest pipeline). The Bigadic geothermal field is located 38 km south of the city of Balıkesir which is in the west of Turkey (Fig. 7.1). Bigadic geothermal field covers a total used area of about 1 km². As of the end of 2007, there were three wells ranging between depth of 307 and 429 m, respectively. The well head temperature is 98°C. There were five pumps operational in the Bigadic geothermal field. Three of these are used for the wells and the other two are used to pump fluid to mechanical rooms. The wells 1 and 2 are basically artesian wells. The Pump-3 is designed to pump automatically when the flow rate requirement becomes 100 kg/s, and is generally not used because of the elevation difference between the geothermal source and the mechanical room. This elevation difference is about 200 m and provides enough pressure difference to drive the geothermal fluid. If the mass flow rate demand increases significantly, the Pump-3 will start automatically.

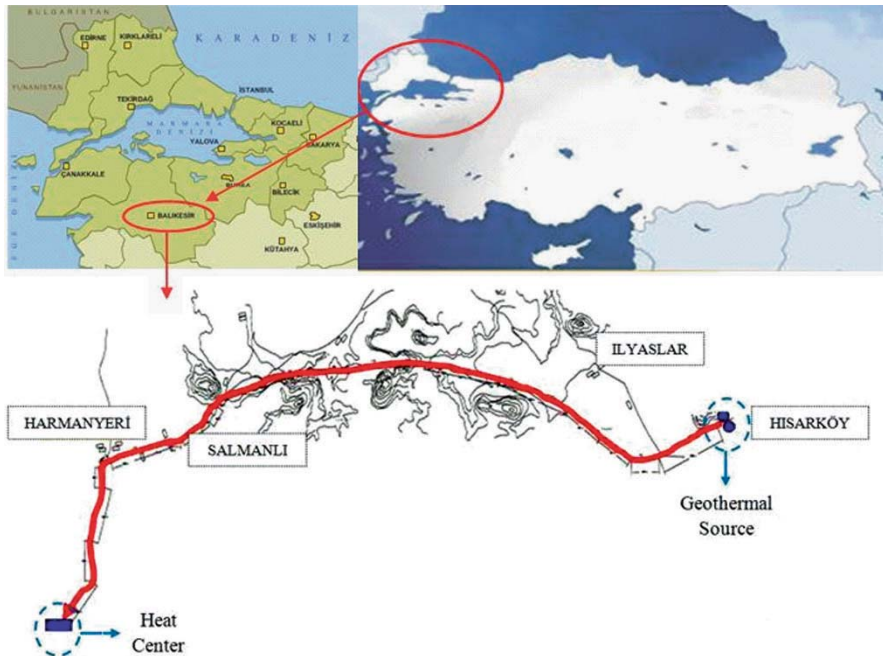


Fig. 7.1 Map of the geothermal field in Bigadic.

Here, we can explain the system in three main parts as shown in Fig. 7.2. In the first part, the geothermal fluid is pumped into the ‘mud and gas separator unit’ to separate undesirable particles. After passing through the mud and gas separator unit, the geothermal fluid flows into the first heat exchanger. There is an 18 km long pipeline between the geothermal source and the mechanical room. In-between the geothermal source and the mechanical room, the geothermal fluid temperature decreases between 3 and 4°C, respectively, which essentially causes some high amount of energy losses. In the second part, the geothermal fluid transfers its heat to the tap water for residential buildings and is cooled to about 44°C in the first and second heat exchangers available in the mechanical room. After the heat transfer takes place in the first and second heat exchangers, the geothermal fluid is sent to the first and second center-pipeline. In the third part, clean hot water is pumped to the heat exchangers located under each building. The system is designed to have one or two heat exchangers for each building. One heat exchanger is for heating building and the other is for hot-water requirements. Presently, each building has one or two heat exchanger(s) to supply heat and hot water requirements. Nearly 10% of the total residences in Bigadic may have extra water heaters in case the desired temperature is not obtained. There are three pipelines to transfer the hot water along the different pipelines. The second and third center-pipelines supply the heat requirement of the dwellings, one post office, one dormitory, eight colleges, one state hospital, two police stations, and ten government agency buildings.

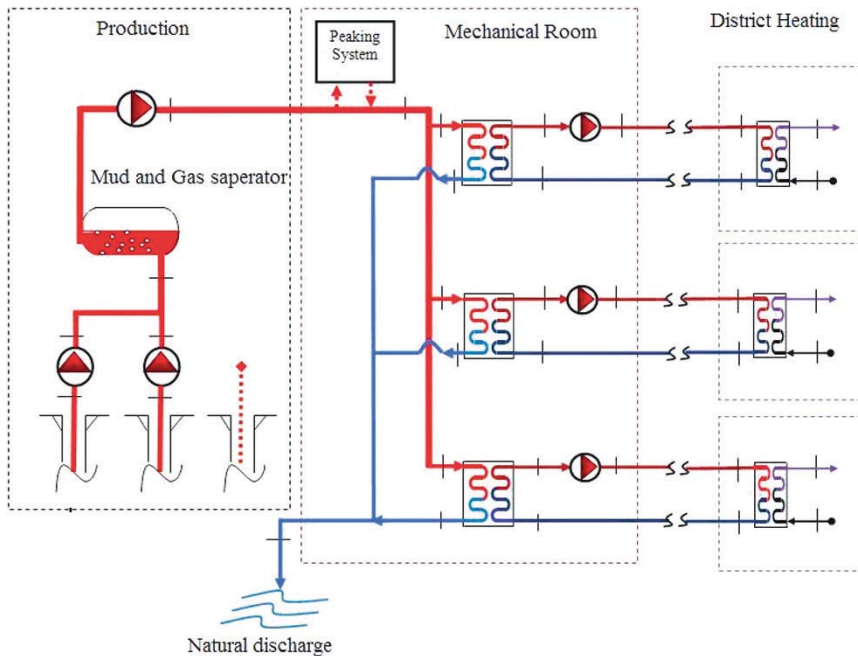


Fig. 7.2 A flowchart of the Bigadic GDHS.

Although we have calculated and presented the heating energy demand for winter season of Bigadic GDHS in a recent study (Oktay et al., 2007b), we now focus on its cooling energy demand for summer season. In the following sections, methods and calculations of cooling load are given and explained clearly.

7.3 Methodology

7.3.1 Analysis method for building energy demand

A wide variety of building energy analysis methods are currently available to HVAC engineers and range from simple to sophisticated. The simplest methods involve the largest number of simplifying assumptions and therefore tend to be the least accurate. The most sophisticated methods involve the fewest assumptions and thus can provide the most accurate results. Generally, methods for building energy analysis can be categorized into three and are as follows:

- Single Measure Method (example: Equivalent Full Load Hours)
- Simplified Multiple Measure Method (example: Bin Method)
- Detailed Multiple Measure Method (example: Hour by Hour)

Here, calculations are made via detailed multiple measure method. In this method, energy calculations are on hour-by-hour basis. As a result, they have the potential

to satisfy all the requirements listed earlier for high-quality energy analysis results. There is, however, a certain amount of variation among different detailed multiple measure methods, leading some methods to meet the accuracy requirements better than others. Within the detailed multiple measure category, there are two major sub-categories worth discussing: The Reduced Hour-By-Hour Method and 8760 Hour-By-Hour Method. In our calculation the second method is used.

7.3.1.1 The 8760 hour-by-hour method

This method simulates building and equipment performance for all 8,760 hours in the year using the proper sequence of days and actual weather data. No weighting of results or simplifications are necessary. The fundamental principle is that the way to produce the most accurate energy and operating cost estimates is to mimic the real-time operating experience of a building over the course of a year. All the requirements listed earlier for high-quality energy analysis results can be met with this approach. The actual weather data account for the range and timing of weather conditions in great detail. Further, the hourly and daily variation of building occupancy, lightning, and equipment utilization can be easily accounted for. In addition, the full year simulation tracks the dynamic hour-to-hour and day-to-day thermal behavior of the building, and the response of HVAC equipment to this behavior. The ultimate result is high-quality data that can be utilized to produce accurate, detailed data about the quantity and timing of energy utilized. Both are requirements for accurate operating cost estimates (Pegues, 2002).

The 8760-hour method produces a diverse, realistic set of cooling and heating loads for the month. So in this study, 8760 Hour-By-Hour Method is utilized to determine the cooling load.

7.3.2. Description of the ACS considered

The present study simulates a building and an ACS which utilizes a solution of lithium bromide and water, as the working fluid pair (see Fig. 7.3). Water is the refrigerant and lithium bromide, a non toxic salt, is the absorbent. Refrigerant, liberated by heat from the solution, produces a refrigerating effect in the evaporator when cooling water is circulated through the condenser and absorber. The absorption cycle is energized by a heat medium (hot water) at 70–95°C and the condenser is water cooled through a cooling tower. When the heat medium inlet temperature exceeds 67.7°C, the solution pump forces dilute lithium bromide solution into the generator. The solution boils vigorously under a vacuum and droplets of concentrated solution are carried with refrigerant vapor to the primary separator. Subsequent to separation, refrigerant vapor flows to the condenser and concentrated solution is pre-cooled in the heat exchanger prior flowing to the absorber. In the condenser, refrigerant vapor is condensed on the surface of the cooling coil and latent heat, removed by the cooling water, is rejected to a cooling tower. Refrigerant liquid accumulates in the condenser and then passes through an orifice into the evaporator. In the evaporator, the refrigerant liquid is exposed to a substantially deeper vacuum than in the condenser due to the influence of the absorber. As refrigerant liquid flows over the surface of the evaporator coil it boils

and removes heat, equivalent to the latent heat of the refrigerant, from the chilled water circuit. The recirculation chilled water is cooled to 7°C, and the refrigerant vapor is attracted to the absorber. A deep vacuum in the absorber is maintained by the affinity of the concentrated solution from the generator with the refrigerant vapor formed in the evaporator. The refrigerant vapor is absorbed by the concentrated lithium bromide solution flowing across the surface of the absorber coil. Heat of condensation and dilution are removed by the cooling water and rejected to a cooling tower. The resulting dilute solution is preheated in a heat exchanger prior returning to the generator where the cycle is repeated (for details, see Yazaki Energy Systems, 2008).

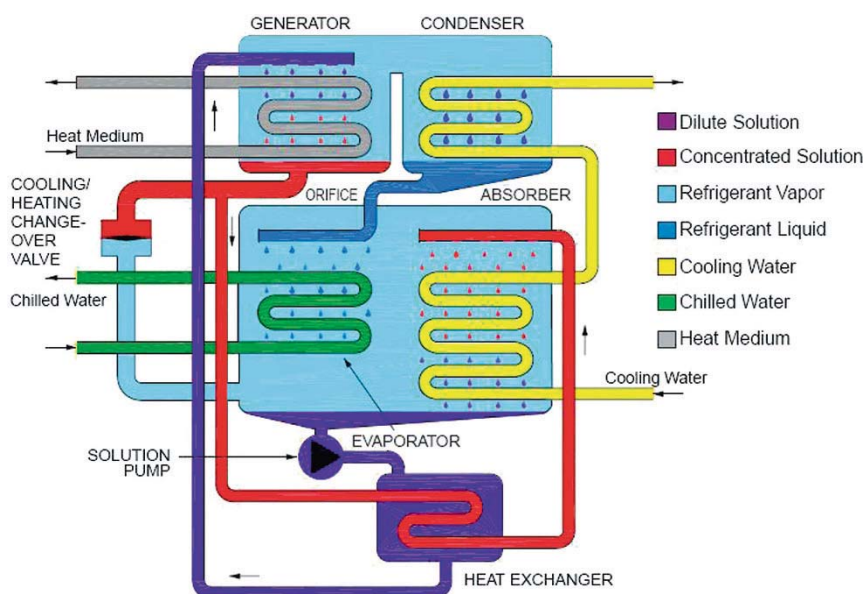


Fig. 7.3 An ACS considered for the building in Bigadic (Yazaki Energy Systems, 2008).

7.3.3. Model building

The wall structures may vary from one region to another. The materials used in the construction of buildings consist of stones, concrete, bricks, and reinforcement iron bars. In Bigadic, brick walls, and polystyrene of 2 cm thickness is commonly used as an insulation material. Table 7.1 gives commonly used wall structure for buildings in Balikesir and its thermal characteristics, including the conductance U -value, thermal resistance, heat gain, and infiltration information. In calculations, U , A , and UA are used as the heat transfer coefficient, heat transfer area, and overall heat transfer coefficient, respectively. Method simulates building and equipment Chosen absorption system utilizes a solution of lithium bromide and water.

Table 7.1 Some data and properties of the model dwelling.

Element types	Area (m ²)	U (W/m ² °C)	UA (W/ °C)
<i>Outside wall</i> (20 cm hallow brick + 2 cm insulation)	96	0.52	49.92
<i>Double-pane windows</i>	24	2.70	64.8
<i>Roof</i> (with 8 cm insulation)	100	0.38	38
Total UA (W/°C)			152.72

7.4 Methodology

First, a residence is selected for modeling, and the overall heat transfer coefficient is calculated according to chosen residence's general construction elements given in Table 7.2. Then, using degree-hours values, cooling load of the residence is determined. Degree-hours values were also calculated by using data taken from Turkish meteorological data station for 23 years. Degree-hours values are calculated for three conditions: the warmest year, the coldest year, and the average values for 23 years, using hourly average temperatures. Degree-hours values are calculated for three conditions to realize how to change its range for best and worst conditions.

Table 7.2 Calculation of cooling load for an hour.

Outdoor temperature and relative humidity		35°C/50%			
Indoor temperature and relative humidity		25°C/50%			
Floor dimensions / volume of floor		10m×10m×3m/ 300 m ³			
Infiltration		4.5 times for 24 hours			
Person		4 persons (staying 16 hours)			
Lighting and electrical equipment		Works 16 hours			
		Area (m ²)	U (W/m ² °C)	ΔT (°C)	Heat gain (W)
Outside wall	North	24	0.52	10	124.8
	South (+2%)	24	0.52	10	127.3
	East (+3%)	24	0.52	10	128.5
	West (+3%)	24	0.52	10	128.5
Windows		24	2.7	10	648
Roof		100	0.38	10	380
Heat gain from walls, windows, and roof ^[1]					1537
Infiltration heat gain ^[2]					1930
Heat gains from persons ^[3]					536
Heat gains from lighting					300
Heat gains from electrical equipment ^[4]					300
Cooling load					4600

^[1] $Q = \text{Area} \times U \times \Delta T$

^[2] Infiltration heat gain = Volume of floor × Infiltration × Air density (1.143 kg/m³) × Δh(air).

^[3] Heat gain from person = Number of person × Sensible/latent load per person (134 W).

^[4] Heat gain from lighting = Number of lamps × Power of the lamps

- For the first condition, hourly average temperatures for 23 years were figured out and referred to as average temperature condition (ATC).
- For second condition, degree-hours values were computed for the warmest year and referred to as maximum temperature condition (MxTC).
- For third condition, degree-hours values were computed for the coldest year and referred to as minimum temperature condition (MnTC).

The cooling loads are determined using degree-hours method for three conditions (as listed above in the forms of ATC, MxTC, MnTC) according to every hour in each day. The calculation results are given in Table 7.2.

Moreover detailed calculation of the cooling load for 10 hours is demonstrated in Table 7.3 for 23–25°C by considering the total heat gain via temperature difference, infiltration, electrical equipment, etc. As the indoor temperature is taken between 20–25°C, the change in degree-hours value for different conditions is found and given in Table 7.4.

Annual cooling load is calculated considering the total heat gain via temperature difference, infiltration, and electrical equipment. The COP value of the absorption system selected for cooling at 75°C generator temperature is 0.4 (Fig. 7.4). Table 7.5 gives required cooling load and needed geothermal energy for three conditions in the temperature range of 20–25°C.

Table 7.3 Heat gains calculated for various indoor temperatures ranging from 23 to 25°C.

Hours	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00
Temperature (°C)	26.05	27.24	28.1	28.84	29.14	29.05	28.66	27.97	26.86
Heat gains for 25°C									
Infiltration	0.203	0.432	0.598	0.741	0.799	0.781	0.706	0.573	0.359
Walls, windows, and roof	0.161	0.343	0.474	0.588	0.633	0.620	0.560	0.454	0.285
Persons, lighting, and electrical equipment	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136
Total (kW)	1.5	1.91	2.208	2.46	2.57	2.54	2.4	2.16	1.78
Heat gains for 24°C									
Infiltration	0.395	0.625	0.791	0.934	0.992	0.974	0.899	0.766	0.552
Walls, windows, and roof	0.314	0.496	0.627	0.741	0.786	0.773	0.713	0.607	0.438
Persons, lighting, and electrical equipment	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136
Total (kW)	1.845	2.257	2.554	2.811	2.914	2.883	2.748	2.509	2.126
Heat gains for 23°C									
Infiltration	0.588	0.818	0.984	1.127	1.184	1.167	1.092	0.959	0.745
Walls, windows, and roof	0.467	0.649	0.780	0.894	0.939	0.926	0.866	0.760	0.591
Persons, lighting, and electrical equipment	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136
Total (kW)	2.191	2.603	2.9	3.157	3.259	3.229	3.094	2.855	2.472

Table 7.4 Degree-hours for various indoor temperatures ranging from 20 to 25°C.

Degree-hours for the ATC (°C -hours)	Indoor temp (°C)	20 °C	21 °C	22 °C	23 °C	24 °C	25 °C
	April	208	143	92	51	28	16
	May	529	390	280	195	132	85
	June	2799	2364	1976	1622	1308	1036
	July	2546	2016	1608	1251	940	671
	August	2715	2166	1731	1357	1033	751
	September	1895	1495	1145	845	594	392
	October	347	246	165	109	69	43
Total		11039	8820	6997	5430	4104	2994
Degree-hours for the MnTC (°C -hours)	Indoor Temp (°C)	20 °C	21 °C	22 °C	23 °C	24 °C	25 °C
	April	166	102	60	33	15	5
	May	543	364	224	120	50	17
	June	1814	1312	1003	736	510	335
	July	2963	2519	2071	1672	1318	1014
	August	1566	1232	944	708	508	346
	September	1444	1115	876	671	499	361
	October	342	340	234	153	101	64
Total		8838	6984	5412	4093	3001	2142
Degree-hours for the MxTC (°C -hours)	Indoor Temp (°C)	20 °C	21 °C	22 °C	23 °C	24 °C	25 °C
	April	546	411	302	220	160	113
	May	1829	1536	1273	1038	833	652
	June	2399	1995	1638	1325	1051	815
	July	3553	3266	2653	2142	1710	1330
	August	4228	3862	3259	2719	2240	1818
	September	3712	3112	2588	2131	1730	1375
	October	880	669	513	401	316	243
Total		17147	14851	12226	9976	8040	6346

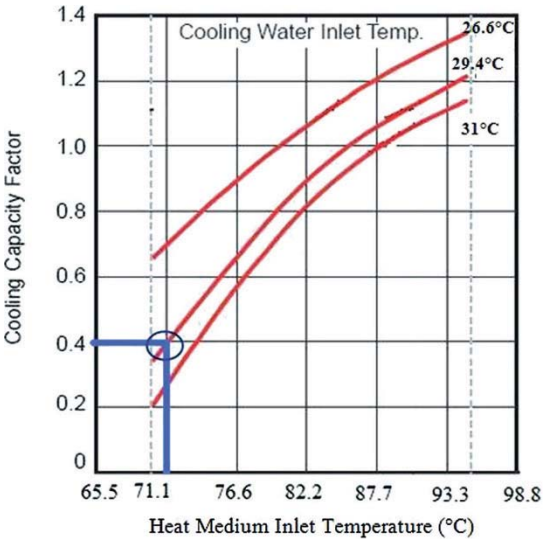


Fig. 7.4 Cooling capacity factor profiles (modified from Yazaki Energy Systems, 2008).

The COP value of the HVAC system for cooling changes generally in the range of 2.5 and 3.5. In this study, COP value is taken as 3 for conventional cooling system. Electricity requirement for this cooling system is found to depend on the cooling loads and COP value, using the following equation:

$$W = Q_c / \text{COP}$$

where Q_c represents cooling load of the residence in kWh and W represents electrical work in kWh. Annual cooling load and electrical energy requirement for the residence are given in Fig. 7.5.

Table 7.5 Cooling load and geothermal energy requirement for three different conditions.

Inside temperature (°C)		20	21	22	23	24	25
Cooling load (kWh)	ATC	5465	4829	4272	3782	3353	2984
	MnTC	4793	4285	3847	3470	3145	2881
	MxTC	7163	6358	5643	5022	4487	4006
Required geothermal energy (kWh)	ATC	13662	12073	10680	9455	8383	7460
	MnTC	11982	10713	9618	8674	7864	7202
	MxTC	17907	15895	14107	12554	11216	10015

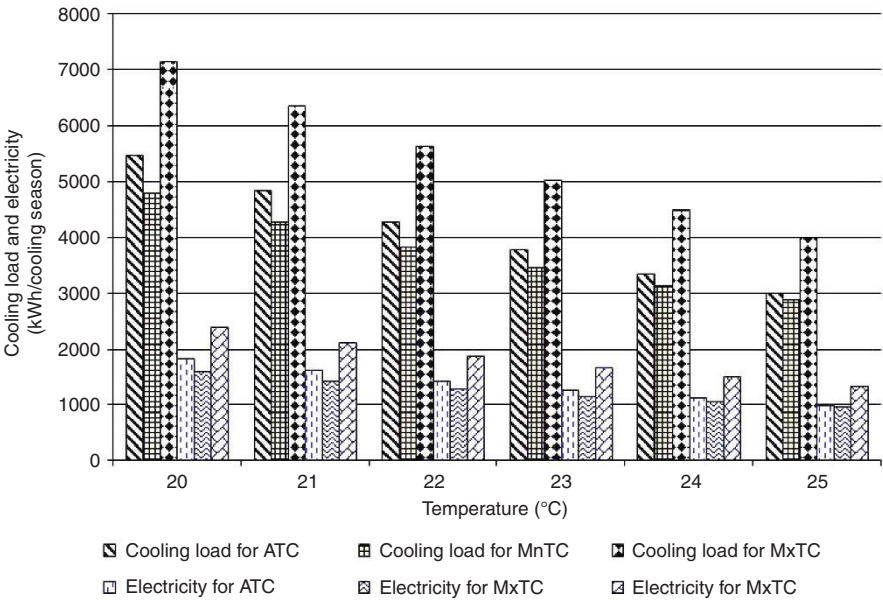


Fig. 7.5 Cooling load and electricity requirement.

7.5 Environmental Benefits

Environment protection is one of our most important obligations, whose goals were defined during some key UN Summits in Rio (1991), Kyoto (1997), and Johannesburg (2001). Any type of energy production, transportation, transformation, conversion, and consumption has some impact on the environment, and the magnitude of such an impact will depend closely on the technologies and methods used. The typical CO₂ emissions from fossil-fueled electrical power plants become 915 g/kWh for coal at a 35% power plant efficiency, 760 g/kWh for fuel oil at a 35% power plant efficiency, and 315 g/kWh for natural gas at a 60% power plant efficiency. The emission of air pollutants, such as nitrogen oxides, sulfur dioxide, and carbon dioxide, will be greatly reduced if we manage to limit our consumption of fossil fuels (Oktay et al., 2007c; and Bertani et al., 2002). Fossil fuels emissions are given in Table 7.6.

Table 7.6 Fossil fuels emissions.

<i>Fuel</i>	Emissions (g/kWh)		
	CO ₂	SO ₂	NO _x
Coal	915	3.15	2.72
Fuel oil	760	22.57	2.27
Natural gas	315	0.04	1.59

7.6 Result and Discussion

Bigadic geothermal sources are mainly utilized for district heating, although the source temperature is suitable for the absorption cooling. That is why in this study, geothermal energy-assisted absorption cooling and its environmental effects on global warming are investigated. It is known that electricity usage has an indirect effect on air pollution. For each kWh of electricity production, the power plants emit 315–915 g of CO₂; 0.04 and 3.15 g of SO₂, respectively. Figure. 7.6 shows the potential of CO₂, SO₂, and NO_x emissions reduction for a house in summer season.

Environmental benefits of the Bigadic GDHS for heating season are investigated and given as follows: (i) it is obtained that maximum heating demand for a total of 2200 dwellings is 15.25 MW and the energy savings achieved with this system amounts to 3876.24 tons of oil equivalent (TOE) per year (1 TOE is equal to 8,000,000 kcal); (ii) the amount of emissions of CO₂ and SO₂ are reduced drastically. If other fuels, namely coal, fuel oil, and electricity were used, the annual emissions of such gases would have been 29, 996/355.49, 11, 206/53.65, 136, 313/3097 tons/year, respectively. If the system worked with full capacity, the number of the equivalent of the dwelling would have increased from 2200 to 4593. When Bigadic geothermal district heating system reaches full capacity, a total of 8092.54 TOE/year energy will be saved (Oktay et al., 2007c).

Cooling load for ATC in cooling season changes between 13,715 and 16,896 MWh when we consider a total of 2200 dwellings. The electrical energy saving achieved with absorption cooling system amounts to between 2112 and 5253 MWh. The amount of emissions of SO₂, CO₂, and NO_x can be reduced drastically if the absorption cooling system is utilized. The reductions in CO₂ emissions from coal, fuel oil, and natural gas-fired power plant are calculated to be 1933 and 4806; 1605 and 3992; and 689 and 1654 tons based on the average and best case scenarios, respectively.

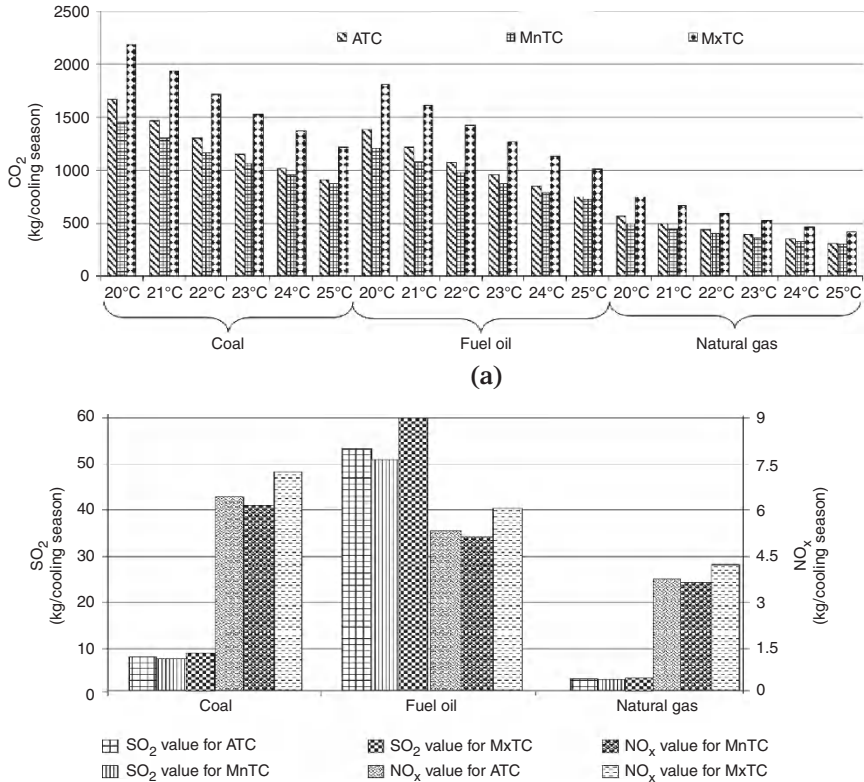


Fig. 7.6 Reduced emission values for a house in summer season (a) for CO₂, (b) SO₂ and NO_x at a 23°C indoor temperature.

7.7 Concluding Remarks

This chapter deals with a study on the effect of using a geothermal-based absorption cooling system and its impact on the environment through greenhouse gas reductions. It also compares the emissions for various fuel options and discusses opportunities for combating the global warming. It is shown that using such absorption systems will help reduce greenhouse gas emissions. Moreover, it is observed that increasing the indoor air temperature by 5°C (e.g., from 20 to 25°C) will increase the SO₂, CO₂, and NO_x emissions by about 80%, respectively.

References

- Akpınar, A, Kömürcü, M İ, Önsoy H, and Kaygusuz K, (2008). Status of geothermal energy amongst Turkey's energy sources. *Renewable and Sustainable Energy Reviews* 12: 1148–1161.
- Bertani, R, Thain, I (2002) Geothermal power generating plant CO₂ emission survey. *IGA Newsletter* 49: 1–3.
- Bassols, J, Kuckelkorn, B, Langreck, J, Schneider, R and Veelken, H (2002) Trigeneration in the food industry. *Apply Therm. Eng.* 22 (6):595–602.
- Misra, RD, Sahoo, PK and Gupta, A (2006) Thermoeconomic evaluation and optimization of an aqua-ammonia vapour-absorption refrigeration system. *Int J Refrig.* 29(1):47–59.
- Oktay, Z, Aslan, A, (2007a). Geothermal district heating in Turkey: The Gonen case study. *Geothermics* 36:167–182.
- Oktay, Z, Coskun, C, Dincer, I, (2007b) Performance analysis of the Bigadic geothermal district heating system. *International 3th Energy, Exergy and Environment Symposium*.
- Oktay, Z, and Dincer, I (2007c) Energetic, Exergetic, Economic and Environmental Assessments of the Bigadic Geothermal District Heating System. *International Journal of Green Energy* 4: 549–569.
- Pegues, J (2002) The benefits of 8760 hour-by-hour building energy analysis. *Carrier Software Systems*. New York, USA: HVAC Systems Engineer.
- Saravanan, R and Maiya, MP (1998) Thermodynamic comparison of waterbased working fluid combinations for a vapor absorption refrigeration system. *Apply Therm Eng* 18(7):553–568.
- Sozen, A (2001) Effect of heat exchangers on performance of absorption refrigeration systems. *Energy Convers Management* 42(14):1699–1716.
- Sun, DW (1998) Comparison of the performance of NH₃–H₂O, NH₃–LiNO₃ and NH₃–NaSCN absorption refrigeration systems. *Energy Convers* 39(5/6):357–368.
- Yazaki Energy Systems (2008). Water Fired Chiller/Chiller-Heater, Yazaki Energy Systems, Inc., Texas, USA, Accessed at <http://www.yazakienergy.com/>.

Reducing Greenhouse Gas Emissions from a Landfill Site Using Various Thermal Systems

C. Ozgur Colpan, Ibrahim Dincer and Feridun Hamdullahpur

8.1 Introduction

Global warming, which is a specific case of global climate change, refers to the increase in the average temperature of the atmosphere and oceans in recent decades, and the projected continuation of this increase. The drivers of climate change are seen as: changes in the atmospheric concentrations of GHGs and aerosols, land cover, and solar radiation (IPCC, 2007). According to the Intergovernmental Panel on Climate Change (IPCC, 2007), most of the increase in global average temperatures since the mid-20th century is linked to the observed increase in the anthropogenic GHG concentrations.

The four long-lived GHGs, which are released due to human activity, are CO₂, CH₄, N₂O, and halocarbons. The effect of these gases on global warming is assessed using an index called 'global warming potential' (GWP), which is a measure of how much a given mass of GHG contributes to global warming relative to a reference gas (usually CO₂) for which the GWP is set to 1. For a 100-year time horizon, GWPs of CO₂, CH₄, and N₂O are reported to be 1, 25, and 298, respectively (IPCC, 2007). Using this index, one can calculate the equivalent CO₂ emission by multiplying the emission of a GHG by its GWP.

Municipal solid waste may have significant effects on the production of GHG as well as other environmental problems and human health if it is disposed in landfills where there are no treatments and processes. There are several steps in the production of GHG from waste. Waste is first decomposed by aerobic bacteria until all the oxygen is consumed. Then, organic acids are produced in the absence of oxygen, which is followed by methanogenic state in which organic materials are decomposed

This paper draws on earlier publications of the authors (Colpan et al., 2008a, 2009).

into CH_4 and CO_2 . The leachate is also produced, which may contaminate the groundwater. There are also explosion risks due to the release of flammable gases, e.g., CH_4 . To prevent the health and environmental effects of landfills, these sites should be properly designed and operated. For example, while the groundwater may be protected by using liners and leachate collection systems, gas collection, treatment and processing systems must be used to reduce the GHG effect.

Energy may be produced from MSW through technologies, such as incineration, gasification, and generation of biogas and its utilization. Murphy and McKeogh (2004) investigated these technologies and concluded that generation of biogas and its conversion to transport fuel requires the least gate fee. Landfill gas can be converted into fuel and energy forms by direct combustion, chemical energy storage, introducing into the natural gas grid, and electricity generation. Qin et al. (2001) analyzed LFG combustion through experimental and numerical studies. Their experiments include the determination of laminar flame speeds, extinction strain rates, stable species and NO concentrations, and flame structures. Electricity generation from landfill gas can be accomplished by technologies such as the internal combustion engine, gas turbine, the Stirling engine, and fuel cells. Bove and Ubertini (2006) compared several technologies used to generate electricity from landfill gases, and showed that the internal combustion engine, which is the most widely used technology due to economical reasons, presents the poorest environmental performance. On the contrary, fuel cells are shown to be the cleanest electricity generating systems; however, they are not yet economically advantageous. There are different types of fuel cells and most of them may be fueled by LFG. However, low temperature fuel cells need a reformer to convert the fuel into hydrogen. Additionally, in all fuel cell types, LFG should be cleaned according to the impurity tolerance levels of the fuel cell. Lombardi et al. (2006) compared conventional treatments with the following alternatives: the direct LFG feeding to a fuel cell; the production of a hydrogen-rich gas by means of steam reforming and CO_2 capture to feed a stationary FC; and the production of a hydrogen-rich gas by means of steam reforming and CO_2 capture to feed a vehicle FC. Their study reveals that LFG reforming to a vehicle FC has the lowest specific greenhouse effect emission. Spiegel et al. (1999) demonstrated the operation of a commercial phosphoric acid fuel cell (PAFC) with LFG. Their system produces up to 137 kW power, 37.1% efficiency at 120 kW, and exceptionally low secondary emissions. Lunghi et al. (2004) conducted life cycle assessment analysis of a molten carbonate fuel cell (MCFC) system for LFG recovery for an evaluation of environmental consequences, and to provide a guide for further environmental impact reduction. Duerr et al. (2007) analyzed a biogas fueled alkaline fuel cell (AFC). They chose the AFC because of its very low freezing point of the potassium hydroxide electrolyte ($\sim -50^\circ\text{C}$).

The SOFC has the highest operating temperature level among the fuel cell types. According to the manufacturing type, i.e., electrolyte, electrode or interconnect supported, the SOFC may operate between 500 and 1000°C, which enables successful integration with other systems. Currently, there is more research on intermediate and low temperature SOFCs since they have better structural integrity and a lower start-up time. Another important advantage of SOFCs over other fuel cell types is that gas mixtures including hydrocarbons may be reformed inside the

fuel cell, which is called direct reforming. This feature together with the other advantages of SOFCs makes this fuel cell type very appropriate for production of electricity in landfill sites. A review of the SOFC and its modeling may be found in the paper by Colpan et al. (2008b).

In this study, GHG emissions from an uncontrolled landfill site are compared with those from controlled landfill sites in which flaring, conventional electricity generation technologies such as internal combustion engine and gas turbine, and an emerging technology, the SOFC, are utilized. For this comparison, GHG emission from each technology is first found for each year of its lifetime for a selected case study using the method developed by the authors. Then, the GHG reduction ratio and specific lifetime GHG emission are calculated for each case. Consequently, the most effective technology is determined. It should be noted that GHG emissions are calculated using on-site direct emissions (from flaring, ICE, GT, or SOFC), without taking into consideration the life cycle emissions occurring during manufacture of the infrastructure (engine, flares, cells, pipes), production and delivery of auxiliary materials, auxiliary energy consumption, gas-cleaning treatment, and so on.

8.2 Landfill Processes

In a landfill site, LFG, which is composed of methane, carbon dioxide, and non-methane organic compound (NMOC), i.e., ethane, butane, hexane, hydrogen sulfide, etc., is generated due to a series of biological processes. Over time, the amount of gas generated increases until such time the site reaches its capacity. Subsequently, the amount of gas generated begins to decrease due to the reduction in the organic material components. Because of the adverse environmental effects of the LFG, this gas should be collected and properly utilized by flaring or electricity generation technologies. In the following subsections, LFG generation and collection processes are discussed.

8.2.1 Calculation of landfill gas generation

Landfill gas generation from MSW can be calculated using the software called LandGEM, which was developed by the US Environmental Protection Agency (LandGEM, 2008). This software is based on a first order decomposition rate equation for quantifying emissions from the decomposition of landfilled waste in MSW landfills, which is shown in the following equation. (Alexander et al., 2005)

$$Q_{CH_4} = \sum_{i=1}^n \sum_{j=0.1}^1 kL_o \left(\frac{M_i}{10} \right) e^{-k \cdot t_{ij}} \quad (8.1)$$

From Eq. (8.1), annual methane generation in a year can be calculated. Generally, it is assumed that landfill gas has a composition of 50% CH₄ and 50% CO₂. Hence, total landfill gas generation may be found by doubling the result from Eq. (8.1). Methane generation rate, k , is a function of factors such as moisture content, availability of

nutrients for methane-generating bacteria, pH, and temperature of the waste mass. The potential methane generation capacity, L_o , depends on the type and composition of the waste placed in the landfill. The Clean Air Act (CAA) default values, which are based on federal regulations for MSW landfills laid out by the CAA for k and L_o , are 0.05 year^{-1} and $170 \text{ m}^3/\text{ton}$, respectively (Alexander et al., 2005).

8.2.2 Landfill gas collection

Landfill gas generated by the decomposition of organic materials should be collected in a well designed and managed site due to environmental, health, and energetic considerations. The quantity of gas collected is estimated by multiplying the generated landfill gas by collection efficiency. According to the EPA (1998), collection efficiencies at well-designed landfills typically range from 60 to 85%, with an average of 75%. A very well-designed collection system, i.e., 85% efficiency, should have the following features: a composite bottom liner consisting of a synthetic (plastic) layer over 2 feet (0.6 meter) of clay or similar material; soil cover applied over newly deposited refuse on a daily basis; no significant off-site lateral migration of landfill gas; a comprehensive landfill gas collection system with vertical wells and/or horizontal collectors providing 100% collection system coverage of all areas with waste within a few years after the waste is deposited; a gas collection system which is operating effectively so that all wells are fully functioning (i.e., relatively free of liquids and drawing landfill gas under vacuum) (Stege, 2003).

The GHG emission routes in a well-designed landfill site with a collection system are shown in Fig. 8.1. These routes will be discussed in detail in the following sections.

8.3 Thermal Systems Considered

Flaring (direct combustion) is the traditional approach to utilize the collected LFG for reducing the GHGs in a landfill site. The flaring of LFG is an economical approach, and also it reduces the risk of explosion of uncontrolled LFG emissions. The operation principle of landfill gas flare is simple; LFG is ignited by bringing it into contact with a supply of air. Different configurations of conduit and chambers can be used for this purpose. In today's market, open and closed flare types are available. Open flares burn landfill gas as open flames, whereas closed flares burn landfill gas in a vertical, cylindrical, or rectilinear enclosure. Details of these flare types may be found in the report by Environment Agency and Scottish Environment Protection Agency (2002). On the other hand, since the collected gas has a considerable amount of heating value, it may be utilized to produce electricity and/or heat. The most commonly used technology for utilizing LFG is internal combustion engines, followed by gas turbines. Additionally, SOFCs are very promising candidates to be used in landfill sites in the future due to their advantages discussed in the previous and following sections. These technologies are discussed in detail in the following subsections.

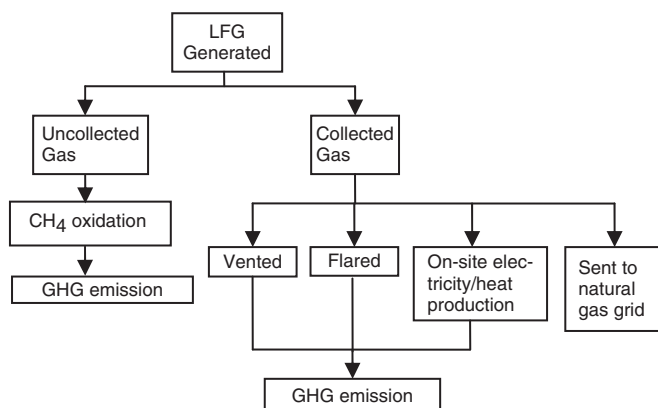


Fig. 8.1 Greenhouse gas emission routes in a landfill site with LFG collection system.

8.3.1 Internal combustion engine (ICE)

The internal combustion engine is the most widely used technology for electricity generation from LFG, mainly because of its economical feasibility. These engines are attractive because they are compact and easy to transport. The main disadvantage is the high amounts of NO_x and CO emissions produced by these engines as compared with other technologies, which contribute to the air pollution. Lean-burn spark ignition engines are the most common type of ICE used in landfill sites. When these engines are operated using LFG, engine power ratings are commonly reduced by 5–10% (SCS Engineers, 1994) compared to operation using natural gas. It should be noted that before the LFG is fed to the ICE, moisture and particulates must be removed according to the tolerance limits of the engine, so as not to reduce the engine efficiency and reliability and increase the necessity for more regular maintenance.

The power output of these engines varies between 300 kW and 3.6 MW for an individual unit (Environment Agency and Scottish Environment Protection Agency, 2004). Generally, many ICEs operate together according to the LFG generated to produce more power. A typical landfill site operating with this type of engine should also include a gas flare to burn any LFG collected in excess of maximum requirements of the engine, to burn LFG when the generated gases are low enough to justify the operation of the engine, and to operate during the maintenance.

8.3.2 Gas turbine (GT)

Gas turbines are the second most popular technologies that utilize LFG. The majority of gas turbines presently operating at landfills are the simple cycle, single shaft type. They are very similar to natural gas turbines except that, because of the low heating value, the number of fuel regulating valves and injectors are doubled (SCS Engineers, 1997). During its operation, large quantities of air enter the compressor.

After the air is compressed, it mixes with fuel in the combustor, and the combusted gas expands in the turbine where power is produced. Some amount of this power is used to drive the compressor.

Compared to ICEs, gas turbines have lower NO_x and CO emissions, and also fewer moving parts. Their exhaust can also be utilized in a cogeneration application. However, if electricity generation is more important in an application, the gas turbine is disadvantageous since it has a lower electrical efficiency than the ICE. Other disadvantages are having a high capital cost, being sensitive to LFG supply loads and ambient air temperature variations, and not being suitable for moderate size landfills. For small-size landfills, microturbines are generally selected instead of gas turbines.

8.3.3 Solid oxide fuel cell (SOFC)

The SOFC is an emerging technology that is expected to replace conventional energy systems like ICEs and gas turbines once it has become economically competitive. The SOFC has higher electrical efficiency, lower emissions, a higher exhaust gas temperature that makes it possible to be used in cogeneration applications, quieter operation, and fewer moving parts compared to conventional systems.

There have been demonstrations of SOFC operation using biogas (News, 2005, 2007). These demonstrations include biogas production from wastewater in a sewage treatment plant and animal waste. It has been recently reported that a planar SOFC unit in Finland, which will produce 20 kW of electric power and 14–17 kW of thermal output, is believed to be the first SOFC in the world that is fueled by LFG (News, 2008).

The SOFC is a very attractive option for LFG application since it can use hydrogen and carbon monoxide as fuels, which are reformed from methane. In high temperature SOFCs, this reformation occurs inside the fuel cell; this is called direct reforming. The reforming mechanism is controlled by water–gas shift and steam reforming reactions, which are shown by Eqs. 8.2–8.3. In some cases, it is preferable to use a dry reformer before the LFG enters the SOFC to prevent the carbon deposition at the anode catalyst. The dry reforming reaction is shown in Eq. (8.4).



It should be noted that the collected LFG must be subjected to an extensive gas cleanup process before it enters to SOFC due to high levels of contaminants in the gas. The tolerance limits of SOFCs to these contaminants may be found in the literature (Sime et al., 2002; Xenenergy, 2002).

8.4 Analysis of Greenhouse Gas Emissions

In this section, a method for calculating GHG emission from a landfill site without an active collection system is first described. Then, methods for calculating GHG emissions from landfill sites in which the collected LFG is utilized by flaring, conventional electricity generation technologies such as ICE and GT, and SOFC, are discussed. Finally, some parameters for comparing these technologies are introduced.

8.4.1 Landfill site without an active collection system

In a landfill site without an active collection system, not all of the methane generated is emitted into the atmosphere. A portion of the methane generated is oxidized while passing through soil and landfill covers. The fraction of methane that is oxidized is generally taken as 10% (Climate Leaders, 2004). The oxidation of methane reaction is given as follows:



If we neglect the NMOC portion of the LFG, total GHG emissions from this kind of a site may be expressed as shown in Eq. (8.6). It should be noted that the equations in this chapter are derived for a LFG composition of 50% CH_4 and 50% CO_2 . However, similar equations may be derived with simple modifications to these equations for different ratios of CH_4 and CO_2 .

$$m_{\text{GHG.uncoll}} = \sum_{y=1}^{t_{\text{final}}} \left(m_{\text{CH}_4 \cdot \text{gen}} \times (1 - \text{OX}) \times \text{GWP}_{\text{CH}_4} + \left(m_{\text{CO}_2 \cdot \text{gen}} + \text{OX} \times m_{\text{CH}_4 \cdot \text{gen}} \times \frac{\rho_{\text{CO}_2}}{\rho_{\text{CH}_4}} \right) \right) \quad (8.6)$$

8.4.2 Landfill site with an active collection system

In a landfill site with an active collection system, LFG is recovered by vertical wells or horizontal collectors. The recovered gas can be flared or utilized to generate electricity by technologies such as gas turbines, ICEs, or fuel cells. In the following subsections, the methodologies for calculating the GHG emissions from landfill sites, which consist of flare and these electricity generating technologies, are discussed.

8.4.2.1 Flaring

The combustion of methane may also be represented by Eq. (8.5). If we assume that all of the collected gas is flared, and a small portion of the collected gas is vented during the routine and unscheduled maintenance, total GHG emissions from the site can be found by using Eq. (8.7).

$$m_{\text{GHG.coll}} = \sum_{y=1}^{t_{\text{final}}} \left((1 - \eta_{\text{coll}}) \times (m_{\text{GHG.uncoll}})_y + \eta_{\text{coll}} \times (m_{\text{GHG.flare}})_y \right) \quad (8.7)$$

where GHG generated due to flaring is

$$m_{\text{GHG.flare}} = m_{\text{CH}_4.\text{gen}} \times \text{vent} \times \text{GWP}_{\text{CH}_4} + \left(m_{\text{CO}_2.\text{gen}} + (1 - \text{vent}) \times m_{\text{CH}_4.\text{gen}} \times \frac{\rho_{\text{CO}_2}}{\rho_{\text{CH}_4}} \right) \quad (8.8)$$

8.4.2.2 Electricity generation technologies from LFG

8.4.2.2.1 Internal combustion engine

GHG emissions per energy output of ICEs suitable for LFG operation are given in the literature (Lombardi et al., 2006). Using this emission data, the amount of collected LFG, electrical efficiency of the ICE, days of operation of the engine per year, and higher heating value of the fuel, one may calculate the total GHG emissions from such a landfill site using Eq. (8.9). In this equation, it is assumed that after year, t_{down} , engines stop operating and collected LFG is burned. There is also enough number of ICEs that can utilize LFG even at the year when its generation is at maximum level.

$$m_{\text{GHG.coll}} = \sum_{y=1}^{t_{\text{down}}} \left((1 - \eta_{\text{coll}}) \times (m_{\text{GHG.uncoll}})_y + \eta_{\text{coll}} \times (m_{\text{GHG.ICE}})_y \right) + \sum_{y=t_{\text{down}}}^{t_{\text{final}}} \left((1 - \eta_{\text{coll}}) \times (m_{\text{GHG.uncoll}})_y + \eta_{\text{coll}} \times (m_{\text{GHG.flare}})_y \right) \quad (8.9)$$

where GHG generated from ICE can be calculated as

$$m_{\text{GHG.ICE}} = (\tau / 365) \times (m_{\text{LFG.gen}} \times hhv \times \eta_{\text{ICE}} \times \varepsilon_{\text{ICE}} / 3600) + (1 - \tau / 365) \times m_{\text{GHG.flare}} \quad (8.10)$$

8.4.2.2.2 Gas turbine

Since there is insufficient data in the literature regarding GHG emissions from LFG fueled gas turbines, a simple model is developed by the authors. In this model, it is assumed that air gas composition is: 77.48% N₂, 20.59 O₂, 0.03% CO₂, and 1.9% H₂O. For the fuel–air ratio, $\bar{\lambda}$, the combustion equation may be written as shown in Eq. (8.11).

$$\bar{\lambda}(0.5\text{CH}_4 + 0.5\text{CO}_2) + (0.7748\text{N}_2 + 0.2059\text{O}_2 + 0.0003\text{CO}_2 + 0.019\text{H}_2\text{O}) \rightarrow (1 + \bar{\lambda})(x_{\text{N}_2}\text{N}_2 + x_{\text{O}_2}\text{O}_2 + x_{\text{CO}_2}\text{CO}_2 + x_{\text{H}_2\text{O}}\text{H}_2\text{O}) \quad (8.11)$$

Exit gas composition of the combustor may be shown using Eqs. (8.12)–(8.15).

$$x_{\text{N}_2} = \frac{0.7748}{1 + \bar{\lambda}} \quad (8.12)$$

$$x_{\text{O}_2} = \frac{0.2059 - \bar{\lambda}}{1 + \bar{\lambda}} \quad (8.13)$$

$$x_{\text{CO}_2} = \frac{\bar{\lambda} + 0.0003}{1 + \bar{\lambda}} \quad (8.14)$$

$$x_{\text{H}_2\text{O}} = \frac{0.019 + \bar{\lambda}}{1 + \bar{\lambda}} \quad (8.15)$$

Solving the energy balance around the control volume enclosing the combustor, as shown in Eq. (8.16), $\bar{\lambda}$ hence exit gas composition may be calculated.

$$0 = -0.02 \cdot \dot{n}_f \cdot \text{LHV} + \dot{n}_f \cdot \bar{h}_f + \dot{n}_{\text{c,i}} \cdot \bar{h}_{\text{c,i}} - \dot{n}_{\text{c,o}} \cdot \bar{h}_{\text{c,o}} \quad (8.16)$$

The first term in the right-hand side of Eq. (8.16) denotes the assumed heat loss from the combustor.

The total GHG emissions from a landfill site, where a gas turbine is used for electricity production, may be calculated using Eq. (8.9), if the $m_{\text{GHG,ICE}}$ is replaced with $m_{\text{GHG,GT}}$ which is shown in Eq. (8.17).

$$m_{\text{GHG,GT}} = (\tau/365) \times \left(m_{\text{LFG,gen}} \times \frac{\bar{\lambda} + 0.0003}{\bar{\lambda}} \times \frac{M_{\text{CO}_2}}{M_{\text{LFG}}} \right) + (1 - \tau/365) \times m_{\text{GHG,flare}} \quad (8.17)$$

8.4.2.2.3 Solid oxide fuel cell

GHG emissions per LFG entering the system may be found using the SOFC model developed by the authors (Colpan et al., 2007). This SOFC model may be described as follows. The gas composition of the fuel channel exit can be found using chemical equilibrium equations and the relation between the electric current and the molar flow rate of hydrogen that is utilized. Then, the air utilization ratio, which measures the amount of excess air that should be sent to the air channel to carry away the unutilized heat in the fuel cell, is calculated. Hence, cell voltage, work output of the cell, and electrical efficiency of the cell are found. After finding the GHG emissions from the SOFC, the total GHG emissions from the landfill site may be calculated in a similar method as conducted with ICEs and gas turbines.

8.4.3 Comparison of LFG utilization technologies

The authors propose three parameters for comparing the usefulness of technologies in reducing the global warming in landfill sites. The first parameter is called ‘GHG reduction ratio’, as shown in Eq. (8.18). This ratio quantifies the GHG emission reduction when an active collection system is used. If there is no emission from the landfill site when an active system is used, this ratio is equal to 100%. If this ratio is equal to 1, it also means there is no contribution to global warming from this landfill site.

$$\Gamma = (m_{\text{GHG.uncoll}} - m_{\text{GHG.coll}}) / m_{\text{GHG.uncoll}} \quad (8.18)$$

The second parameter is called ‘specific lifetime GHG emission’ which may be defined as the ratio of the total GHG emission from the landfill site in its lifetime to the total amount of useful energy produced from LFG. This ratio is shown in Eq. (8.19) and is useful to compare GHG emissions for the same amount of power produced from different technologies. From the point of view of global warming and energy, the lower the ratio is, the more effective the technology is.

$$\sigma = \frac{m_{\text{GHG.coll}}}{\left(m_{\text{CH}_4.\text{gen}} + m_{\text{CO}_2.\text{gen}} \right) \times \eta_{\text{coll}} \times \tau / 365 \times h\nu / 3.6 \times \eta_{\text{el}}} \quad (8.19)$$

The third parameter is called environmental impact factor, which could be used to rank the electricity generation technologies according to their effectiveness in reducing the greenhouse gases. This ratio changes between 0 and 1. If it is equal to 1, it means it is the least effective way to reduce the greenhouse gases among the possibilities that have been studied. This parameter is shown in Eq. (8.20).

$$\lambda = \sigma_i / \sigma_{\text{max}} \quad (8.20)$$

8.5 Case Study

For our case study, we considered that the landfill site, which is filled with municipal solid waste, opened in 2008 and it will be accept waste for 20 years. The annual waste acceptance rate is taken as 200,000 ton/year. CAA default values, which are based on federal regulations for MSW landfills laid out by the Clean Air Act, are considered for the methane generation rate and the potential methane generation capacity. The LFG composition is considered as 50% CH₄ and 50% CO₂. Other input data are given in Table 8.1. The results obtained using the data in Table 8.1 are presented in the following section.

Table 8.1 Input data for case studies.

Fraction of oxidized methane	10%
Fraction of vented gas in flare	1%
Collection efficiency	75%
The year that the electricity production ends	2088
Number of days that electricity producing technology operates per year	320
Higher heating value of LFG	14,829 MJ/tonnes
Specific GHG emission ratio of ICE	0.551 tonnes eq.CO ₂ /MWh (Lombardi et al., 2006). tonnes eq.CO ₂ /MWh
Electrical efficiency of ICE	35%
Combustion chamber inlet temperature of GT	850 K
Gas turbine inlet temperature	1520 K
Gas turbine electrical efficiency	28%
Operating cell voltage of SOFC	0.65 V
Fuel utilization ratio of SOFC	85%
Inlet gas temperature of SOFC	850°C
Exit gas temperature of SOFC	950°C
Active surface area of a single cell	100 cm ²

8.6 Results and Discussion

Generated and collected LFG and GHG emissions for each scenario were calculated using the methodology described in Sections 8.4 and 8.5. Then, to find the most effective technology, a comparison of the different scenarios was carried out.

Annual gas generation rates for all components of the LFG, i.e., methane, carbon dioxide, and NMOC, were calculated by LandGEM software. The results are shown in Fig. 8.2. As can be seen from this figure, LFG generation increases until the final year it accepts the waste. Then it decreases exponentially. For this landfill site, which has a 20-year lifetime, the site continues releasing GHGs for 120 years more after it stops accepting waste as can be seen from this figure.

Taking an average collection efficiency of 75%, collected and uncollected LFG and its components were calculated for each year and shown in Fig. 8.3.

For a landfill site without an active collection system, some amount of methane will be oxidized and converted into carbon dioxide. Remaining gases will be released into the atmosphere. Given that high amounts of methane, which is 25 times more contributing to global warming than carbon dioxide, are released in this case, this gas should be collected and utilized since it has a considerable amount of heating value and high global warming potential. In this study, different technologies for utilizing the collected gas were considered. These include flaring, electricity generation technologies such as ICE, gas turbine, and SOFC. Annual GHG emission from the landfill site for each technology is shown in Fig. 8.4. For example, in the final year that the site will accept waste, i.e. 2028; 366,831 tonnes CO₂ eq. could be released to the atmosphere from a site without an active collection system. Using the

most economical solution, which is flaring, GHG emissions would be much lower, 153,456 tonnes CO₂ eq. However, there is no electricity production when flaring is used. In the case where a gas turbine is used to utilize the LFG, GHG emissions would be slightly lower than the case of flaring, which is found to be 151,404 tonnes CO₂ eq. The most effective technologies for reducing GHG emissions are ICE and SOFC. For the peak year, when ICE and SOFC are utilized, the site produces GHG emissions of 127,430 and 134,208 tonnes CO₂ eq, respectively. It should be noted that, for all technologies, it is considered in the calculations that many power generators of the same type operate together, and they may be replaced with new ones if necessary. Additionally, after the year 2088, due to the low methane generation, it is assumed that collected gas will be sent to gas flare instead of the power generator.

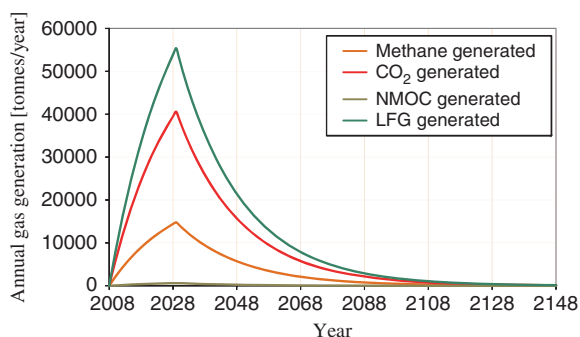


Fig. 8.2 Annual gas generation of LFG and its components.

As previously mentioned, the results obtained by using the methodology discussed in Section 8.4 were used in constructing Fig. 8.4. When modeling an ICE, the specific GHG emission ratio of the ICE, which has unit of tonnes eq.CO₂/MWh of an existing engine, was taken from literature (Lombardi et al., 2006) and used in Eq. (8.10). In the case of the gas turbine, a simple model was developed by the authors as discussed in Section 8.4.2.2.2. Using input data given in Table 8.1, the fuel/air ratio on a molar basis was calculated to be 0.070935. According to this ratio, exit gas composition of the gas turbine was found to be 72.3% N₂, 12.6% O₂, 6.7% CO₂, and 8.4% H₂O. Finally, in the case of the SOFC, the model is discussed in Section 8.4.2.2.3. For the type of fuel used in this study, it is reasonable to assume a 0.65 V cell voltage. At this voltage, the corresponding current density and electrical efficiency are 0.28 A/cm² and 40.3%, respectively. It is also found that for

1 ton of LFG entering a SOFC system, 0.98595 ton CO₂.eq GHG is emitted to the atmosphere.

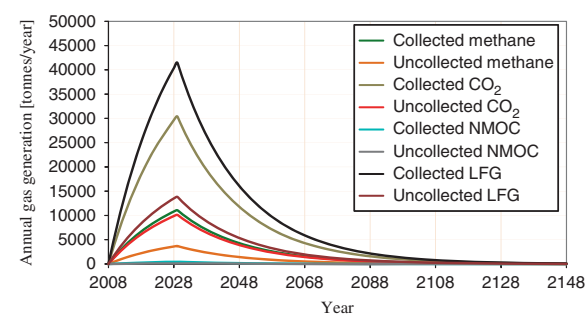


Fig. 8.3 Collected and uncollected amount of LFG and its components.

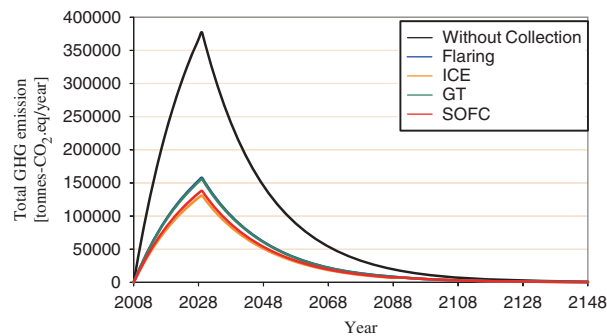


Figure 8.4 Total GHG emissions for various LFG utilization methods.

Figure 8.5 shows the comparison between different technologies operating at controlled landfill sites in terms of their effect on production of GHGs. As shown in Fig. 8.5, the simplest solution, which is flaring, will reduce the GHGs by 58%. Hence, this result reveals the fact that an active collection system together with a

gas flare would be very effective in reducing the GHG emission if an economical solution is desired and there is no consideration of getting benefit from this gas to convert it into electricity. This figure also shows that using an ICE results in the highest GHG reduction ratio, which is slightly higher than the ratio when SOFC is used. The gas turbine has the least global warming reduction potential of the electricity production technologies studied in this chapter.

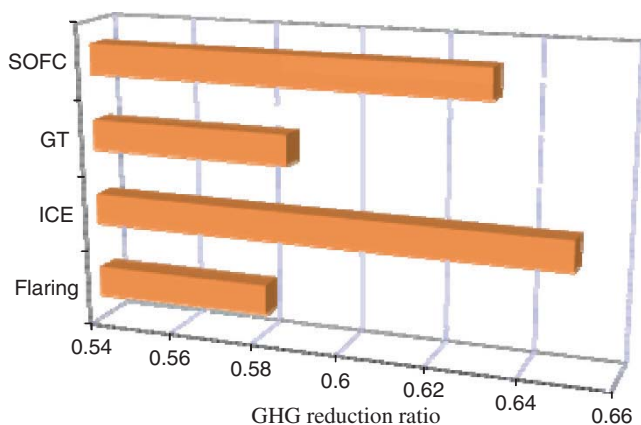


Fig. 8.5 GHG reduction ratio for different scenarios.

Since each technology has different electrical efficiency and global warming potential, a more meaningful comparison between the controlled landfill sites studied may be conducted calculating the total GHG emissions in the lifetime per total amount of energy produced for each technology. The results of this comparison are shown in Fig. 8.6. It may be seen from this figure that the SOFC has the lowest specific lifetime GHG emission among the technologies studied, which is 2.3836 tonnes CO₂.eq/MWh, when the SOFC is only used for electricity generation. Since the SOFC has a high exhaust temperature, useful heat may be produced which would increase the fuel utilization efficiency of the system. Producing work and heat at the same time, which is called cogeneration, the specific lifetime GHG emission may be further reduced to 1.1217 tonnes CO₂.eq/MWh, as shown in Fig. 8.6. In Fig. 8.7, environmental impact factor of the electricity generation technologies are compared. As it can be seen from this figure, gas turbine has an environmental impact factor of 1, since it has the highest specific lifetime GHG emission, and SOFC with cogeneration case has the lowest environmental impact factor, which is equal to 29%.

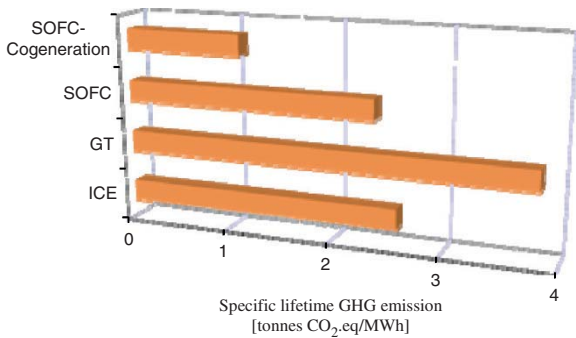


Fig. 8.6 Specific lifetime GHG emission for different scenarios.

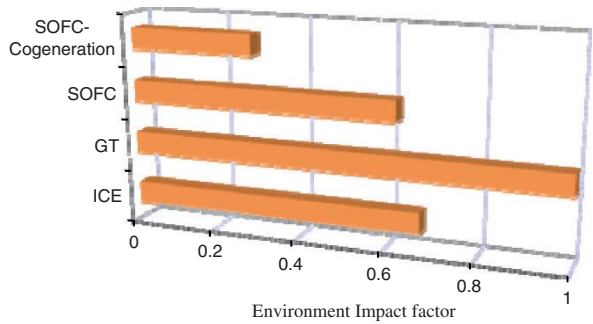


Fig. 8.7 Environmental impact factor for different scenarios.

8.7 Conclusions

In this chapter, GHG emissions from an uncontrolled landfill site are compared with those from controlled landfill sites in which flaring, conventional electricity generation technologies such as ICE and GT, and SOFC are utilized. It is shown

that even with the simplest solution, which is flaring, total GHG emissions in the lifetime of the site can be reduced by 58% compared to the uncontrolled case. Among the different technologies, the SOFC seems to be the best option, as it reduces the GHG emissions by 63%, and has a specific lifetime GHG emission of 2.38 tonnes CO₂.eq/MWh when it only produces electricity and 1.12 tonnes CO₂.eq/MWh when it is used in a cogeneration application. The latter case has the lowest environmental impact factor, which is equal to 29%. Hence, this study has shown that SOFC is very effective in combating global warming in landfill sites in addition to its other advantages like low emissions and noise and high efficiency. A future study will include an optimization of a SOFC in a landfill site. In this study, operating variables will be optimized to maximize the energetic performance and minimize the greenhouse gas effect.

Acknowledgment

The financial and technical support of an Ontario Premier's Research Excellence Award, the Natural Sciences and Engineering Research Council of Canada, Carleton University, and University of Ontario and Institute of Technology is gratefully acknowledged.

Nomenclature

GWP	global warming potential
$\bar{h}$	specific enthalpy, J/mol
hhv	higher heating value of landfill gas, MJ/tonnes
k	methane generation rate, year ⁻¹
L_o	potential methane generation capacity, m ³ /tonnes
LHV	lower heating value, J/mol
m	mass, tonnes CO ₂ .eq
$\dot{n}$	molar flow rate, mol/s
M_i	mass of waste accepted in the i th year, tonnes
OX	fraction of methane oxidized in the soil
Q_{CH_4}	annual methane generation, m ³ /year
t_{ij}	age of the j th section of waste mass M_i accepted in the i th year, years
x	molar concentration
vent	fraction of vented gas in flare

Greek Letters

$\mathcal{E}_{ICE}$	specific GHG emission ratio of internal combustion engine, tonnes eq.CO ₂ /MWh
ρ	density, g/cm ³
σ	specific lifetime GHG emission, tonnes eq.CO ₂ /MWh
η_{el}	electrical efficiency
η_{coll}	collection efficiency
η_{ICE}	electrical efficiency of internal combustion engine

Γ	greenhouse gas reduction ratio
τ	Number of days that electricity producing technology operates per year, days
$\bar{\lambda}$	fuel–air ratio on molar basis

Subscripts

c,i	combustor inlet
c,o	combustor outlet
f	fuel

References

- Alexander, A., Burklin, C., Singleton, A. 2005. Landfill Gas Emissions Model (LandGEM) Version 3.02 User's Guide. Washington, USA: United States Environmental Protection Agency.
- Bove, R., Lunghi, P. 2006. Electric power generation from landfill gas using traditional and innovative technologies. *Energy Conversion and Management*. 47:1391–1401.
- Climate Leaders. 2004. Direct Emissions from Municipal Solid Waste Landfilling. US Environmental Protection Agency.
- Colpan, C.O., Dincer, I., and Hamdullahpur, F. 2007. Thermodynamic modeling of direct internal reforming solid oxide fuel cells operating with syngas. *International Journal of Hydrogen Energy*. 32:787–795.
- Colpan, C.O., Dincer, I., and Hamdullahpur, F. 2008a. Reduction of greenhouse gas emissions using various thermal systems in a landfill site. *Proceedings of the Global Conference on Global Warming-2008*, 6–10 July 2008, Istanbul, Turkey.
- Colpan, C.O., Dincer, I., and Hamdullahpur, F. 2008b. A review on macro-level modeling of planar solid oxide fuel cells. *International Journal of Energy Research*. 32:336–355.
- Colpan, C.O., Dincer, I., Hamdullahpur, F. 2009. Reduction of greenhouse gas emissions using various thermal systems in a landfill site. *International Journal of Global Warming*. 1(1–3):89–105.
- Department of Foreign Affairs and International Trade. 2002. Fuel Cell Technologies Ltd., CanadExport, 20(10):1–4.
- Duerr, M., Gair, S., Cruden, A., McDonald, J. 2007. Hydrogen and electrical energy from organic waste treatment. *International Journal of Hydrogen Energy*. 32: 705–709.
- Environment Agency and Scottish Environment Protection Agency. 2002. Guidance on Landfill Gas Flaring.
- Environment Agency and Scottish Environment Protection Agency. 2004. Guidance for Monitoring Landfill Gas Engine Emissions.
- EPA, 1998. *Compilation of Air Pollutant Emission Factors, AP-42, Volume 1: Stationary Point and Area Sources*, 5th ed., Chapter 2.4. Office of Air Quality Planning and Standards. Research Triangle Park, NC, US: Environmental Protection Agency.

- Intergovernmental Panel on Climate Change (IPCC). 2007. *Climate Change 2007: Synthesis Report*. An Assessment of the Intergovernmental Panel on Climate Change.
- LandGEM. <http://www.epa.gov/ttn/catc/products.html#software>. Accessed on March 29, 2008.
- Lombardi, L., Carnevale, E., Corti, A. 2006. Greenhouse effect reduction and energy recovery from waste landfill. *Energy*. 31: 3208–3219.
- Lunghi, P., Bove, R., Desideri, U. 2004. Life-cycle-assessment of fuel-cells-based landfill-gas energy conversion technologies. *Journal of Power Sources*. 131:120–126.
- Murphy, J.D., McKeogh, E. 2004. Technical, economic and environmental analysis of energy production from municipal solid waste. *Renewable Energy*. 29:1043–1057.
- News. 2005. GTI runs SOFC on gasified chicken waste. *Fuel Cells Bulletin*. 9:4.
- News. 2007. TMI demos SOFC using agricultural waste. *Fuel Cells Bulletin*. 9:4.
- News. 2008. Wärtsilä to deliver SOFC system using landfill gas. *Fuel Cells Bulletin*. 3:1.
- Qin, W., Egolfopoulos, F.N., Tsotsis, T.T. 2001. Fundamental and environmental aspects of landfill gas utilization for power generation. *Chemical Engineering Journal*. 82:57–172.
- Sime, R., Stucki, S., Biollaz, S., Wiasmitinow, A. 2002. Linking Wood Gasification with SOFC Hybrid Processes, *Proceedings*, 5th European SOFC Forum, Lucerne, Switzerland.
- SCS Engineers. 1994. Implementation Guide for Landfill Gas Recovery Projects in the Northeast. Final Report.
- SCS Engineers. 1997. Comparative Analysis of Landfill Gas Utilization Technologies.
- Spiegel, R.J., Preston, J.L., Trocciola, J.C. 1999. Fuel cell operation on landfill gas at Penrose Power Station. *Energy*. 24: 723–742.
- Stege, A. 2003. User's Manual Mexico Landfill Gas Model Version 1.0. Prepared for SEDESOL IIE CONAE.
- XENERGY. 2002. Toward a Renewable Power Supply: The Use of Biobased Fuels in Stationary Fuel Cells. Washington, DC: Prepared for the Northeast Regional Biomass Program.

Partial Gasification for CO₂ Emissions Reduction

Nirmal V. Gnanapragasam, Bale V. Reddy and Marc A. Rosen

9.1 Introduction

From the perspective of energy security and environmental sustainability, highly effective uses for fossil fuel in energy industries are demanded. Power plants having integrated gasification combined cycle (IGCC) with advanced configurations are being developed worldwide to use coal and biomass more efficiently and thus cleanly. Gasification forms the major component within the IGCC systems and has the best fuel flexibility of any of the advanced technologies for power production, with the current technology well adapted to use biomass and other low-value feedstock that have high-ash residues (Liu and Niksa, 2004). Gasification also provides an opportunity to control and reduce gaseous pollutant emissions, and a lowest cost approach to concentrate the carbon dioxide at high pressure to facilitate sequestration (Trapp, 2005).

The gasifier operating conditions include temperature, pressure, air/oxygen stream, steam requirement, and the end product conditions (Higman and Burgt, 2003). Sugiyama et al. (2003) reported the performance of gasification process in multi-staged enthalpy extraction technology (MEET) system. Numerical simulation of coal gasification in entrained flow coal gasifier was performed and the corresponding gasification details were reported by Watanabe and Otaka (2006) in support of the numerical model. Performance of gasification in a pressurized fluidized bed gasifier were observed through the high temperature Winkler process setup by Bhattacharya (2006) with about 90% carbon conversion of Australian lignite. Yun et al. (2007) found various factors that affect the performance of the gasifier in an IGCC system. The factors considered were conversion efficiencies, moisture content, sulphur content, ash content, ash-melting temperature, slag viscosity, slag characteristics, and coal reactivity. They found that the best coal type for IGCC applications appears to be the one that contains low ash content with low-enough slag viscosity and high reactivity in coal. A review of co-gasification of coal, petroleum coke, and up to 10% of several types of biomass was done by

Valero and Uson (2006). The influence of fuel variation in gasifier efficiency and modifications in operation that should be made in oxy-co-gasification are obtained. The performance enhancement for an IGCC using different supplementary firing options revealed (Gnanaprasam et al., 2008) that the specific net CO₂ emissions are the highest for the case without supplementary firing and the lowest for the case with partial gasification.

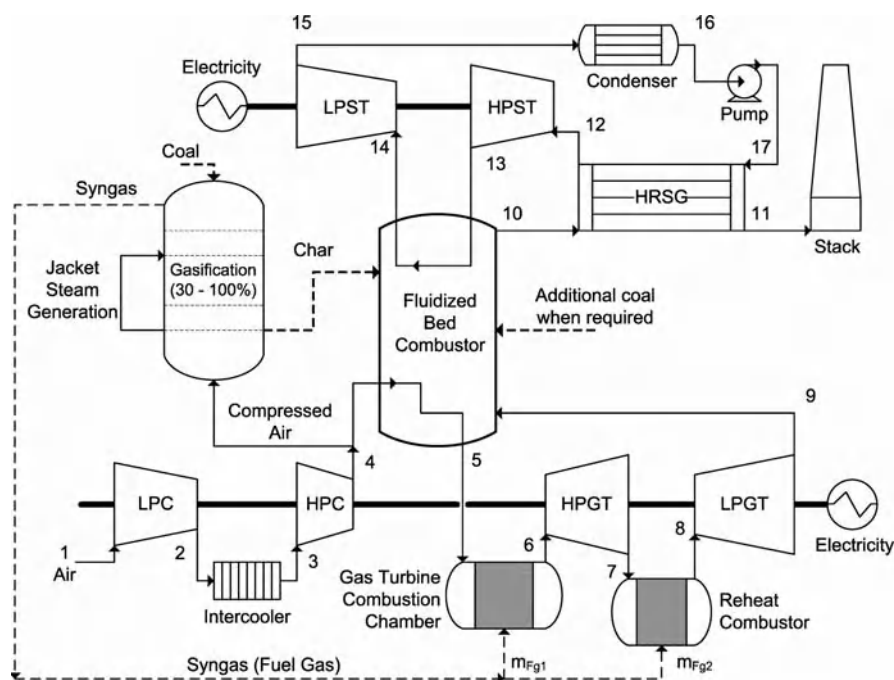


Fig. 9.1 Integrated gasification combined cycle power plant configuration under investigation to study the performance of the gasifier.

The effect of the gasifier/gasification performance within an IGCC power generation system as shown in Fig. 9.1 is hard to find since the proposed system is new way of improving the IGCC performance with lower CO₂ emissions. The current work focuses on the performance of gasification process based on two of the gasifier-operating conditions: (i) air flow rate and (ii) steam flow rate. The effect of these two conditions on the CO₂ emissions of the IGCC system is investigated. The relation between feedstock (source fuels) and CO₂ emissions of gas and steam cycles are established by using four different solid fuels in the gasification process. The fuels are selected based on decreasing carbon content and heating value and they are anthracite, lignite, loblolly pine, and wood chips. The amount of CO₂ emitted is correlated to the carbon content and heating value of the feedstock based on the estimation of specific CO₂ emission. The effect of operating conditions of the combined cycle within the IGCC system on the gasifier performance

is also investigated. This is achieved by setting different temperature conditions at three locations within the IGCC, namely compressed air inlet temperature to the gas turbine combustion chamber; gas turbine inlet temperature; and inlet temperature to the HRSG. The effect of temperature conditions of the combined cycle on relative CO₂ emission is estimated to find the optimal cycle operating temperature where moderate network output and corresponding CO₂ emission are expected. The proposed IGCC system provides opportunities to investigate these effects in detail so that it can be applied for full scale IGCC facility.

9.2 Partial Gasification-Based IGCC System

9.2.1 Partial gasification process

Partial gasification allows only part of the solids fed into the gasifier to be converted into gas, while retaining some of the solid carbon elements to be combusted in a supplementary combustor to improve the system performance. Gasification (partial or full) of coal and its pressurized fluidized bed combustion are the two most important developments for the topping gas cycle (McMullan et al., 1997) in a combined cycle arrangement for power generation. As an improvement to the basic combined cycle, simultaneous introduction of partial gasification and pressurized fluidized bed combustion of coal in the topping gas cycle has already been proposed (De and Nag, 2000a). A synthesis of some existing proposals (Cai and Gou, 2007) adopts partial gasification to reduce the primary investment of the gasification equipment. The un-gasified surplus solid is then fed to a pressurized fluidized bed boiler similar to the system in this work as shown in Fig. 9.1.

9.2.2 Proposed IGCC system with supplementary firing

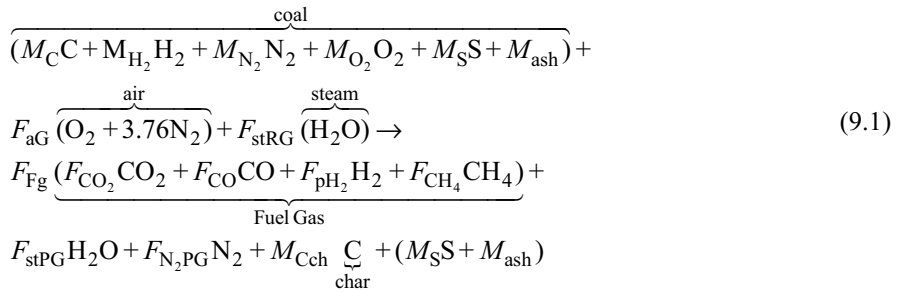
The IGCC configuration considered in this study (Fig. 9.1) uses coal gasification to convert coal to a fuel gas (syngas) which is fired in the gas turbine combustion chamber (GTCC) creating high-temperature pressurized gas which expands in the high-pressure gas turbine (HPGT). The gas is then reheated in the reheat combustor (RHC) which also uses syngas from the gasifier to generate the required thermal energy. The heated low-pressure gas expands in the low-pressure gas turbine (LPGT). The LPGT exhaust is directed to the supplementary firing arrangement to increase its temperature before entering the heat recovery steam generator (HRSG). The resulting high-temperature gases pass through the HRSG, generating steam that drives a two-stage steam turbine in the bottoming cycle. The supplementary firing combustor/furnace has three purposes: (i) reheat the gas turbine exhaust (from T_9 to T_{10}); (ii) pre-heat the compressed air before it enters the gas turbine combustion chamber (from T_4 to T_5); and (iii) reheat the low-pressure steam in the steam cycle (from T_{13} to T_{14}).

9.3 Thermodynamic Analysis

The mass balance is accompanied by the chemical balance of species involved with reactants and products. The gas turbine combustion chamber, reheat combustor, supplementary firing combustors involve combustion processes burning syn-gas (fuel gas) and char/coal in them. The enthalpy at each state is estimated based on basic thermodynamic relations, here the chemical balance of the combustion processes are listed followed by the mass and energy balance of the combustion processes.

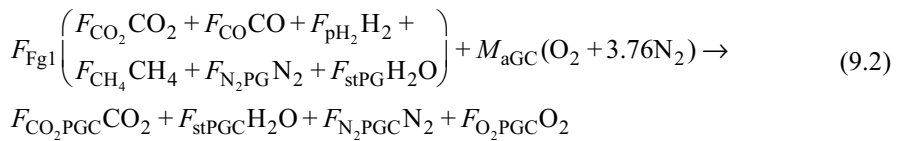
9.3.1 Gasification and combustion reactions

The chemical reaction during partial gasification of coal follows the form (Nag and Raha, 1994) which is based on the Amagat model for ideal gas mixtures:

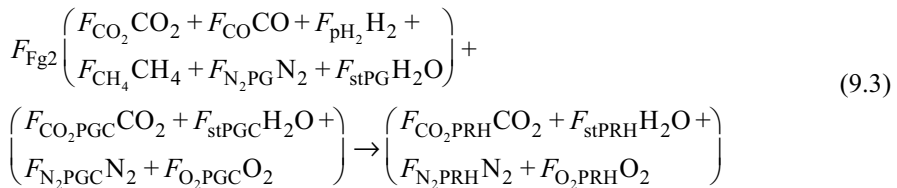


The combustion reactions for the GTCC and the reheat combustor within the gas cycle for all cases are as follows:

(i) Gas turbine combustion chamber (GTCC)



(ii) Reheat combustor



(iii) Char combustor

$$\left(\overbrace{M_{\text{CCC}}C + M_{\text{H}_2\text{CC}}\text{H}_2 + M_{\text{N}_2\text{CC}}\text{N}_2 + M_{\text{O}_2\text{CC}}\text{O}_2}^{\text{Additional coal when used}} \right) +$$

$$M_{\text{Cch}}(C) + (F_{\text{CO}_2\text{PRH}}\text{CO}_2 + F_{\text{stPRH}}\text{H}_2\text{O} + F_{\text{N}_2\text{PRH}}\text{N}_2 + F_{\text{O}_2\text{PRH}}\text{O}_2) +$$

$$M_{\text{aCC}}(\text{O}_2 + 3.76\text{N}_2) \rightarrow$$

$$(F_{\text{CO}_2\text{PCC}}\text{CO}_2 + F_{\text{stPCC}}\text{H}_2\text{O} + F_{\text{N}_2\text{PCC}}\text{N}_2 + F_{\text{O}_2\text{PCC}}\text{O}_2)$$
(9.4)

Materials are supplied such that, following the balances, there is always sufficient oxygen present in the product gases to permit any subsequent combustion.

9.3.2 Mass and energy balance

The mass and energy balances for the gas cycle (GTCC, HPGT, RHC, and LPGT) are the same for all four supplementary cases. The enthalpy and mass flow rate of the GTCC products exiting at state 6 are

$$h_6 = (\dot{m}_{\text{aGC}}h_5 + F_{\text{Fg1}}\dot{m}_{\text{Fg}}h_{\text{Fg}} + F_{\text{Fg1}}\dot{m}_{\text{Fg}}\text{HHV}_{\text{Fg}}) / (\dot{m}_{\text{GC}})$$
(9.5)

$$\dot{m}_{\text{GC}} = \dot{m}_{\text{aGC}} + F_{\text{Fg1}}\dot{m}_{\text{Fg}}$$
(9.6)

The enthalpy and mass flow rate of the reheat combustor products exiting at state 8 are

$$h_8 = (\dot{m}_{\text{GC}}h_7 + F_{\text{Fg2}}\dot{m}_{\text{Fg}}h_{\text{Fg}} + F_{\text{Fg2}}\dot{m}_{\text{Fg}}\text{HHV}_{\text{Fg}}) / (\dot{m}_{\text{RH}})$$
(9.7)

$$\dot{m}_{\text{RH}} = \dot{m}_{\text{GC}} + F_{\text{Fg2}}\dot{m}_{\text{Fg}} = \dot{m}_{\text{aGC}} + F_{\text{Fg1}}\dot{m}_{\text{Fg}} + F_{\text{Fg2}}\dot{m}_{\text{Fg}}$$
(9.8)

The enthalpy and mass flow rate of the char combustor products exiting at state 10 are

$$h_{10} = \left\{ \left[\dot{m}_{\text{RH}}h_9 + \dot{m}_{\text{Cch}}\text{CV}_{\text{ch}} + \dot{m}_{\text{cC}}\text{HHV}_{\text{c}} \right] \right\} / \dot{m}_{\text{Ch}}$$
(9.9)

$$\dot{m}_{\text{Ch}} = \dot{m}_{\text{RH}} + \dot{m}_{\text{Cch}} + \dot{m}_{\text{cC}} = \dot{m}_{\text{aGC}} + F_{\text{Fg1}}\dot{m}_{\text{Fg}} + F_{\text{Fg2}}\dot{m}_{\text{Fg}} + \dot{m}_{\text{Cch}} + \dot{m}_{\text{cC}}$$
(9.10)

9.3.3 Gas cycle performance

The net work output rate of the gas cycle can be expressed as

$$\dot{W}_{\text{netGC}} = \dot{m}_a (h_2 - h_1) + \dot{m}_a (h_4 - h_3) - \dot{m}_{\text{GC}} (h_6 - h_7) - \dot{m}_{\text{RH}} (h_8 - h_9) \quad (9.11)$$

and the rate of heat supplied to the gas cycle as

$$\dot{Q}_{\text{GC}} = \dot{Q}_L [\dot{m}_{\text{GC}} h_6 - \dot{m}_{\text{aGC}} h_5 + \dot{m}_{\text{RH}} h_8 - \dot{m}_{\text{GC}} h_7] \quad (9.12)$$

Thermal efficiency of gas cycle is subsequently

$$\eta_{\text{thGC}} = \frac{\dot{W}_{\text{netGC}}}{\dot{Q}_{\text{GC}}} \quad (9.13)$$

Constant polytropic efficiency for the compressor and isentropic efficiencies for gas turbine and steam turbine are assumed and a value of 85% is used (Shi and Che, 2007; Polyzakis et al., 2008).

9.3.4 Steam cycle performance

The net work output rate of the steam cycle, accounting for additional air ($\dot{m}_{\text{air}}$) that may be required depending on the excess oxygen balance, follows

$$\dot{W}_{\text{netSC}} = \dot{m}_{\text{st}} [(h_{12} - h_{13}) + (h_{14} - h_{15}) - (h_{17} - h_{16})] - \dot{m}_{\text{air}} h_1 \quad (9.14)$$

The rate of heat supplied to the steam cycle, not accounting for the mass flow rate of any solids since they are retained within the combustor as ash and bed material, follows

$$\dot{Q}_{\text{SC}} = \dot{Q}_L [\dot{m}_{\text{PRH}} (h_{10} - h_{11}) + \dot{m}_{\text{st}} (h_{14} - h_{13})] \quad (9.15)$$

Thermal efficiency of steam cycle is as follows:

$$\eta_{\text{thSC}} = \frac{\dot{W}_{\text{netSC}}}{\dot{Q}_{\text{SC}}} \quad (9.16)$$

An overall fractional heat loss $\dot{Q}_L$ of 3% of the heat input is assumed, and accounted for by setting $\dot{Q}_L = 0.97$ (Ramaprabhu and Roy, 2004).

9.3.5 Combined cycle performance

The net work output rate of the combined cycle can be written as

$$\dot{W}_{\text{net}} = \dot{W}_{\text{netGC}} + \dot{W}_{\text{netSC}} \quad (9.17)$$

and the combined cycle thermal efficiency as

$$\eta_{\text{comb}} = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{GC}} + \dot{Q}_{\text{SC}}} \quad (9.18)$$

9.4 System Performance Analysis

The results for the proposed IGCC configuration shown in Fig. 9.1 is computed based on fixed temperature conditions (except for the analyses explicitly involving parameter variations). That is, $T_3 = 370$ K, $T_5 = T_4$, $T_6 = 1,600$ K, $T_8 = 1600$ K, $T_{10} = 1100$ K, $T_{11} = 400$ K, $T_{12} = 900$ K, and $T_{14} = 900$ K. These temperatures are chosen in such a way that it is close to the maximum operating value for the corresponding components. The mass flow rates of fuel (coal, syngas, char) are estimated from the calculations for different operating conditions in the analysis. The results are discussed based on variations of parameters (efficiency, work output, coal/char consumption, steam production, and CO₂ emission) with respect to operating conditions such as pressure ratio (5–50), GTCC air inlet temperature ($T_5 = T_4$ and $T_5 = T_4 + 100$ K), gas turbine inlet temperature (1,000–1,700 K), and supplementary firing temperature (1,000 and 1,100 K). The pressure of steam used in the steam cycle are $P_{12} = P_{17} = 80$ bar and $P_{13} = 40$ bar. The chemical composition of four different solid fuels is given in Table 9.1 (Parikh et al., 2005), anthracite will be used for all the analyses when compared to other three fuel types.

Table 9.1 Four different solid fuels with the corresponding chemical composition (dry mass % wt) and higher heating values (Parikh et al., 2005).

Elements	Anthracite	Lignite	Pine	Wood chips
C	83.67	63.89	56.3	48.1
H ₂	3.56	4.97	5.6	5.99
O ₂	2.84	24.54	37.7	45.74
N ₂	0.55	0.57	0.00001	0.08
S	1.05	0.48	0.00001	0.00001
Ash	8.32	4.5	0.4	0.1
HHV (MJ)	32.85	25.1	21.77	19.92

9.4.1 Effect of gasification on combined cycle performance

The operating conditions of the combined cycle unit within the IGCC system will affect the output of the gasifier since the amount of coal consumed by gasifier is determined by operating temperatures at each state of the cycle as shown in Fig. 9.1. For the given set of temperature conditions as mentioned in the passage above, the change in values of different parameters with respect to percentage gasification are shown in Fig. 9.2. The parameters include combined cycle efficiency (CC eff), coal consumed in the gasifier (Coal,Gasif), coal consumed in the char combustor (Coal,CFBC), total coal consumed (Coal,Total), steam produced in the

steam cycle (Steam), char produced in the gasifier (Char,Prod), char used in the char combustor (Char,Used), and the net work output rate (Wnet). There is significant change in the values of all the parameters up to about 45% of gasification since the amount of total coal used and char produced are highest in the region below 45% gasification. The combined cycle efficiency is lower at 30% gasification and increases rapidly up to 45% gasification and then is almost constant until full gasification is achieved. The net work output rate decreases with increase in gasification due to the reduction in mass flow rate of the stream since, the fuel input and corresponding airflow are reduced to the gasifier as gasification is increased. Total coal and coal consumed in the gasifier are same up to 75% gasification, beyond which additional coal is consumed in the char combustor to furnish the energy required to increase the temperature of the gas turbine exhaust to $T_{10} = 1,100$ K. Since the efficiency is almost constant at this point (beyond 75%) and network output is higher than at full gasification, for an IGCC shown in Fig. 9.1 partial gasification of 80% can be adapted to save coal consumption, but will have to wait till the discussion on CO_2 emissions for the same conditions.

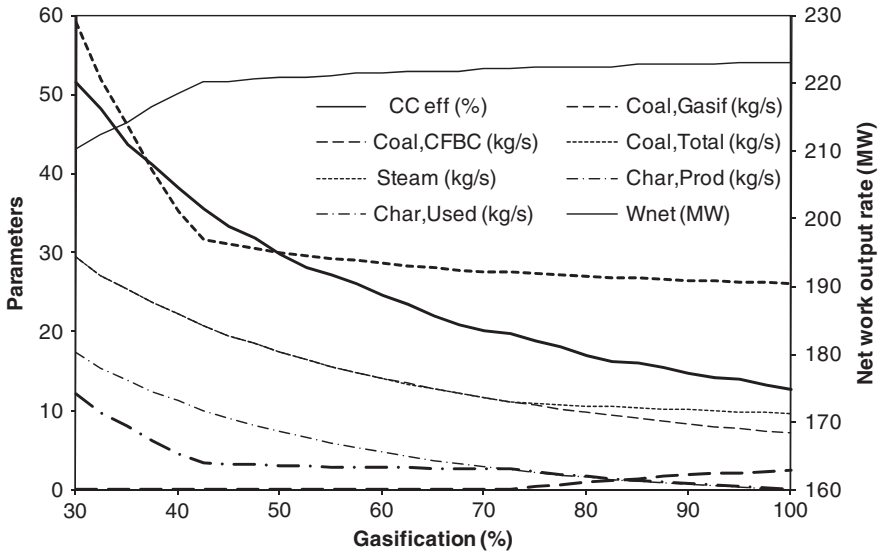


Fig. 9.2 Variation in values of parameters under investigation for the given IGCC configuration with increase in percentage gasification.

9.4.2 Effect of operating temperatures on combined cycle performance with respect to gasification

Operating temperatures refer to the inlet temperatures at three different locations within the IGCC configuration as shown in Fig. 9.1; inlet to the gas turbine combustion chamber at state 5, inlet to the gas turbine at state 6, and inlet to the HRSG

at state 10. In Fig. 9.3 eight different combinations of these three temperatures are used to observe the changes in relative net work output rate with respect to increasing gasification.

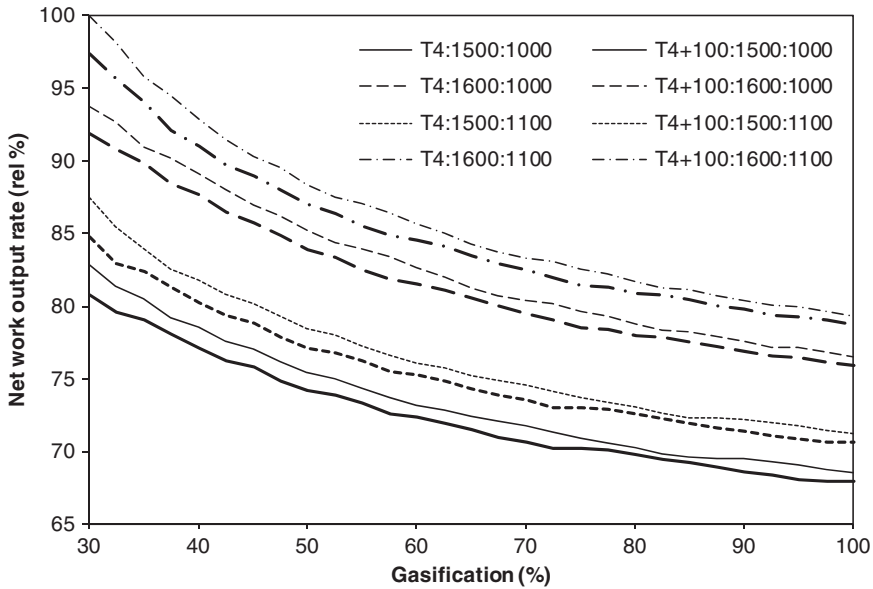


Fig. 9.3 Comparison of *relative net work output* among eight different temperature conditions for the IGCC configuration with increase in percentage gasification.

The legends are representing values of three temperatures in this fashion $T_5:T_6:T_{10}$. From the trends in Fig. 9.3 it is clear that the temperature condition of $T_4:1,600:1,100$ has the highest net work output rate and the lowest is with conditions of $T_4+100:1,500:1,000$. Increasing the temperature of air (T_5) before it enters the gas turbine combustion chamber by 100 K decreases the net work output for all the temperature cases (four thick lines). The reason for this is that an increase in T_5 reduces the syngas use in the gas turbine combustion chamber thus reducing the coal/air input to the gasifier which decreases the mass flow of the total stream bringing down the net work output. The same action happens when there is an increase in T_{10} (third number in each legend) which can be observed from the results in Fig. 9.3 for the respective curves where T_{10} is higher. Using a supplementary firing arrangement as shown in Fig. 9.1 gives an opportunity to study the influence of demand for syngas on cycle performance, based on different temperature conditions. From the set of results given in Fig. 9.3 it is better to run the unit at $T_4:1,600:1,100$ temperature conditions.

9.4.3 Effect of operating temperature on net CO₂ emissions with respect to gasification

The relative net CO₂ emissions (includes CO₂ emissions from gas turbine combustion chamber, reheat combustor, char combustor) for the same set of eight different temperature conditions are shown in Fig. 9.4 with increasing gasification. There is rapid decrease in CO₂ emission up to about 75% of gasification mainly for the temperature cases where $T_5 = T_4$. The reason for this is the similar behaviour exhibited by coal and char consumption in Fig. 9.2. The CO₂ emissions are higher for cases involving increase in T_5 by 100 K (four thick lines) beyond 60% gasification compared to the four cases with $T_5 = T_4$. The reason for this is the generation of CO₂ in the char combustor due to combustion of char and additional amount of coal in these cases (observed in Fig. 9.4 as abrupt change in CO₂ emission trend). Because of the additional coal combusted in char combustor for supplementary firing, the trend in maximum CO₂ emissions is reversed in the respective cases. Toward full gasification (beyond 70%) the highest CO₂ emission is for the temperature condition of $T_4+100:1,500:1,100$.

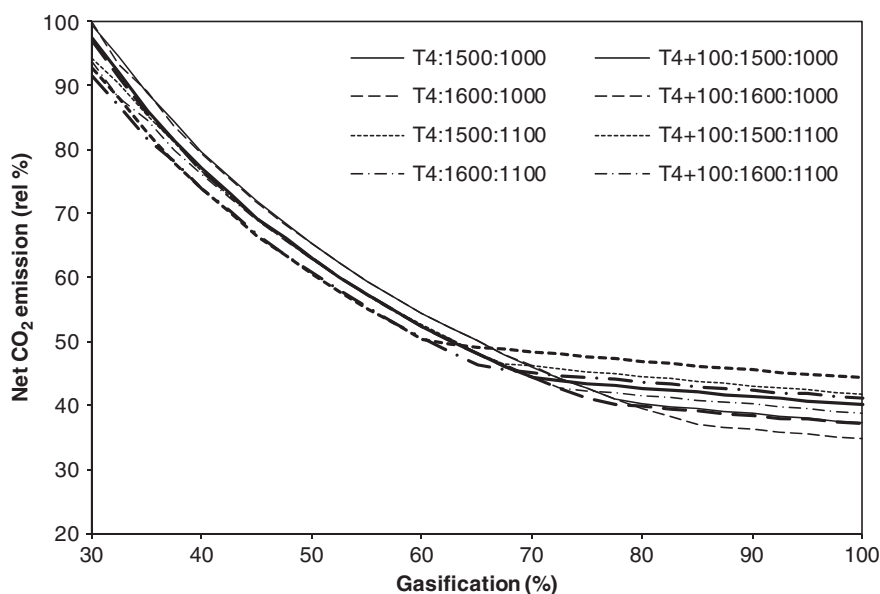


Fig. 9.4 Comparison of *relative CO₂ emission* among eight different temperature conditions for the IGCC configuration with increase in percentage gasification.

This clearly proves the point discussed regarding additional coal bringing in more CO₂ emission, since this temperature condition puts three loads on the char combustor – increase in T_5 , decrease in T_6 , and increase in T_{10} . On the contrary the

lowest CO₂ emission (beyond 70% gasification) is reported for the temperature condition of T_4 :1,600:1,000 which is when all the three loads for the char combustor are removed.

9.4.4 Effect of gasifier-operating conditions on net specific CO₂ emissions with respect to gasification

The operating conditions of gasifiers vary depending on the type of gasifier. In the current work air gasification is used and so a Lurgi moving bed gasifier is assumed. Mass flow of steam and air are the only variable-operating conditions that are tested in the current work. Figure 9.5 shows the use of four different mass flow rate of steam (40, 50, 60, 70) and four different air flow rate (50, 60, 70, 80) conditions chosen arbitrarily to study the effect of the variation.

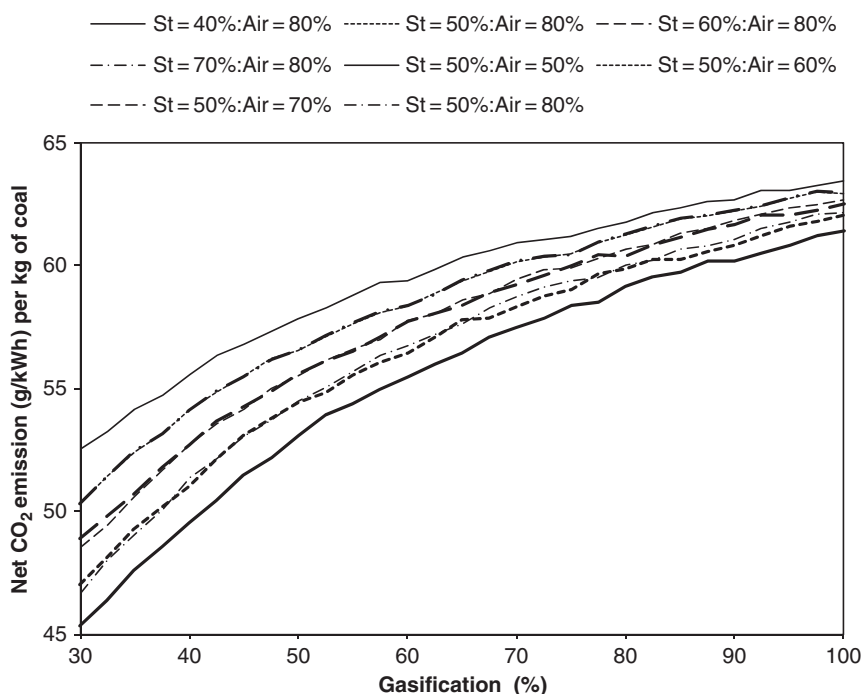


Fig. 9.5 Comparison of CO₂ emission per kg of coal in gas and steam cycles among four different flow rates of steam (St) and air (Air), respectively, used as the operating condition for the gasifier.

The mass flow rates are specified here as percentage of coal used. The effect of these operating conditions on the net specific CO₂ emissions is shown in Fig. 9.5. The specific CO₂ emissions increase with gasification which is an established fact

about gasification processes (Damen et al., 2006). This trend is not to be confused with that from Fig. 9.4, since that is relative CO₂ emissions. The clarity of the result curves in Fig. 9.5 can be understood by looking at the thin lines first, starting with St=40%:Air=80% which has the highest CO₂ emissions and the rest of the thin lines representing increase in steam mass flow percentage have equally lower CO₂ emissions with one another and have merged (equal values) with decreasing air flow rate conditions. For the thick lines the condition at St=50%:Air=50% has the lowest specific CO₂ emissions. With increasing steam flow rate there is decrease in specific CO₂ emissions and with increase in air flow rate there is increase in the specific CO₂ emissions. Remember these conditions are percentage of coal used in the gasifier. When the flow rates are increased the use of coal will also increase suggesting increased CO₂ emissions. When steam flow is increased no major increase in the net stream (includes all the gases put together which exit through the stack as shown in Fig. 9.1) is observed since steam will be used for gas conversion reactions. But when air flow is increased, the inert nitrogen gas in the air continues throughout the cycle which increases the bulk of the net stream. The increase of air flow in gasifier also suggests higher syngas production, which has about 14% CO₂ by weight and this contributes to the increase in specific CO₂ emission. The specific CO₂ emission results as shown in Fig. 9.5 suggest that it is better to send equal amounts of air and steam with corresponding quantity of coal to have lower specific CO₂ emissions.

9.4.5 Effect of feedstock on net specific CO₂ emissions with respect to gasification

The gasifier performance is mainly affected by the nature and chemical composition of the feedstock. In actual gasifier units, for each feedstock the corresponding syngas composition will vary. In this work the syngas composition is fixed so that the unified effect of feedstock composition on the specific CO₂ emissions can be estimated. Four types of solid fuels are used as feedstock in the calculations one at a time. As listed in Table 9.1, four different fuels are chosen with decreasing heating values (which corresponds to decreasing carbon percentage). The specific CO₂ emissions by the gas cycle (includes CO₂ from gas turbine combustion chamber and reheat combustor) which uses syngas and by steam cycle (CO₂ from the char combustor) which uses char and coal are compared with increasing gasification in Fig. 9.6. Within the gas cycle the anthracite coal emits the maximum amount of specific CO₂ due to the higher carbon content of the fuel. The wood chip emits the lowest specific CO₂ due to lower carbon content. The trends can be attributed to the heating value as well, since anthracite has highest heating value of all the four fuels will be consumed less thus increasing the specific emission. But since they are not relatively compared, the corresponding specific CO₂ emission suggests the impact of carbon content in source fuel (feedstock). The sudden change in the CO₂ emissions after certain percentage of gasification (70 for anthracite, 60 for lignite, 50 for pine, and 40 for wood chip) is caused mainly by the operating conditions of the combined cycle and is nothing to do with the composition of feedstock. For steam cycle the trend among the feedstock in terms of the difference in specific

CO₂ emission values follows the gas cycle (anthracite the most and wood the least). The steam cycle has reverse trend with respect to gasification when compared to gas cycle. The reason for this is the amount of the respective fuel used from low to full gasification. Based on the net work output data (not presented) using anthracite coal is efficient especially at higher gasification but it is associated with higher CO₂ emission as well. Using lignite or blend of lignite and anthracite will have moderate work output as well as CO₂ emissions.

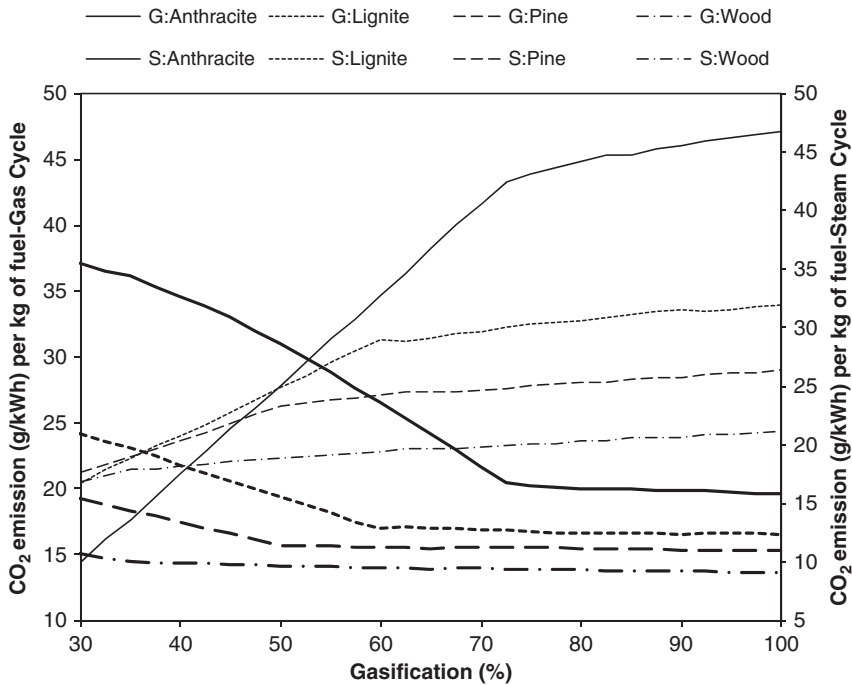


Fig. 9.6 Comparison of *CO₂ emission per kg coal* in gas and steam cycles among four different solid fuel types as mentioned in Table 9.1. In the legends G represents gas cycle and S represents steam cycle.

9.4.6 Validation of the current results with published results

Validation of the results of the current work was made by comparing them with published results. The validation becomes inconsistent since the considered IGCC design differs and the comparison based on gasification percentage is not observed. Nonetheless, the efficiency (50–56%) and net work output (150–190 MW) for the current work for varying inlet temperature conditions to the gas turbine combustion chamber (T_3) and gas turbine (T_6) are similar in behavior to the trends

published in several gasification and combined cycle works. The operating conditions used in these works differ from those used here. For example, De and Nag (2000a, 200b) considered pressure ratios of 4–40 and obtained overall efficiencies of 37–53%, Srinivas et al. (2006) used pressure ratios of 4–32 and obtained specific work values of 2–10 MJ/kg, Butcher and Reddy (2007) used net work output (10–17 MW) and observed exhaust gas inlet temperatures of $T_9 = 500\text{--}600\text{ }^{\circ}\text{C}$. The latter is the same range as in the current work. The enthalpy values for the steam cycle at each state are within the operating range when compared with an existing power plant (Dsouza and Li, 2006). The resulting CO_2 emissions (from 200 to 1400 g/kWh for all ranges of operating conditions used in this work) are within the range reported in some other works including Garcia et al. (2006), who compared three gasifiers from 750 to 900 g/kWh. Other CO_2 emissions reported include 0.709 kg/kWh (Amelio et al., 2007), 0.735 and 0.777 kg/kWh (Kanniche and Bouallou, 2007), and 710–920 g/kWh (Wall, 2007). Thus the thermodynamic calculations used in the current work appear to be reliable within the range of operating conditions and for the assumptions used.

9.5 Conclusions

The effect of combined cycle and gasifier-operating conditions on the CO_2 emissions and performance of an IGCC power generation system was investigated. The following conclusions were inferred from the results and discussion:

- Since the efficiency is almost constant beyond 75% gasification for the given conditions and network output is higher than at full gasification, partial gasification of about 75% can be adapted to save coal consumption.
- Supplementary firing arrangement as shown in Fig. 9.1 affects the demand for syngas in the gas cycle based on different temperature conditions of the IGCC. To have higher work output and lower CO_2 emissions it is better not to increase the compressed air temperature before it enters the gas turbine combustion chamber.
- CO_2 emission increases with gasification and the lowest relative CO_2 emission at higher gasification is observed for the temperature condition with lower compressed air temperature and lower HRSG inlet temperature.
- Based on the operating conditions of the gasifier, the specific CO_2 emission can be moderated when equal amounts of air and steam with corresponding quantity of coal are sent into the gasifier.
- High carbon content of the feedstock generates more CO_2 but is efficient especially at higher gasification. Using lignite (low carbon coal) or blend of lignite and anthracite (high carbon coal) will have moderate work output as well as CO_2 emissions. When CO_2 emission reduction is the priority, wood chips are best for gasification.

Acknowledgment

The authors kindly acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

Nomenclature

C	Elemental carbon
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
F	Fraction
h	Specific enthalpy [J/kg]
H_2	Elemental hydrogen
H_2O	Water
M	Molar mass
$\dot{m}$	Mass flow rate [kg/s]
N_2	Elemental nitrogen
O_2	Elemental oxygen
$\dot{Q}$	Heat rate [J/s]
Q_L	Heat loss
$\dot{W}$	Work rate [J/s]
Subscripts	
a	Air
CC	Coal/char combustor
CCC	Carbon of coal in combustor
Cch	Carbon of char
Ch	Char
GC	Gas cycle or gas combustor (GTCC)
FF	Fuel gas furnace
Fg	Fuel gas
Fg1	Fuel gas used in GTCC
Fg2	Fuel gas used in reheat combustor
PCC	Product of char combustor or coal combustor
PFF	Product of fuel gas furnace
PGC	Product of GTCC
PRH	Product of reheat combustor
RH	Reheat combustor
SC	Steam cycle
st	Steam
th	Thermal

Greek symbols

η Energy efficiency

Abbreviations

GT	Gas turbine
GTCC	Gas turbine combustion chamber
HHV	Higher heating value [J/kg]
HPC	High pressure compressor
HPGT	High pressure gas turbine
HPST	High pressure steam turbine
HRSG	Heat recovery steam generator
LPC	Low pressure compressor
LPGT	Low pressure gas turbine
LPST	Low pressure steam turbine

References

- Amelio, M, Marrone, P, Gallucci, F, Basile, A. 2007. Integrated gasification gas combined cycle plant with membrane reactors: Technological and economical analysis. *Energy Conversion and Management* 48:2680–2693.
- Bhattacharya, SP. 2006. Gasification performance of Australian lignites in a pressurized fluidized bed gasifier process development unit under air and oxygen-enriched air blown conditions. *Process Safety and Environmental Protection* 84:453–460.
- Butcher, C, Reddy, BV. 2007. Second law analysis of a waste heat recovery based power generation system. *International Journal of Heat and Mass Transfer* 50:2355–2363.
- Cai, R, Gou, C. 2007. A proposed scheme for coal fired combined cycle and its concise performance. *Applied Thermal Engineering* 27:1338–344.
- Damen, K, Troost, Mv, Faaij, A, Turkenberg W. 2006. A comparison of electricity and hydrogen production systems with CO₂ capture and storage. Part A: Review and selection of promising conversion and capture technologies. *Progress in Energy and Combustion Science* 32:215–246.
- De, S, Nag, PK. 2000a. Thermodynamic analysis of a partial gasification pressurized combustion and supercritical steam combined cycle. *Institution of Mechanical Engineers, Part A* 214(A6):565–574.
- De, S, Nag, PK. 2000b. Effect of supplementary firing on the performance of an integrated gasification combined cycle power plant. *Institution of Mechanical Engineers, Part A* 214(A1):53–60.
- Dsouza, N, Li, K. 2006. Introduction to Energy Systems. Design project report. Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, Oshawa, Ontario, Canada.
- Garcia, GO, Douglas, P, Croiset, E, Zheng, L. 2006. Technoeconomic evaluation of IGCC power plants for CO₂ avoidance. *Energy Conversion and Management* 47:2250–2259.

- Gnanapragasam, NV, Reddy, BV, Rosen, MA. 2008. Effect of supplementary firing options on cycle performance and CO₂ emissions of an IGCC power generation system. *International Journal of Energy Research*. DOI: 10.1002/er.1499.
- Higman, C, Burgt, Mvd. 2003. *Gasification*. Gulf Professional Publishing, Elsevier Science, USA.
- Kanniche M, Bouallou C. 2007. CO₂ capture study in advanced integrated gasification combined cycle. *Applied Thermal Energy* 27:2693–2702.
- Liu, G-S, Niksa, S. 2004. Coal conversion submodels for design applications at elevated pressures. Part II. Char gasification. *Progress in Energy and Combustion Science* 30:679–717.
- McMullan, JT, Willams, BC, Sloan, EP. 1997. Clean coal technologies. *Institution of Mechanical Engineers, Part A* 211(A4):95–107.
- Nag, PK, Raha, D. 1994. Thermodynamic analysis of a coal-based combined cycle power plant. *Heat Recovery Systems & CHP* 15:115–129.
- Parikh, J, Channiwala, SA, Ghosal, GK. 2005. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel* 84:487–494.
- Polyzakis, AL, Koroneos, C, Xydis, G. 2008. Optimum gas turbine cycle for combined cycle power plant. *Energy Conversion and Management* 49:551–563.
- Ramaprabhu, V, Roy, PR. 2004. A computational model of a combined cycle power generation unit. *Journal of Energy Resources Technology* 128:231–240.
- Shi X, Che, D. 2007. Thermodynamic analysis of an LNG fuelled combined cycle power plant with waste heat recovery and utilization system. *International Journal of Energy Research* 31:975–998.
- Srinivas, T, Gupta, AVSSKS, Reddy, BV, Nag, PK. 2006. Parametric analysis of a coal based combined cycle power plant. *International Journal of Energy Research* 30:19–36.
- Sugiyama, S, Suzuki, N, Kato, Y. 2005. Gasification performance of coals using high temperature air. *Energy* 30:399–413.
- Trapp, B. 2005. Coal gasification: When does it make sense? *Process Powergen Conference, IGCC session, Las Vegas*, available at www.gasification.org/Docs/Penwell%202005/Eastman.pdf
- Valero, A, Uson, S. 2006. Oxy-co-gasification of coal and biomass in an integrated gasification combined cycle (IGCC) power plant. *Energy* 31:1643–1655.
- Wall, TF. 2007. Combustion processes for carbon capture. *Proceedings of the Combustion Institute* 31:31–47.
- Watanabe, H, Otaka, M. 2006. Numerical simulation of coal gasification in entrained flow coal gasifier. *Fuel* 85:1935–1943.
- Yun, Y, Yoo, YD, Chung, SW. 2007. Selection of IGCC candidate coals by pilot-scale gasifier operation. *Fuel Processing Technology* 88:107–116.

A Strategic Program to Reduce Greenhouse Gas Emissions from Food Industry

Aydin Kilic, Adnan Midilli and Ibrahim Dincer

10.1 Introduction

Global warming is considered a problem caused by combined worldwide greenhouse gases (GHG) emissions. Many greenhouse gases occur naturally as a result of Earth's geological, hydrological, and biological cycles. They include water vapor, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and ozone (O₃). In addition, other photochemically important gases, such as carbon monoxide (CO), oxides of nitrogen (NO_x), and non-methane volatile organic compounds (NMVOCs), while they do not function as greenhouse gas, contribute indirectly to the greenhouse effect (Anonymous, 1998; ICF, 2007).

Energy resources are closely linked with the development of agriculture sector. Therefore, energy is a particularly significant input in the so-called 'industrial' food and farming systems, with farm systems based on synthetic external inputs and producing for the processing or global markets (i.e., several manufacturing stages and long transport distances) (Ziesemer, 2007). Agriculture and food processing systems play an important role to increase the fossil fuel consumption and climate change because of their significant energy use and agriculture's potential to serve as a sink for the negative externalities of energy use. In food industry, energy is used not only in planting, cultivating, and harvesting the agricultural products, but also in manufacturing and transporting the inputs, such as pesticides, fertilizers, and machinery and in processing, packaging, and distribution of final products. In terms of energy consumption, the food supply chain including production, processing, transportation, and consumption of food products can cause the environmental impacts, such as global warming. In other words, utilization of fossil fuels in food industry using these food supply chain releases carbon dioxide (CO₂) and other greenhouse gases that contribute to an increase in global warming (e.g., Dalgaard and Abbotts, 2000; Pelulessy, 2000).

Considering the above explanations, we need to find a better solution and propose some potential sustainability strategies and programs to reduce global

warming effect caused by food industry. Therefore, permanent and effective food strategies and programs should be put forward to increase the use and application of renewable energy sources and technologies in food industry.

Nowadays there is a great interest in studying the linkages between food industry and its energetic, environmental, and sustainability aspects. Therefore, in this chapter we present some potential sustainability strategies and programs to reduce global warming effect caused by food industry. This lack of information is the motivation for this work. Thus, the primary objectives of this work are to improve the understanding and to promote the strategic use of some potential sustainability strategies and programs that may help reduce the global warming effect caused by food industry.

10.2 Analysis

In order to develop and propose the required potential sustainability strategies, programs, and factors that may help reduce global warming effects caused by food industry, the following are important and are studied and discussed in the subsections:

- relationship between food supply chain and global warming,
- general processes in food industry,
- energy use steps for food processes, and
- energy demand and global warming potentials for some food products commonly used.

10.2.1 Food supply chain

In general, the food supply chain includes the number of steps such as production, processing, transportation, packaging, and consumption. These steps can create the environmental pollution that is one of the most important parameter to cause and increase global warming effects. In this regard, Fig. 10.1 illustrates the general food supply chain modified from the literature (Foster et al., 2006). As shown in this figure, raw material and energy enter the food supply chain. During processing, emissions including greenhouse gases and liquid and solid pollutants are produced. These emissions can pollute the land, air, and water and also create environmental pollution. Following environmental pollution, global warming effects can be observed locally, regionally, and globally. Therefore, it is recommended that emission-free energy sources such as solar, hydropower, wind should be utilized in food industry to minimize the environmental pollution increasing the global warming effects and to save fossil fuel sources that can be utilized in food industry.

10.2.2 General processes in food industry

The discussion concerning the energy burden of transportation is often distilled to examine the distance food travels from the farm to the consumer, or the ‘food

miles' of the product. The true energy expenditures of transportation, however, are much more complex. Method of transportation, fuel and loading efficiency of vehicles, and consumer travel all factor into the final analysis of energy consumption for food products. Transportation energy must be considered along with energy costs of production, processing, packaging, and storage of products, as higher energy expenditure for transportation can be offset by lower energy use in one of these areas (Ziesemer, 2007). In this regard, Fig. 10.2 presents a combination of some common processes in food industry.

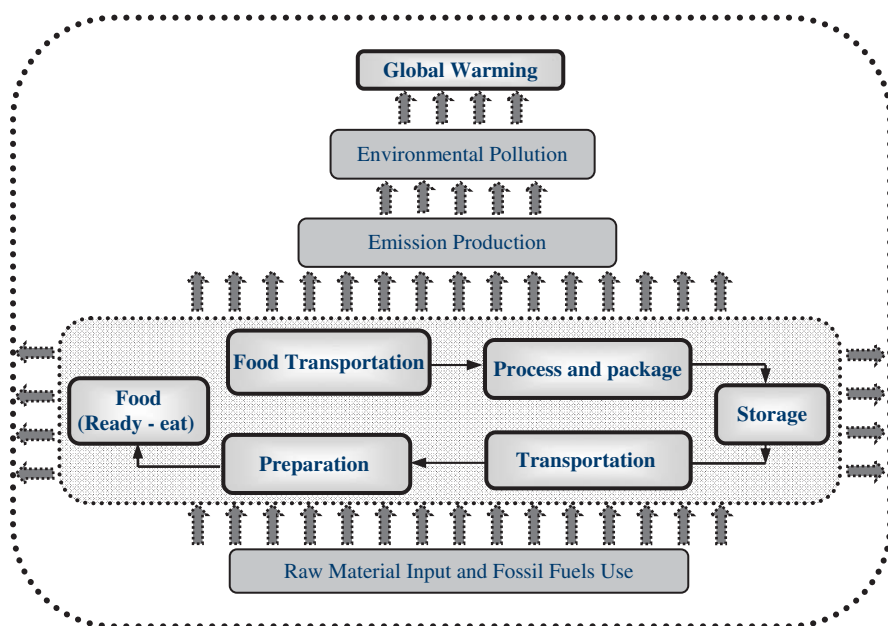


Fig. 10.1 Relationship between food supply chain and global warming in terms of raw material and fossil fuel use (modified from Foster et al. 2006).

The world's total energy utilization for food production, processing, distribution, preparation, etc., is known to be 1600 liters of oil per capita per year (Maul, 2003). In this, transportation plays a key role in the food system and is vastly more complex than just shipping directly from the farm to homes. There is no doubt that for many foods the environmental impacts of organic agriculture are lower than for the equivalent conventionally grown food (Anon., 2001a,b). So, there is sufficient evidence available to state that organic agriculture overall would have less environmental impact than conventional agriculture since it uses more material and energy and produces more greenhouse gases. Since there is a wide variation in the agricultural impacts of food grown in different parts of the world, global sourcing could be a better environmental option for particular foods. Usually, the processes include a mixture of boiling, pasteurization, evaporation, cooking, baking, and frying. Electrical consumption (besides for lighting and ventilation) is

primarily used for pumps, cyclones, milling, conveyers and other transport systems, and in compressed air and cooling systems. The cooling system often represents approximately 50% of the total electricity consumption (e.g., Pimentel and Pimentel, 1996; Dalsgaard and Abbotts, 2000; Pelupessy, 2000).

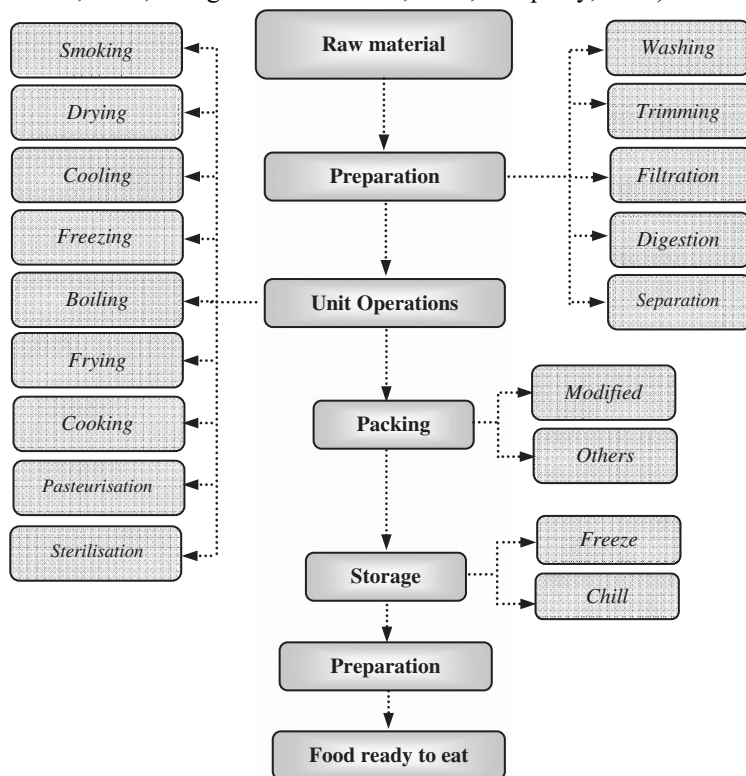


Fig. 10.2 A flowchart of general process steps in food industry.

10.2.3 Energy use in food supply steps

Most of food processing operations are highly energy intensive and cause a high degree of environmental impact. Energy consumption in the food industry, as in most other industries, consists of a mix of energy use necessary for the operation of the existing equipment and energy use. The unnecessary use of energy caused by suboptimal operation of the production plant can be reduced by introducing energy management methods and systems. Processing step has energy consumption, water use, cleaning chemical production and consumption, the use of intermediate packaging than possibly extra transport. In this regard, Fig. 10.3 shows crucial energy consumption points and common process flows during food supply chain.

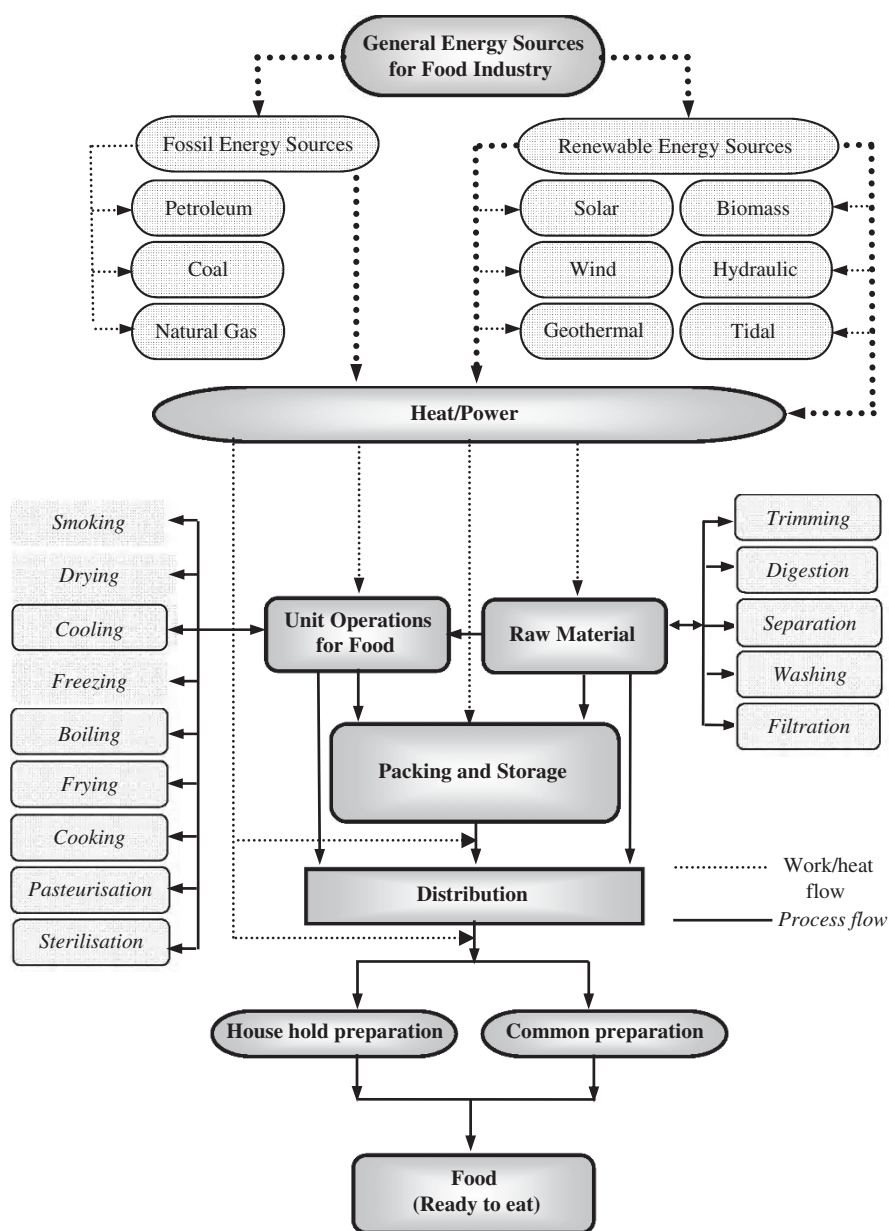


Fig. 10.3 A flowchart of energy consumption points and process flows during the food supply chain.

10.2.4 Energy demand and global warming potentials

As an example for energy demand and global warming potentials in food industry, Table 10.1 gives a list of various research results presented in the literature for some food products.

Table 10.1 Energy demand and global warming potentials for some food products.

	Packing	Retail	Transport	Consumption	Storage	Process
Energy demand (MJ/kg product)						
Org. potato	0.3	0.2	1.4	0.65	–	–
Potato (UK)	0.3	0.2	1.27	1.2	0.5	–
Local fruit (D)	–0.65	1.2	–0.49	–	–0.81	–
Imported fruit	–0.65	1.2	–3.57	–	–	–
Ketchup	13.8	1.2	1.4	–	1.3	7.1
Beef	–	2.2	–	–	0.15	5.11
Fish finger (LE)	–	4.2	–	3.25	–	10.75
Fish finger (HE)	–	4.75	–	26.5	–	10.08
Chilled salmon	–	2.25	–	4	–	2.5
Bread (Swedish)	–	–	3.50	2	–	3.9
GWP (g CO ₂ eq. Per kg)						
Organic potato	5	4	125	85	–	–
Carrot	4.78 ^{–3}	2.23 ^{–2}	–	1.86 ^{–1}	–	0
Frozen carrot	1.50 ^{–2}	37106	–	3.22 ^{–1}	–	37348
Canned carrot	4.44 ^{–1}	–	–	37318	–	1.34 ^{–1}
Tomato	520	135	95	–	–	440
Fish finger (LE)	–	141	–	216	–	540
Fish finger (HE)	–	216	–	812	–	540
Bread (Swedish)	–	–	380	10	–	210

Source: Mattsson and Sonnesson (2000); Nemry et al. (2001); Cederberg, (2003); Williams et al. (2006); Foster et al. (2006).

10.3 Results and Discussion

In order to reduce the effects of global warming effect based on the emissions coming from food industry, the following actions are proposed and discussed to reduce the greenhouse gases emitted from food industry: (i) some key drivers and strategies; (ii) a strategic program; and (iii) an alternative solution. In this regard, Fig. 10.4 proposes the driving forces and possible strategies for reducing the global warming effects while Fig. 10.5 proposes a strategic program for food

industry. Moreover, Fig. 10.6 presents an alternative solution to reduce the greenhouse gas emissions produced by food industry. This is expected to reduce greenhouse gas emissions and hence combat global warming.

10.3.1 Some key drivers and strategies

Widespread use of renewable energy in food industry can be important for achieving food sustainability and reducing the global warming effect. If so, renewable energy and technologies are needed for food industry. In this regard, in order to reduce the global warming effects caused by food industry, the urgent need is to develop some potential strategies for sustainability in food industry and find a sustainable alternative energy-based food supply chain. Actually, sustainable development requires a supply of energy resources that is sustainable and available at reasonable cost and causes no or minimal negative effects. In fact, fossil energy resources are finite, and thus lack the characteristics needed for stability and sustainability, while green energy sources are sustainable over the relatively long term (Midilli and Dincer, 2007). Particularly, cost-effective and environmentally benign renewable energy can be the most essential means for increasing the energy stability and sustainability in food industry. If a comprehensive renewable energy-based food technologies is effectively put into practice, this key example will encourage many food producers for implementation. The food industry may then maximize the benefits from the renewable energy-based food supply chain, while minimizing the global warming effect associated with the use of fossil fuel energy sources. In this regard, it is expected that these potential strategies proposed in this chapter can contribute to the development of food industry and make it more sustainable. Consequently, the use of renewable energy sources in food industry can help safe production, transportation, distribution, etc., of food and thus contribute to ensure the sustainability in food sector. Renewable energy is mostly expected in the future to replace the fossil fuel in food industry. Considering this important feature, the required strategies for sustainability in food industry are presented in Fig. 10.4 as modified from Dincer and Rosen (2004; 2005) and Midilli et al. (2005). As shown in Fig. 10.4, the main factors considered in the development of strategies for food industry are education, media, societies and organizations, public institutions, private sector, government, and research and development units.

These driving forces should be related to food strategy, programming, and planning units. These units produce the required strategies for stability and sustainability in food industry. If these strategies are put into practice, then it will be possible to ensure the social, environmental, energy, economical, and industrial stabilities in food industry.

10.3.2 A strategic program

In order to put into practice the required strategies to reduce the global warming effect caused by food industry, a strategic program should be developed. In this regard, Fig. 10.5 presents a possible strategic program for reducing greenhouse gas emissions from food industry.

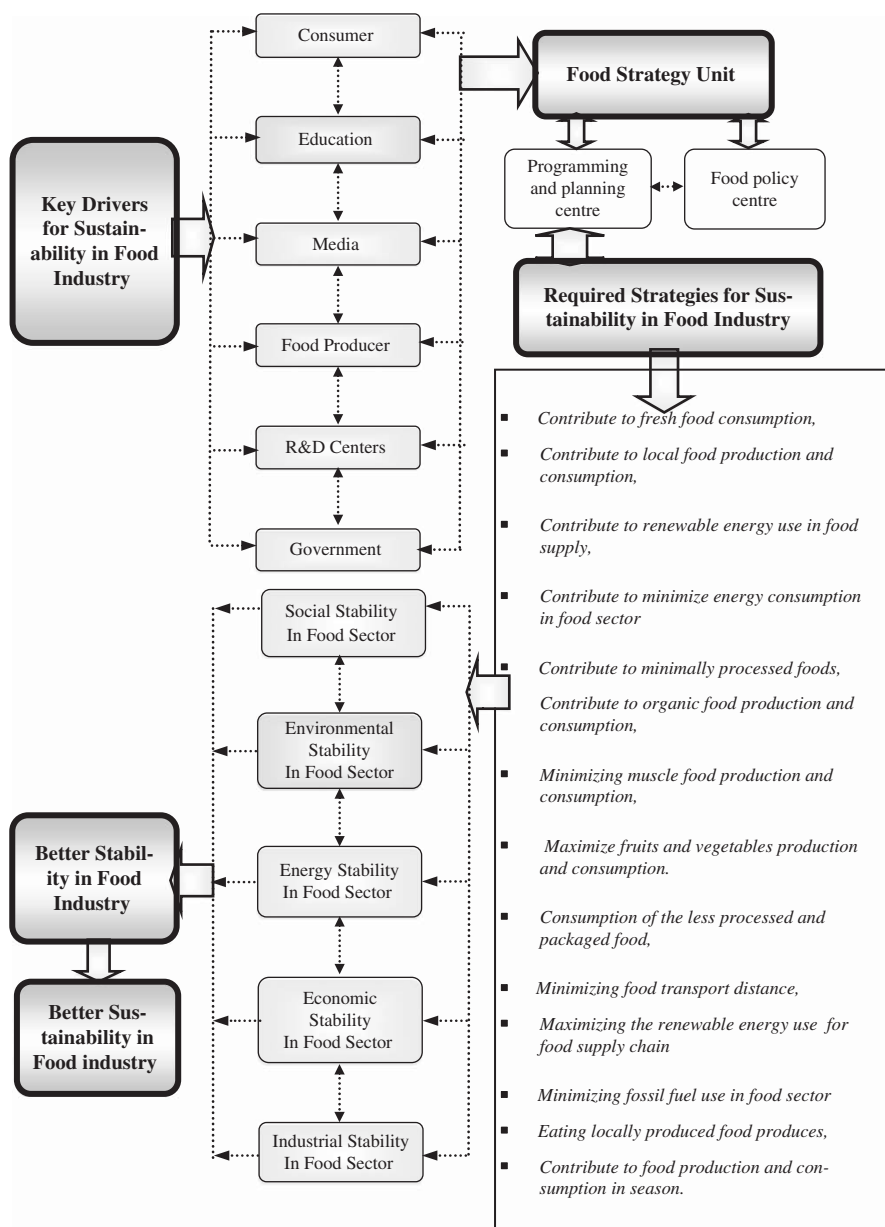


Fig. 10.4 Possible strategies for reducing the greenhouse gas emissions produced by food industry.

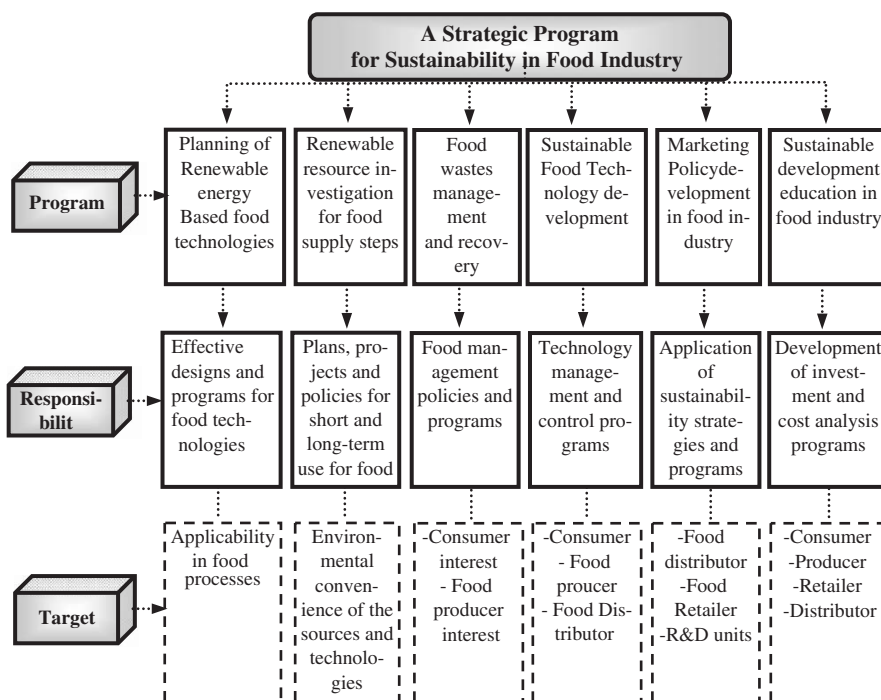


Fig. 10.5 A strategic program for food industry.

10.3.3 An alternative solution

Global warming that is observed locally, regionally, and globally has recently been a key problem as a result of fossil fuel consumption. In the past, fossil fuel sources could be used to solve world energy problems. However, fossil fuels cannot continue indefinitely as the principal energy sources due to the rapid increase of world energy demand for industrial, residential, commercial, and sectoral applications and also for different needs of the human beings.

One of the requirements of human beings is food supply. Particularly, population growth and development of new technologies are very important parameters affecting the fossil fuel consumption in food industry. In the case of fossil fuels in food industry, this industry will probably produce some pollutants such as tar, dust, and harmful gases including CO_x , SO_x , and NO_x , causing air pollution, as well. The pollutants produced by food industry are discharged to the atmosphere and create some problems.

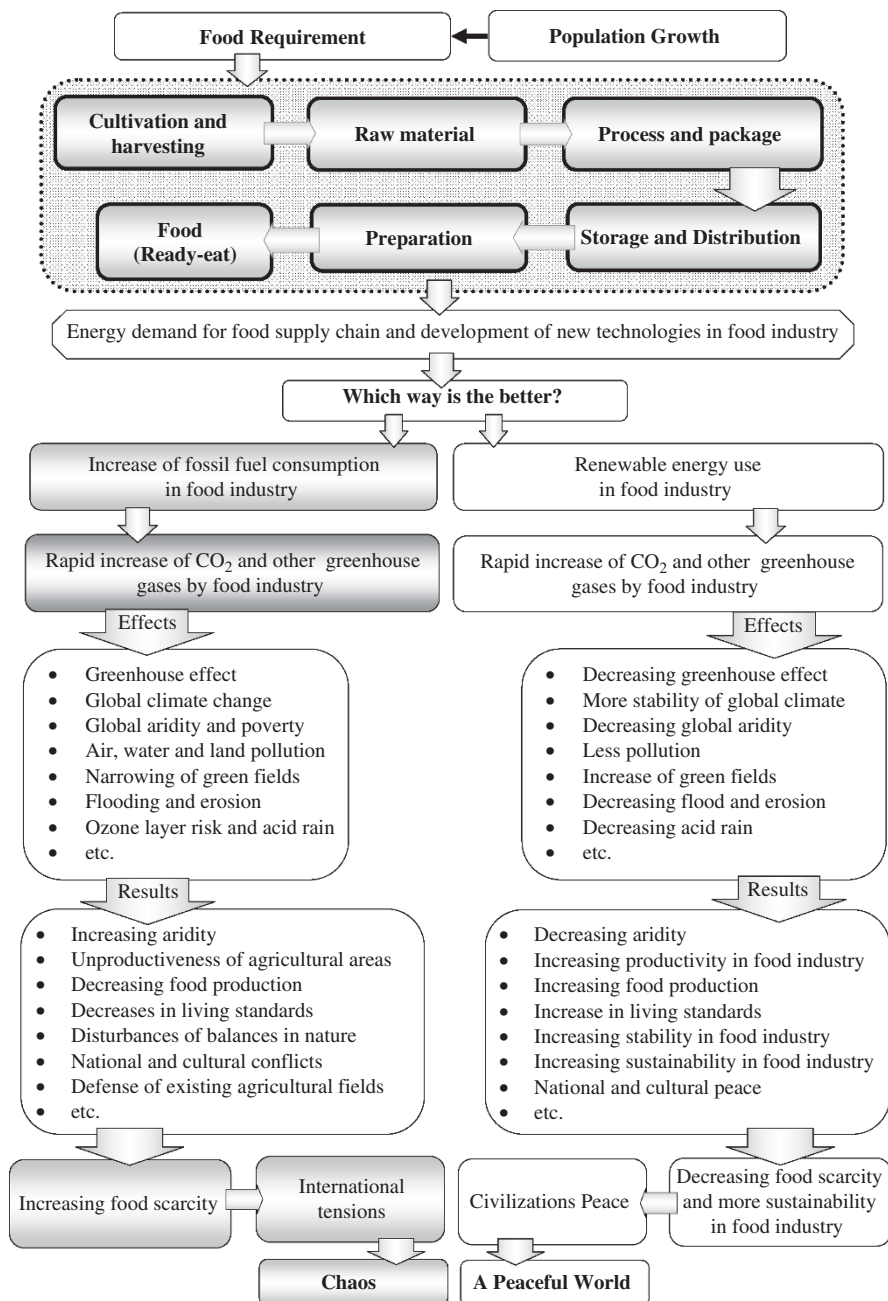


Fig. 10.6 An alternative solution to reduce greenhouse gas emissions from food industry.

For example, gas, particulate matter, and dust clouds in the atmosphere absorb a significant portion of the solar radiation directed at the Earth and cause a decrease in the oxygen available for living things. This can cause the global warming and change the climates locally, regionally, and/or globally. For instance, the average annual temperature of Earth has increased 0.7°C since 1860. If the utilization of fossil fuels continues at today's pace, the world's annual average temperature is predicted by some to increase 1.25°C by 2025, 2.2°C by 2050, 3.5°C by 2075 and 5.4°C by 2100, due to the rise in atmospheric CO_2 concentration (Ulltanir, 1997; TUSIAD, 1998; Midilli et al., 2005). If the utilization of fossil fuels reaches to 1000 EJ (1 exajoule = 10^9 GJ = 22.7×10^6 TEP (ton equivalent petrol)) in 2050, world average temperature will likely rise between 3°C and 5°C . This increase in temperature is sufficiently high to affect significantly life across the world. A 1°C rise in temperature may change climates in many areas of the northern and southern hemispheres. An annual average world temperature increase of almost 5°C would likely raise the levels of seas and oceans more than 1 m due to ice melting in the poles, and cause agricultural poverty, erosion, and floods (e.g., TUSIAD, 1998).

In fact, these negative effects of fossil fuel utilization can be created not only by food industry but also by all applications that consume fossil fuel sources. If increasing use is made of fossil fuels in food industry, significant global problems will probably increasingly occur. These are listed in Fig. 10.6 indicating and focusing on the important results of this study. Considering the above negative effects and the results, listed in Fig. 10.6, of fossil fuel consumption, it can be said that it is impossible to reduce the global warming effects caused by food industry and to ensure the energy stability and sustainability in food sector. Actually, this can allow us to use the renewable energy sources and technologies in this sector. In fact, in the near future, it is expected that, in case of increasing global warming and its immediate effects, the renewable energy and technologies will also become increasingly important to compensate for clean energy need in food industry.

Considering the above explanations, it should be emphasized that one of the main global problem affecting food industry is population growth. Increasing population needs much more food. Thus, in order to supply much more food for human beings, the following main processes in food industry should be taken into consideration: cultivation and harvesting, raw material production, food processing and packing, food storage and distribution, and finally food preparation. To achieve these food process steps and develop new technologies in food industry, energy is absolutely required. For this purpose, we have two ways. One is to utilize fossil fuel-based energy and technologies in food industry. Second way is to use renewable energy and technologies. If we use fossil fuel-based energy and technologies in food industry, it is certain to produce the above pollutants and greenhouse gases. If so, some possible effects of greenhouse gas emission produced by food industry can be observed locally, regionally, and globally. These effects can cause (i) increasing aridity, (ii) unproductiveness of agricultural areas, (iii) decreasing food production, (iv) degrading living standards, (v) disturbances

of balances in nature, (vi) national and cultural conflicts, and (vii) defense of existing agricultural fields. These negative results can probably increase the food scarcity and decrease the food stability. As a result of these, local, regional, and global tensions can be observed. Accordingly, these tensions can likely cause a chaos in the world. Considering these important explanations, it can be said that fossil fuel consumption in food industry can accelerate the global warming effect. Therefore, the second way should be taken into consideration to decrease the effects of global warming. As understood from Fig. 10.6, renewable energy and technology can provide more energy sustainability in food industry. In this regard, if renewable energy and technologies are used in food industry, the emissions of greenhouse gases can be likely reduced. In such a way that, this attempt, can rapidly decrease the concentration of greenhouse gases produced by food industry. If so, the main contribution of renewable energy use in food industry can be enumerated as follows: (i) decreasing greenhouse effect, (ii) more stable climatic conditions, (iii) decreasing global aridity, (iv) less pollution, (v) increasing green agriculture, (vi) decreasing flood and erosion, and (vii) greener and cleaner technologies and their use. Thus, the results of these positive effects can be enumerated as follows: (i) decreasing aridity, (ii) increasing productivity in food sector, (iii) increasing food production and living standards, (iv) increasing stability and energy sustainability in food industry, and (v) national and cultural peace. Consequently, it can be deduced that these important results can decrease the food scarcity and increase the energy stability and sustainability in food industry. As a result of this, the peace of civilizations may be ensured and thus, a peaceful world may be constituted. Meanwhile, it should be emphasized that renewable energy and technologies will not be entirely replace fossil fuels and technologies in food industry. However, it will be an important advantage to meet partially the energy requirements for food supply chain and developments of new technologies in food industry by using renewable energy sources and technologies.

10.4 Conclusions

This chapter aimed to analyze the aspects of energy consumption and greenhouse gas production in food industry and discuss potential solutions and strategies for reducing energy consumption and greenhouse gases for better environment and sustainable development.

Acknowledgment

The authors acknowledge the support provided by Nigde University in Turkey and the Natural Sciences and Engineering Research Council in Canada.

References

- Anon. (1998) California Energy Commission, historical and forecasted greenhouse gas emissions inventories for California staff report.
- Anon. (2001a) A Report of working group I of the intergovernmental panel on climate Change (IPCC).
- Anon. (2001b) Greenhouse gas emissions from management of selected materials in municipal Solid Waste, US.
- Cederberg, C (2003) Life cycle assessment of animal products. In Environmental-Friendly Food Production Woodhead-Publishing, England.
- Dalsgaard, H, Abbotts, AW (2000) Improving energy efficiency, ed. Mattsson, B. and U. Sonesson, Environmentally-Friendly Food Processing, ed B. Mattsson and U. Sonesson, CRC Press, Boca Raton, FL.
- Dincer, I, Rosen, MA (2004) Exergy as a driver for achieving sustainability. *International Journal of Green Energy* 1(1): 1–19.
- Dincer, I, Rosen, MA (2005) Thermodynamic aspects of renewables and sustainable development. *Renewable Sustainable Energy Review* 9: 169–189.
- Earle, RL (2004) Unit Operations in Food Processing. Web Edition. The New Zealand Institute of Food Science & Technology Inc.
- Foster, C, Green, K, Bleda, M, Dewick, P, Evans, B, Flynn, A, Mylan, J (2006) Environmental Impacts of Food Production and Consumption: A Report to the Department for Environment, Food and Rural Affairs. London.
- ICF (2007) Jones & Stokes climate change/greenhouse gas emissions analysis, City of Solana Beach, Climate Change/Greenhouse Gas Emissions Report.
- Mattsson, B, Sonesson, U (2000) Environmentally-Friendly Food Processing, 1: 33–431, eds Mattsson B. and Sonesson, U., CRC Press, Boca Raton, FL.
- Maul LK (2003) Lane county food system assessment report: A compilation of findings and suggestions for future research at www.fresh-energy.org.
- Midilli, A, Dincer, I (2007) Key strategies of hydrogen energy systems for sustainability. *International Journal of Hydrogen Energy*, 32(5): 511–524.
- Midilli, A, Ay, M, Dincer, I, Rosen, MA (2005) On hydrogen and hydrogen energy strategies-I: current status and needs. *Renewable Sustainable Energy Review*, 9(3): 255–271.
- Nemry, F, Theunis, J, Breceht, TH, Lopez, P (2001) Green gas emissions reduction and material Flows. Federal Office for Scientific, Technical and Cultural Affairs, Belgium.
- Pelupessy, W (2000) Environmental Issues in the Production of Beverages: the Global Coffee Chain. Cap. 7. pp 95–115. In: Mattsson B, Sonesson U, Environmentally-friendly food processing. Woodhead Publishing Limited, Cambridge England.
- Pimentel, D, Pimentel M (1996) Energy use in livestock production. *Food, Energy and Society*, ed. Pimentel D and Pimentel, M, Boulder, CO. University Press of Colorado, 77–84, US.
- TUSIAD (1998) Evaluation of energy strategy of Turkey towards 21. Century (in Turkish). No: TUSIAD-T/98-12/239, Istanbul.
- Ultanir, MO (1997) Hidrojenin yakıt olarak kullanımı ve özellikleri. Çevre-Enerji Kongresi, TMMOB Makine Mühendisleri Odası, 295–315.
- Williams, AG, Audsley, E, Sandars, DL (2006) Determining the environmental burdens and resource use in the production of agricultural and horticultural commodities. Main Report Defra Research Project IS0205. Cranfield University and Defra, Bedford. Available on www.silsoe.cranfield.ac.uk, and www.defra.gov.uk.
- Ziesemer, J (2007) Energy use In organic food systems, Natural Resources Management and Environment Department Food and Agriculture Organization of the United Nations, Rome.

Environmental and Economic Issues from Changing a Major Fuel Type as Energy Resource in an Industrial City in Korea

Byeong-Kyu Lee and Hung-Suck Park

11.1 Introduction

Ulsan is the largest industrial city of Korea with a population of more than 1.1 million people and national-scale industrial complexes (ICs) including non-ferrous metallic IC, petrochemical IC, automobile and shipbuilding IC. Main sources of air pollutants in major metropolitan cities are traffic emissions (Mamane et al., 2008). However, they are quite different from the main sources from industrial cities. According to the recent study of air pollution source apportionment (Koo and Kim, 2007), 77%, 66%, 87%, and 58% of the total sulfur oxides (SO_x), nitrogen oxides (NO_x), PM_{10} , and volatile organic compounds (VOCs), respectively, are from point sources such as power plants and manufacturing plants in Ulsan. In Seoul, the capital city of Korea, with a population of 12 million people, however, 72% and 63% of the total emissions of SO_x and VOCs are from area sources. Mobile sources are responsible for 16%, 83%, 93%, and 35% of the total emissions of SO_x , NO_x , PM_{10} , and VOCs in Seoul, respectively.

Because of heavy contribution from industrial sources to air pollution in Ulsan, the government of Korea had designated Ulsan as an area particularly requiring countermeasures to air pollution. Also, the local government of Ulsan has adopted many regulations to cut down emissions of air pollutants or improve its air quality. For example, the use of solid fuel such as coal was prohibited except in few big facilities in 1985. In addition, gradual increase in the use of low-sulfur fuel and clean fuel such as liquefied natural gas has been required since 1988. The regulations to limit maximum content of sulfur in fuel have also been reinforced since their adoption in 1981. The sulfur content in fuels such as bunker fuel oil C (B-C) was 4.0% and 2.5% in early and late 1980s, respectively. The current sulfur content in B-C oil applied to new and some existing plants in Ulsan has been 0.3%, an ultra low sulfur fuel, since 2001, with 1.6% in 1991 and 0.5% in 1997.

Thanks to these regulations and efforts for reduction of air emissions, the air pollution levels in Ulsan have greatly improved. In order to reduce the total air emissions of SO_x (Stern, 2005), NO_x , and PM from industrial areas in Ulsan, a volunteered agreement between the big sources and the national and local governments has been made. The agreement includes increase in use of clean fuel and ultra low sulfur B-C oil of 0.3% and more investment for air pollution control (APC) equipment. At this moment the plants that use ultra low sulfur fuel are waived operation or attachment of control equipment for removal or reduction of SO_x emissions. However, the recent improvement in the air pollution levels in Ulsan would be mainly due to low energy consumption via energy savings or efficiency increase rather than the strict application of the volunteered agreement (Park and Lee, 2007).

The business success of the industries in Ulsan is highly dependent upon energy costs. The recent fuel or energy prices have sharply increased during the last 2 years. Thus already a few companies could not operate their plants any more because of rising fuel or energy costs (Borchers et al., 2008). Many companies, due to the required high energy costs, have considered business shutdown in the near future if the fuel or energy costs have a kind of skyscraper rise (Zhang, 2008). Thus most companies in Ulsan have filed a lot of petitions that they want to use high-sulfur fuel such as B-C oil of 4.0% with conditions of strict operation of APC equipment. Also, they have requested to use solid fuel like coal with conditions of strict operation of APC equipment. However, most of the people who live in Ulsan want to keep the air environment clean. The local government of Ulsan wants to continue their previous policies or strategies, such as increasing the use of clean fuel or ultra low sulfur fuel, for improvement of its air environment. However, the government also needs to boost up active industrial business in Ulsan. Thus the local government is faced with a kind of dilemma on strategies of industrial fuel use in Ulsan. The purpose of this study is to evaluate environmental impacts and economic benefits associated with changing the ultra low sulfur B-C oil of 0.3% with high-sulfur B-C oil of 4.0%, coal, natural gas, and nuclear power.

11.2 Methods

The local and national regulations or strategies for the air environment improvement in Ulsan have been reviewed. The change of annual average concentrations of SO_x in Ulsan was analyzed as a function of introduction of low or ultra low sulfur fuels. In particular, the cause of the recent improvement on SO_x levels in Ulsan was investigated. The main methods to reduce SO_x levels in Ulsan would include increasing control efficiency of SO_x removal equipment, changing to low sulfur containing fuel, tightening of SO_x emission standards at sources, and increasing fines on exceeding the standards.

This study analyzed which method was the main cause of the reduction in SO_x concentrations. Then this study evaluated the environmental problems and

economic benefits expected when ultra low sulfur bunker C oil of 0.3% is replaced by high-sulfur B-C oil of 4.0%, coal, natural gas, and nuclear power. The first evaluation was focused on the current environmental issues related to increased use of B-C oil of 0.3% S. The second evaluation was to analyze environmental impacts related to the considered options of fuel change including a comparison of pros and cons of each alternative option. In particular, this study highlighted the environmental issues and economic benefits resulting from increased use of high-sulfur B-C oil of 4.0%, coal, natural gas, and nuclear power to solve current environmental and economical problems associated with current use of B-C oil of 0.3% S and energy crisis. This study also discussed the issues related to administrative consistency such as keeping the environmental policies on increased use of low or ultra sulfur fuel or clean fuel.

11.3 Results and Discussion

11.3.1 Comparison of SO_x levels in major cities

Fig. 11.1 shows change of annual average concentrations of SO_x in major cities in Korea. SO_x levels gradually decreased with time. SO_x levels in the largest industrial city, Ulsan, were much higher than those in the Korean capital city, Seoul. This fact indicates that the main sources of SO_x are not traffic emissions but industrial emissions. Comparison of the average SO_x levels among Busan, Daegu, and Ulsan cities showed that their SO_x concentrations were quite similar in 1996. However, SO_x levels in Busan (the largest port city with a population of 3.7 million) and Daegu (an inland basin city with a population of 2.5 million) have become much lower than those in Ulsan since 1999. Korea had economical aids from the International Monetary Fund (IMF) in December 1997 because of economical crisis, by a shortage of foreign currency, throughout the country. During 1998, the activity levels of business greatly shrank, resulting in business shutdown of many companies and reduction of SO_x emissions. When the economic situations improved in 1999, a lot of companies in Ulsan substantially recovered from the economic crisis. However, many companies in Busan and Daegu that had weak infrastructure of business or industries had much trouble to recover. Thus business activities were still sluggish in Busan and Daegu in 1999 and early 2000s. The difference in city business activities or economic situations between Ulsan and Busan (or Daegu) resulted in the difference in their SO_x levels.

The control efficiencies of SO_x removal equipment, which is one of the main methods to reduce SO_x levels, and the emission standards of SO_x at sources have not changed greatly over the past 10 years. However, the limit of sulfur content in fuel for industries has gradually decreased in Korea and, in particular, Ulsan. Also, a lot of industries in Ulsan have been required to reduce their SO_x emission levels by local and central governments. One of the major efforts to reduce SO_x emission levels at industrial sources was to increase the use of low-sulfur

fuel, such as 0.5% S bunker C (B-C) oil, with the operation of SO_x removal equipment, or clean fuel (natural gas) or ultra low sulfur fuel (0.3% S B-C oil) in Ulsan. For example, the largest power plants in Ulsan are currently using a high sulfur content B-C, oil with desulfurization facilities (DSFs), 0.3% B-C, and natural gas with no DSFs as their fuel. Thus they reduced a large amount of their SO_x emissions. In Ulsan, the SO_x emissions from mobile sources, such as road vehicles, ships, and aircrafts, were only a small fraction of the total SO_x emissions as compared to those from stationary sources such as power plants and industrial stacks. Thus the main cause of the recent improvement in SO_x levels in Ulsan was due to the increased use of ultra low sulfur fuel or clean fuel for industries. Also, the increased operation of DSFs in case of using high-sulfur fuel could contribute to the recent improvement in SO_x levels in Ulsan.

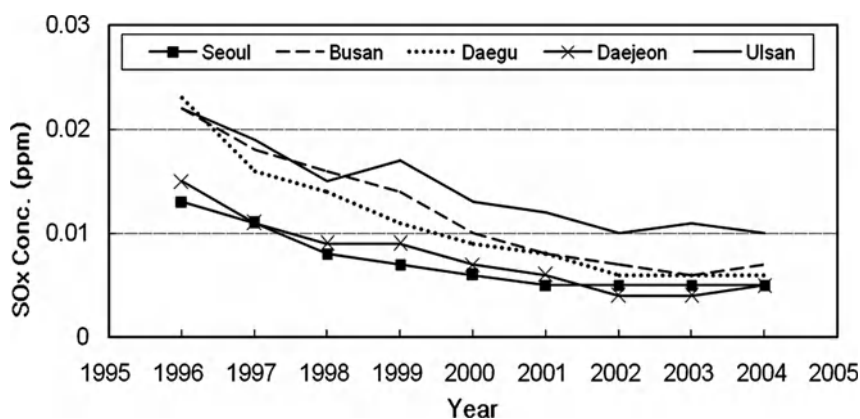


Fig. 11.1 Change annual average SO_x in major cities in Korea.

11.3.2 SO_x levels with change of sulfur content in fuel

Fig. 11.2 shows the change of annual average SO_x and the regulation change of sulfur content limit of major fuel, B-C oils, in Ulsan. The highest peak concentration of SO_x was observed in 1991; however, the annual averages decreased with decreasing sulfur content in major fuel. When actively changed from B-C oil of 2.5% S to 0.5% S via 1.6% S during the period 1991–1997, in spite of a large increase in terms of total energy use, the annual average SO_x levels sharply decreased. This is because of the large change of sulfur content in fuel as well as substantial improvement in removal or collection efficiencies of APC equipment to keep reducing air emissions from companies. After adopting 0.5% S limit in B-C oil, the degree of improvement of annual SO_x levels was not that satisfactory as

compared to the improvement degree expected before adopting the regulations of the sulfur content limit. Thus the local Ulsan government has adopted 0.3% S limit in B-C oil, a kind of ultra low sulfur fuel, to get further reduction of SO_x levels in spite of reducing the costs to purchase more expensive B-C oil of 0.3% S. The annual SO_x levels were not significantly improved during the first 3 years after adopting the 0.3% S limit in major fuel. This is because the government waived the responsibility to operate SO_x control facilities for companies that use 0.3% S B-C oil. The SO_x emission concentrations from the stacks of plants which use high sulfur content fuel such as 4.0%, 2.5%, and 1.6% S B-C oils were much less than 100 ppm.

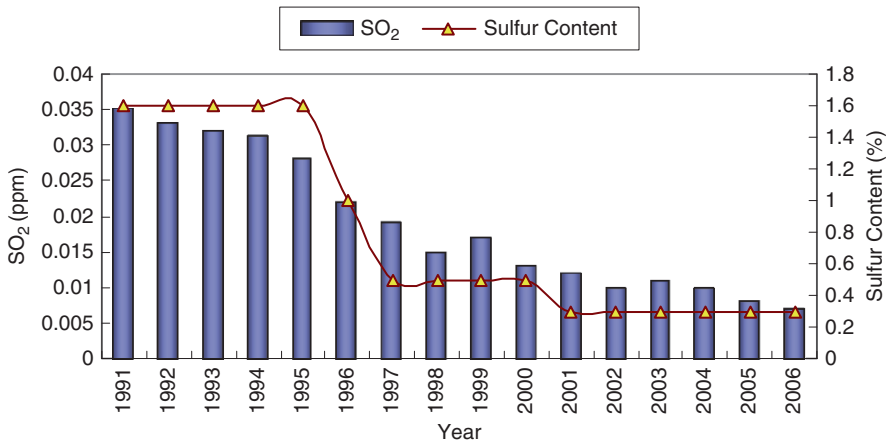


Fig. 11.2 Change of annual average SO_x and sulfur content of major fuel in Ulsan.

In fact many big companies that use fuel with high sulfur content are emitting less than 30 ppm. Also, the SO_x emission levels from the stacks of plants that use low-sulfur B-C oil of 1.0% S or 0.5% S ranged from 50 to 90 ppm. However, the SO_x emission levels from the stacks of plants that use ultra low sulfur B-C oil of 0.3% S, which is not required to operate SO_x removal devices of the stacks, ranged from 160 to 150 ppm which is slightly lower than the current emission standard, 180 ppm. The total SO_x emissions did not greatly reduce, but they could slightly increase with use of B-C oil of 0.3% S. The volunteered agreement of air pollution reduction between the local government and the big companies that consume a lot of energy use or emit a large amount of air pollution was signed in 2004. Even though the local government has encouraged the increased use of ultra low sulfur fuel instead of high sulfur content fuel, the total consumption of B-C oil of 4.0%, 2.5%, 1.0%, and 0.3% S reduced by 21.4%, 25.7%, 11.3%, and 24.5%, respectively, in 2005 based on those of 2003 (Table 11.1). Therefore, the reduction of 27.3% in the annual SO_x levels during the period 2003–2005 would be mainly due to decrease of total energy use rather than

increase of use of low-sulfur B-C oil of 0.3% S (see next section for detailed discussion).

Table 11.1 Annual oil consumption in Ulsan.

Year	Total oil*	unit: 1000 bbl					
		Bunker fuel oil C					
		B-C total	4.0% S	2.5% S	1.0% S	0.5% S	0.3% S
2005	138,525	23,239	10,095	6,707	454	1,140	4,843
2004	140,017	27,034	11,222	9,412	453	1,059	4,879
2003	135,377	29,844	12,846	9,032	512	1,039	6,415
2002	132,703	30,720	12,260	9,024	638	820	7,978

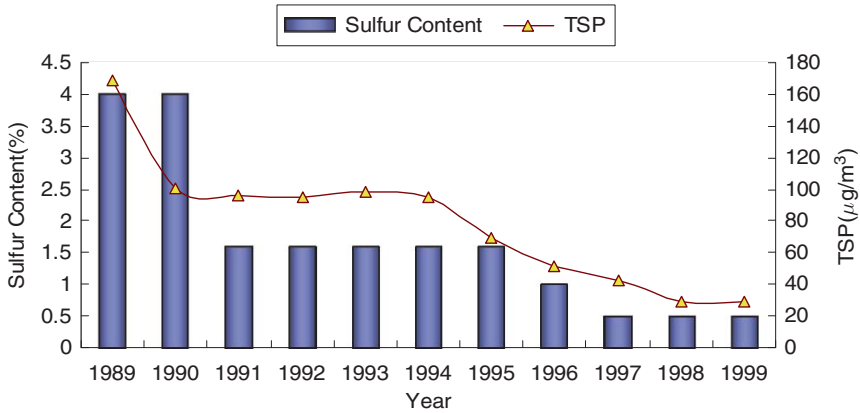
*Total oil means a sum-up of consumption of light oil, bunker fuel oils A, B, and C in Ulsan.

Table 11.2 shows the production and emissions of SO_x associated with consumption of major industrial energy resources in Ulsan for 2004. The highest energy resources based on ton of oil equivalent (TOE) was bunker fuel oil C followed by liquefied natural gas (LNG) and coal. The highest SO_x production from major industrial energy use in Ulsan was from B-C oil of 4.0% S followed by B-C oil of 2.5% S and coal. The highest SO_x emission from major industrial energy use in Ulsan was from B-C oil of 4.0% S followed by B-C oil of 2.5% S and B-C oil of 0.3% S. Utilization of clean fuel, such as LNG, and ultra low sulfur fuel, such as B-C oil of 0.3% S, as fuel resources in Ulsan does not require the operation of SO_x control equipment. However, other B-C oils must have proper SO_x control equipment, keeping an average control efficiency of 87% in Ulsan. The production of SO_x from utilization of B-C oil of 0.3% S was only 2.5% of the total SO_x produced from major energy use.

Table 11.2 Production and emissions of SO_x associated with consumption of major industrial energy resources in Ulsan for 2004.

	Bunker fuel oil C					LNG	Coal	
	4.0% S	2.5% S	1.0% S	0.5% S	0.3% S		Soft	Hard
Relative TOE (%)	25.5	18.6	1.7	4.0	15.3	14.2	10.6	10.0
SO_x production (tonne/yr)	60,988	27,830	1,030	1,203	2,741	5.5	6,745	8,640
Relative SO_x production (%)	55.8	25.5	0.9	1.1	2.5	0.1	6.2	7.9
Total SO_x emission (tonne/yr)	7,921	3,618	134	156	2,741	5.6	877	1,123
Relative emission of SO_x (%)	47.8	21.8	0.8	0.9	16.5	0.0	5.3	6.8

However, the air emission of SO_x from the B-C oil of 0.3% S reached 16.5% of the total SO_x emissions, based on the SO_x emitted from each energy source after passing SO_x control equipment, in Ulsan for 2004. Thus, the SO_x emissions from B-C oil of 0.3% S must be controlled by proper SO_x control equipment or replaced by clean fuel or other B-C oils. If industries want to utilize other B-C oils, they must operate proper SO_x control equipment resulting in total emissions reduction of SO_x .



(3a): TSP

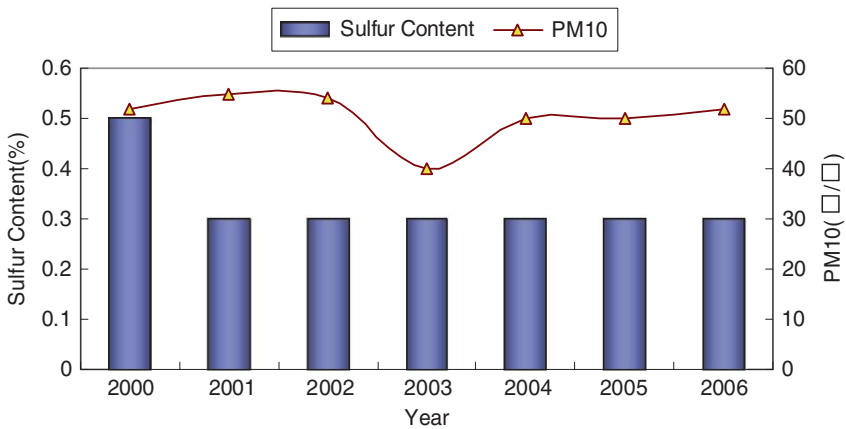
(3b): PM₁₀

Fig. 11.3 Change annual average TSP or PM₁₀ concentrations with change of sulfur content in major fuel in Ulsan.

Fig. 11.3a and b shows change of annual average concentrations of total suspended particulate [TSP (shown in PM_{10} values since 1995)] and of PM_{10} , respectively, with change of the regulations to limit maximum sulfur content in major fuel, B-C oil, in Ulsan. The annual levels of particulate matter (TSP or PM_{10}) substantially decreased with decreasing sulfur content of the fuel in Ulsan. When correlation was analyzed between annual SO_x and TSP levels associated with decrease of sulfur content in major fuel, a high correlation ($r = 0.850$) was obtained during 9 years in 1990s (Fig. 11.4). This fact shows that reduction of sulfur content in major fuel or improvement in removal or collection efficiency of particulate and SO_x control equipment could greatly contribute to the reduction in annual levels of particulate matter, particularly TSP levels. However, a significant correlation was not identified between annual SO_x and PM_{10} levels when B-C oil of 0.3% S introduced.

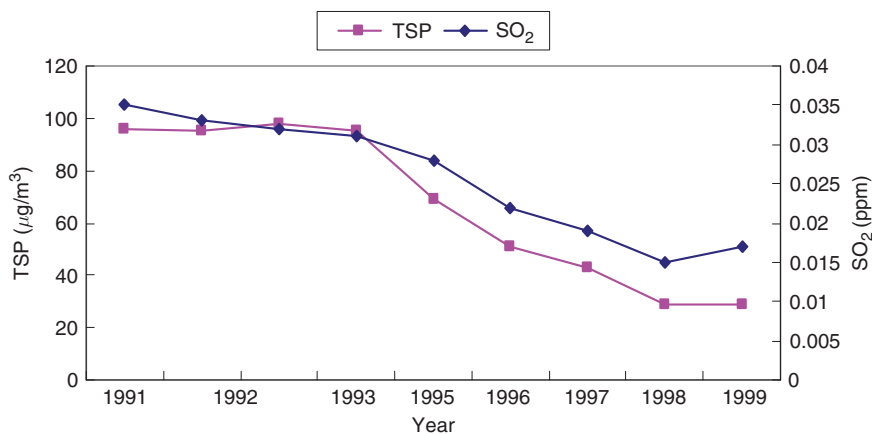


Fig. 11.4 Correlation between annual SO_x and TSP levels in Ulsan during 1990s.

11.3.3 Issues associated with conversion to high-sulfur fuel

Table 11.3 shows SO_x production by conversion rate when clean and ultra low sulfur fuels (LNG and B-C oil of 0.3% S) are replaced by high-sulfur fuel (B-C oil of 4.0% S) according to the conversion scenarios. If 50% and 100% of the current consumption of LNG and B-C oil of 0.3% S is replaced by B-C oil of 4.0% S, the total SO_x production increased by 31% (33,905 tonne/year) and 62% (67,810 tonne/year), respectively. When control efficiency of SO_x control equipment is assumed as 87%, the SO_x emissions in these scenarios only increased as much as 4408 tonne/year (4.0%) and 8815 tonne/year (8.0%) after control of produced SO_x . If the control efficiency of SO_x control equipment goes up to 94%, there would be no additional emissions of SO_x . The additional cost required for upgrading control efficiency of existing control equipment from 87% to 94% is necessary. If some plants do not have control equipment of SO_x , they need to purchase new control facilities of SO_x . In that case their expenditure will be more than that of other plants with existing control equipment.

Table 11.3 SO_x production by conversion of clean and ultra low sulfur fuels to B-C oil of 4.0% S.

Scenario	Con- version rate (%) to 4.0% S B-C	SO _x production (tonne/yr)			Increase by conver- sion	SO _x emis- sion after control [tonne/yr (%)]
		LNG + 0.3% S B-C	4.0% S B-C	Total (B-A, B, C + LNG + coal)		
Original	0	2,746	106,437	109,814	–	–
Scenario 1	10	2,472	113,493	115,965	6,781 (6%)	881 (0.8%)
Scenario 2	30	1,922	127,604	129,527	20,343 (19%)	2,645 (2.4%)
Scenario 3	50	1,373	141,716	143,089	33,905 (31%)	4,408 (4.0%)
Scenario 4	80	549	162,883	163,432	54,248 (50%)	7,052 (6.4%)
Scenario 5	100	0	176,994	176,994	67,810 (62%)	8,815 (8.0%)

The unit prices of B-C oil of 0.3% S and LNG were 25% and 38%, respectively, higher than that of B-C oil of 4.0% S based on unit price per TOE of 2004. However, the unit prices of B-C oil of 0.3% S and LNG were 10 and 15%, respectively, higher than that of B-C oil of 4.0% S based on unit price per TOE in January 2008. Also, the January 2008 unit prices of LNG, B-C oil of 0.3% S, and B-C oil of 4.0% S increased as high as 39%, 49%, and 69%, respectively, as compared to those for 2004. The unit price increase of B-C oil of 4.0% S much exceeded those of LNG or B-C oil of 0.3% S. In addition, oil prices have sharply increased since 2005, and thus currently they are increasing almost every day. Also, there is high uncertainty of purchase and operation/maintenance costs of air pollutant or SO_x control facilities because of severe fluctuation of energy costs. In addition, current emissions of carbon dioxide additionally increased by 3.7% when 100% of current use of LNG and B-C oil of 0.3% S is converted into B-C oil of 4.0% S. The additional emission increase of carbon dioxide would also be an additional economic expenditure with increased use of B-C oil of 4.0% S. Therefore, it is not easy to exactly evaluate economic benefits associated with conversion of LNG or B-C oil of 0.3% S into B-C oil of 4.0% S.

The other important issue that should be addressed with increasing use of high-sulfur fuel like B-C oil of 4.0% S would be increase of SO₃ emissions (increased proportional to SO₂ emission increase) resulting in increased corrosion of facilities and more frequent generation of white plume. Even though there are some available technologies for reduction of SO₃ emission and white plume problems, it is still difficult to apply those technologies to solve the problems based on current technology situations.

11.3.4 Issues associated with conversion into coal

Currently, the highest emission of carbon dioxide from energy resources in Ulsan industries for year 2004 was from B-C of 4.0% S, followed by coal, B-C of 2.5% S, and B-C of 0.5% S (Table 11.4). Even though the energy consumption as TOE of coal was 18.4% of the total TOE in Ulsan, carbon dioxide produced from coal use reached up to 22.6% of the total emission in Ulsan. This shows that coal has much higher emission factors of carbon dioxide per TOE as compared to other clean fuel or B-C oils (Kaygusuz, 2009).

Table 11.4 Carbon dioxide emissions from energy resources in Ulsan industries for 2004.

Fuel type	Bunker fuel oil C					Light oil	LNG	Coal	
	4.0% S	2.5% S	1.0% S	0.5% S	0.3% S			Hard	Soft
Fuel consumed (TOE%)	22.9	16.8	1.6	3.6	13.8	10.0	12.8	8.2	10.2
Emission factor (C ton /TOE)	0.875	0.875	0.875	0.875	0.875	0.837	0.637	1.100	1.059
CO ₂ emission (1,000 TCO ₂ /yr)	3,387	2,473	229	535	2,029	1,414	1,374	1,528	1,821
CO ₂ percentage (%)	22.9	16.7	1.5	3.6	13.7	9.6	9.3	10.3	12.3

Table 11.5 shows carbon dioxide emission depending upon conversion rates when clean and ultra low sulfur fuels (LNG and B-C oil of 0.3% S) are replaced by soft coal, according to the conversion scenarios. When 50% and 100% of current consumption of LNG and B-C oil of 0.3% S is replaced by coal, 5% and 10% of carbon dioxide emission would be added. Even though Korea is currently not classified in the Annex I countries, according to the Kyoto Protocol for global warming mitigation (Shackley and Verma, 2008), it would be forced to reduce air emissions of greenhouse gases after 2012. According to a recent report (Han, 2008), the required costs for proper treatment of carbon dioxide additionally emitted by use of coal instead of B-C oils would be added as high as 39% of current energy costs. The current purchase costs of coal are around 40% of those of B-C oil of 0.3% S. Costs for treatment or trading of carbon dioxide could increase further in future (Bartsch and Muller, 2000). Even though current economic savings by converting into coal are great, they have high vulnerability in future (Moriarty and Honnery 2008).

Table 11.5 Carbon dioxide emissions by conversion of clean and ultra low sulfur fuels to coal.

Scenario	Conversion rate into soft coal (%)	CO ₂ production (1,000 ton/yr)				CO ₂ emission increase (%)
		LNG + 0.3% S B-C	Soft coal	Total (B-A, B, C + LNG + coal)	Increase by conversion	
Original	0	3,403	1,821	13,376	–	–
Scenario 1	10	3,063	2,295	13,510	134	1
Scenario 2	30	2,383	3,243	13,778	402	3
Scenario 3	50	1,703	4,191	14,046	670	5
Scenario 4	80	681	5,613	14,448	1,072	8
Scenario 5	100	0	6,561	176,994	1,340	10

Table 11.6 summarizes emission factors of air pollutants associated with utilization of major energy resources for 2004 in Ulsan. B-C oils represented the highest emissions of NO_x and SO_x because of their largest amount of energy utilization and their high emission factors. However, soft coal showed the highest emission factors of SO_x, TSP, and PM₁₀ and the second highest emission factors of NO_x. Based on this information, another big concern associated with coal use increase would be to increase concentrations of air pollutants such as TSP, PM₁₀, NO_x, and SO_x. In the past Ulsan was called as a pollution city in Korea. Currently, Ulsan also has the highest annual level of SO_x in Korea. Thus, the Ulsan government and people would not to take the coal option to overcome current energy crisis without significant reduction in total air emissions or further improvement in its urban air quality.

Table 11.6 Emission factors of air pollutants associated with utilization of major energy resources in Ulsan for 2004, unit: kg/TOE.

	2004 TOE	CO	NO _x	SO _x	TSP	PM ₁₀	VOC	Total
B-C	2,696,808	1.359	11.968	9.127	0.570	0.368	0.370	23.761
Light oil	538,565	8.333	22.603	7.594	1.454	1.426	2.223	43.633
LNG	588,609	2.054	6.772	0.015	0.044	0.042	0.311	9.239
Hard coal	465,050	0.067	1.221	0.213	0.080	0.054	0.032	1.667
Soft coal	392,460	0.492	12.840	9.654	21.523	14.419	0.059	58.987

11.3.5 Issues associated with natural gas and nuclear power options

Other options for current energy crisis would be natural gas (NG) which can provide for much lower pollution burden as compared to other energy resources. Supply contracts of NG are usually based on longer terms like 15 or 20 years unlike usually conducted short-term contract of oils. Currently, Korean government has got long-term purchase contracts for NG with middle-east countries and Russia in the periods which had been maintained for relatively low prices of natural gas (Stern, 2008). The consumer price per TOE of NG for industrial use for 2004 was 40% expensive as that of B-C oil of 4.0% S. However, the current consumer price for industrial use for January 2008 is just around 15% higher than that of B-C oil of 4.0% S. Also, the estimated price increase rate of 8.68% for NG is much lower than that of 12.52% for B-C oil of 0.3% S which would be similar to B-C oil of 4.0% S. Therefore, NG should also be considered as another option. However, there are a couple of drawbacks for this option. One of the big concerns would be the problems associated with a supply system of natural gas. It is not that easy to expand the supply system of NG in a short time period.

Nuclear power energy is an almost environmentally free option, except nuclear waste problems. Nuclear power plants almost do not produce greenhouse gases (Sovacool, 2008). Also, nuclear power energy is currently the cheapest energy in Korea. Ulsan has successfully and safely operated many nuclear power plants for more than 30 years since 1977. Thus, the utilization of nuclear power energy can be a good option for current energy and economy crisis. Concerns for nuclear energy are safety problems which could occur in the operation processes of nuclear power plants including proper disposal or storage of nuclear waste. However, accidents in the operation of nuclear power plants are not common and most power plants have very good safety systems to prevent any accidents. Even though the power plants have been safely operated, the general public is still worried about the accidents that could occur in power plants. We still remember the horrible accident that occurred in the nuclear power plants of Chernobyl, Russia, in 1986.

11.4 Conclusions

The annual average concentrations of SO_x and particulate matter, especially TSP, decreased with decreasing sulfur content in fuel in the largest industrial city in Korea. The recent improvement in SO_x levels was due to the reduced energy consumption of high sulfur content fuel rather than the increased utilization of ultra low sulfur fuel, such as B-C oil of 0.3% S, which does not require control equipment of SO_x . Four options were considered to solve the current energy crisis and economic expenditure for industries. Because each option has its own pros and cons, industries should choose the proper option for their situation considering the following. One option is to use B-C oil of 4.0% S but operation of control equipment with high control efficiency of SO_x is essential. The other option is to utilize coal with strict operation of air pollution control equipment; however,

treatment costs of additionally emitted carbon dioxide should be considered. One of the big drawbacks for the natural gas option is the establishment of transport or supply systems to expand supply of NG. The option of nuclear power energy needs to overcome public resistance of the horrible accidents which may occur in nuclear power plants.

Acknowledgment

This research was supported by a grant (code 08 RTI B-03) from Regional Technology Innovation Program funded by Ministry of Land Transport & Maritime Affairs of Korean government. The authors appreciate the funding and the generous help provided by the Department of Environmental Policy in the metropolitan city of Ulsan, Korea.

References

- Bartsch, U, Muller, B (2000) Fossil fuels in a changing climate. Oxford, NY.
- Borchers, M, Euston-Brown, M, Mahomed, L (2008) Energy Planning in South African cities. In: *Urban Energy Transition: From Fossil Fuels to Renewable Power*, Peter Droege, Ed., pp. 563–584.
- Han, K-H (2008) Utilization of solid fuel and strategies for treatment of air pollutants. Debate on fuel and environmental policies to overcome energy crisis. Presented in the University of Ulsan, March 6, 2008.
- Kaygusuz, K (2009) Energy and environmental issues relating to greenhouse gas emissions for sustainable development in Turkey. *Renewable and Sustainable Energy Reviews* 13: 253–270.
- Koo, Y-S, Kim, Y-K (2007) Evaluation and prediction of air pollution potential in Ulsan. Ulsan Regional Environmental Technology Development Center Report.
- Mamane, Y, Perrino, C, Yossef, O, Catrambone, M (2008) Source characterization of fine and coarse particles at the East Mediterranean coast. *Atmospheric Environment* 42: 6114–6130.
- Moriarty, R, Honnery, D (2008) Mitigating greenhouse: Limited time, limited options. *Energy Policy* 36: 1251–1256.
- Park, H-S, Lee, BK (2007). Review of fuel policies and effective use of fuel and facilities in Ulsan. Report of Sharp Heavy Industries Co. Ltd.
- Shackley, S, Verma, P (2008) Tackling CO₂ reduction in India through use of CO₂ capture and storage (CCS): Prospects and challenges. *Energy Policy* 36: 3554–3561.
- Sovacool, BK (2008) Valuing the greenhouse gas emissions from nuclear power: A critical survey. *Energy Policy* 36: 2950–2963.
- Stern, DI (2005). Global sulfur emissions from 1850 to 2000. *Chemosphere* 58: 163–175.
- Stern, J (2008) *Natural gas in Asia: The challenges of growth in China, India, Japan, and Korea*, 2nd ed. Oxford Institute for Energy Studies.
- Zhang, ZX (2008) Asian energy and environmental policy: Promoting growth while preserving the environment. *Energy Policy* 36: 3905–3924.

Emission Characteristics of Diesel Engine-Powered Cogeneration Systems

Aysegul Abusoglu and Mehmet Kanoglu

12.1 Introduction

The industrial sector is a major electricity consumer. The growth rate of electricity demand is high especially in the developing countries and a continuous growth is anticipated for coming years. Many governments revise their energy policy introducing legislative and economic incentives to encourage private participation in the power generation investments. Generally, a favorable economic environment is created for the industries that make use of energy conservation, and cogeneration is an effective method of achieving this. Unfortunately power facilities have the potential of environmental pollution by the emission of harmful gases and other hazardous components. Power plants and cogeneration facilities emit some undesirable content in exhaust gases including solid particles, and these emissions, depending on their level, can be very harmful for human beings and other organisms (Frangopoulos, 1993; EPA, 2000).

Cogeneration or combined heat and power production (CHP) is a technology used by many industries all over the world since the beginning of the 20th century as an economic means of providing industrial plant energy requirements. Reciprocating engine-powered cogeneration systems are commonly applied in the 2.5–50 MW range for power production. They are widely available as compact, fully packaged, and skid-mounted units that are easy to install. Reciprocating engine systems usually use turbocharged, intercooled industrial engines. The main fuel used is heavy fuel oil. Natural gas, diesel oil, LPG, propane, and biogas can also be used. For the diesel engine-powered cogeneration (DEPC) applications, heavy fuel oil and natural gas are the major fuels due to lower cost and high availability (Stenhede, 2004).

A major portion of environmental pollution is caused by the exhaust emission from the internal combustion engines. The three main pollutants which are subject to exhaust emission legislation are carbon monoxide (CO), unburned

hydrocarbons (HC), and nitrogen oxides (NO_x) (Abdel-Rahman, 1998). Normally nitrogen is very inert but at high temperatures oxygen and nitrogen get the chance to mate for the formation of NO_x as in the case of combustion processes of diesel engines. Other important pollutants contained in exhaust emissions are aldehydes (H-C-O compounds), lead components produced by use of leaded fuels, sulfur dioxide (SO_2), and particulates especially with diesel engines.

Heavy fuel oil has a high share in fossil fuel consumption especially for diesel engine-powered cogeneration applications. Two major categories of heavy fuel oil are distillate oils and residual oils. Being more viscous and less volatile than distillate oils, the heavier residual oils may need to be heated for ease of use and to facilitate proper atomization for combustion. Residual oils are used mainly in industrial applications, especially in power production facilities.

In the utilization of residual heavy fuel oils for industrial power production, two major problems arise: hazardous emissions and depletion of fuel reserves in the world. Cogeneration which generates heat and power simultaneously from same fuel supply may be the most appropriate method to address these concerns (Kaarsberg et al., 1999; Stenhede, 2004). In literature, two methods were used for measuring the effectiveness of cogeneration systems in fuel savings and emission reduction. In the first method, emissions were compared between cogeneration systems and separate power heat systems (SPHS) by using the difference between the heat rates of conventional fossil fuel-fired systems and the cogeneration systems (Kaarsberg et al., 1999; Voorspools and D'haeseleer, 2000a; 2000b). In the second method, emissions released from cogeneration systems were distributed to the products (power and heat) and compared to the conventional power and heat production systems separately (Sevilgen et al., 2003). In these studies, fuel saving analysis (FSA) was performed in terms of the first law efficiency (also called fuel utilization efficiency). The first law efficiency treats power and heat equally and this is a weakness for its use as a performance parameter for environmental studies as in the case of thermoeconomic analysis of cogeneration systems.

In this chapter, the exergetic efficiency is used for environmental assessment of the diesel engine-powered cogeneration systems. For this, emissions released from an actual diesel engine-powered cogeneration system (DEPCS) are investigated and the operations of desulfurization (DeSO_x) and denitrification (DeNO_x) units are described. The emissions assessment from DEPCS are performed by using fuel saving analysis method based on the exergetic efficiency rather than fuel utilization efficiency that is commonly used in literature. Exhaust emission reduction is expressed with an analogy to fuel savings and compared to SPHS. First, we present information on air pollution and environmental concerns in Turkey.

12.2 Air Pollution and Environmental Concerns in Turkey

Air pollution is becoming a great environmental concern in Turkey. Air pollution from energy utilization in the country is due to the combustion of coal, lignite, petroleum, natural gas, wood and agricultural and animal wastes. On the other hand, owing mainly to the rapid growth of primary energy consumption and the increasing use of domestic lignite, NO_x and SO_2 emissions, in particular, have increased rapidly in recent years in Turkey. The major source of these emissions is the power sector, contributing more than 50% of the total emissions (IEA, 2005).

12.2.1 CO_2 Emissions and greenhouse gases

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) emissions are all produced during fuel oil combustion. Nearly all of the fuel carbon in fuel oil is converted to CO_2 during combustion process. Turkey's total carbon dioxide (CO_2) emissions amounted to 193 million tons (Mt) in 2002. Public electricity and heat production were the largest contributors of CO_2 emissions, accounting for 28% of the country's total. The industry was the second largest, representing 26% of total emissions, followed by transport, which represented 19%, and direct fossil fuel use in the residential sector with 10% (Hepbasli, 2005; IEA, 2005; Say and Yucel, 2006;). In Fig. 12.1, CO_2 emissions by fuel types between 1973 and 2002 are given (IEA, 2005). Other sectors, including other energy industries, account for 17% of total emissions. Since 1990, emissions from public electricity and heat production have grown rapidly than in other sectors, increasing by 6%. Simultaneously, the shares of emissions from the residential and transport sectors both dropped by 7% and 3%, respectively, while the share of emissions from the power production and manufacturing industries and construction sector remained stable (Hepbasli, 2005; Say and Yucel, 2006).

12.2.2 NO_x and SO_x emissions

The main air pollutants related to the power production and use of energy are sulfur oxides (SO_x) – in particular sulfur dioxide (SO_2), – nitrogen oxides (NO_x), and suspended particulates. Sulfur oxides (SO_x) emissions are generated during oil combustion from the oxidation of sulfur contained in the fuel. The emissions of SO_x from conventional combustion systems are predominantly in the form of SO_2 . On average more than 95% of the fuel sulfur is converted to SO_2 , about 1–5% is further oxidized to sulfur trioxide (SO_3), and 1–3% is emitted as sulfur particulate. SO_3 readily reacts with water vapor (both in the atmosphere and in flue gases) to form a sulfuric acid mist. The use of high-sulfur lignite in particular is an important source of air pollution. In 2002, Turkey emitted a total of 2.08 Mt of SO_2 , equivalent to 30.4 kg per capita. This is slightly below the OECD average, which at the end of the 1990s was 32.9 kg per capita (IEA, 2005). Electricity generation and industry are by far the largest contributors to SO_2 emissions in the

country, representing respectively 65% and 21% of total emissions in 2001 (Ocak et al., 2004).

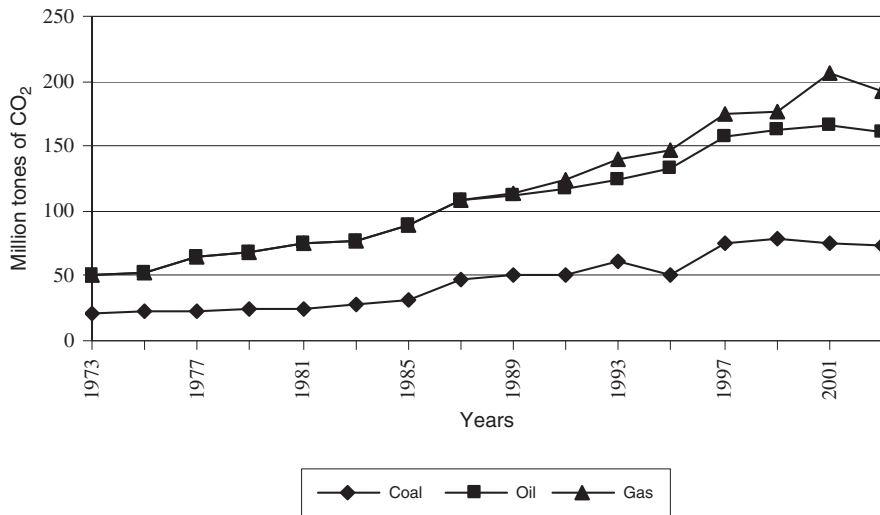


Fig. 12.1 CO₂ emissions by fuel types between 1973 and 2002 in Turkey (IEA, 2005).

The term NO_x refers to the composite of nitric oxide (NO) and nitrogen dioxide (NO₂). For most fossil fuel combustion systems, over 95% of the emitted NO_x is in the form of nitric oxide. Nitrous oxide (N₂O) is not included in NO_x but has recently received increased interest because of atmospheric effects. Emissions of NO_x totaled approximately 0.90 Mt in 2003, slightly below the 2000 levels of 0.92 Mt. On a per capita level, emissions were of 12.8 kg in 2003, substantially below the OECD average of approximately 40 kg at the end of the 1990s. Transportation and predominantly road-based transport, is the largest source of NO_x emissions, representing 36% of total emissions. Electricity generation and industry represent over 20% each (IEA, 2005; Ocak et al., 2004).

12.2.3 Particulate matter (PM) emissions

Particulate emissions maybe categorized as either filterable or condensable. Filterable particulate matter emissions depend predominantly on the grade of fuel fired. Combustion of lighter distillate oils results in significantly lower PM formation than does combustion of heavier residual oils. In general, filterable PM emissions depend on the completeness of combustion as well as on the oil ash content (EPA, 2000). The PM emitted by distillate oil-fired combustion processes primarily comprises carbonaceous particles resulting from incomplete combustion of oil and is not correlated to the ash or sulfur content of the oil. However, PM

emissions from residual oil burning are related to the oil sulfur content. This is because low-sulfur residual oil (heavy fuel oil no. 6), either from naturally low-sulfur crude oil or desulfurized by several processes, exhibits substantially lower viscosity and reduced asphaltene, ash, and sulfur contents, which results in better atomization and more complete combustion (IEA, 2005). The emission standards for power plants in Turkey are given in Table 12.1 with the revision in 2004. These standards remain significantly less stringent than those currently in force at the EU (European Union) level as defined by the revised Large Combustion Plants (LCP) directive (IEA, 2005; Ulutas, 2005). For example, for new liquid fuel-fired power plants (authorized after November 2003) with a thermal input greater than 300 MW, the NO_x emissions limit is set at 200 mg/Nm^3 at the EU level, while the NO_x emissions limit is 800 mg/Nm^3 in Turkey.

Table 12.1 Emission standards for power plants in Turkey (IEA, 2005).

1986 REGULATION (mg/Nm^3)									
	PM		CO	NO _x		SO ₂			
	OP	NP		OP	NP	<300 MW _{th}		>300 MW _{th}	
						ROH>20,000	NP	ROH<50,000 and OP	ROH>50,000 and NP
SFFP	250	150	250	1000	800	3200	2000	3200	1000
LFFP	110	110	175	1000	800	3200	1700	1700	800
GFP	10	10	100	500	500	60	60	60	60
2004 REGULATION (mg/Nm^3)									
SFFP	100		200	800		2000 (<100 MW _{th}) 1300 (100–300 MW _{th})		1000 ≥300 MW _{th}	
LFFP	110–170 ≥15 MW _{th}		150	800		1700 (1% S) 2400 (1.5% S) (<100 MW _{th}) 1700 (100–200 MW _{th})		800 ≥300 MW _{th}	
GFP	10		100	500		60		60	

SFFP: solid fuel-fired plants, LFFP: liquid fuel-fired plants, GFP: gas-fired plants,
OP & NP: old plants and new plants, refer to power plants built before and after Air Quality Protection
regulation came into force in 1986

ROH: remaining operating hours

^a Sulfur content (mass percentage) of the fuel used

12.3 Description of Exhaust Flow in the DEPC Plant

The actual DEPC plant, SANKO Energy, is located in the southeastern Turkey, the city of Gaziantep (Abusoglu and Kanoglu, 2008). The electricity is generated by three, diesel engine-actuated generator sets each having two turbochargers.

Each diesel engine-generator set in the plant produces 8.44 MW electricity and 2.7 tons/h saturated steam at 8 bars and 170°C. The engine operating and performance characteristics are listed in Table 12.2. For calculated engine parameters, related data can be found from related papers and reference books (Abusoglu and Kanoglu, 2008, 2009a, 2009b; Pulkrabek, 1997). The schematic diagram of the plant's exhaust flow line for one engine set is shown in Fig. 12.2. The permissible annual electricity production is 217 GWh and the annual heavy fuel oil consumption is nearly 45,000 tons at designed operating conditions.

The exhaust gases leaving the engine flow through the turbine of the turbocharger unit to produce the necessary shaft work for the compressor. The exhaust gases leaving the turbine is sent to the DeNO_x (denitrification) unit in which the NO_x emission is lowered to acceptable legal values by spraying urea solution onto the exhaust gases. Then, the exhaust gases leaving the turbine enter the waste heat recovery unit to transfer heat to the feedwater to produce steam for manufacturing facilities in the factory and for preheating of streams in the auxiliary equipments such as fuel forwarding module and fuel oil in daily usage tank. Finally, the exhaust gases flow through a DeSO_x (desulfurization) unit before being exhausted to the atmosphere.

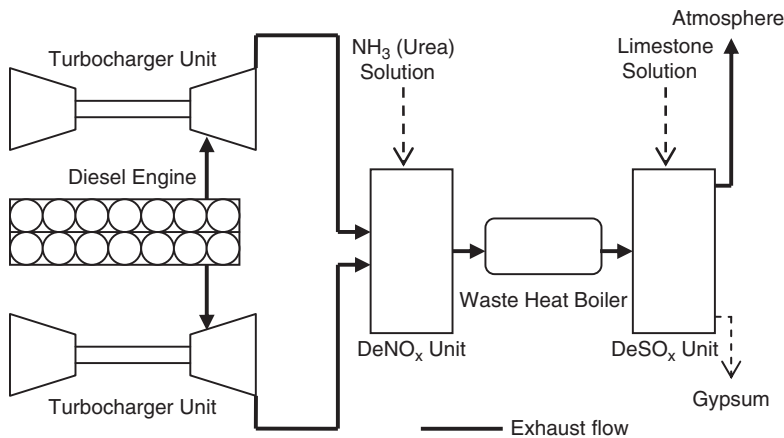


Fig. 12.2 Exhaust flow schematic of the DEPC plant. Only one engine set is shown.

12.3.1 Denitrification unit (DeNO_x)

The main aim of the denitrification unit is to treat NO_x exhaust emissions as N_2 and water. During burning of fuel the molecules including nitrogen reacts with oxygen in the intake air and produce NO. If the amount of oxygen is less, then instead of NO, the product will be N_2 . This process is the basic of the denitrification principle by improving the quality of combustion. For each engine-

generator set one DeNO_x unit is installed. Casing of the units are insulated to prevent heat transfer. NO_x emissions are treated into the nitrogen (N₂) and water (H₂O) by selective catalytic reduction (SCR) process. The SCR reaction is catalyzed by vanadium/titanium catalysts at temperatures in the range 300–500°C as shown below:



The catalytic reactors are made of special ceramics shaped in honeycomb modules. Ammonia (NH₃) obtained from urea in liquid form is used as reductor element. The exhaust gas at 300–450°C is transferred from cylinders to DeNO_x units by insulated exhaust ducts. Exhaust gases at high temperature pass through the catalytic reactors; here NH₃ is injected into the exhaust gases, and so NO_x react with NH₃ and produce nitrogen (N₂) and water (H₂O).

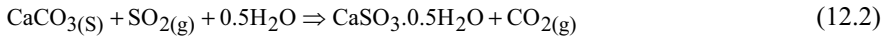
Table 12.2 Operating and performance characteristics of Diesel 32 V 40 engine.

Cylinder diameter, D (mm)	320
Cylinder bore, B (mm)	320
Stroke, S (mm)	400
Crank offset, a (mm)	200
Number of cylinders, N_c	18
Piston area, A_p (m ²)	0.08
Compression ratio, r_c	12.37
Displacement volume, V_d (m ³)	0.03217
Clearance volume, V_c (m ³)	0.00283
Air flow rate, $\dot{m}_a$ (kg/s)	18.4
Fuel flow rate, $\dot{m}_f$ (kg/s)	0.46
Air–fuel ratio, AF	40.0
Exhaust flow rate (kg/s)	17.0
Piston mean speed, U_p (m/s)	10.0
Engine speed, N (rpm)	750
Break power, $\dot{W}_b$ (kW)	8440
Brake mean effective pressure, bmep (kPa)	2490
Torque, τ (Nm)	114.6
Brake-specific fuel consumption, bsfc (g/kWh)	184.0
Specific power, SP (kW/m ²)	6217
Specific volume, SV (m ³ /MW)	0.06434
Output per displacement, OPD (kW/L)	14.58
Combustion efficiency, η_c	0.98
Volumetric efficiency, η_v	1.29
Thermal efficiency, η_{th}	0.47

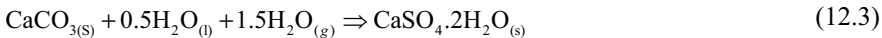
These two final products are natural materials and have no harmful effect on the environment. The total solid urea consumption of DeNO_x unit is about 260 kg/h, where total NO_x mass flow is 402 kg/h. The treated flue gas should include NO_x at a total amount less than 800 mg/Nm³ as indicated in Table 12.1.

12.3.2 Desulfurization unit (DeSO_x)

From process point of view the proposed flue gas desulfurization system is referred to as “limestone–gypsum” process, based on the use of common limestone (CaCO₃) in powder form as reagent and the production of gypsum as by-product. The limestone consumption is nearly 750 kg/h. The waste gas purification process is performed for each gas stream in a scrubber with integrated quencher where SO₂ and other pollutants (SO₃ – HCl) are removed by washing liquid which is a suspension of limestone in water. The waste gas enters laterally above the bottom of the scrubber into the quenching zone of the scrubber. The waste air is cooled down to the saturation temperature in the quencher zone. From here the waste gas flows vertically upward to the subsequent nozzle lever where the pollutants absorption, as well as some dust separation takes place. During the absorption of SO₂, SO₃, and HF, hardly soluble deposits such as CaSO₄, H₂O, CaSO₃, and CaF₂ are formed and suspended in the scrubbing solution. In order to prevent larger deposits in the scrubbing liquid tank, an agitator is installed in the scrubber sump. This serves at the same time for dispersing the oxidation air. The reaction that takes place during the desulfurization process is



When the oxidation with air take place



Due to the continuous recirculation and subsequent formation of some sulfites and sulfates a portion of recirculated liquid is bled off to a dewatering system that provides a reduction of moisture down to 15% residual water content, in order to handle the gypsum removal. The scrubbing and cooling liquid suspension is accumulated in the scrubber lower sump from where it is taken and recirculated by suitable wear-resistant recirculation pumps. The treated flue gas should include SO₂ at a total amount less than 2400 mg/Nm³ (see Table 12.1). In Tables 12.3 and 12.4, emission content of exhaust gases before and after the flue gas treatment units (DeNO_x and DeSO_x) are given.

12.4 Fuel Savings Analysis

The diesel engine-powered cogeneration system (DEPCS) converts waste heat, which is a consequence of electricity production by diesel engines, to useful heat. In these systems, the conversion ratio of fuel chemical or heat energy to electrical energy can be defined as electricity (or thermal – first law) efficiency η_e and the

conversion ratio to heat energy is defined as heat efficiency η_h . Electricity and heat generation are denoted by $\dot{W}$ and $\dot{Q}$, respectively.

Table 12.3 Emission content of exhaust gases before the flue gas treatment for the DEPC plant.

Content	Engine 1	Engine 2	Engine 3
O ₂ (%)	13.40	13.45	13.55
CO ₂ (%)	5.55	5.55	5.45
CO (mg/m ³)	75.5	90	105
NO (mg/m ³)	1485	1500	1532
SO ₂ (mg/m ³)	935.5	1149	1053
Gas temperature (°C)	309.5	312.5	310

In separate power heat systems (SPHS), separate fuels are used to obtain electricity and heat. Fuel consumption in these systems was treated as dependent parameter on electricity generation system efficiency η_{sc} and boiler heat efficiency η_{sh} in literature (Kaarsberg et al., 1998, 1999, Voorspools and D'haeseleer, 2000a, 2000b; Sevilgen et al., 2003).

Table 12.4 Emission values of exhaust gases after the flue gas treatment for the DEPC plant.

Type of fuel	Fuel oil no. 6
Power produced (MW)	25.32
Exit exhaust temperature (°C)	53.7
Velocity of exhaust gas at the exit (m/s)	8.1±0.1
Mass flow rate of exhaust gas at the exit (m ³ /h)	123,464
Particulate matter concentration (mg/m ³)	96.78
Particulate matter emission (kg/h)	11.8695±2.6904 (limit value: 15)
CO concentration (mg/m ³)	101.67
CO emission (kg/h)	12.5507±1.4898 (limit value: 5)
SO ₂ concentration (mg/m ³)	40.95
SO ₂ emission (kg/h)	5.0673±0.6036 (limit value: 100)
NO concentration (mg/m ³)	1282.14
NO emission (kg/h)	158.3056±18.7665 (limit value: 20)
NO ₂ concentration (mg/m ³)	1983.75
NO ₂ emission (kg/h)	244.94
O ₂ concentration (%)	12.8
CO ₂ concentration (%)	6.3

In the analysis of fuel savings, the exergetic efficiency is used for environmental assessment of DEPCS system versus SPHS. In comparing DEPCS and SPHS, it is assumed that they produce the same amount of electricity and heat. Electricity and heat generation are calculated from

$$\dot{W} = \dot{m}_f LHV_f \varepsilon_e \quad (12.4)$$

$$\dot{Q} = \dot{m}_f LHV_f \varepsilon_h \quad (12.5)$$

where LHV_f is the lower heating value of the fuel, $\dot{m}_f$ is the rate of fuel used, ε_e and ε_h are the exergetic efficiencies of DEPCS in terms of electric power produced and steam generated, respectively. The amount of fuel required to produce the same amount of electricity in SPHS can be determined from

$$\dot{m}_{sef} = \dot{m}_f \zeta_e \left(\frac{\varepsilon_e}{\varepsilon_{se}} \right) \quad (12.6)$$

where ζ_e is the ratio of the lower heating value of the fuel used in DEPCS to the lower heating value of the fuel used in SPHS, and ε_{se} is the exergetic efficiency of SPHS in terms of power produced. The amount of fuel required to produce heat in the boiler, which is equal to the heat produced in DEPCS, is calculated from

$$\dot{m}_{shf} = \dot{m}_f \zeta_h \left(\frac{\varepsilon_h}{\varepsilon_{sh}} \right) \quad (12.7)$$

where ζ_h is the ratio of the lower heating value of the fuel used in DEPCS to the lower heating value of the fuel used in the boiler of SPHS, and ε_{sh} is the exergetic efficiency of SPHS in terms of steam generated. The amount of fuel savings in this case can be expressed as (Kaarsberg et al., 1999)

$$\Delta \dot{m} = \dot{m}_f \left[\zeta_e \left(\frac{\varepsilon_e}{\varepsilon_{se}} \right) + \zeta_h \left(\frac{\varepsilon_h}{\varepsilon_{sh}} \right) - 1 \right] \quad (12.8)$$

The limit condition in Eq. (12.8) that needs to be satisfied to obtain fuel savings in DEPCS is

$$\left[\zeta_e \left(\frac{\varepsilon_e}{\varepsilon_{se}} \right) + \zeta_h \left(\frac{\varepsilon_h}{\varepsilon_{sh}} \right) \right] > 1 \quad (12.9)$$

In case of using the same fuel in both systems $\zeta_e = \zeta_h = 1$, and Eq. (12.9) becomes

$$\left(\frac{\varepsilon_e}{\varepsilon_{se}} \right) + \left(\frac{\varepsilon_h}{\varepsilon_{sh}} \right) > 1 \quad (12.10)$$

The required data and the results of thermodynamic calculations for DEPCS are given in Table 12.5 (Abusoglu and Kanoglu, 2008, 2009a, 2009b). For SPHS, required data is taken from literature (Sevilgen et al., 2003). The net electrical power produced and steam generated for DEPCS are 25,320 kW and 176.1 kW, respectively. The mass flow rate of fuel oil in DEPCS is 1.38 kg/s (see Table 12.5).

Using the equations in this section, the mass flow rates of fuel for the power production unit and the boiler unit of SPHS are determined to be 1.66 kg/s and 0.20 kg/s, respectively. It is clear that using separate units of power and heat production increases the fuel consumption by 34.8% with respect to the existing DEPCS.

Table 12.5 The data of the DEPC plant for the fuel savings analysis (Abusoglu and Kanoglu, 2008, 2009a, 2009b).

Mass flow rate of fuel oil (kg/s)	1.38
Lower heating value of fuel oil (kJ/kg)	42,700
Power produced (MW)	25.32
Generated steam output (kW)	176.1
Mass flow rate of exhaust gas (kg/s)	51.0
Exergetic efficiency of DEPC plant, ε_e (%)	40.6
Exergetic efficiency of diesel engine, ε_{DE} (%)	40.4
Exergetic efficiency of waste heat boiler, ε_h (%)	11.4

12.5 Emission Difference Analysis

The amount of emission produced depends on the electricity production in DEPCS while it depends on both electricity and heat generation in SPHS. The amount of emission released by DEPCS is calculated from

$$M_{DEPC,i} = \dot{W}\theta_{DEPC,i} \quad (12.11)$$

where θ_{DEPC} stands for the specific emission of DEPCS (amount of emission released per unit electricity production) and “i” represents emission type (CO_2 , SO_2 , and NO_x). Emission amounts of SPHS for electricity and heat production are given respectively as (Kaarsberg et al., 1999)

$$M_{SP,i} = \dot{W}\theta_{SP,i} \quad (12.12)$$

$$M_{SH,i} = \dot{Q}\theta_{SH,i} \quad (12.13)$$

where $M_{SP,i}$ and $M_{SH,i}$ are emission amounts of SPHS for power and heat production respectively, and θ_{SP} and θ_{SH} are the specific emissions of power and heat produced in SPHS, respectively. The amount of emission reduction (ΔM) owing to DEPCS is given by

$$\Delta M = \dot{W}(\theta_{SP,i} + \beta\theta_{SH,i} - \theta_{DEPC,i}) \quad (12.14)$$

where β is the heat–power ratio (ratio of heat energy to electrical energy in the cogeneration system). The limit condition for the emission reduction is given as

$$\theta_{SP,i} + \beta\theta_{SH,i} > \theta_{DEPC,i} \quad (12.15)$$

When specific emissions are constant, a change in heat–power ratio will change the emission reduction provided by DEPCS or any cogeneration facility. The heat–power ratio for the case of equal emission production from the DEPC and SPH systems is defined as critical heat–power ratio β^* and expressed as

$$\beta^* = \frac{\theta_{\text{DEPC},i} - \theta_{\text{SP},i}}{\theta_{\text{SH},i}} \quad (12.16)$$

Average specific emissions of the DEPC plant can be obtained using the values in Table 12.5. For SPHS, these values can be taken from literature (Kaarsberg et al., 1998, 1999; Voorspools and D’haeseleer, 2000a, 2000b; Sevilgen et al., 2003). Table 12.6 contains specific emissions for gas turbines, DEPC, and gas engines for both cogeneration and conventional power plant applications. Comparison of these specific emissions and the efficiencies of the DEPC and SPH systems are given in Figs. 12.3 and 12.4, respectively. Exergetic efficiencies and the heat–power ratio of the DEPC plant are given in Table 12.7. Natural gas, lignite, and heavy fuel oil are considered as fuels in boilers used for heat production in SPHS and average specific emissions of these fuels are shown in Table 12.8.

Table 12.6 Specific emissions of various cogeneration plants and conventional power plants (g/kW_eh) (Kaarsberg et al., 1998, 1999; Voorspools and D’haeseleer, 2000a, 2000b; Sevilgen et al., 2003).

Emission	Cogeneration systems			Conventional power plants	
	Gas turbine	DEPC	Gas engine	SPH	Combined cycle
NO _x	0.25	0.41	1.34	3.3	0.18
CO ₂	580	500	529.1	997.3	400
SO ₂	–	2.20	–	3.7	–

By using the emission values in Table 12.4, the amount of each emission can be calculated for DEPCS for full load power production as 10.381 kg for NO_x, 12.66 m³ for CO₂, and 55.704 kg for SO₂. Corresponding values for SPHS owing to the same amount of power produced and steam generated as DEPCS are determined, respectively, as 83.56 kg and 0.110 kg for NO_x, 25.25 m³ and 0.05 m³ for CO₂, and 93.68 kg and 1.28 kg for SO₂. It is clear that the DEPC plant can reduce NO_x, CO₂, and SO₂ emissions by 87.6%, 50% and 41.3%, respectively, in comparison to SPHSs.

Table 12.7 Exergetic efficiencies and heat–power ratios for the DEPCS and SPHS (Abusoglu and Kanoglu, 2008, 2009a, 2000b; Sevilgen et al., 2003).

	ε	β
DEPC	0.404	0.007
SPHS		
Steam turbine power system	0.334	–
Combined cycle system	0.480	–
boiler	0.770	

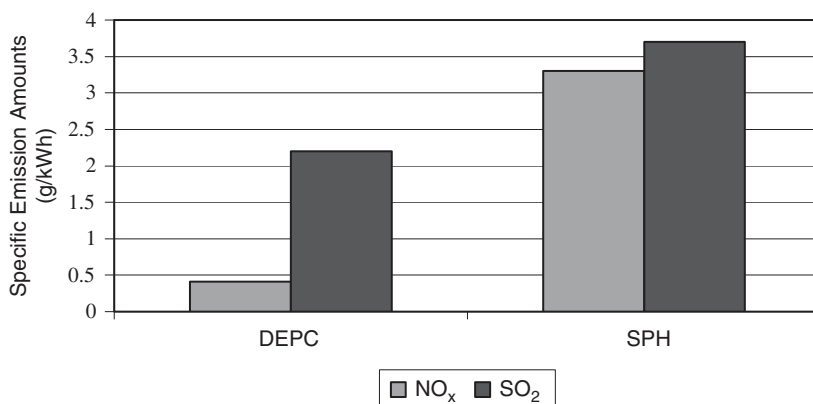


Fig. 12.3 NO_x and SO₂ emissions comparison of DEPC and SPH at full load condition.

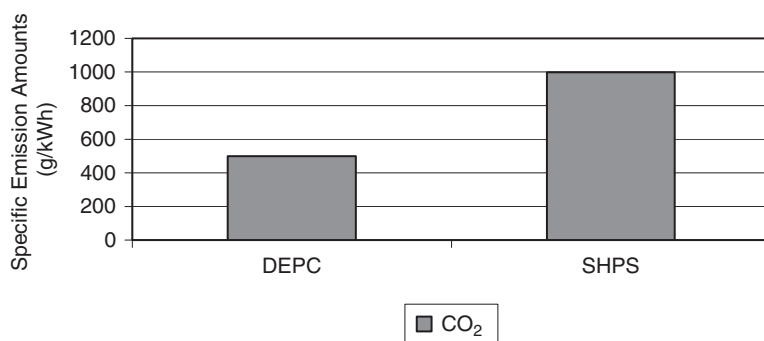


Fig. 12.4 CO₂ emissions comparison of DEPC and SPH at full load condition.

Table 12.8 Emissions produced in boiler for producing heat (g/kWh) (Kaarsberg et al., 1999; Voorspools and D'haeseleer, 2000a, 2000b; Sevilgen et al., 2003).

Fuel type	NO _x	CO ₂	SO ₂
Natural gas	0.93	201.92	–
Coal (lignite)	0.89	364.25	9.21
Fuel oil no. 6	0.62	263.95	7.25

In DEPCS, amount of emissions increase with load as shown in Fig. 12.5 since specific emissions are constant. However, determining emissions reduction by using fuel savings method may cause errors because it ignores specific emission differences for different technologies utilizing the same fuel type. It can be seen that these differences are important parameters which should be taken into consideration. Parameters affecting emission differences are specific emissions, fuel type in cogeneration (i.e., emissions will be different when diesel oil or heavy fuel oil is used in DEPCS) and SPHS, and heat–power ratios of the cogeneration system.

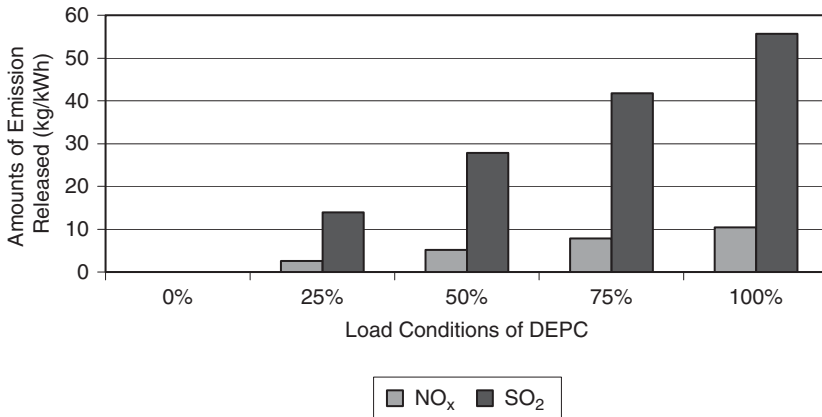


Fig. 12.5 Variation of NO_x and SO₂ emissions with respect to the load variation in DEPCS.

12.6 Conclusions

In this chapter, exhaust emission characteristics of an actual DEPC plant and the operations of denitrification (DeNO_x) and desulfurization (DeSO_x) flue gas treatment units in the facility are studied. Exhaust emission assessment is performed by using fuel savings analysis method and exergetic efficiency. Exhaust emission reduction is expressed using an analogy to fuel savings. The results show that replacing separate heat–power producing applications by cogeneration applications such as DEPC greatly reduces unwanted emissions, namely, the DEPC plant can reduce NO_x, CO₂, and SO₂ emissions by 87.6%, 50% and 41.3%, respectively, in comparison to SPHS. However, in light of actual case study presented in this chapter the following conclusions can be listed for using fuel saving analysis methodology and emission reduction:

- Emission reduction is affected by system parameters such as specific emission amounts, fuel types, cogeneration types, and different specific heat and power applications.

- Emission reduction calculated by fuel saving method can cause errors since with this method, specific emission differences are ignored for different technologies which use the same type of fuel.
- Fuel saving analysis method cannot determine the limit conditions for required emission reduction. For this reason cogeneration applications cannot always reduce emissions (Sevilgen et al., 2003).
- The emissions assessment from DEPCS is performed by using fuel saving analysis method based on the exergetic efficiency rather than fuel utilization efficiency that is commonly used in literature (Kaarsberg et al., 1999; Voorspools and D'haeseleer, 2000a, 2000b; Sevilgen et al., 2003). Exergy-based fuel saving analysis methodology usage accounts for the quality of outputs of power production systems and thus the arbitrariness of the results can be removed. However, for rational results, with the exergy-based evaluation methodologies, the allocation of emissions to the power and heat produced should be performed directly.

Acknowledgments

The authors acknowledge the support provided by the Scientific Research Projects Unit at the University of Gaziantep and greatly appreciate the plant management and engineers of SANKO Energy for their cooperation throughout this study and for supplying data for the plant.

Nomenclature

$\dot{W}$	power, kW
$\dot{Q}$	heat rate, kW
LHV	lower heating value, kJ/kg
$\dot{m}$	mass flow rate, kg/s
M	amount of emission (mg/Nm ³)
Greek letters	
η	first law (energy) efficiency
ε	second law (exergetic) efficiency
Θ	specific amount of emission (g/kWh)
β	heat to power ratio
β^*	critical heat to power ratio
Subscripts	
se	separate electricity
sh	separate heat
e	electricity
h	heat
f	fuel

References

- Abdel-Rahman, AA (1998) On the emissions from internal-combustion engines: A review. *International Journal of Energy Research*, 22: 483–513.
- Abusoglu, A, Kanoglu, M (2008) First and second law analysis of diesel engine powered cogeneration systems. *Energy Conversion and Management*, 49: 2026–2031.
- Abusoglu, A, Kanoglu, M (2009a) Exergetic and thermoeconomic analyses of Diesel engine powered cogeneration: Part 1 – formulations. *Applied Thermal Engineering* 29: 234–241.
- Abusoglu, A, Kanoglu, M (2009b) Exergetic and thermoeconomic analyses of Diesel engine powered cogeneration: Part 2 – applications. *Applied Thermal Engineering* 29: 242–249.
- EPA Report – AP 42 (2000) Compilation of air pollutant emission factors. 5th edition, Washington DC, USA.
- Frangopoulos, CA (1993), Cogeneration of heat and power – The way forward. Proceedings of a European Conference-Greek Productivity Center, Athens, Greece.
- Hepbasli, A (2005) Development and restructuring of Turkey's electricity sector: a review. *Renewable & Sustainable Energy Reviews* 9: 311–343.
- IEA (International Energy Agency) (2005) Energy Policies of IEA Countries: Turkey Review. OECD/EA, France.
- Kaarsberg, T, Elliott, RN, Spurr, M (1999) An integrated assessment of the energy savings and emissions-reduction potential of combined heat and power. American Council for an Energy-Efficient Economy (ACEEE'99), Washington DC, USA.
- Ocak, M, Ocak, Z, Bilgen, S, Keles, S, Kaygusuz, K (2004) Energy utilization, environmental pollution and renewable energy sources in Turkey. *Energy Conversion and Management* 45: 845–864.
- Say, NP, Yucel, M (2006), Energy consumption and CO₂ emissions in Turkey: empirical analysis and future projection based on economic growth. *Energy Policy*, 34: 3870–3876.
- Sevilgen, SH, Erdem, HH, Akkaya, AV, Cetin, B (2003) Comparison cogeneration system with conventional power plant and evaluation of their environmental impacts. Proceedings of the First International Energy, Exergy and Environment Symposium, İzmir, Turkey.
- Stenhede, T (2004) Cogeneration and emissions. 10th International Energy and Environmental Technology Systems Fair and Conference, ICCI'2004, Istanbul, Turkey.
- Ulutas, BH (2005) Determination of the appropriate energy policy of Turkey. *Energy*, 30: 1146–1161.
- Voorspools, K, D'haeseleer, W (2000a) Dynamic simulation of the entire electric power generation system for evaluating CO₂ emissions. The Third Asia-Pacific Conference on Sustainable Energy and Environmental Technologies, Hong-Kong.
- Voorspools, K, D'haeseleer, W (2000b) The impact of cogeneration in a given energetic context. 5th International Conference on Greenhouse-Gas Control Technologies (GHGT-5), Cairns, Australia.

Effects of Fuel Consumption of Commercial Turbofans on Global Warming

Onder Turan and T. Hikmet Karakoc

13.1 Introduction

The main objective of this study is to parametrically investigate the fuel consumption effect of commercial turbofans on global warming. In this regard, of the important parameters, specific fuel consumption of commercial turbofans is taken into consideration. In order to minimize the effect of fuel consumption on global warming, the values of engine design parameters are optimized for maintaining minimum specific fuel consumption (SFC^* , $g/kN\ s$) of high-bypass turbofan engine under different flight conditions and design criteria. The backbones of optimization approach consisted of elitism-based genetic algorithm coupled with real parametric cycle analysis of a turbofan engine. For solving optimization problem a new software program is developed in MATLAB, while objective function is determined for minimizing the specific fuel consumption by considering parameters such as the fan pressure ratio (π_f), bypass ratio (α), and the fuel heating value [h_{PR} (kJ/kg)]. Accordingly, it may be concluded that the software program developed can successfully solve optimization problems at $1.2 \leq \pi_f \leq 2$, $2 \leq \alpha \leq 8$, and $23,000 \leq h_{PR} \leq 120,000$ with aircraft flight Mach number ≤ 0.8 . Fuel types used in preliminary engine cycle analysis were JP-4, JP-5, JP-8, and hydrogen in this chapter. As a conclusion, SFC^* was found to be 5.50, 18.31, and 34.25 $g/kN\ s$ at cruising condition for hydrogen, kerosene, and ethanol, respectively.

For making aircraft propulsion systems applicable for all types of aircraft, the following development goals were being pursued (Mattingly, 2006):

- higher overall efficiency;
- larger power output engines;
- larger ratios of power output to engine weight, volume, and frontal area;
- greater service life, endurance, and reliability; and
- reduced noise.

For supersonic flights, the overall efficiency of turbojet engines was clearly noticeable. However, for high subsonic flight speeds, the velocity of the exhaust gas jet was too high to obtain a best propulsive efficiency. Under these conditions, the bypass engine became a very good choice for improving the propulsive efficiency. Highest possible thermodynamic and propulsive efficiencies of aircraft propulsion systems led to some engine characteristics (Oates, 1997) as very high compressor pressure ratios, turbine inlet temperature, and bypass ratios.

The advantages of the high-bypass ratio turbofan engines can be summarized as follows:

- high overall efficiency, resulting in long flight range;
- lower jet velocity, leading to great noise reduction;
- increase in thrust; and
- low specific fuel consumption, which reduces chemical emissions.

Since the deregulation of the airline market in 1978, the pressure on the engine manufacturers to produce more efficient, low-cost aircraft has increased dramatically (Schipper and Rietveld, 1997). The increased competition forced the airline companies to reduce their commitment as launch customers for new airframe and engines (Nightingale, 2000). In addition, environmental concerns pushed for more stringent legislation on pollutant emissions and noise. The standard regulating NO_x emissions of aero-engines was first adopted in 1981 (ICAO, 1999), then was made more stringent in 1993 with a reduction of the permitted levels by 20%. It was followed in 1999 by a further reduction of the standard by about 16% on average for engines to be certified from December 31, 2003.

The financial uncertainties pushed manufacturers to reduce their time to market from 5 years to 39 months for the Trent series (Robins, 1996). In addition Rolls-Royce now plans to reduce its engine development timescale by a further 30% (Anand and Priddin, 2001). The increased competition in conjunction with the environmental concerns changed the market drivers which could be classified as follows (Mari, 2001):

- Life cycle cost: acquisition, fuel burn, maintenance.
- Environmental impact: pollutants emissions, noise.
- Performance: thrust, weight, specific fuel consumption.

Owing to growing up of the intercontinental transportation necessity, it has become inevitable to make more powerful engines. It is estimated that there are currently 16,800 jet airplanes in the world and this figure is expected to grow to 35,300 by 2024. Also, the passenger traffic activities have increased on average 4.8% per year (Boeing, 2007). On the other hand, 2–5% of the world energy consumption belongs to aviation industries (Koroneos et al., 2007). Rolls-Royce predicts continued strong long-term growth in all major segments of the commercial aircraft and jet engine market. Over the next 20 years, the forecasts demand for 132,000 engines, worth \$701 billion. Markets within Asia, both short-haul and intercontinental, will drive much of this growth. However, the more mature markets in Europe and North America require over 6000 new airliner deliveries to replace older aircraft in today's fleet. Delivery of these engines also creates an aftermarket opportunity of \$550 billion for services in lifetime (Rolls-Royce, 2007).

Over the last 20 years Rolls-Royce's outlook has seen a steady move toward higher thrust engines. Airlines have demanded aircraft with better payload-range performance, more flexibility to takeoff from short runways and improved climb rates. There is no sign of the drive for performance declining. Therefore, Rolls-Royce continues to forecast that the sectors above 200.17 kN (45,000 lb) takeoff thrust will be the largest in terms of value. The forecast for the engine market naturally reflects the size distribution and dynamics of the aircraft market. The market has been segmented into takeoff thrust categories, which can be roughly matched against aircraft classes. For example, below 26.7 kN (6,000 lb) is the domain of smaller business jets, while 26.7–97.86 kN (6,000–22,000 lb) engines predominantly power business jets and regional jets. The 97.86–200.17 kN (22,000–45,000 lb) category covers the single-aisle market and engines above 200.17 kN (45,000 lb) thrust are for twin-aisle aircraft. While there has been little change in the relationship between takeoff thrust required and the maximum takeoff weight (MTOW) of the aircraft, there have been continued reductions in the MTOW required for a given mission. This is due to more fuel-efficient engines, which require less weight of fuel to be carried and lighter airframe structures. There is also now more focus on 'hot-and-high' engine performance, with airlines wishing to have the flexibility to operate without payload restrictions from regions such as the Middle East, India, and Latin America. Although the largest quantity of engines is for the 97.86–200.17 kN (22,000–45,000 lb) thrust band, the market value is dominated by high thrust engines for long-haul twin-aisle aircraft. This sector has expanded at a rapid rate over the last 15–20 years and is forecast to continue to grow in the coming decades (Rolls-Royce, 2007).

High-bypass turbofan engines can be modeled at various levels of detail, ranging from simple algebraic relations to full three-dimensional (3-D) description of the gas path. Aerothermodynamic models are considered in this study. Some models are massively used by the manufacturers throughout an engine program: for preliminary design and performance prediction, for the synthesis of the control laws, for condition monitoring, as well as for the engine-airframe integration (Borguet et al., 2007).

In this study, we report the development of a modular aircraft high-bypass turbofan engine simulation in the MATLAB (Matrix Laboratory) environment. A new software program was developed for multi-design point optimization of a high-bypass turbofan engine. The newly developed software program's name is TURBOGENf (turbofan genetic fan). It can search optimum thermodynamic points of a high-bypass turbofan engine coupled with elitism-based genetic algorithm method (EBGA) for minimum specific fuel consumption for different fuel usages. The genetic algorithms (GAs), initially developed by Holland (1975), are the most recognized and practiced form of evolutionary algorithms which are stochastic optimization techniques that mimic Darwin's principles of natural selection and survival of the fittest. GAs can be used in the case of discontinuous objective functions, within disjointed and/or non-convex design spaces, and together with discrete, continuous, or integer design variables. With respect to local search methods (e.g., gradient-based) GAs minimize the risk to converge to a local optimum, thanks to the simultaneous processing of the whole candidate solutions.

Moreover, they are particularly suitable for multiobjective optimization problems which are often encountered in real design problems. Because of these advantages, GAs are more and more widely used in various disciplines. However, GAs generally require a large number of iterations and they converge slowly. Optimization using genetic algorithms is thus advantageous when the objective functions evaluation is not too expensive in terms of calculating time (Borguet et al., 2007). Therefore, GAs are efficient when coupled to approximation methods (Pierret, 2005), to parametric reconstructions (Grondin et al., 2005), or to 0-D (zero-dimensional) models.

13.2 High-Bypass Turbofan Engine Modeling

In the following, we focus on a particular type of jet engine: the separated flows and non-afterburning turbofan. With the current level of technology, this one has revealed to be the optimum configuration for high subsonic commercial aircraft (Cumpsty, 2000). A schematic of the engine is sketched in Fig. 13.1.

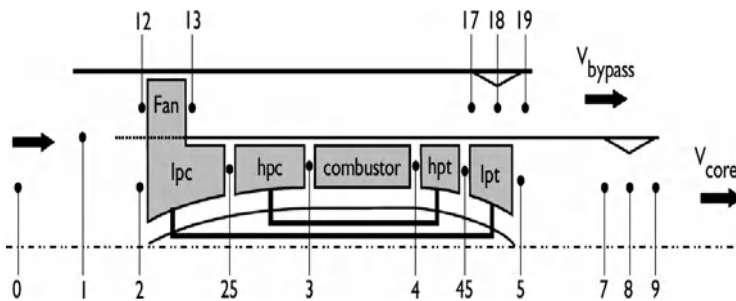


Fig. 13.1 General station numbering of a turbofan engine.

The assumptions for the analysis of the turbofan engine cycle with losses are as follows:

- Perfect gas upstream of main burner with constant properties γ_c , R_c , C_{pc} .
- Perfect gas downstream of main burner with constant properties γ_t , R_t , C_{pt} .
- All components are adiabatic (no turbine cooling).
- The efficiencies of the compressor, fan, and turbine are described through the use of (constant) polytropic efficiencies e_c , e_f , and e_t , respectively.

The steps of cycle analysis can be easily seen in Mattingly (1996). But the most important parameters, specific thrust and specific fuel consumption, are given as follows:

$$\frac{F}{\dot{m}_0} = \frac{1}{1 + \alpha} \frac{a_0}{g_c} \left[\begin{aligned} & \left((1 + f) \frac{V_9}{V_0} - M_0 \right) \\ & + (1 + f) \frac{R_i T_9 / T_0}{R_c V_9 / a_0} \frac{1 - P_0 / P_9}{\gamma_c} \end{aligned} \right] \\ + \frac{\alpha}{1 + \alpha} \frac{a_0}{g_c} \left(\frac{V_{19}}{V_0} - M_0 + \frac{T_{19} / T_0}{V_{19} / a_0} \frac{1 - P_0 / P_{19}}{\gamma_c} \right) \quad (13.1)$$

$$(13.2)$$

$$SFC = \frac{\dot{m}_f}{F} = \frac{f}{(1 + \alpha) F / \dot{m}_0}$$

Table 13.1 Parameters of genetic algorithm and design point of a high-bypass turbofan engine-I.

Flight conditions and design-point parameters of TURBOGENf			
$M_0=0.8$	$T_0=220$ K	$h_{PR}=23,000$ kJ/kg	$\pi_c=20$
T_4 (K)=1,500	C_{pc} kJ/(kg. K)=1.00488	$C_{pt}=1.147$ kJ/(kg K)	$\gamma_c=1.4$
$\gamma_t=1.33$	$p_{t4} / p_{t3}=0.99$	$p_{t19} / p_{t13}=0.99$	$e_c=0.90$
$e_f=e_t=0.89$	$\eta_b=\eta_m=0.99$	$p_0 / p_9=0.90$	$p_0 / p_{19}=0.90$
Genetic algorithm parameters of TURBOGENf			
$Pn=200$	$Gn=300$	$Ct=0.6$	$Mr=0.003$
$1.2 \leq \pi_f \leq 2$	$has_{\pi_f}=0.1$	$2 \leq \alpha \leq 8$	$has_{\alpha}=0.1$

13.3 Preliminary Design Curves with TURBOGENf

In the following, TURBOGENf (turbofan genetic fan) software program developed by Turan (2007) is introduced. TURBOGENf is a software program developed in MATLAB programming environment which analyses parametric cycle of a non-afterburning, separate exhaust flow turbofan engine at different design points in SI unit and gets optimum design points at different flight conditions and design criteria via elitism-based genetic algorithm simultaneously. Main purpose of TURBOGENf is minimizing specific fuel consumption of a high-bypass turbofan engine under different design criteria, different fuels and flight conditions. Decision variables of TURBOGENf are fan pressure ratio (π_f) and bypass ratio (α). It is possible to see some 3-D performance curves of an engine in TURBOGENf. TURBOGENf is able to draw 3-D color-scaled counter plot corresponding to specific fuel consumption, specific thrust, propulsive, thermal, and overall efficiency coupled with decision variables such as the fan pressure ratio and the bypass ratio. Table 13.1 consists of design-point parameters of an

example turbofan engine. From Figs. 13.2 to Fig. 13.4 3-D color-scaled counter plot coupled with decision variables (π_f and α) and specific fuel consumption (SFC) according to Tables 13.1–13.3 for which h_{PR} is 23,000, 43,000, and 120,000 kJ/kg, respectively can be seen. Each mesh plot color in these figures represents value of the specific fuel consumption as a objection function curve.

Table 13.2 Parameters of genetic algorithm and design points of a high-bypass turbofan engine-II.

Flight conditions and design-point parameters of TURBOGENf			
$M_0=0.8$	$T_0=220$ K	$h_{PR}=43,100$ kJ/kg	$\pi_c=20$
T_4 (K)=1,500	C_{pc} kJ/(kg K)=1.00488	$C_{pt}=1.147$ kJ/(kg K)	$\gamma_c=1.4$
$\gamma_t=1.33$	$P_{t4}/P_{t3}=0.99$	$P_{t19}/P_{t13}=0.99$	$e_c=0.90$
$e_f=e_t=0.89$	$\eta_b=\eta_m=0.99$	$p_0/p_9=0.90$	$p_0/p_{19}=0.90$
Genetic algorithm parameters of TURBOGENf			
$Pn=200$	$Gn=300$	$Cr=0.6$	$Mr=0.003$
$1.2 \leq \pi_f \leq 2$	$has_{\pi_f}=0.1$	$2 \leq \alpha \leq 8$	$has_{\alpha}=0.1$

Table 13.3 Parameters of genetic algorithm and design points of a high-bypass turbofan engine-III.

Flight conditions and design-point parameters of TURBOGENf			
$M_0=0.8$	$T_0=220$ K	$h_{PR}=120,00$ kJ/kg	$\pi_c=20$
T_4 (K)=1,500	C_{pc} kJ/(kg K)=1.00488	$C_{pt}=1.147$ kJ/(kg K)	$\gamma_c=1.4$
$\gamma_t=1.33$	$P_{t4}/P_{t3}=0.99$	$P_{t19}/P_{t13}=0.99$	$e_c=0.90$
$e_f=e_t=0.89$	$\eta_b=\eta_m=0.99$	$p_0/p_9=0.90$	$p_0/p_{19}=0.90$
Genetic algorithm parameters of TURBOGENf			
$Pn=200$	$Gn=300$	$Cr=0.6$	$Mr=0.003$
$1.2 \leq \pi_f \leq 2$	$has_{\pi_f}=0.1$	$2 \leq \alpha \leq 8$	$has_{\alpha}=0.1$

Until now, fossil fuels have contributed to over 80% of energy expenses, and among them, oil played the dominant role. It is expected that its use will not decline until the next two or three decades. The transportation sector, including aviation, an essential part of our modern society, represents the largest part of the petroleum-based fuels consumption. Its importance has continuously grown at a very fast rate over the last century. Future global energy and environmental issues have imposed changes in the operating conditions of jet engines. As in other sectors, research is now oriented on saving energy, in parallel with enhanced protection of our environment (reduction of the emissions of pollutants and green house gases) and fuel reformulation. The detailed modeling of the combustion of jet fuels is a useful tool to solve the problem of combustion control as well as to reduce emissions and fuel consumption.

Table 13.4 Main characteristics of kerosene jet fuel.

Property	JP-8	JP-8	JP-8/Jet A-1	Jet A	JP-8	Kerosene
Molecular weight		152		162		
Approximate formula	–	$C_{10.9}H_{20.9}$	$C_{11}H_{21}$	$C_{11.6}H_{22}$	–	–
Number of C atoms in the fuel	–	10.9	11	11.6	–	9–13
H/C ratio	–	1.92	1.91	1.9	–	1.9–2.1
Boiling range °C	140–300	Average 204	165–265	Average 216	–	140–280
Specific gravity at 15°C	0.81		0.81		–	0.77–0.83
Av. composition in vol%						
Aromatics	20		18		18(monoaro.) + 2(diario.)	10–20
Cycloalkenes	20		20		20	20–30
Paraffin	58		60		28(n-par.) + 29(i-par.)	50–65
Olefins	2		2		–	0

Source: Dagaut and Cathonette (2006).

Table 13.5 Main characteristics of kerosene jet fuel.

Fuel type	Energy density (MJ/kg)	Energy per unit volume (MJ/L)	Motivity factor	Specific carbon emission (kg C/kg fuel)
Liquid hydrogen	141.90	10.10	1.00	0.00
Gaseous hydrogen	141.90	0.013	1.00	0.00
Fuel oil	45.50	38.65	0.78	0.84
Gasoline	47.40	34.85	0.76	0.86
Jet fuel	46.50	35.30	0.75	–
LPG	48.80	24.40	0.62	–
LNG	50.00	23.00	0.61	–
Methanol	22.30	18.10	0.23	0.50
Ethanol	29.90	23.60	0.37	0.50
Bio diesel	37.00	33.00	–	0.50
Natural gas	50.00	0.04	0.75	0.46
Charcoal	30.00	–	–	0.50

Source: Midilli et al. (2005).

Table 13.6 Computer experiment results for different fuel types usage in preliminary design of turbofans.

Engine number	h_{PR} (kJ/kg)	SFC* [g/(kN s)]
I	23,000	34.25
II	43,000	18.31
III	120,000	5.50

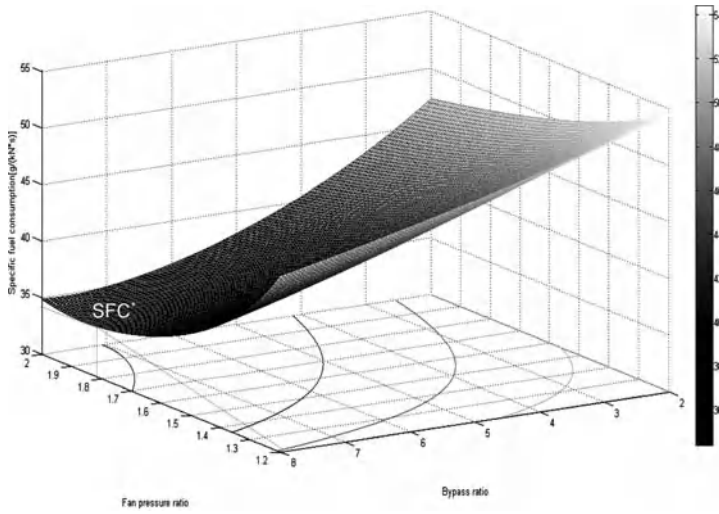


Fig. 13.2 Specific fuel consumption–fan pressure ratio–bypass ratio 3-D curves in TURBOGENf for $h_{pr}=23,000$ kJ/kg.

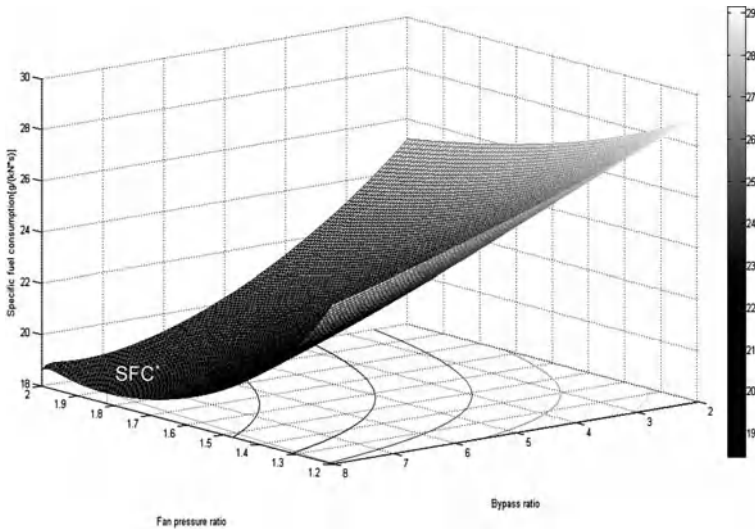


Fig. 13.3 Specific fuel consumption–fan pressure ratio–bypass ratio 3-D curves in TURBOGENf for $h_{pr}=43,000$ kJ/kg.

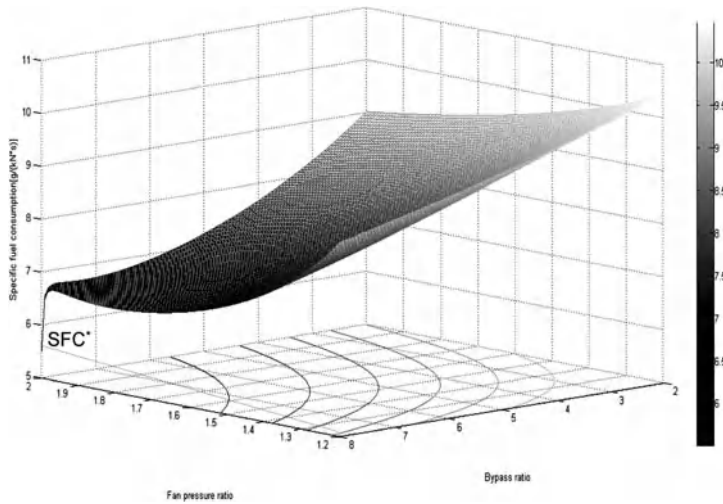


Fig. 13.4 Specific fuel consumption–fan pressure ratio–bypass ratio 3-D curves in TURBOGENf for $h_{pr}=120,000$ kJ/kg.

Such a modeling represents a real challenge because practical jet fuels are complex mixtures of several hundreds of hydrocarbons including alkenes, cycloalkenes, aromatics, and polycyclic compounds. Table 13.4 gives the main characteristics of JP-8 and Jet A-1 reported by several authors compared with the general characteristic of kerosene (Guibet, 1999; Edwards and Maurice, 2001; Violi et al., 2002; Dagaut and Cathonette, 2006). Kerosene usage chain with indications of inputs and outputs including environmental impacts is shown in Fig. 13.5. Main characteristics of kerosene jet fuel can be listed in Table 13.5.

13.4 Results and Discussion

In this study, we have presented optimization analysis results of a high-bypass turbofan engine for minimizing specific fuel consumption according to decision variables such as the fan pressure ratio (π_f) and the bypass ratio (α) using different fuels. In this regard, upper and lower limits of π_f and α were determined, while engine design-point parameters were identified such as in Tables 13.1–13.3. It can be shown that some computer experiment results of TURBOGENf for three different fuel usages are summarized in Table 13.6 for the values of $1.2 \leq \pi_f \leq 2$, $2 \leq \alpha \leq 8$, and $23,000 \leq h_{pr} \text{ (kJ/kg)} \leq 120,000$.

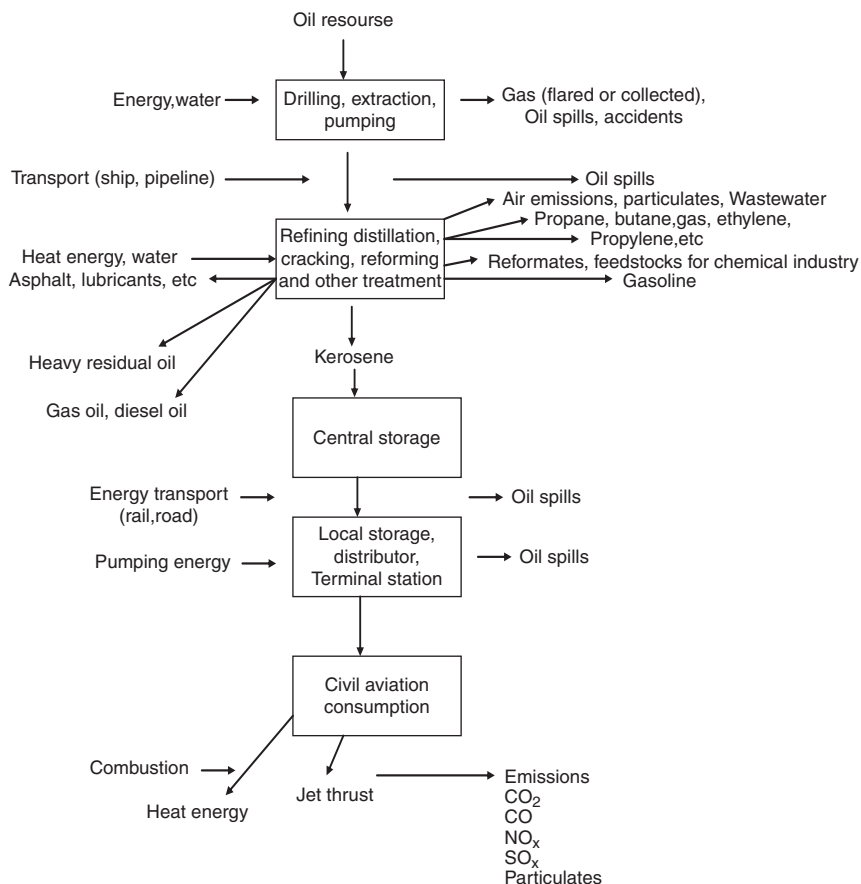


Fig. 13.5 Kerosene usage chain with indications of inputs and outputs including environmental impacts (modified from Koroneos et al., 2007).

According to the values in Table 13.6, the specific fuel consumption is lower for hydrogen-fueled engine than JP-5- and JP-8-fueled engine because hydrogen has higher fuel heating value than the others. Moreover it was observed that the fuel heating value was a very effective parameter on specific fuel consumption surface shape in this study. In Fig. 13.4, hydrogen's specific fuel consumption surface is sharply decreased at optimum point (i.e., $\pi_f=2$ and $\alpha=8$ for this computer experiment) than the JP-5 and JP-8s' surfaces (optimum points for JP-5 and JP-8 are $\pi_f=1.8$ and $\alpha=8$, respectively). Figure 13.6 shows cycle design point

of some modern commercial engines used in long and middle range aircraft. Selected engine are V2500-A5, CFM56-5C4, RB211-524H, Trent890, PW2040, CFM56-7B26, CF6-80C2, and Trent500 (Aviationnow, 2007; CFM56, 2007; Janes, 2007; RollsRoyce, 2007). It can be easily shown that real engine values can be yielded in optimization solution space in this chapter.

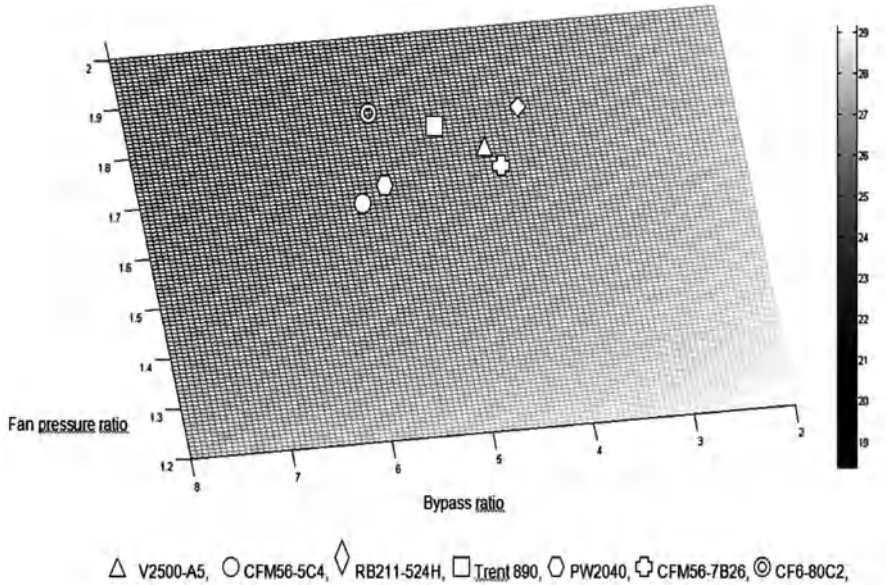


Fig. 13.6 Parametric design points of some modern commercial turbofan engines in TURBOGENf.

13.5 Conclusions

In this study, elitism-based genetic algorithm method was applied for minimum specific fuel consumption of high-bypass turbofan engine in the conceptual design phase for different fuels. In this regard, TURBOGENf software program was developed. Decision variables in this software were the fan pressure ratio (π_f) and the bypass ratio (α). The main conclusions drawn from the results of this study may be listed as follows:

- Depending on the application, it can be seen that elitism-based genetic algorithm method is a successful tool for solving this optimization problem.
- The ability of an elitism-based genetic algorithm to provide a family of optimal solution to this particular problem has been demonstrated.
- Optimization problem was solved easily in TURBOGENf.
- TURBOGENf can successfully solve optimization problems at $1.2 \leq \pi_f \leq 2$, $2 \leq \alpha \leq 10$, and $23,000 \leq h_{PR} \text{ (kJ/kg)} \leq 120,000$ with $M_0 \leq 0.8$.

- 3-D color-scaled surface performance plots of a high-bypass turbofan engine can be drawn easily from TURBOGENf.
- It can be observed that $Gn \geq 200$, $Pn \geq 300$, and $Mr = 0.003$ are sufficient for yielding optimum points in TURBOGENf.

However, it has to be realized that the proposed application is rather academic. First, constrained problem could be considered. Then, additional effects such as the weight, noise, exergy efficiency, and thrust of the commercial engine or its pollutant emissions should be introduced in the model to define new figures of merit.

Nomenclature

a_0	Speed of sound at freestream, m/s
C_p	Specific heat at constant pressure, kJ/(kg K)
Cr	Crossover rate
C_v	Specific heat at constant volume, kJ/(kg K)
e	Polytropic efficiency
f	Fuel–air ratio
F	Thrust, kN
$F/\dot{m}_0$	Specific thrust, N s/kg
GA	Genetic algorithm
g_c	Newton's constant
Gn	Generation number
has	Sensitivity
h_{PR}	Fuel heating value, kJ/kg
M_0	Mach number at freestream
Mr	Mutation rate
P	Pressure, Pa
Pn	Population number
R	Universal gas constant, m ² /(s ² K)
SFC	Specific fuel consumption, g/(kN s)
T	Temperature, K
V	Velocity, m/s
α	Bypass ratio
γ	Specific heat ratio
π	Pressure ratio
Subscripts and superscripts	
c	Compressor
f	Fuel; fan
t	Turbine
$*$	Optimum
0,1,2,...,19	Different locations in engine stations

References

- Anand MS, Priddin CH (2001) Combustion CFD. A Key driver to reducing development cost and time. Fifteenth International Symposium on Air Breathing Engines, Bangalore, India.
- Aviationnow (2007) http://www.aviationnow.com/media/pdf/spec_04_gas_turbines.pdf. Access date: March 20.
- Boeing (2007) <http://www.boeing.com> Access date: November 20.
- Borguet, S, Kelner, V, Leonard, O (2007) Cycle optimization of a turbine engine: an approach based on genetic algorithms; <http://www.ulg.ac.be/turbo/research/paper/NCTAM2006.pdf>, Access date: November 20.
- CFM56 (2007) <http://www.geae.com>, Access date: September 12.
- Cumpsty, N (2000) Jet propulsion. Cambridge University Press.
- Dagaut P, Cathonette, M (2006) The ignition, oxidation, and combustion of kerosene: A review of experimental and kinetic modeling, *Progress in Energy and Combustion Science* 32: 48–92.
- Edwards, T, Maurice, LQ (2001) Surrogate mixtures to represent complex aviation and rocket fuels. *Journal of Propulsion and Power* 17: 461–6.
- Grondin, G, Kelner, V, Ferrand, P, Moreau, S (2005) Robust design and parametric performance study of an automotive fan blade by coupling multi-objective genetic optimization and flow parameterization. *Proc. of the International Congress on Fluid Dynamics Applications in Ground Transportation*, Lyon, France.
- Guibet, JC (1999) Fuels and engines. Paris: Editions Technic.
- Holland, J (1975) Adaptation in natural and artificial systems. University of Michigan Press
- ICAO (1999) Adopts new aircraft engine emissions and noise standards. Council of the International Civil Aviation Organization (ICAO).
- Janes (2007) http://www.janes.com/aerospace/civil/news/jae/jae010213_2_n.s.html, Access date: March 18.
- Koroneos, C, Dompros, AR, Moussiopoulos, N (2007) Advantages of use of hydrogen fuel as compared to kerosene. *Conservation and Recycling* 44(2): 99–113.
- Mari, C (2001) Trends in the technological development of aero engines: an overview. Fifteenth International Symposium on Air Breathing Engines, Bangalore, India.
- Mattingly, J (1996) Elements of gas turbine propulsion. McGraw-Hill.
- Mattingly, J (2006) Elements of propulsion: gas turbines and rockets. AIAA Education series, USA.
- Midilli, A, Dincer, I, Rosen, MA (2005) On hydrogen and hydrogen energy strategies II: future projections affecting global stability and unrest. *Renewable & Sustainable Energy Reviews*, 9: 273–287.
- Nightingale, P (2000) The product-process-organization relationship in complex development projects. *Research Policy* 29: 913–930, Elsevier.
- Oates, GC (1997) Aerothermodynamics of gas turbine and rocket propulsion. AIAA Education series, USA.
- Pierret, S (2005) Multiobjectives and multidisciplinary optimization of three-dimensional turbomachinery blades. *Proc. of the 6th World Congress of Structural and Multidisciplinary Optimization*. Rio de Janeiro, Brazil.
- Robins, SR (1996) The Trent program. A further step in engineering evolution. Christopher Hilton Lecture at the Royal Institute of Engineers.
- Rolls Royce (2007) www.rollsroyce.com/civilaerospace. Access date: March 18.
- Schipper, Y, Rietveld, P (1997) Economics and environmental effects of airline deregulation. *Tinbergen Institute Discussion Papers* 97: 031/3.
- Turan, O (2007) Optimization of turbofan engines with elitism-based genetic algorithm method. Doctoral Thesis, Anadolu University, Natural and Applied Sciences.
- Violi, A, Yan, S, Eddings, EG, Sarofim, AF, Granata, S, Favarelli, T (2002) Experimental formulation and kinetic model for JP-8 surrogate mixture. *Combustion Science and Technology*, 174 (11&12): 399–417.

Marnoch Engine Performance for Multiple Pressure Vessel Configurations

I. Marnoch, G. Naterer, M. A. Rosen and J. Weston

14.1 Introduction

A new type of heat recovery and thermal conversion process is analyzed that produces electricity by recovering thermal energy over a wide range of temperature differences, including relatively small ones. The process induces fluid motion and drives a piston assembly connected to an electric generator. Temperature differences as low as 15°C produce useful power from the process. The performance can be enhanced through solar energy input, which would provide temperatures upward of 90°C at the collector side and increase the Carnot efficiency of the process significantly.

As a consequence, the device has the potential to reduce greenhouse gas emissions significantly, by allowing renewable energy resources and waste heat to be utilized and fossil fuel use to be correspondingly decreased. Hence, the device may have a role as a technology for mitigating global warming and the impact it is having via climate change.

The unit consists of two main parts: (i) one that absorbs heat from a higher temperature source and (ii) one that converts thermal to mechanical and finally electrical energy, before discharging the remaining heat to a lower temperature sink (see Fig. 14.1). The device uses pairs of vessels that are pre-pressurized with gas (dry air, hydrogen, or nitrogen) to absorb and transfer heat. The heated gas exits the pressure vessel and flows into an enclosed cylinder, which drives a piston to produce shaft power. Thermal energy is converted to kinetic energy via the working fluid, which is subsequently converted to mechanical energy in the high-pressure pneumatic cylinders, and a transmission system with gears designed to optimize the energy potential of the fluid.

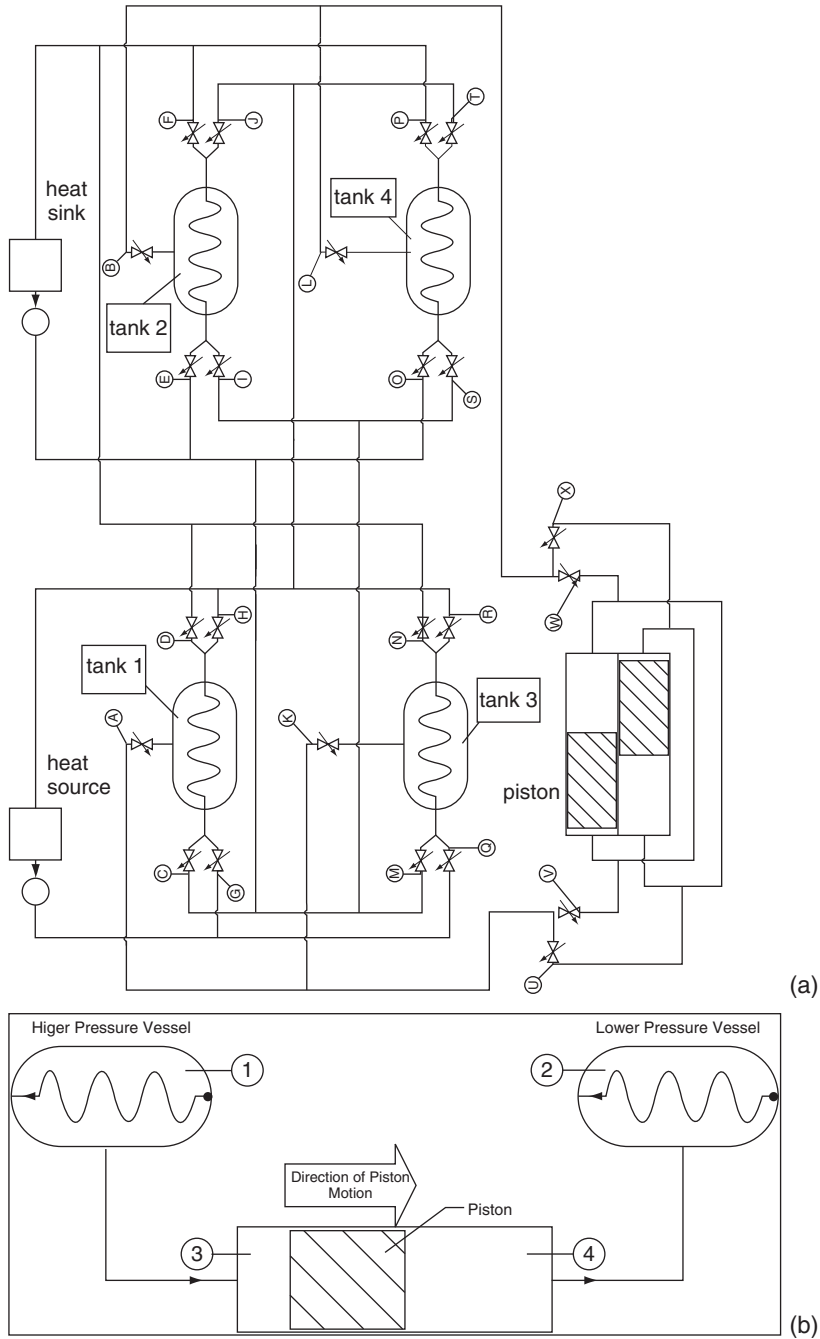


Fig. 14.1 Schematic of Marnoch power device. (a) schematic of overall system and (b) piston assembly.

Finally, the mechanical energy is transferred to an electric generator sized appropriately to the system. The device uses pairs of highly pressurized tanks in a closed loop, with operating principles similar to a Stirling engine, except the manner of heat inflows/outflows; valve assembly and other unique changes are aimed at overcoming the deficiencies of a Stirling engine.

The process operates similar to a conventional heat engine, which absorbs heat from a high-temperature source, produces power, and rejects waste heat to a lower temperature medium. In contrast to conventional heat engines that combust fossil fuels, however, the proposed system does not emit greenhouse gases and can operate effectively over relatively small temperature differences. Such heat source temperatures are available in many applications.

The Marnoch unit (Fig. 14.1a) consists of four cylindrical tanks, each fitted with helical copper tube coil heat exchangers. Each tank is connected to both a hot source and a cold source, via tubes and valves that allow a controlled mass flow at any step of the process.

In this chapter, which extends previous work (Armstrong et al., 2007), the operating performance and economic viability of the Marnoch unit for various operating circumstances and applications are examined. In particular, the performance and operation are studied of a prototype Marnoch engine developed at UOIT, for a range of operating temperatures and tank configurations. The environmental performance of the device, particularly with respect to global warming, is also assessed.

14.2 Modeling and Analysis of Engine Performance

The Marnoch engine uses a pneumatic rotary actuator and a transmission system that converts mechanical energy provided through a flywheel to electricity in an electrical generator. Any cylinder configuration can be used and it is not restricted to a rotary actuator. The transmission can be a belt drive or direct drive, similar to systems used in wind turbines. The differential in pressure between the heated tank and the cooled tank drives the actuator. The size of the actuator depends on the size of the generator used. When the gas is highly compressed within the piston cylinder, the temperature differential needed to generate a sufficient pressure change is proportionately less than at a lower initial pressure. A prototype Marnoch engine is shown in Fig. 14.2.

A thermodynamic model was developed to predict the performance and efficiency of the Marnoch system. Also, a control system was developed for automation of valves and flow exchange between the pressure vessels.

Analysis results are presented in Figs. 14.3 and 14.4 and Tables 14.1–14.5 of operating performance over a range of operating temperatures and time intervals. Based on the results, the performance of the device is promising and significant potential exists for higher power output at higher pressures within the pressure vessels.

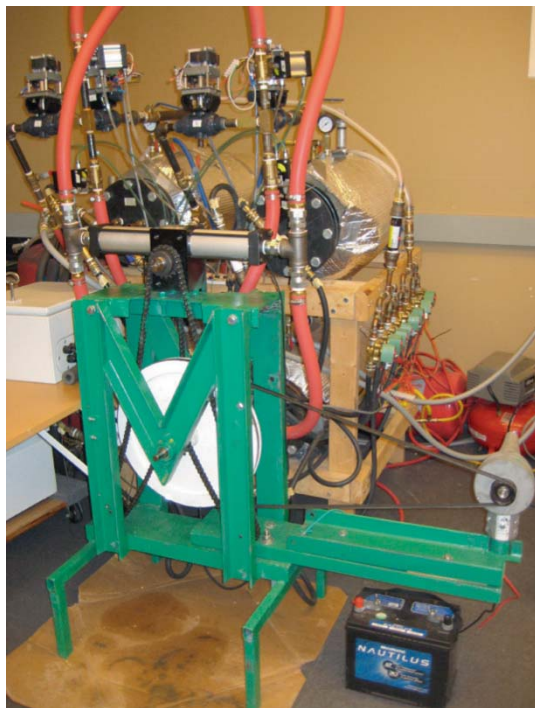


Fig. 14.2 Photograph of Marnoch prototype engine.

A pressure differential is initially created between two pressure vessels, through a temperature difference. When the device begins operation, these vessels have the same initial condition. Heat exchangers within the vessels are used to transfer heat from an external source to the interior of the vessel. Depending on whether the system is heated or cooled, a thermal energy source or sink is connected accordingly. Once a pressure differential has been generated between the vessels, a specialized piston assembly is utilized to convert the pressure differential to mechanical energy.

The assembly consists of two chambers separated by the piston. The piston moves back and forth, thereby varying the sizes of the chambers. As the volume of the first chamber increases, that of the second decreases. The chamber of minimum volume is connected to the vessel with a higher pressure, while the lower pressure vessel is connected to the chamber with the larger volume. The pressure difference between the two chambers results in a net force on the piston, causing it to move. Once the piston has reached the end of the cylinder, a valve is activated. This yields a net mass flow from the high pressure to low pressure vessel, as the gas within the chamber of decreasing volume is transferred to the low pressure vessel.

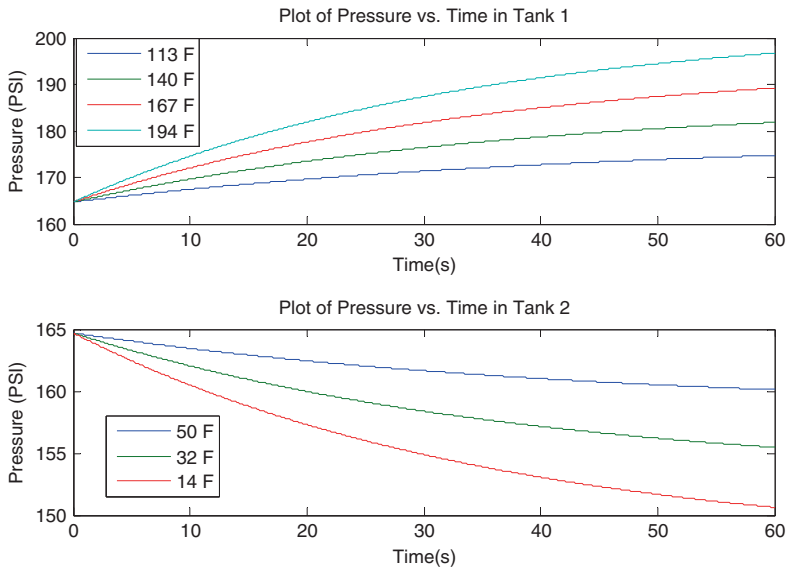


Fig. 14.3 Variations of pressures in tanks at varying source temperatures, for initial conditions in the tank of 69.8°F and 164.7 psia.

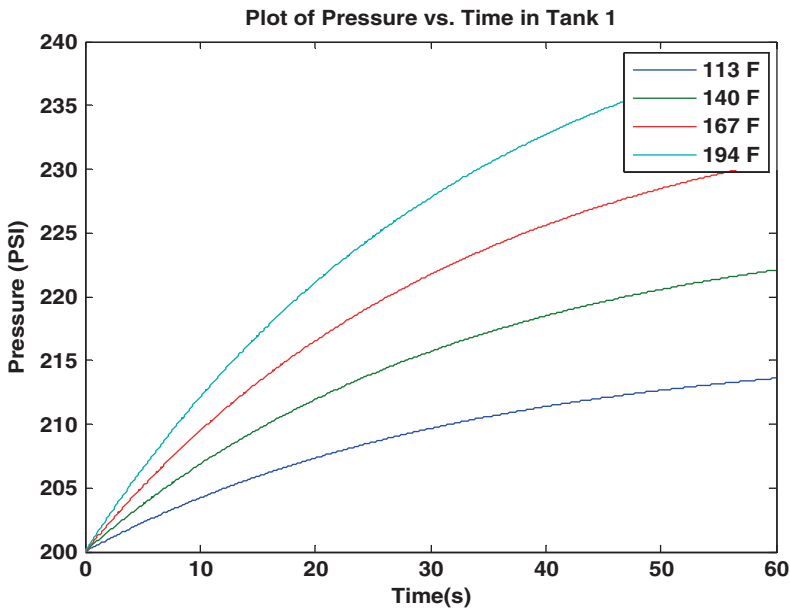


Fig. 14.4 Pressure in tank 1 at varying source temperatures, for initial conditions in the tank of 69.8°F and 200 psia.

Table 14.1 System operating parameters (for case 2 with a 40 °C temperature difference in Table 14.4).

Tank inner diameter (in.)	23.5
Tank volume (US gallons)	431.83
Tank operating pressure (psig)	3000 (205.08 atm absolute)
Tank design pressure (psig)	3500
Coil tube outer diameter (in.)	1.5
Coil tube thickness (in.)	0.109
Coil tube inner diameter (in.)	1.282
Number of turns	160
Pitch (in.)	1.5
Coil outer diameter (in.)	22
Coil length (in.)	210.00
Coil tube length (ft)	921.53
Percent of total tank volume in tubes	19.59
Total surface area of coil (ft ²)	361.89
Inner surface area of tank (ft ²)	117.92

An analytical model was developed to predict the power output and number of strokes, based on the initial conditions within the pressure vessels. This model is based on principles of conservation of mass and Bernoulli's equation (Cengel and Kern, 1950; Mulley, 2004; Turner, 2005). For a fixed time interval, it is assumed that each side of the system is at constant temperature and no losses occur during the pressure transfer. Using the Bernoulli equation, it can be shown that

$$\frac{dm}{dt} = C \cdot A \sqrt{2 \cdot p_u \cdot \rho_u \cdot \left[\left(\frac{p_d}{p_u} \right)^{\left(\frac{2}{k} \right)} - \left(\frac{p_d}{p_u} \right)^{\left(\frac{k+1}{k} \right)} \right]} \quad (14.1)$$

In Eq. (14.1), k denotes the ratio of specific heats. Also, m , t , A , p , and ρ , respectively, denote mass, time, area, pressure, and density, and the subscripts u and d denote upstream and downstream, respectively. Using this equation, the mass flow rate from each tank into the cylinder can be determined. Based on the mass flow rates, numerical integration of the functions below lead to the predicted change of mass with time in each tank as follows:

$$m_1(t) = m_1(0) - \int_{t_1}^{t_2} \frac{dm_1}{dt} dt \quad (14.2)$$

$$m_2(t) = m_2(0) + \int_{t_1}^{t_2} \frac{dm_2}{dt} dt \quad (14.3)$$

Table 14.2 Data for heat exchangers (for case 2 with a 40 °C temperature difference in Table 14.4).

Gas thermal conductivity (Btu/h ft F)	0.016
Gas molecular weight	29
Gas specific heat (Btu/lb F)	0.24
Gas temperature (F)	50.00
Gas viscosity (cP)	0.01
Gas density (lb/ft ³)	16.0000
Thermal expansivity	0.001961
Water temperature (F)	122.00
Water fouling factor	0.001
Gas fouling factor	0.001
Wall thermal conductivity (Btu/h ft F)	231
Wall thermal resistance (h ft ² F/Btu)	0.0000393
Overall heat transfer coefficient, U (Btu/h ft ² F)	23.19
Heat transfer rate, Q (Btu/h)	604,312

Table 14.3 System performance with a 80 °C (144 °F) temperature difference.

Temperature of heat source (°C/°F)	90/194
Temperature of cold sink (°C/°F)	10/50
48 gallon tank configuration (×4 tanks)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	9.88
Heat transfer rate, Q (Btu/h)*(per tank)	62,165
Operating pressure (psig)	300
Carnot efficiency (%)	22.03
Projected hourly output for 4-tank (2 pair) configuration, each tank having 48 gal. (kW h)	8.06
Projected daily output for 4-tank configuration, for 10 h/day operation (kW h)	80
Revenue for 10 h operation at \$110/MW h (\$)	8.80
Annual revenue for 10 h operation/day at \$110/MW h (\$)	3212.00
432 gallon tank configuration (×8 pair of tanks)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	9.46
Heat transfer rate, Q (Btu/h)* (per tank)	492,811
Operating pressure (psig)	300
Carnot efficiency (%)	22.03
Projected hourly output for 8-pair tank configuration, each tank having 432 gal., at 50% efficiency (kW h)	128
Projected daily output for 8-pair tank configuration, for 10 h/day operation (kW h)	1277
Projected daily output for 8-tank configuration, operating 10 h/day high output and 14 h/day low output (kW h)	2171
Projected daily output for 8-tank configuration, for 24 h/day steady operation (kW h)	3065
Revenue per day at \$110/MW h for 10 h/day high output and 14 h/day low output (\$)	238.84
Revenue per day at \$110/MW h for 24 h/day steady operation (\$)	337.19
Revenue per annum at \$110/MW h for 24 h steady operation (\$)	123,074

* The heat transfer rate is evaluated as $Q = UA\Delta T$.

These equations are based on the pistons and pressure vessels having the configuration shown in Fig. 14.1b. Based on the mass within each of the piston chambers, the pressures at points 3 and 4 are also calculated as a function of time. With this information, it can be shown that the boundary work produced by the system during a given power stroke can be calculated as follows:

$$W_b = \int_1^2 p_3 dV - \int_1^2 p_4 dV \quad (14.4)$$

These calculations are repeated for several strokes, until the difference between p_1 and p_2 is negligibly small. The resulting boundary work terms of all strokes are added to give a total value, and then the result is divided by the time required for the strokes to occur to obtain the average power output of the system.

Table 14.4 System performance with a 40 °C (72 °F) temperature difference at 300 psi.

Temperature of heat source (°C/°F)	50/122
Temperature of cold sink (°C/°F)	10/50
48 gallon tank configuration (2 pair)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	8.36
Heat transfer rate, Q (Btu/h)*(per tank)	26,304
Operating pressure (psig)	300
Carnot efficiency (%)	12.38
Projected hourly output for 4-tank configuration, each tank having 48 gal. (kW h)	1.92
Projected daily output for 4-tank configuration, for 10 h/day operation (kW h)	20
Revenue for 10 h operation at \$110/MW h (\$)	2.20
Annual revenue for 10 h operation/day at \$110/MW h (\$)	803
432 gallon tank configuration (8 tanks)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	8.00
Heat transfer rate, Q (Btu/h)*	208,469
Operating pressure (psig)	300
Carnot efficiency (%)	12.38
Projected hourly output for 8 pair-tank configuration, each tank having 432 gal. at 50% efficiency (kW h)	30
Projected daily output for 8-pair tank configuration, for 10 h/day operation (kW h)	304
Projected daily output for 8-pair tank configuration, operating 10 h/day high output and 14 h/day low output (kW h)	516
Projected hourly output for 8-pair tank configuration, for 24 h/day steady operation (kW h)	729
Revenue per day at \$110/MW h for 10 h/day high output and 14 h/day low output (\$)	56.77
Revenue per day at \$110/MW h for 24 h/day steady operation (\$)	80.15
Revenue per annum at \$110/MW h for 24 h steady operation (\$)	29,253

* The heat transfer rate is evaluated as $Q = UA\Delta T$.

14.3 Results and Discussion

Results are presented for initial pressures of 164.7 and 200 psia. The conditions are intended to replicate working conditions of a prototype at UOIT, as well as planned future extensions to higher pressure units. In modeling the unit, heat transfer within the pressure vessels and pressure changes within the piston–cylinder device are included.

Table 14.5 System performance with a 40 °C (72 °F) temperature difference at 3,000 psi.

Temperature of heat source (°C/°F)	50/122
Temperature of cold sink (°C/°F)	10/50
48 gallon tank configuration (2 pairs)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	24.17
Heat transfer rate, Q (Btu/h)*(per tank)	76,034
Daily heat transfer, for 24 h/day operation (Btu)	1,824,823
Operating pressure (psig)	3,000
Carnot efficiency (%)	12.38
Projected hourly output for 4-tank configuration, each tank having 48 gal. (kW h)	5.54
Projected daily output for 4-tank configuration, for 10 h/day operation (kW h)	133
Revenue for 10 h operation at \$110/MW h (\$)	14.63
Annual revenue for 10 h operation/day at \$110/MW h (\$)	5340
432 gallon tank configuration (8 tanks)	
Overall heat transfer coefficient, U (Btu/h ft ² F)	23.2
Heat transfer rate, Q (Btu/h)*	604,312
Operating pressure (psig)	3000
Carnot efficiency (%)	12.38
Projected hourly output for 8-pair tank configuration, each tank having 432 gal. at 50% efficiency (kW h)	88
Projected daily output for 8-pair tank configuration, for 10 h/day operation (kW h)	880
Projected daily output for 8-pair tank configuration, operating 10 h/day high output and 14 h/day low output (kW h)	1496
Projected hourly output for 8-pair tank configuration, for 24 h/day steady operation (kW h)	2112
Revenue per day at \$110/MW h for 10 h/day high output and 14 h/day low output (\$)	164.57
Revenue per day at \$110/MW h for 24 h/day steady operation (\$)	232.33
Revenue per annum at \$110/MW h for 24 h steady operation (\$)	84,800

* The heat transfer rate is evaluated as $Q = UA\Delta T$.

In the lab prototype, the current experimental setup includes a thermal source, thermal sink, four pressure vessels (each containing a helical coil heat exchanger), and a system of pipes and valves to direct the flows. Mechanical energy is extracted from the pressure differential by means of the piston assembly. The device is comprised of two sealed compartments and a rack and pinion gear assembly.

A pressure differential between the two sealed compartments causes the piston to move, which in turn rotates the gear. By directing the flow of pressurized gases from two pressure vessels into the appropriate sealed compartments, mechanical energy is produced in the gear system of the lab prototype.

The model is used to predict the power output of the device. Results are obtained on a per-stroke basis and simulations are performed for several pressure vessel sizes and initial pressures. For all cases, a time delay of 0.2 s per stroke is included, accounting for the time required for the valve configuration to change. The results are summarized in Tables 14.1–14.3. Based on the results of the thermodynamic models, several observations can be made regarding the performance of the device. Concerning the heat exchangers, the induced pressure difference resulting from heating or cooling in the pressure vessels increases significantly when the magnitude of the difference between the heat exchanger working fluid temperature and the gas temperature increases. By increasing the temperature difference between the water and gas, a significant pressure difference can be generated. Using the parameters of the current test unit with an initial pressure of 164.7 psia, a source temperature of 113°F and a sink temperature of 50°F, a pressure differential of 14.6 psia between the two pressure vessels can be generated after a period of 60 s.

The model can be extended to higher or lower temperature differences. For the temperature differences possible with cogeneration or solar thermal panels as heat sources, for example, large temperature differences can be generated. With a source temperature of 167°F and a sink temperature of 32°F, a pressure difference of 33.7 psia is predicted.

Using the heat exchanger model to predict thermal performance with higher initial pressures also yields promising results. By increasing the initial pressure in the tank, there is a dramatic increase in the induced pressure difference, due to a temperature difference arising over a 60 s period. This result demonstrates that system operation at a higher initial pressure will produce a significantly larger pressure difference, and thus a larger energy output. The model underestimates the time required between each stroke, meaning it could take longer for the pressure difference between vessels to equalize than predicted. In an actual system, some energy is dissipated within the flywheel, thereby allowing for a slight increase in delay between strokes.

The results demonstrate the benefit of operating the system at higher pressures. The total power output of the system increases significantly if the initial pressure in the tank is increased. With higher initial pressures, a greater pressure difference results from the same temperature difference. This result has important implications for the design of future generation units, as increasing the initial pres-

sure would increase the power output of the system, although equipment costs would also be increased.

Figure 14.5 illustrates a multiple pair configuration with piston assemblies for each pair of tanks. This design overcomes the stroke disparity of the single piston design between tank changes. Each pair of tanks in the multiple unit design will have sequential stroke timing and be connected to a common driveshaft which will result in a steady stroke power value to the flywheel and ultimately the generator.

By supporting the use of renewable energy resources and waste heat and a reduction in fossil fuel utilization, the device has the potential to reduce greenhouse gas emissions significantly. Hence, the device may serve a meaningful role in efforts to mitigate global warming and climate change.

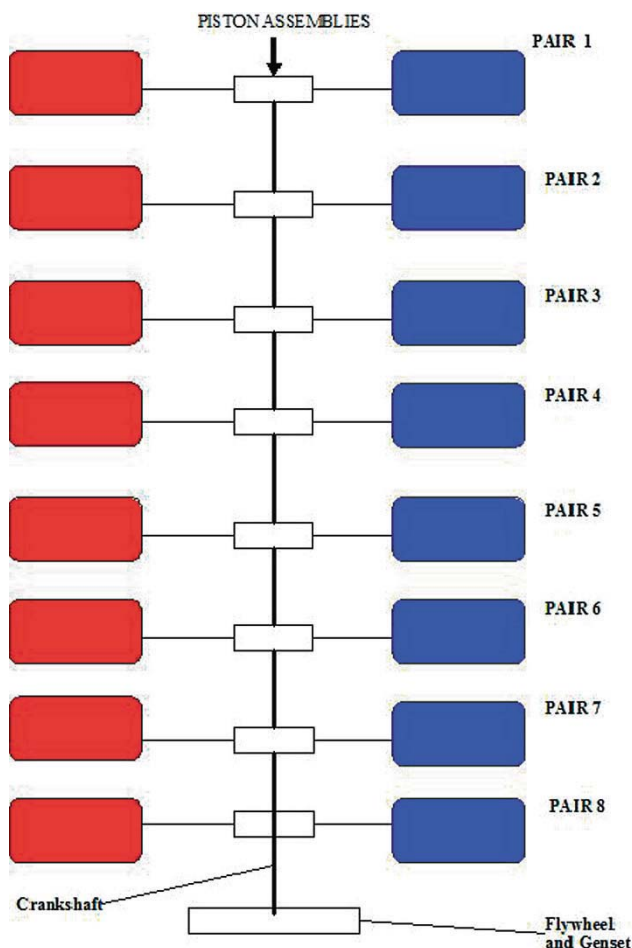


Fig. 14.5 Multiple tank configuration.

14.4 Conclusions

The performance and operation are investigated for a Marnoch thermal energy conversion device, a novel heat engine for converting heat to electricity. A thermodynamic model was developed to predict the performance of the system and used to generate performance results over a range of operating pressures and time intervals.

The performance results for the device are promising, suggesting significant potential exists for higher power output at higher pressures within the air vessels. A control system used for automation of the valves and flow exchange between the pressure vessels is able to initialize the device, monitor operations, detect pneumatic, thermal, or other changes, make operating decisions, and control peripherals automatically.

The Marnoch thermal energy conversion device could play a meaningful role as a device for mitigating global warming. This is because the device possesses significant potential to facilitate the utilization of renewable energy resources and waste heat, and thereby to reduce fossil fuel use and corresponding greenhouse gas emissions. Hence, the device may assist in combating climate change.

Acknowledgments

Financial support for this research from the Natural Sciences and Engineering Research Council of Canada, as well as the NRC Industrial Research Assistance Program, is gratefully acknowledged.

References

- Armstrong, A, Haseen, F, Marnoch, I, Weston, J, Naterer, GF, Lu, L, Rosen, MA, Dincer, I (2007) Thermodynamic optimization and control of a Marnoch thermal energy conversion device. *Proc. 21st Canadian Congress of Applied Mechanics*, Toronto, Ontario, pp. 284–285.
- Cengel YA, Turner RH (2005) *Fundamentals of Thermal Fluid Science*, 2nd edition. New York: McGraw Hill.
- Kern, DQ (1950) *Process Heat Transfer*. New York: McGraw Hill, pp. 216–217.
- Mulley, R (2004) *Flow of Industrial Fluids-Theory and Equations*. Boca Raton, FL: CRC Press, p. 407.

Exergy Analysis of Food Drying Processes

Neslihan Colak, Mustafa T. Balta, Filiz İçier, Ebru Kuzgunkaya, Arif Hepbasli and Zafer Erbay

15.1 Introduction

It is well known that micro-level system parameters may have some great impact on macro-level energy aspects, the environment, and sustainability. Of course, if one wants to approach these thermodynamically, there are two ways: energy analysis through the first law of thermodynamics and exergy analysis through the second law of thermodynamics. Exergy analysis is an essential tool to expose the impacts of a power generating device on exergy-based sustainability; sustainability is necessary to overcome current ecological, economic, and developmental problems (Dincer and Rosen, 2005). In this regard, some new exergy-based sustainability parameters for a PEM fuel cell have been developed and studied parametrically to investigate how they will help measure the level of environmental impact and sustainable development (Midilli and Dincer, 2009). These types of parameters may also be applied to other energy-related systems.

Drying has been used worldwide for centuries to preserve different food and agricultural products. Nowadays, the drying process is one of the major procedures of food preservation. The basic target of food dehydration is to remove water to a final concentration, which assures microbial spoilage of the product and minimizes chemical and physical changes of the food during storage (Crapiste and Rotstein, 1997). Drying is an energy-intensive operation consuming 9–25% of national energy in the developed countries (Mujumdar, 1995). In many practical applications, drying is a process that requires high-energy input because of the high latent heat of water evaporation and relatively low-energy efficiency of industrial dryers.

For development of sustainable energy, three important technological changes have been required: energy economies on the demand side, efficiency improvements in the energy production, and renewing of fossil fuels by various sources of renewable energy.

Heat pumps (HPs) are devices for raising the temperature of low grade heat energy to a more useful level using a relatively small amount of high grade energy. Using HPs in convective hot air dryers has been recognized as an ideal area for HP applications (Schmidt et al., 1998). The energy efficiencies of conventional dryers are generally very low, a value of 35% being representative of the upper performance range (Lawton, 1978). Strommen et al. (2002) found that HPDs consume between 60% and 80% less energy than conventional dryers operating at the same temperature. This makes such dryers a feasible option for users who are not satisfied with the comparatively high energy consumption of directly heated dryers (Schmidt et al., 1998).

The most effective way to reduce energy demand is to use energy more efficiently. In this regard, exergy analysis, based on the second law of thermodynamics, successfully identifies the magnitudes and locations of energy degradations, inefficient uses of natural resources, and the pollution of the environment by means of waste energy (Kotas, 1985). If the less energy goes into production and marketing of foods, the less global warming pollution is created.

Exergy analysis evaluates the available energy at different points in a system. In the design of a system, the exergy method can be used to extract useful information to aid the task of choosing the most appropriate component design and operation procedure. This information is much more effective in determining the plant and operation costs, energy conservation, fuel versatility, and pollution levels. Bejan (1982) pointed out that the minimization of lost work in the system would provide the most efficient system. Moreover, Bejan (1988) and Szargut *et al.* (1988) emphasized that the effect of operating conditions on the system efficiency was much stronger for lost-work analysis than it is for the heat balance analysis. This explanation is required to determine the inefficient processes, equipment, or operating procedures during drying. For evaluating the performance of food drying systems, energy analysis method has been widely used, while the studies on exergy analysis are relatively few in number.

Fresh fruits and vegetables have both important nutritional and economic value. Recently, the market demand for naturally processed fruits and vegetables has undergone an important rise because of increasing health-conscious consumers. In vegetables broccoli is described as a vegetable with a high nutritional value due to its important content of vitamins, antioxidants, and anti-carcinogenic compounds (Nestle, 1998). Broccoli dehydration has not been investigated to a great extent and a few data are available in the literature (Bon et al., 1997; Simal et al., 1998; Mulet et al., 1999; Sanjuan et al., 2001; Mrkic et al., 2007). Annual broccoli production of Turkey increased 90.3% from 2005 to 2006 and reached 16,178 tonnes (Turkish Statistical Institute, 2006). It is estimated that production of this vegetable will rise gradually in Turkey and the world.

In this study, exergy analysis of food drying processes is presented and applied to broccoli drying process in a heat pump-driven conveyor dryer as a case study. Broccoli florets were dried at 45°C, 50°C, or 55°C drying air temperatures and 0.5 m/s, 1 m/s, or 1.5 m/s, drying air velocities. Effects of temperatures and mass flow rates on the exergy losses, exergy efficiencies, and improvement potentials of the drying process were investigated.

15.2 Case Study: Broccoli Drying

Fresh broccoli (*Brassica oleracea*) was purchased from a local market in Izmir, Turkey. It was processed within 24 h. Broccoli samples were washed with water, and then the excess water on the surface of broccoli was removed with filter paper. Afterward, florets of broccoli were separated.

Broccoli florets were dried in a heat pump conveyor dryer designed and constructed in the Department of Mechanical Engineering, Faculty of Engineering, Ege University, Izmir, Turkey, shown schematically in Fig. 15.1. Drying system consists of two main parts: (i) heat pump and (ii) drying chamber. The air was heated by heat pump system that included a scroll compressor, two condenser (an internal and an external ones), expansion valve, evaporator, and a heat recovery unit and air temperature was controlled by a control unit. R407C was used as refrigerant in heat pump system. The drying air velocity was regulated by a fan and fan speed control unit and drying air was recycled. Drying compartment dimensions were 3 m × 1 m × 1 m and drying material was moved by a conveyor band system worked by a motor.

15.2.1 Drying procedure and measurements

After the dryer reached steady-state conditions, broccoli florets were spread onto a couple of trays as thin layer settled onto the conveyor band. Drying experiments were carried out at the drying air temperatures of 45°C, 50°C, or 55°C, and drying air velocities of 0.5 m/s, 1.0 m/s, or 1.5 m/s, respectively.

Moisture loss was recorded at 30 min intervals during drying process for determination of drying curves. The sample moisture content was determined with vacuum-oven method (AOAC, 1990). The initial moisture content of the broccoli floret samples was determined 86.44% on a wet basis. The composition of broccoli florets used in this study is given in Table 15.1 (Anon., 2008).

Table 15.1 Composition of broccoli florets (Anon, 2008).

Component	Amount (%)
Water	86.44
Protein	2.91
Oil	0.38
Carbohydrate	6.69
Fiber	2.68
Ash	0.90

Humidities, temperatures, and velocities were measured in drying chamber with robust humidity probes (Testo, 0636.2140, Freiburg, Germany), vane/temperature probes (Testo, 0635.9540, Freiburg, Germany), professional telescopic handle for plug-in vane probes (Testo, 0430.0941, Freiburg, Germany), respectively. Measurements of drying air temperature, velocity, and relative humidity were recorded at inlet and outlet holes at every 10 min. The surface temperature of drying material was measured by an infrared thermometer (Testo 525-T2, infrared

thermometer with laser sighting). The temperature of the drying chamber walls was measured with a digital multimeter (METEX ME-32) during drying process. A digital balance (Scaltec SBA 61, Goettingen, Germany) was used to measure the weight loss of sample during drying experiments. The ambient temperature and the relative humidity were also measured and recorded. Pressures and temperatures of the refrigerant were measured with pressure probes (Testo, low/high-pressure probes, 0638.01941) and surface temperature probes (Testo, temperature probes, 0628.0019), respectively. All measured values were observed and recorded with a multi-function instrument (Testo 350-XL/454, control unit, Freiburg, Germany) and loggers. The schematic diagram of the drying process and measurements were shown in Fig. 15.1.

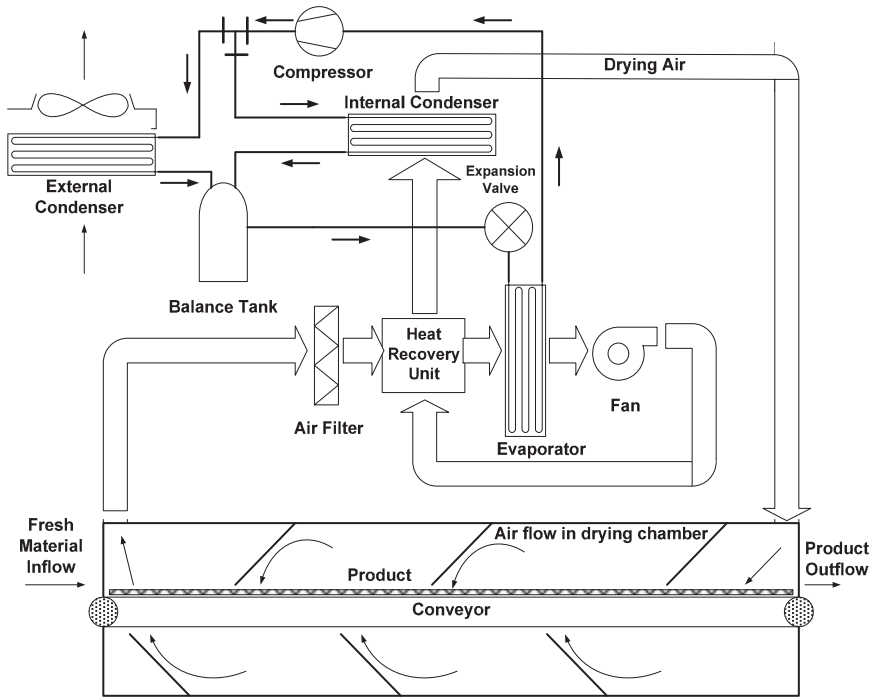


Fig. 15.1 Schematic illustration of heat pump conveyor dryer system.

15.2.2 Determination of thermal properties of food and drying air

Specific heat of food materials has been determined experimentally by several methods, including the method of mixtures, method of guard plate, and using a differential scanning calorimeter (Choi and Okos, 1986; Singh, 1992). Choi and Okos (1986) have suggested the following model for the specific heat for foods:

$$C = \sum C_i X_i \quad (15.1)$$

with the specific heat of pure components given as

$$C = C_w X_w + C_p X_p + C_f X_f + C_c X_c + C_{fi} X_{fi} + C_{ash} X_{ash} \quad (15.2)$$

$$C_w = 4.1762 - 9.0864 \times 10^{-5} T + 5.4731 \times 10^{-6} T^2 \quad \text{for water} \quad (15.3)$$

$$C_p = 2.0082 + 1.2089 \times 10^{-3} T - 1.3129 \times 10^{-6} T^2 \quad \text{for protein} \quad (15.4)$$

$$C_f = 1.9842 + 1.4733 \times 10^{-3} T - 4.8008 \times 10^{-6} T^2 \quad \text{for fat} \quad (15.5)$$

$$C_c = 1.5488 + 1.9625 \times 10^{-3} T - 5.9399 \times 10^{-6} T^2 \quad \text{for carbohydrate} \quad (15.6)$$

$$C_{fi} = 1.8459 + 1.8306 \times 10^{-3} T - 4.6509 \times 10^{-6} T^2 \quad \text{for fiber} \quad (15.7)$$

$$C_{ash} = 1.0926 + 1.8896 \times 10^{-3} T - 3.6817 \times 10^{-6} T^2 \quad \text{for ash} \quad (15.8)$$

where T is the temperature of food; the units of the specific heats and temperatures are kJ/kg °C and °C, respectively. The composition of the broccoli used in this study was given in Table 15.1.

The above theoretical models are based on proportions by compositions. There is deviation between the experimental values and the above model due to (1) specific heat of the component phases varied with the source or origin, (2) bound water or unfrozen water has a different specific heat than bulk water, (3) excess specific heat due to the interaction of the component phases (Rahman, 1995).

The enthalpy of drying air can be written as

$$h_{da} = c_{Pda} T + \omega h_{sat @ T} \quad (15.9)$$

where c_{Pda} defines the specific heat of drying air, T the drying air temperature, ω the specific humidity, and $h_{sat @ T}$ is the enthalpy of the saturated vapor.

The enthalpy of broccoli can be written in terms of specific heat as (Rahman, 1995)

$$h = \sum h_i X_i = \sum \int_{T_1}^{T_2} C_i X_i dT \quad (15.10)$$

where h is the enthalpy of the individual food components and X_i is the mass fraction of food components.

The specific entropies of broccoli are given as (Syahrul et al., 2002)

$$s_{m1} - s_{m0} = C_{m1} \ln(T_{m1} / T_{m0}) \quad (15.11)$$

$$s_{m2} - s_{m0} = C_{m2} \ln(T_{m2} / T_{m0}) \quad (15.12)$$

where T_{m0} was the reference temperature, which was taken to be 23°C in this study

and T_{m2} was the temperature of food item in °C.

To evaluate the entropy of moist air, the contribution of each component in the mixture is determined at the mixture temperature and the partial pressure of the component (Syahrul et al, 2002):

$$s_{da} = s_a - R_a \ln \frac{P_a}{P_0} + w \left(s_v - R_v \ln \frac{P_v}{P_0} \right) \quad (15.13)$$

15.2.3 Energy and exergy balance equations

For a general steady-state, steady-flow process, the four balance equations are applied to find the work and heat interactions, the rate of exergy decrease, the rate of irreversibility, the energy and exergy efficiencies (Kotas, 1985).

The general energy balance can be expressed as

$$\sum \dot{E}_{in} = \sum \dot{E}_{out} \quad \text{or} \quad \dot{Q} + \sum \dot{m}_{in} \dot{h}_{in} = \dot{W} + \sum \dot{m}_{out} \dot{h}_{out} \quad (15.14)$$

where $\dot{m}$ is the mass flow rate and the subscript *in* stands for inlet and *out* for outlet, $\dot{E}_{in}$ is the rate of net energy transfer in, $\dot{E}_{out}$ is the rate of net energy transfer out by heat, work, and mass, $\dot{Q} = \dot{Q}_{net,in} = \dot{Q}_{in} - \dot{Q}_{out}$ is the rate of net heat input, $\dot{W} = \dot{W}_{net,out} = \dot{W}_{out} - \dot{W}_{in}$ is the rate of net work output, and h is the enthalpy per unit mass.

The general exergy balance can be expressed in the rate form as

$$\sum \dot{E}x_{in} - \sum \dot{E}x_{out} = \sum \dot{E}x_{dest} \quad \text{or} \quad \sum \left(1 - \frac{T_0}{T_k} \right) \dot{Q}_k - \dot{W} + \sum \dot{m}_{in} \psi - \sum \dot{m}_{out} \psi = \dot{E}x_{dest} \quad (15.15)$$

$$\psi = (h - h_0) - T_0 (s - s_0) \quad (15.16)$$

where $\dot{Q}_k$ is the heat transfer rate through the boundary at temperature T_k at location k , $\dot{W}$ is the work rate, ψ is the flow exergy, s is the specific entropy, and the subscript zero indicates properties at the dead state of P_0 and T_0 .

The exergy destroyed or the irreversibility may be expressed as follows:

$$\dot{I} = \dot{E}x_{dest} = T_0 \dot{S}_{gen} \quad (15.17)$$

where $\dot{S}_{gen}$ is the rate of entropy.

Van Gool (1997) has also proposed that maximum improvement in the exergy efficiency for a process or system is obviously achieved when the exergy loss

or irreversibility ($\dot{Ex}_{in} - \dot{Ex}_{out}$) is minimized. Consequently, he suggested that it is useful to employ the concept of an exergetic '*improvement potential rate*' when analyzing different processes or sectors of the economy. This improvement potential in the rate form, denoted $\dot{IP}$, is given as (Hammond and Stapleton, 2001)

$$\dot{IP} = (1 - \eta)(\dot{Ex}_{in} - \dot{Ex}_{out}) \quad (15.18)$$

Total exergy inflow, outflow, and losses of the tray and the drying chamber were estimated based on the exergy analysis, which determined the exergy values at steady-state points and the reason of exergy variation for the process.

Exergy analysis was performed for conveyor dryer framed with cutting lines in Fig. 15.1. Exergy balance equation for the conveyor dryer was

$$\dot{Ex}_{m2} - \dot{Ex}_{m1} = \dot{Ex}_{da1} - \dot{Ex}_{da2} + \dot{Ex}_{evap} - \dot{Ex}_{loss} - \dot{Ex}_{dest} \quad (15.19)$$

where $\dot{Ex}_m$ was the exergy transfer rate of the material, $\dot{Ex}_{da}$ was the exergy transfer rate of the drying air, $\dot{Ex}_{evap}$ was the exergy evaporation rate of the dryer, $\dot{Ex}_{loss}$ was the rate of exergy loss in the surrounding, and $\dot{Ex}_D$ was the rate of exergy destruction in the dryer.

The specific exergies at inlets (ψ_{m1}) and outlets (ψ_{m2}) of the material were given as follows (Syahrul et al., 2002):

$$\psi_{m1} = (h_{m1} - h_{m0}) - T_0(s_{m1} - s_{m0}) \quad (15.20)$$

$$\psi_{m2} = (h_{m2} - h_{m0}) - T_0(s_{m2} - s_{m0}) \quad (15.21)$$

Specific exergies with a stream of drying air entering and leaving the dryer were as follows (Syahrul et al., 2002):

$$\psi_{da1} = (h_1 - h_0) - T_0(s_1 - s_0) \quad (15.22)$$

$$\psi_{da2} = (h_2 - h_0) - T_0(s_2 - s_0) \quad (15.23)$$

where ψ_{da1} and ψ_{da2} were the specific exergy transfers at inlets and outlets, respectively; h_0 , s_0 denoted the specific enthalpy and specific entropy at the temperature of dead state (T_0), respectively; h_1 and s_1 denoted the specific enthalpy and the specific entropy at the temperature of drying air entering the dryer (T_{da1}), respectively; h_2 and s_2 denoted the specific enthalpy and the specific entropy of drying air at the temperature of the drying air exiting, respectively. The potential and kinetic exergies were negligible.

The heat transfer rate due to phase change was (Syahrul et al., 2002)

$$\dot{Q}_{evap} = \dot{m}_w \cdot h_{fg} \quad (15.24)$$

The rate of exergy transfer due to evaporation of the dryer was (Syahrul et al., 2002)

$$\dot{Ex}_{evap} = \left[1 - \frac{T_0}{T_{m2}} \right] \dot{Q}_{evap} \quad (15.25)$$

Heat transfer rate to the environment was (Syahrul et al., 2002)

$$\dot{Q}_{loss} = \dot{Q}_{evap} - \dot{m}_1(h_{m2} - h_{m1}) + \dot{m}_{da}(h_{da1} - h_{da2}) \quad (15.26)$$

The following equation was used to calculate the rate of exergy loss to the surrounding, where T_b is the boundary temperature (Syahrul et al., 2002):

$$\dot{Ex}_{loss} = \left(1 - \frac{T_0}{T_b} \right) \dot{Q}_{loss} \quad (15.27)$$

The exergy efficiency of the dryer can be defined as the ratio of the product exergy to exergy inflow for the chamber. Thus, the general form of exergy efficiency was written as

$$\eta_{ex} = 1 - \frac{\dot{Ex}_{loss}}{\dot{Ex}_{in}} \quad (15.28)$$

15.2.4 Results for the case study

In this section, effects of the drying air temperature and the mass flow rate of drying air on the system performance were discussed. Specific heats, enthalpies, and entropies of the broccoli florets were calculated from Eqs. (15.2), (15.10), and (15.11–15.12), respectively. The properties of the inlet and outlet air were calculated from the computer aided thermodynamic tables. The reference (dead state) temperature for exergy analyses was taken to be 23°C. Exergy analyses of single-layer drying process of broccoli florets in a heat pump conveyor dryer were performed by using the data obtained from the experiments (Table 15.2).

The variations of exergy efficiency and improvement potentials with drying air temperatures at various drying air velocities were illustrated in Figs. 15.2 and 15.3, respectively. As can be seen in Fig. 15.2, exergy efficiency of the drying chamber decreased as the drying air temperature increased at all velocities. When the air temperature was 45°C and velocity was 1.5 m/s, exergy efficiency of the system was determined to be 76.58%. It was obvious from Fig. 15.3 that the improvement potential rate of the drying chamber at 55°C and 0.5 m/s was found to be 13.86 kW as minimum value. Also, improvement potential value for 1.5 m/s was lower than the other velocities at 45°C.

Figures 15.4 and 15.5 show the exergy loss and destructions changing with drying air temperatures at various drying air velocities.

Table 15.2 Data from the experiments and calculations made.

T_{dal} (°C)	V (m/s)	ω_1 (g/g)	ω_2 (g/g)	h_1 (kJ/kg)	H_2 (kJ/kg)	S_1 (kW/°C)	S_2 (kW/°C)	C_{m1} (kJ/kg °C)	C_{m2} (kJ/kg °C)
45	0.5	0.0068	0.0073	337.278	336.041	6.914	6.919	3.845	2.096
	1.0	0.0075	0.0082	339.087	338.364	6.919	6.926	3.845	2.096
	1.5	0.0068	0.0073	336.771	335.634	6.915	6.919	3.845	2.096
50	0.5	0.0076	0.0078	343.599	339.455	6.919	6.922	3.845	2.101
	1.0	0.0082	0.0086	346.071	343.248	6.923	6.927	3.845	2.101
	1.5	0.0084	0.0089	345.673	343.724	6.926	6.930	3.845	2.101
55	0.5	0.0090	0.0097	351.191	348.642	6.929	6.935	3.845	2.106
	1.0	0.0094	0.0097	351.731	348.533	6.931	6.935	3.845	2.106
	1.5	0.0101	0.0109	355.480	353.985	6.936	6.943	3.845	2.106

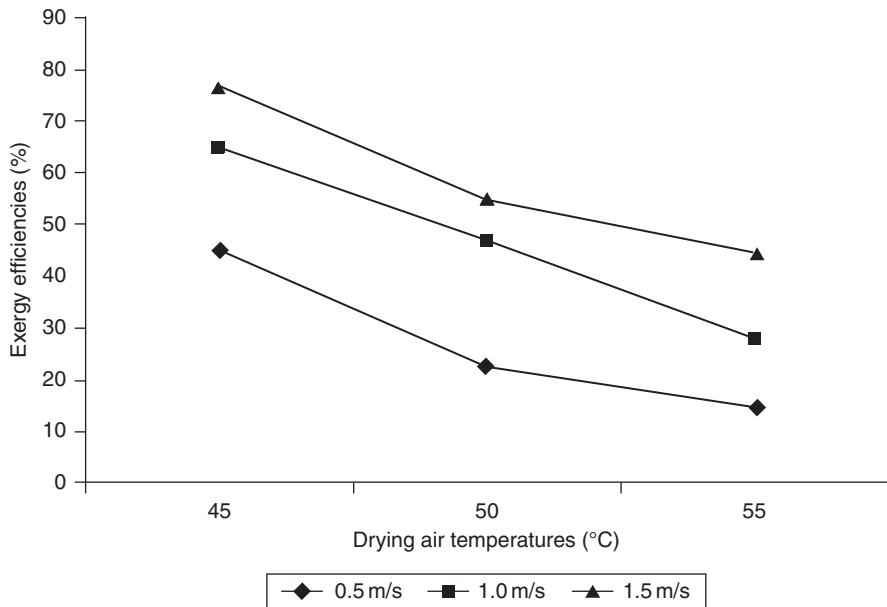


Fig. 15.2 The variations of exergy efficiencies with drying air temperatures at different drying air velocities.

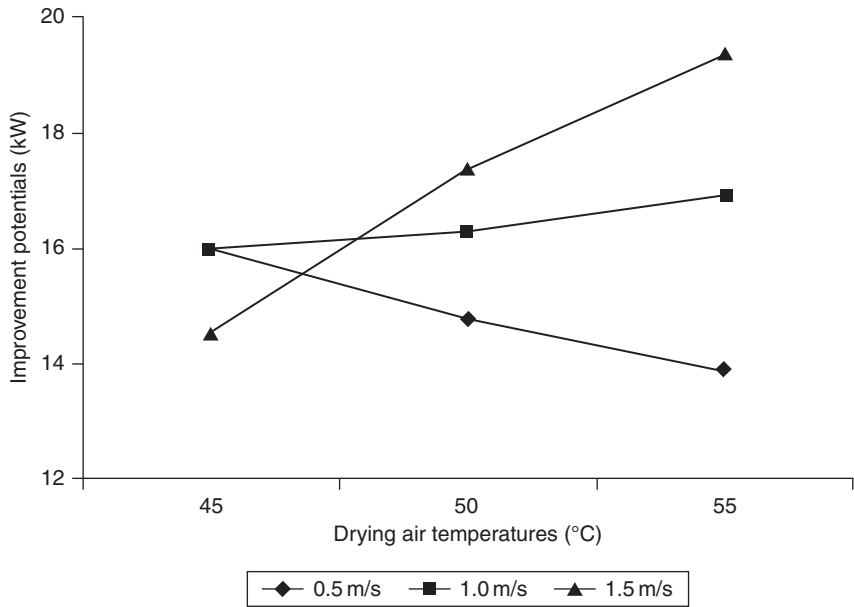


Fig. 15.3 The variations of improvement potentials with drying air temperatures at different drying air velocities.

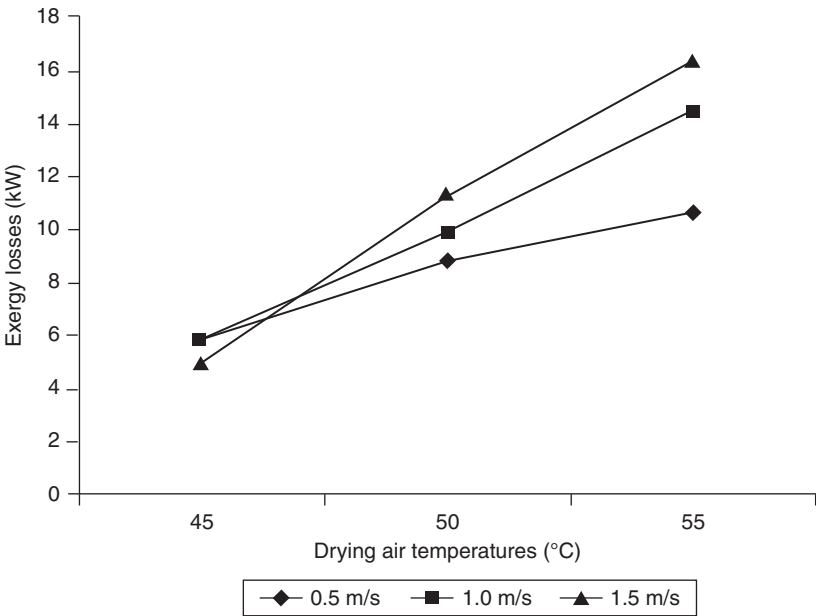


Fig. 15.4 Variations of exergy losses with drying air temperatures at different air velocities.

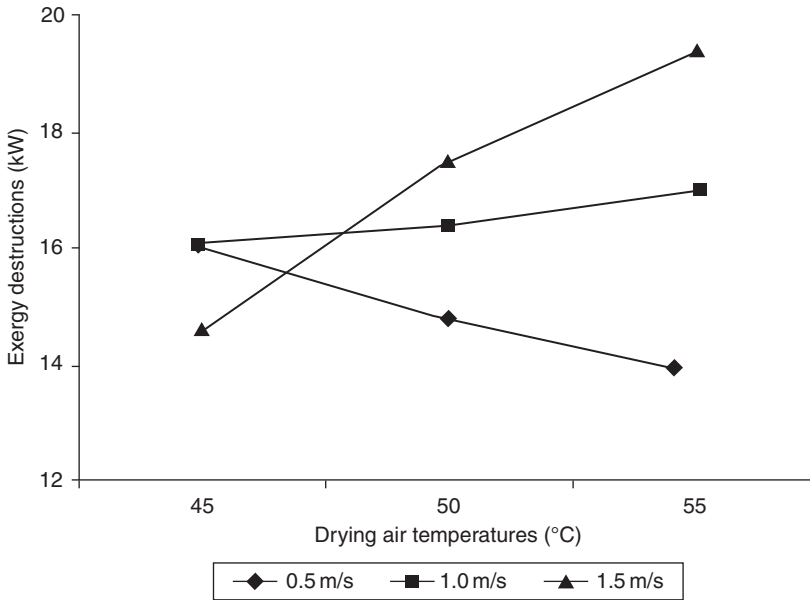


Fig. 15.5 Variations of exergy destructions with drying air temperatures at different air velocities.

15.3 Conclusions

For better environment and sustainability it is really important to improve food drying systems and processes and their efficiencies. This chapter presents an exergy analysis of drying process of broccoli florets in a heat pump conveyor dryer. Some concluding remarks are drawn from this study as follows:

- Exergy efficiency and the improvement potential rate of the drying chamber vary from 14.79% to 76.58% and 13.86 kW to 19.29 kW, respectively.
- Exergy loss of this system increases with raising the temperatures of drying air, when exergy destruction was decreased at 0.5 m/s drying air velocity.
- The maximum exergy efficiency value becomes 76.58% at a drying air temperature of 45°C and a velocity of 1.5 m/s.

Acknowledgments

The authors are grateful for the financial support provided for the project entitled “Design, test and performance evaluation of a gas engine driven solar assisted band conveyor heat pump drying system” under Project No. 106M482 by The Scientific and Technological Research Council of Turkey (TUBITAK).

Nomenclature

C	Specific heat (kJ/kg °C)
$\dot{E}$	Net energy transfer rate (kW)
$\dot{E}x$	Exergy rate (kW)
h	Specific enthalpy (kJ/kg)
$\dot{I}P$	Rate of improvement potential (kW)
$\dot{Q}$	Heat transfer rate (kW)
$\dot{m}$	Mass flow rate (kg/s)
P	Pressure (kPa)
R	Gas constant (J/kg °C)
$\dot{S}$	Entropy rate (kJ/s °C)
s	Specific entropy (kJ/kg °C)
T	Temperature (°C)
$\dot{W}$	Work rate (kW)
X	Weight fraction of dry matter
V	Air velocity (kg/s)
Greek Symbols	
η	Exergy efficiency
ψ	Specific flow exergy (kJ/kg)
ω	Specific humidity (g/g)
Subscripts	
0	Restricted dead state
a	Air
b	Boundary
c	Carbohydrate
$dest$	Destroyed, destruction
$evap$	Evaporation
ex	Exergetic, exergy
f	Fat
fi	Fiber
gen	Generation
p	Protein
v	Vapor
w	Water
da	Drying air
m	Material
$sat@T$	Saturated

References

- Anon (2008) www.nal.usda.gov/fnic/foodcomp. Accessed on May 20, 2008.
- AOAC (1990) Official Method of Analysis. Association of Official Analytical Chemist, Washington, DC, (No: 934.06).
- Bejan, A. (1982) *Entropy Generation Through Heat and Fluid Flow*, Wiley, New York, NY.
- Bejan, A. (1988) *Advanced Engineering Thermodynamics*, Wiley, New York, NY.
- Bon, J, Simal, S, Rossello, C, Mulet, A (1997) Drying characteristics of hemispherical solids. *Journal of Food Engineering* 34: 109–122.
- Choi, Y, Okos, MR (1986) Effects of temperature and composition on the thermal properties of foods. *Food Engineering and Process Applications*, Vol. 1, Transport Phenomenon. Edited by Maguer, L., Jelen, P. Elsevier, New York, 93–101.
- Crapiste, GH, Rotstein, E (1997) Design and performance evaluation of dryers. *Handbook of Food Engineering Practice*. Edited by K.J. Valentas, E. Rotstein and R.P. Singh, CRC Press, New York, 125–166.
- Dincer, I, Rosen, MA (2005) Thermodynamic aspects of renewables and sustainable development. *Renewable and Sustainable Energy Reviews* 9(2): 169–189.
- Hammond, GP, Stapleton, AJ (2001) Exergy analysis of the United Kingdom energy system. *Proceedings of the Institution of Mechanical Engineers* 215(2): 141–162.
- Kotas, TJ (1985) *The Exergy Method of Thermal Plant Analysis*. Essex, Brendon Ltd.
- Lawton, J (1978) Drying: the role of heat pumps and electromagnetic fields. *Physics Technology* 9: 214–220.
- Midilli, A, Dincer, I (2009) Development of some exergetic parameters for PEM fuel cells for measuring environmental impact and sustainability. In Press: *International Journal of Hydrogen Energy*. doi:10.1016/j.ijhydene.2009.02.066.
- Mrkic, V, Ukrainczyk, M, Tripalo, B (2007) Applicability of moisture transfer Bi–Di correlation for convective drying of broccoli. *Journal of Food Engineering* 79: 640–646.
- Mujumdar, AS (1995) *Handbook of Industrial Drying*, Vol. 2, Marcel Dekker Inc., New York.
- Mulet, A, Sanju'an, N, Bon, J, Simal, S (1999) Drying model for highly porous hemispherical bodies. *European Food Research and Technology* 210: 80–83.
- Nestle, M (1998) Broccoli sprout in cancer prevention. *Nutrition Reviews* 56: 127–130.
- Rahman, S (1995) *Food Properties Handbook*. CRC Press, US, 225–271.
- Sanjuan, N, Clemente, G, Bon, J, Mulet, A (2001) The effect of blanching on the quality of dehydrated broccoli florets. *European Food Research Technology* 213: 474–479.
- Schmidt, EL, Klocker, K, Flacke, N, Steimle, F (1998) Applying the transcritical CO₂ process to a drying heat pump. *International Journal of Refrigeration* 21(3): 202–211.
- Simal, S, Rossello, C, Berna, A, Mulet, A (1998) Drying of shrinking cylinder-shaped bodies. *Journal of Food Engineering* 37: 423–435.
- Singh, RP (1992) *Handbook of Food Engineering*, Edited by Heldman DR, Lund DB. Marcel Dekker Inc: New York; 247–276.
- Strommen, I, Eikevik, TM, Alves-Filho, O, Syverud, K, Jonassen, O (2002) Low temperature drying with heat pumps new generations of high quality dried products. 13th International Drying Symposium.
- Syahrul, S, Hamdullahpur, F, Dincer, I (2002) Exergy analysis of fluidised bed drying of moist particles. *Exergy, an International Journal* 2: 87–98.
- Szargut, J, Morris, DR, Stewart, FR (1988) *Exergy Analysis of Thermal, Chemical and Metallurgical Processes*, Taylor & Francis, New York.
- Van Gool, W (1997) Energy policy: fairly tales and factualities. In: *Innovation and Technology-Strategies and Policies*, ODD. Edited by Soares, A. Martins da Cruz, G. Costa Pereira, IMRT. Soares and AJPS. Kluwer, Dordrecht, 93–105.

Carbon Sequestration: A Comparative Analysis

Christopher J. Koroneos and Dimitrios C. Rovas

16.1 Introduction

Carbon sequestration refers to the provision and safe storage of carbon dioxide that otherwise would be emitted to the atmosphere. The basic idea is the retention, isolation, and final storage of the produced carbon dioxide, utilizing biological, chemical, or mechanical routes. Some methods retain the carbon from the exhaust gas before it is emitted. The retained carbon then can be deposited in underground geological repositories or in the oceans. Additionally, chemical and biological processes can transform carbon into solid products or they can enhance the natural terrestrial cycle. Carbon sequestration can be a useful tool in the minimization of the carbon emissions from fossil fuel combustion and it can be significant in the stabilization of the atmospheric CO₂ concentration.

The dominant carbon sequestration methods are as follows:

- Ocean sequestration
- Land ecosystem sequestration
- Sequestration in geological repositories
- Advanced biological processes
- Advanced chemical processes

The carbon emitted to the atmosphere comes mainly from the combustion of fossil fuels. In order to develop a feasible and economical sequestration methodology, there must be significant alteration done to the existing energy system.

There are four major areas of interest in the development of an efficient carbon sequestration system: The carbon flow, the environmental storage, the existing scientific knowledge, and the fossil fuel combustion. The utilization and comparison of those areas would provide the most efficient carbon sequestration system which will lead to the capture and transportation of carbon, the carbon deposition, the advanced technologies, and the terrestrial carbon cycle (Fig. 16.1).

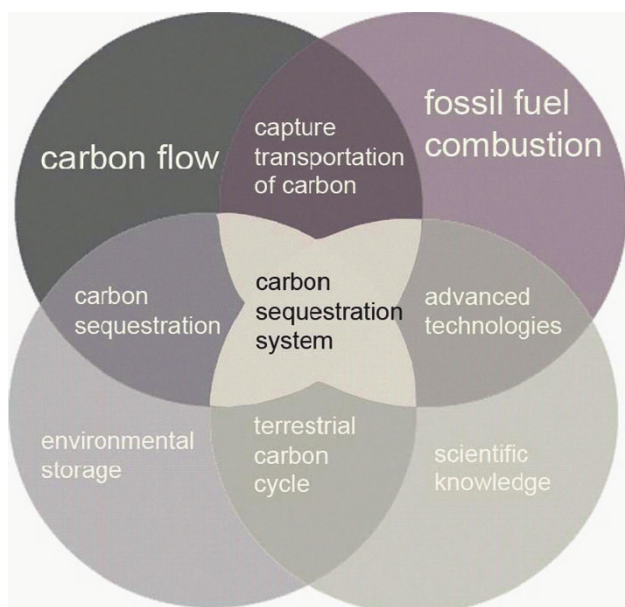


Fig 16.1 The development of an efficient carbon sequestration model.

16.2 Carbon Capture

The scope of carbon capture is the carbon isolation and its storage in such a way as to allow its further treatment. The technologies utilized depend on the carbon source and form, and its compatibility with the sequestration method. The known carbon capture techniques are the following:

- Chemical absorption utilizing solvents
- Physical absorption on solids
- Low-temperature distillation
- Gas separation films
- Mineralization and biomineralization
- Germination–vegetation

These techniques are mentioned due to their simplicity, their low environmental burden, and their relative low cost.

16.2.1 Chemical absorption through solvents

Carbon can be captured from a gas flow, with physical or chemical absorption techniques, utilizing solvents. This process can easily be modeled using Henry's law. CO_2 is an acidic gas, thus its chemical absorption is depending on neutralization reaction using base solvent. The most common solvents utilized are as follows: alcaolamines, such as monoethalomine (MEA), diethelamine (DEA), and

methyldiethelamine (MDEA). Additionally, ammonia and superheated potassium carbonate can be used. The exhaust gases also contain SO_x , NO_x , O_2 , hydrocarbons, and molecules that affect the operation and the efficiency of the chemical absorption. There has to be a pretreatment stage of the exhaust gas, to minimize the content of these gases, which in turn will lead to an increase in the cost of the overall process.

Carbon capture through chemical absorption is a technique that is widely used commercially, especially in the hydrogen production industry, where the carbon is continuously emitted to the atmosphere. This technique is also used to capture CO_2 from biogas. It is important to take into consideration the fact that the absorption rate is not steady and it is strongly depended on the solvents, the CO_2 pressure, the temperature of the exhaust gas, etc. Chemical absorption technique needs further development.

16.2.2 Physical absorption on solids

Carbon capture can be done through physical absorption on large surface solids. Zeolites, for instance, are able to absorb efficiently gases such as steam, oxygen, and carbon. There are two dominant processes of physical absorption: the pressure swing absorption (PSA) and the thermal swing absorption (TSA). Both processes have high energy usage and high operational cost. Notwithstanding, the processes are commercially used in the hydrogen production industry.

16.2.3 Low-temperature distillation

Low-temperature distillation is commercially used for the liquefaction and capture of carbon from exhaust gases with high carbon content, over 90%. Low-temperature distillation is economically feasible for large-scale plants. The advantage of this process is that it produces liquid CO_2 that can be easily stored and transported. Among the disadvantages are the high energy use and the fact that the other gaseous components of the exhaust flow must have their cooling point above the operational temperature.

16.2.4 Gas separation films

Gas separation films are of many types. There are polymer films, palladium films, and inorganic porosity films, metal or ceramic. Their future potential is considered to be acceptable, although their total effectiveness is not proven. The diffusion mechanism that takes place is not unique and varies with the film type. The most efficient gas separation films are the inorganic films, which usually have great permeance and they can be able to operate in high pressure and temperature and in acidic environments. Additionally, they have a long life cycle and construction "flexibility," as they can be produced by a large number of materials and of different porosities. On the other hand, they are extremely costly and some of them are vulnerable due to the fact that they react with sulfur.

16.3 Ocean Sequestration

Ocean is considered to be a great storage facility for the carbon sequestration. Although the feasibility of this technique is not assured, there are two ocean sequestration methods under study: i) direct injection of CO_2 and ii) the iron fertilization.

The ocean carbon “intake” is considered to be around 2 ± 0.8 Gigatons Carbon (GtC) per year. There are thoughts that in the next 1000 years 90% of the today’s carbon emissions will be diffused into oceans. Although the oceans’ biomass represents almost 0.05% of the whole, it transforms annually, almost 50 GtC of inorganic carbon to organic. This process is often referred to as biological pump.

16.3.1 Direct injection

Direct injection starts with the CO_2 capture, continues with the carbon transportation, in tubes or tanks, and it ends up to the ocean sequestration. Carbon can be efficiently sequestered for a period of time of several hundreds of years. In order to achieve that, carbon must be liquefied. Carbon deposition takes place in depths beneath the thermocline; that is to say, depths greater than 1000 m. The technology is mature in order to proceed into a commercial implementation. There is a lack of knowledge of the impact on the climate change and the diversity of the biochemical cycle of the ocean.

There are several techniques in the implementation of the direct injection. There is medium-depth sequestration (1000–2000 m), high-depth sequestration (over 3000 m), sequestration on the bottom of the ocean, or sequestration at the undersea earths’ layer. Carbon sequestration can be done through dissolution or CO_2 hydrate formation, and its efficiency is depending on the actual depth and the injection point. The deeper the injection, the more efficient the sequestration (Fig. 16.2).

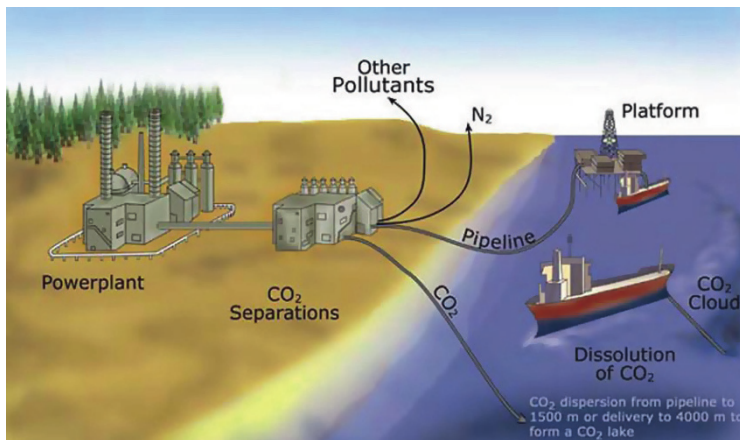


Fig. 16.2 Direct injection methods.

The dominant environmental impact is the lowering of the ocean pH, resulting from the CO_2 reaction with the ocean water, something that will affect the organisms that live in depths beneath 1000 m. The impact scale depends on the pH variation and the exposure duration. Additionally, there might be an impact on the microbial ecology of the ocean that may deflect biochemical reactions relative to the natural ocean carbon cycle. Regionally, these impacts could be minimized if the injection system is designed in a way that the injected carbon will disperse in a wider area and not to the injection point. The ocean sequestration is presented in Fig. 16.3.

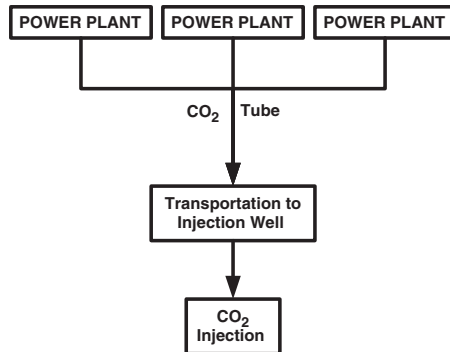


Fig. 16.3 Basic flow of ocean sequestration.

16.3.2 Reinforcement of natural sequestration – iron fertilization

In the natural ocean carbon cycle, the phytoplankton sequesters carbon into ocean. It is estimated that 70–80% of the carbon is recycled on the upper layer of the ocean while the rest is transported to the deep ocean where it is mineralized. Ocean fertilization with substances such as iron, nitrogen, and phosphorus is considered a carbon minimization technique due to the reinforcement of the biological cycle. At ocean areas with high nitrogen and phosphorus content, iron contents' increase or decrease can additionally increase or decrease the phytoplankton biomass. Initial studies have shown that iron fertilization on the upper ocean layer resulted in the phytoplankton increase. For instance, IRONEX I and IRONEX II experiments (US Department of Energy) have shown that the delivery of 500 kg of iron into 72 km in the Pacific Ocean resulted in a 30 times increase of the phytoplankton biomass. Low-scale iron fertilization is already used in the fish cultivation industries.

On the other hand, large-scale fertilization is not an easy task. There are technical and biological constraints in the implementation of this method, related to the lack of knowledge in specific areas. For instance, large-scale fertilization impact on the structure and operation of the seas' ecosystem is unknown. The alteration of the phytoplankton may affect the food net, and additionally, the eutrophication of the ocean is a possibility. If these restraints could be resolved, iron fertilization could be very promising for the future.

16.4 Land Ecosystem Sequestration

Carbon sequestration in land ecosystems refers to the clear abstraction of the atmospheric carbon and to the interception of CO₂ emission production from land ecosystems. Carbon sequestration can be accomplished mainly due to the stabilization of the photosynthesis, the alteration in land use, in a way that this will lead to lower carbon emissions and the use of the biomass as fuel. There are two major approaches on the land ecosystem sequestration: i) the ecosystems protection and maintenance and ii) the ecosystem administration in order to reinforce the carbon sequestration through the increase of the carbon content in the soil, in the subsoil, and in the biomass.

There are several techniques of increasing the carbon content in soil and in subsoil, the dominant of which are as follows: i) increase of carbon density in the soil, ii) increase of the mass and the depth of the trees roots, and iii) minimization of the decay rate. The above can be implemented through soil improvements such as fertilization, decay control, efficient watering, and soil modification, through the cultivation of specific crops, the biotechnology, and the molecular genetics.

16.5 Sequestration in Geological Repositories

Geological repositories such as aquifers, petroleum fields, and carbon deposits can be the first long-range opportunity for massive carbon sequestration. The knowledge is mature due to the former experience in oil and natural gas extraction, the underground aquifer management, and the natural gas storage. Carbon can be sequestered utilizing three basic mechanisms. To begin with, carbon can be “lodged” at its gaseous form, beneath a low permeability mineral, utilizing the same method used in natural gas storage. This technique is promising and it will, in a short term, be the dominant carbon sequestration method. Additionally, carbon can be dissolved in a liquid, such as oil. This is the basic operation for the majority of EOR oil extraction techniques. The oils’ viscosity is minimized; thus, oil flows more easily, entailing economic benefits. At last, carbon reacts directly or indirectly with mineral and the organic matter and becomes a part of their matrix. The formation of calcium, magnesium, and carbonates will be the initial mineral storage procedure. On the other hand, the carbon reaction with the minerals is of a low rate and not understandable in its entirety.

16.5.1 The capacity of the geological repositories

There are three types of geological repositories that are able to store large quantities of carbon:

- Active or depleted oil and gas reservoirs
- High-depth water formations and salt formations
- High-depth carbon plunge and coal-bed methane formations

The storage capacity estimation for geological repositories in the USA is shown in Table 16.1.

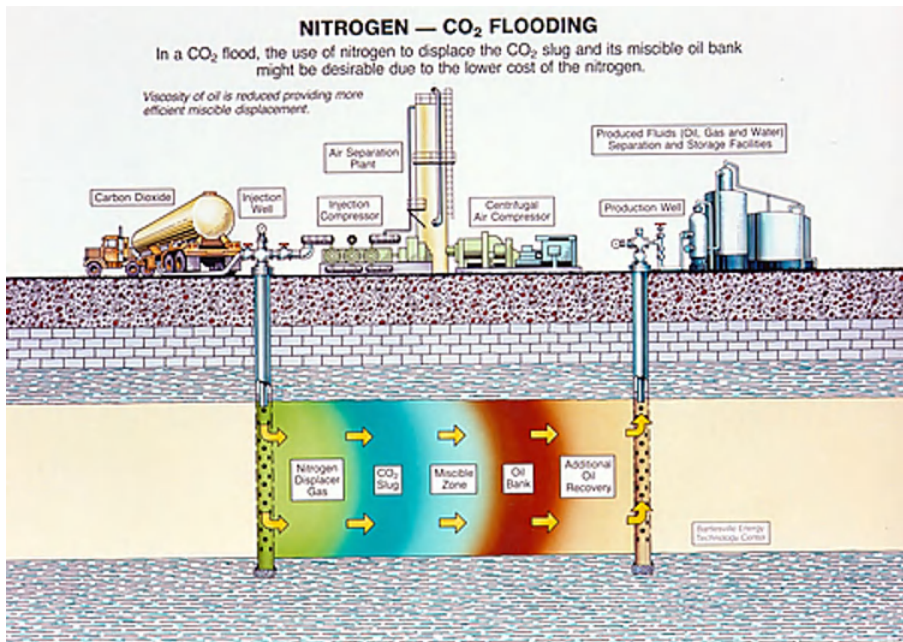
Table 16.1 Storage capacity of geological repositions.

Geological repositions	Capacity estimation (GtC)	References
Salt and water formations	1–130	Bergman and Winter 1995
Natural gas reservoirs	25 ^a	R.C. Burruss 1977
	10 ^b	
Active reservoirs	0.3/year ^c	Baes et al. 1980
Reinforced methane production “coal-bed”	10	Stevens, Kuuskraa and Spector 1998

a: The total carbon is sequestered
b: The excavate natural gas is replaced with carbon
c: The excavate natural gas is replaced with carbon at same pressure

16.5.2 Active or depleted oil and gas reservoirs

Oil and gas reservoirs are a very promising technique of carbon sequestration. Oil and gas reservoirs are formations created naturally inside structural sinks that do not have leakage paths, and additionally, the general geological structure and physical properties are well studied and known, due to the oil and gas excavation industry. The first and more sustainable choice is the carbon sequestration through the EOR oil extraction technique (Fig. 16.4). Almost 80% of the commercially used CO₂ is utilized in the oil industry. This technology is mature and economically applicable. Carbon can be sequestered in depleted gas reservoirs and active gas reservoirs, when the natural gas extraction can be reinforced with the carbon gas injection.

**Fig. 16.4** The EOR method.

The EOR flow diagram is presented in Fig. 16.5. Although the storage potential is the lowest of all, and its industrial compatibility is a matter of concern, this method can be implemented because of the economic feasibility.

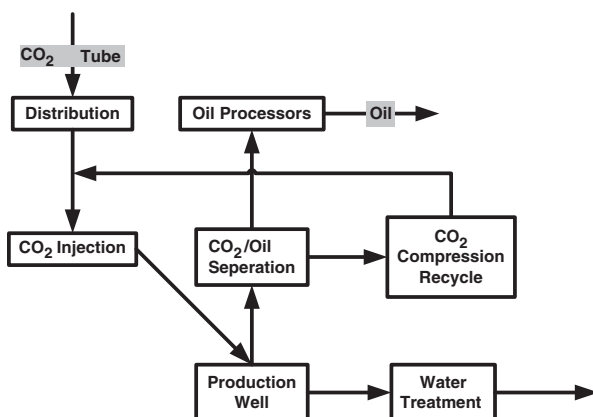


Fig. 16.5 Basic flow diagram of EOR method.

Additionally the basic idea of the sequestration in depleted reservoirs (gas & oil) is presented in Fig. 16.6.

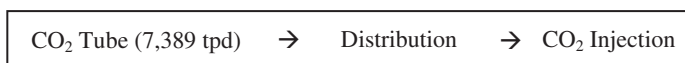


Fig. 16.6 Basic flow diagram of the sequestration in depleted reservoirs

This method has similarities with EOR, but it is much simpler because the reservoir is already depleted.

16.5.3 High-depth liquid formations and saline formations

Unutilized high-depth water formations (>60 m), usually saline water formations, could be a possible storage for carbon sequestration. This formation can be met globally. The knowledge gained from the natural gas storage at these formations can assist the carbon sequestration research. There are two major issues in these methods. Water formation is difficult to be spotted, comparatively with the gas or oil reservoirs, and the water is not removed with the CO₂ injection, something that happens at EOR method. This can result in the pressure increase of the formation, with the possibility of a rock and surface distortion or the possibility of seismic activity. Additionally, the storage capacity is not known and there is always the possibility of CO₂ leakage if the formation has low permeability in gases.

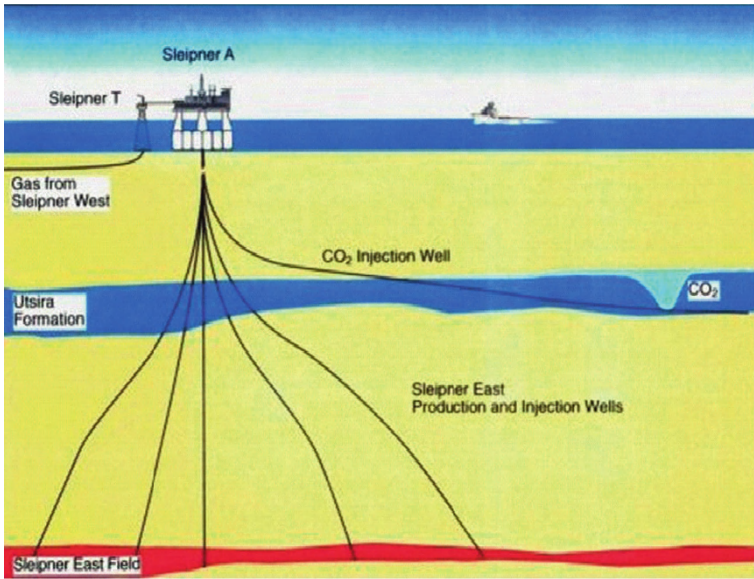


Fig. 16.7 SACS – injection at Sleipner into the Utsira formation under the North Sea.

Saline Aquifer Carbon Dioxide Storage (SACS) (Fig. 16.7) is the first commercial effort for carbon sequestration. It was developed to store the CO₂ co-product from the natural gas extraction. Carbon is injected in the Utsira formation at the North Sea, in a high-depth (800 m) saline storage.

Since the summer of 1996, when the SACS program has been running, almost 10^6 tons of carbon has been sequestered. The SACS program can grant the theory into implementation.

16.5.4 High-depth carbon plunge and coal-bed methane formation

Carbon plunge gives the potential of carbon sequestration and natural gas production reinforcement. Methane production from high-depth carbon plunge can be reinforced with the CO₂ injection, where the CO₂ absorption came along with the methane desorption. This method is already under study in North America. In an experimental field, 85,000 m³ of carbon is injected daily through four injection wells. The initial results have shown that in the total implementation of the project, 75% of the “stored” methane is desorpted.

Coal-bed formations consist of several thick and slim coal seams and intermediate sandstone and shale layers.

16.6 Advanced Biological Processes

The advanced biological technologies reinforce the natural biological processes of carbon sequestration. These technologies cover the usage of new organisms and genetic improvement of land and aquatic bacteria, plants, or animals. This procedure can be followed with the

- development of healthier and more persistent cultivation and plants
- better understanding of the biological diversity and genetics
- development of new injection methods of geological carbon sequestration through microorganisms
- reinforcement of the ocean sequestration through the development of the ocean food chain
- development of alternative polymer bacteria or genetic improved plants

The advanced biological processes reinforce the carbon sequestration, and additionally, they are based on the natural carbon sequestration; thus they can process a gas flow of low carbon content. This means that the carbon storage and transportation steps are not essential; hence, they minimize the total cost and the energy use. They reinforce the carbon recycling, and indirectly they can stage-wise minimize the fossil fuel consumption.

16.7 Advanced Chemical Processes

Advanced chemical processes can develop new sequestration technologies or reinforce the existing sequestration technologies through the better understanding of the chemical reactions, and they can be utilized in both sequestration and capture technologies. Advanced chemical processes are still in progress and they use techniques being developed now for future usage. They are trying to convert the captured CO_2 into long-term aggregates that can be efficiently stored in earth soil or water and have market value. The majority of these technologies make the assumption that the stored carbon will be under pressure, with no mixtures at ambient temperature. A possible approach for carbon sequestration is the transformation of carbon into aggregates such as MgCO_3 . Due to the fact that these materials do not have great market value they could be used in the refilling of magnesium mines. Additionally, oceans could be a viable economic possibility, where carbon can be captured as CO_2 clathrate. At last, carbon from the advanced chemical process point of view can be transformed into plastic or rubber.

16.7.1 Chemical reactions for carbon sequestration

The chemical industry is already mature and there is a large number of chemical procedures developed in the field of carbon capture and sequestration. At the same time, some of the procedures' raw material or energy usage is so intensive that the production of carbon could be of the same quantity as the one being sequestered. The acceptance or not of a process is a difficult task and several criteria must be satisfied:

- The process must be environmentally safe
- The sequestration must be stable and sustainable
- It must be economically competitive
- It must be energy balanced

As mentioned before, there are two major groups of chemical processes: i) The ones that produce products that can be sequestered and ii) the ones that produce products that can be further utilized with economic benefits.

16.7.2 Long-term idle and safe sequestration

The objective of this process is to develop chemical processes that can transform the carbon into products that can be stored safely for a great time period. This procedure is based on the natural CO_2 chemical transformation such as the rock corrosion in order to create calcium and magnesium carbonates or the dissolution of the carbon into the oceans. There are four major approaches for these procedures:

- The transformation of natural silicates for the production of geological stable ores of carbonates and silicon

$$(\text{Mg, Ca})_x\text{Si}_y\text{O}_{x+2y} + x \text{CO}_2 \rightarrow x(\text{Mg,Ca})\text{CO}_3 + y \text{SiO}_2$$
- The CO_2 dissolution into oceans

$$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}_3^-$$
- The development of CO_2 clathrates that can be utilized in large-scale sequestration into cold ocean
- The formation of “formats” and “oxalates.” CO_2 is an acidic gas that can be sequestered with the use of an alkaline compound

16.8 Comparative Analysis

In this section there is a comparative analysis of the dominant carbon sequestration techniques. The characteristics of the sequestration methods are presented in table 16.2. This analysis investigates several sectors concerning the methods such as the advantages and disadvantages, the implementation efficiency and technical maturity, and the industrial compatibility and acceptance. The sequestration methods that are analyzed are as follows:

- Sequestration in aquifers and saline formations
- Sequestration at oil reservoirs utilizing EOR (enhanced oil recovery)
- Sequestration in depleted reservoirs (gas and oil)
- Coal-bed “storage”
- Ocean sequestration
- Reinforcement of forest reservoirs
- Reinforcement of cultivation areas

Table 16.2 Characteristics of several sequestration methods.

Sequestration in aquifers and saline formations	
Advantages	Greatest storage potential among all sequestration methods/CO ₂ residence time is considered to be several thousands years/safe technique
Disadvantages	The potential of carbon release is not entirely studied
Implementation efficiency	Great availability
Technical maturity	There is former experience in chemical deposition in aquifers
Data availability	There are many studies concerning the particular method
Industrial acceptance	There is already CS at Utsira formation at the North Sea, since 1996
Industrial compatibility	Excellent
Sequestration at oil reservoirs utilizing EOR (enhanced oil recovery)	
Advantages	The oil coproduction adds economic benefits to the method/it is safe technique/it is commercially utilized
Disadvantages	Limited storage capacity (<65 GtC)/due to the leakages the CO ₂ , it must be injected under pressure
Implementation efficiency	Restricted to active oil reservoirs
Technical maturity	EOR is applicable over 25 years
Data availability	Excellent
Industrial acceptance	Since 1998 more than 65 oil reservoirs utilize the EOR technique
Industrial compatibility	The CO ₂ injection must be constant (not interrupted)
Sequestration in depleted reservoirs (gas and oil)	
Advantages	Global storage potential is estimated to be 180/the reservoirs have great structural ability/there is great knowledge
Disadvantages	There are not enough depleted reservoirs
Implementation efficiency	Restricted to depleted oil and gas reservoirs
Technical maturity	The technology is same with the EOR technology
Data availability	Great
Industrial acceptance	There is not any industrial implementation
Industrial compatibility	It may require great number of depleted reservoirs
Coal-bed "storage"	
Advantages	CH ₄ production adds economic advantages/efficient sequestration
Disadvantages	Further development for coal-bed methane needed
Implementation efficiency	Uncertainty on how different coal-beds will respond to this technique
Technical maturity	The CO ₂ injection for coal-bed methane production is in early stages
Data availability	Limited
Industrial acceptance	Good
Industrial compatibility	Good

Table 16.3 Characteristics of more sequestration methods.

Ocean sequestration	
Advantages	Storage potential greater than 1000 Gt/no leaking
Disadvantages	It may have distortion on the local SeaWorld/legal problems/residence time restricted
Implementation efficiency	It is applicable in countries close to oceans
Technical maturity	Great experience due the ocean exploration
Data availability	Average
Industrial acceptance	Early stages
Industrial compatibility	Great for power plants close to coastlines
Reinforcement of forest reservoirs	
Advantages	Low implementation costs/great number of forests/Maintenance of the biodiversity
Disadvantages	Lack in audit and verification of the sequestered carbon/Low-term deposition
Implementation efficiency	Easily implemented to isolated areas
Technical maturity	The forestry is technically mature
Data availability	Good
Industrial acceptance	Feasible, low cost method
Industrial compatibility	Its combatable with all the power plants
Reinforcement of cultivation areas	
Advantages	Low cost per ton of sequestered CO ₂ . Additional benefits: better solid quality, no solid corruption, better water utilization, greater production
Disadvantages	Additional need for conventional ploughing
Implementation efficiency	Good
Technical maturity	The technology is already ready for implementation
Data availability	Not good for the carbon sequestration potential
Industrial acceptance	Additional benefits
Industrial compatibility	Good

16.9 Discussion

The objective of this work has been the brief analysis of the dominant carbon sequestration techniques. In order to characterize a carbon sequestration method sustainable, it has to be economically comparative, environmentally friendly, a safe technique, and able to store the sequestered carbon efficiently for a large period of time. The recent developments are promising, but there is much to be done. For instance, the behavior of the sequestered carbon is not entirely understood. The analysis of the reaction of the local environment and its bioecology is not an easy task. The data availability for many methods are in early stages and the possible environmental impacts are in question. Additionally, the implementation and operating costs of the majority of the sequestration methods are not feasible and together some of them consume fossil fuels which produce CO₂. Also, there are

negative reactions from non-government organizations for the implementation of the carbon sequestration methods.

To overcome these restraints, small-scale experiments, pilot programs, and laboratory modeling of the sequestration fields are urgent. Additionally, there must be a new policy aiming to the public information about the benefits of these technologies and financing the research and the development.

16.10 Conclusions

Carbon sequestration is very promising to combat greenhouse effect and global warming. It has the possibility, if the technical restraints are overcome, to minimize the carbon emissions at low levels. However, there must be no inapprehension. As long as the fossil fuels are the dominant energy sources, the problem will remain due to the fact that the most efficient CO₂ minimization “technique” is the CO₂ low productivity. Tables 16.2 and 16.3 give a complete analysis of the advantages and disadvantages of the various sequestration methods described in this work.

References

- Department of Energy, Office of Science, Office of Fossil Energy, Carbon Sequestration, State of the Science, USA (1999) A working paper for road mapping future carbon sequestration R&D.
- Assessment by German Watch (2002) Carbon Dioxide Capture and Storage as a sequestration strategy. www.germanwatch.org/rio/ccs04.htm.
- Bock, BR, Rhudy, RG, Nichols, DE (2001) Economic Evaluation of CO₂ Sequestration Technologies Semi-Annual Technology, Progress Report.
- Diakoulakis, D (2003) Environmental Labeling, National Center for the Environment and Sustainable Development, Greece.
- Hall, DO, House, JI (1994) Trees and Biomass Energy: Carbon Storage and/or Fossil Fuel Substitution? Division of Life Sciences, King's College London, Campden Hill Rd.
- Hellenic Ministry for the Environment (2004) Physical Planning and Public Works, National Planning for the emission trading for the period, In Greek, 2005–2007.
- Herzog, H, Golomb, D (2004) Carbon Capture and Storage from Fossil Fuel Use. MIT Laboratory for Energy and the Environment.
- Herzog, H, Drake, E, Adams, E (1997) CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change. Energy Laboratory, MIT.
- Swisher, JN (1994) Forestry and Biomass Energy Projects: Bottom-up Comparisons of CO₂ Storage and Costs. UNEP Collaborating Center, Rise National Laboratory.

Coal-Based Hydrogen Production with CO₂ Capture in the Aspect of Clean Coal Technologies

Adam Smoliński

17.1 Introduction

Despite the predicted major role of crude oil, mainly in the transport sector, and the growing share of natural gas in power generation, as outlined in the forecast of energy use structure by 2030, coal remains the most important fuel for power generation. Being the most abundant and competitive, coal recoverable reserves could satisfy the world's energy needs in the perspective of about 180 years at the current consumption levels (Energy Information Administration, 2006). At the same time the unstable oil prices as well as stronger environmental regulations regarding greenhouse emissions make the greatest economic powers search a new, price competitive, and environment-friendly energy carrier. According to the specialists in the short- and medium-term hydrogen is likely to become this desired energy carrier. The world research activities in this scope focus on the development of integrated hydrogen and power production technologies, particularly technologies of hydrogen production from coal gasification product – synthesis gas, combined with carbon dioxide capture (Bisio and Boots, 1995; Göttlicher and Pruschek, 1997; Rosen and Scott, 1998; Gray and Tomlinson, 2002; Lin et al., 2002a,b; Chiesa et al., 2005; Collot, 2005; Gambini and Vellini, 2005; Kreutz et al., 2005; Lin et al., 2005a,b; Tzimas and Peteves, 2005; Yamashita and Barreto, 2005; Stiegel and Ramezan, 2006).

This chapter presents the results of laboratory-scale tests of steam gasification of Polish hard coal combined with CO₂ capture in a single step. The main idea of the process is based on applying of Fe₂O₃ as an oxygen transfer compound, enhancing the conversion rate of CO to CO₂ in the water–gas shift reaction, and the CaO for absorption of produced CO₂. Tests of steam gasification of coal were conducted in a laboratory-scale fixed bed reactor in the temperature range of 923–1173 K in three series: steam gasification of coal without additives, with addition of Fe₂O₃ and CaO layered on a coal sample, and mixed with a coal sample, respectively. Coal samples supplier was selected based on the coal mine resources,

Based on Smoliński A (2009) Laboratory scale tests of coal-based hydrogen production with CO₂ capture in the aspect of clean coal technologies. *International Journal of Global Warming* Vol. 1, Nos. 1/2/3: 227–237.

I. Dincer et al. (eds.), *Global Warming, Green Energy and Technology*.
DOI 10.1007/978-1-4419-1017-2_17, © Springer Science+Business Media, LLC 2010

quality, price, and reactivity of coal, suitable for a future Integrated Gasification Combined Cycle system planned to be built in Poland.

17.2 The Idea of the Process

In the steam gasification process coal is converted into synthesis gas, typically composed of 25–30% of hydrogen, 30–60% of carbon monoxide, 5–15% of carbon dioxide, 2–30% of steam, and 0–5% of methane (Smoliński, 2007). Carbon monoxide is further converted into CO_2 in the water–gas shift reaction (WGS) and in the Boudouard reaction, during which CO is converted into amorphous carbon and CO_2 . The idea of hydrogen-rich gas production in the process of steam gasification of coal applied in the study was to use Fe_2O_3 as an oxygen transfer compound to enhance the conversion rates of CO to CO_2 and CaO to absorb the produced CO_2 . Simultaneous addition of Fe_2O_3 and CaO was proved to result in a high content of hydrogen in the product gas (Hauserman, 1994; Hacker et al., 2000; Lin et al., 2002a,b; Hacker, 2003; Kuramoto et al., 2003; Lin et al., 2003; Cox, 2004; Takenaka et al., 2004a,b; Lin et al., 2005a,b; Mondal et al., 2005; Urasaki et al., 2005; Smoliński and Stańczyk, 2006). The reactions of the process of steam gasification of coal to hydrogen-rich gas are presented in Table 17.1. The heats of the reactions were calculated for the temperature range of 873–1173 K using HSC Chemistry ver.3.0.

Table 17.1 The main reactions and the heats of reactions ΔH (kJ/mol) in the process of steam gasification of coal in a temperature range of 873–1173 K.

Reactions	ΔH_{873}	ΔH_{973}	ΔH_{1073}	ΔH_{1173}
$\text{C} + \text{H}_2\text{O}_{(\text{g})} = \text{CO}_{(\text{g})} + \text{H}_{2(\text{g})}$	135,663	135,753	135,742	135,620
$\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} = \text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})}$	–35,734	–34,703	–33,707	–32,750
$2\text{CO}_{(\text{g})} = \text{CO}_{2(\text{g})} + \text{C}$	–171,397	–170,455	–169,449	–168,370
$\text{CH}_{4(\text{g})} + \text{H}_2\text{O}_{(\text{g})} = \text{CO}_{(\text{g})} + 3\text{H}_{2(\text{g})}$	223,967	225,360	226,355	226,999
$\text{CH}_{4(\text{g})} + \text{CO}_{2(\text{g})} = 2\text{CO}_{(\text{g})} + 2\text{H}_{2(\text{g})}$	259,701	260,063	260,062	259,748
$\text{C} + 2\text{H}_{2(\text{g})} = \text{CH}_{4(\text{g})}$	–88,304	–89,607	–90,613	–91,379
$\text{Fe}_2\text{O}_3 + \text{CO}_{(\text{g})} = 2\text{FeO} + \text{CO}_{2(\text{g})}$	–0,554	–3,522	–4,751	–4,650
$\text{Fe}_2\text{O}_3 + \text{C} = \text{CO}_{(\text{g})} + 2\text{FeO}$	170,843	166,934	164,698	163,719
$\text{Fe}_2\text{O}_3 + \text{H}_{2(\text{g})} = 2\text{FeO} + \text{H}_2\text{O}_{(\text{g})}$	35,180	31,181	28,956	28,100
$\text{CaO} + \text{H}_2\text{O}_{(\text{g})} = \text{Ca}(\text{OH})_2$	–98,163	–96,080	–94,025	–92,003
$\text{CaO} + \text{CO}_{2(\text{g})} = \text{CaCO}_3$	–172,091	–170,466	–168,698	–166,786
$\text{Ca}(\text{OH})_2 + \text{CO}_{2(\text{g})} = \text{CaCO}_3 + \text{H}_2\text{O}_{(\text{g})}$	–73,928	–74,386	–74,673	–74,783

17.3 Experimental Procedure and Materials

The tests of hydrogen-rich gas production through steam gasification of coal were conducted in the laboratory-scale fixed bed reactor (Smoliński, 2007). The installation (see Fig. 17.1) consists of gases inlets (valves, flow regulators) (1), a water

pump with a steam generator (2,3), a fixed bed reactor with a resistance furnace (4,5), a water trap (9), a flowmeter (10), and a gas chromatograph – GC(12). The fixed bed reactor is located inside the resistance furnace (see Fig. 17.2). The furnace operation is controlled by a computer (11) and the temperature and the pressure inside the reactor are controlled by a thermocouple (6) and a manometer (7), respectively.

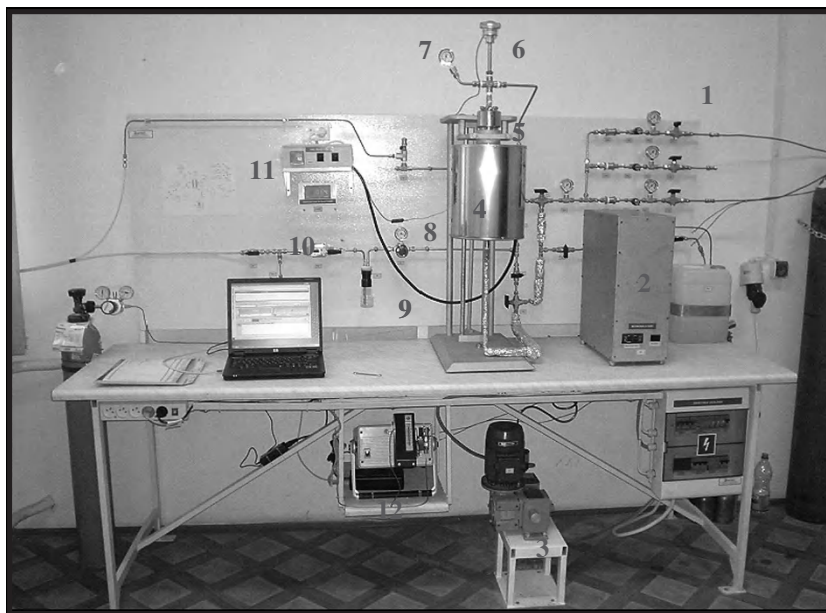


Fig. 17.1 The laboratory-scale fixed bed reactor installation for coal gasification tests: 1 – gases inlets (valves, flow regulators), 2 – steam generator, 3 – pump, 4 – resistance furnace, 5 – fixed bed reactor, 6 – thermocouple, 7 – manometer, 8 – pressure regulator, 9 – water trap, 10 – flowmeter, 11 – furnace temperature control, 12 – gas chromatograph.

The tests of steam gasification of coal were conducted in three series (see Fig. 17.3). In the first one (see Fig. 17.3a) the 3 g of hard coal, with grain diameter below 0.2 mm, was put between the quartz wool and placed at the bottom of the reactor. The quartz wool was used in order to ensure a better temperature distribution and to provide a protection against an entrainment of coal and additives grains by the gaseous media passing through the reactor. In the second and third series of experiments 10 g of Fe₂O₃ and 50 g of CaO were put in layers on a coal sample (see Fig. 17.3b) or mixed with a coal sample (see Fig. 17.3c), respectively.

Then the reactor was heated in an inert gas atmosphere to the set temperatures of 923 K, 973 K, 1023 K, 1073 K, 1123 K, and 1173 K. After the temperature had stabilized, steam was injected upward to the gasifier with a flow rate of $5.33 \cdot 10^{-2}$ ml/s. The gaseous products of the process passed through a water-cooled tar trap, where the condensed liquid products were retained. The amount of cool, dry, and clean

gaseous product was measured with a mass-flowmeter. The composition of the outlet gas mixture was analyzed every 192 s with a gas chromatograph Agilent 3000A.

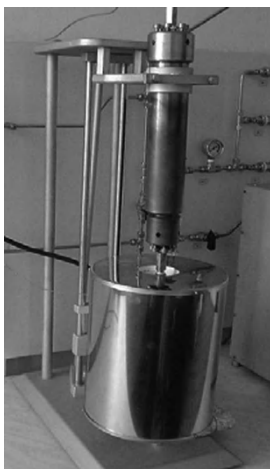


Fig. 17.2 The fixed bed reactor with the resistance furnace.

Based on the results of gaseous products mixture flow rates and percentage compositions, the amounts of the main components of the synthesis gas produced (H_2 , CO, CO_2 , and CH_4) were computed for each of the nineteen, 192 s long time intervals, in 1 h test duration as follows:

$$Q_{ci} = \frac{C_{ci} \cdot Q_i}{100} [\text{ml/s}] \quad (17.1)$$

where Q_{ci} denotes the flow rate of the particular component of the gaseous products mixture (H_2 , CO_2 , CO, or CH_4), C_{ci} denotes the concentration of the given component in the gaseous products mixture measured with GC, and Q_i denotes the flow rate of the gaseous products mixture recorded at the moment of gas sampling by the GC in the i -th time interval. The time interval length resulted from the chromatographic method settings. The volumes of components generated in the time intervals were also computed as follows:

$$V_{ci} = Q_{ci} \cdot t_i [\text{ml}] \quad (17.2)$$

where V_{ci} denotes the volume of the particular component (H_2 , CO_2 , CO, or CH_4) of the gaseous products mixture generated in the i -th time interval and t_i denotes the time interval length.

The coal samples used in the experiments were provided by the Piast coal mine. They were collected from the coal seams planned to be exploited in 5–10 years when a large-scale coal gasification plant is expected to be operated in Poland. The characteristic of the tested coal is presented in Table 17.2.

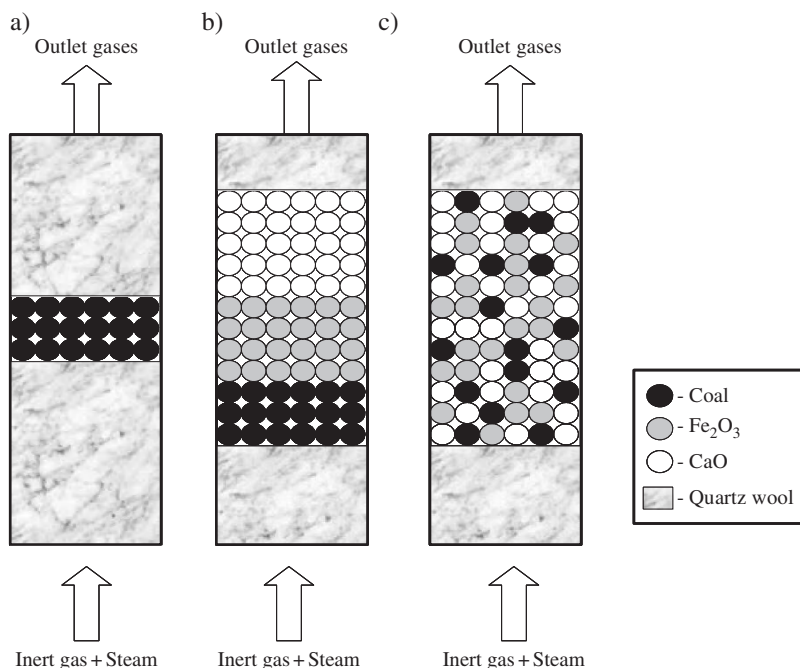


Fig. 17.3 The samples in the series of experiments: (a) sample of coal, (b) coal sample with Fe₂O₃ and CaO layered, and (c) coal sample mixed with Fe₂O₃ and CaO.

17.4 Results and Discussion

In the study the main gaseous products mixture flows and percentage composition of the gaseous product mixture in the steam gasification process were determined using mass flowmeter and GC, respectively. The influence of addition of Fe₂O₃ and CaO on the amount of gaseous product and its composition was analyzed.

The temperature is an important parameter which strongly influences the product gas yield in the gasification process. In Fig. 17.4 the total yield of H₂, CO, CO₂, and CH₄ and the product mixture composition in 1 h tests of steam gasification of coal are presented. The total gas yield at the temperature of 1173 K was about 1.7 times higher than at 923 K. The total amount of hydrogen produced in 1 h gasification tests varied between 2669 ml at the temperature of 923 K and 4836 ml at 1173 K.

Table 17.2 The proximate and ultimate analysis of the tested coal.

Parameter	Value
<i>As-received</i>	
Total moisture W_t^r [%]	8.58
Ash A^r [%]	5.54
Total sulfur S_t^r [%]	0.49
Calorific value Q_i^r [kJ/kg]	26,798
<i>Analytical</i>	
Total moisture W^a [%]	6.02
Ash A^a [%]	5.69
Volatiles V^a [%]	31.12
Heat of combustion Q_s^a [kJ/kg]	28,805
Calorific value Q_i^a [kJ/kg]	27,616
Ash melting point - oxy:	
Sintering point t_s [°C]	990
Softening point t_A [°C]	1270
Melting point t_B [°C]	1350
Flow temp. t_C [°C]	1370
Total sulfur S_t^a [%]	0.5
Carbon C_t^a [%]	70.64
Hydrogen H_t^a [%]	4.08
Nitrogen N^a [%]	0.98
<i>Dry</i>	
Ash A_d [%]	6.05
Total sulfur S_t^d [%]	0.53
Volatiles V^{daf} [%]	35.25
Heat of combustion Q_s^{daf} [kJ/kg]	32625

In the process of steam gasification of coal (see Fig. 17.4) the concentration of hydrogen in the syngas increased from 59% at the temperature of 923 K to 62% at 1173 K, while the CO₂ concentration increased from 20% at 923 K to 24% at 1023 K. In a temperature range of 1073–1173 K the CO₂ concentration decreased and reached 16% at 1173 K. The CO concentration in the produced syngas varied between 19% at the temperature of 923 K and 22% at 1173 K. Moreover, in a temperature range of 923–1023 K the total concentration of CO in the synthesis gas decreased from 19 % to 15%, whereas in a temperature range of 1073–1173 K it increased to 21–22%. The increase in CO and decrease in CO₂ concentrations in the gaseous products mixture in a temperature range of 1073–1173 K can be explained by a reverse Boudouard reaction during which an amorphous carbon and CO₂ are consumed which results in CO enrichment of the gaseous product and by the absence of the water–gas shift reaction at temperatures over 1073 K. Similar results were reported by Mondal et al. (2005). The concentration of CH₄ was low in a temperature range of 923–1023 K and at higher temperatures (1073–1173 K) it decreased to zero. It can be explained by steam and dry reforming of CH₄.

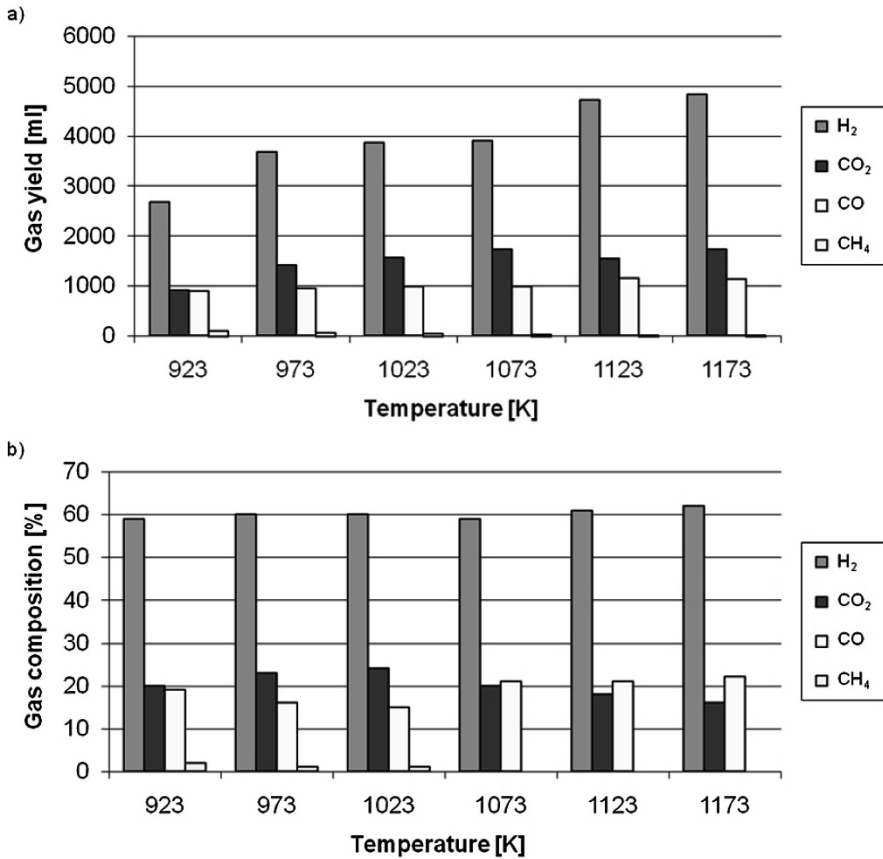


Fig. 17.4 (a) The total gas yield and (b) the gas composition obtained in 1 h tests of the steam gasification of coal.

The simultaneous addition of Fe₂O₃ and CaO significantly increased the hydrogen content in the product gas. In Figs. 17.5 and 17.6 the total yield of H₂, CO, CO₂, and CH₄ and the composition of the gaseous products mixture in 1 h tests of steam gasification of coal with addition of Fe₂O₃ and CaO in layers and mixed, respectively, are presented. Fe₂O₃ oxidized CO to CO₂ and enhanced the water–gas shift reaction which resulted in an increase in H₂ content and in an effective reduction of CO content. Practically all CO was oxidized to CO₂ both in series with Fe₂O₃ layered on and mixed with coal samples.

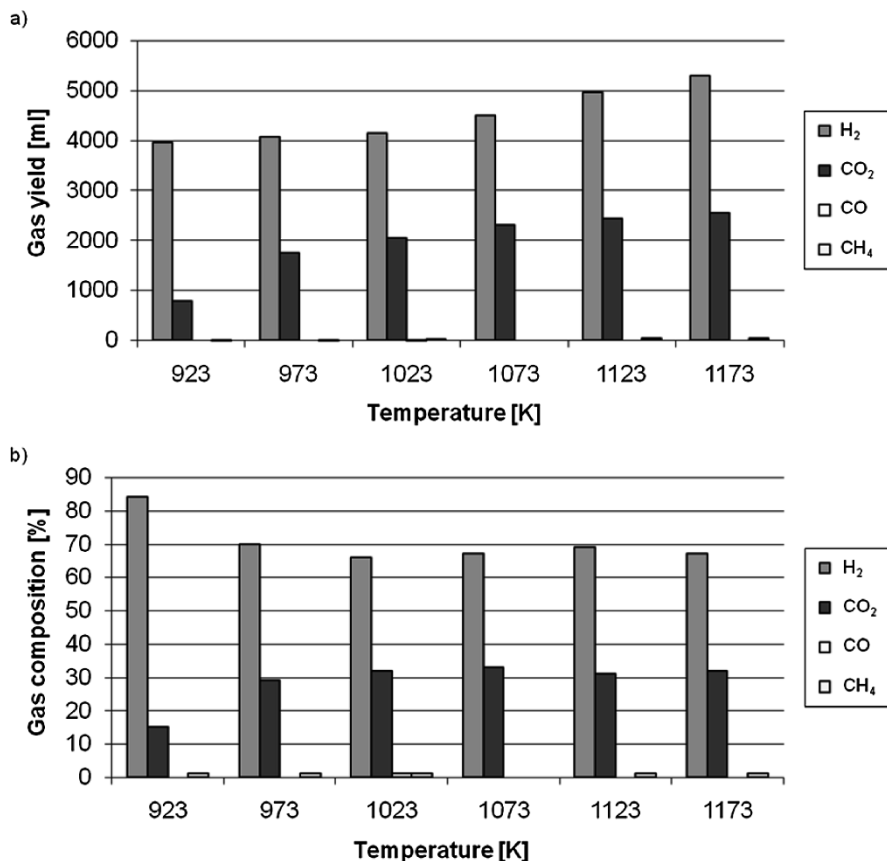


Fig. 17.5 (a) The total gas yield and (b) the gas composition obtained in 1 h tests of steam gasification with addition of Fe₂O₃ and CaO layered on coal samples.

Addition of Fe₂O₃ and CaO in the process of steam gasification of coal enhanced the yield and the content of H₂ in the gaseous product mixture. CaO was added to remove CO₂ produced in the water–gas shift reaction, the Boudouard reaction and in the oxidation reactions with Fe₂O₃. A significant increase in hydrogen content was observed both with addition of Fe₂O₃ and CaO in layers and mixed, but the CO₂ capture was more effective when CaO was mixed with coal and Fe₂O₃. At the temperature of 923 K the hydrogen yield was 3959 ml for layered and 4446 ml for mixed samples, whereas at the temperature of 1173 K the hydrogen yield was 5295 ml and 5901 ml for layered and mixed samples, respectively.

In case of steam gasification of coal with Fe₂O₃ and CaO put in layers in a temperature range of 973–1173 K the total concentration of CO₂ was higher than without iron and calcium oxides (see Figs. 17.5 and 17.6). It can be explained by

by the fact that the whole amount of CO was oxidized by Fe₂O₃ to CO₂ and its absorption by CaO was hindered as the contact surface between agglomerated CaO and CO₂ was limited. Mixing CaO with Fe₂O₃ and coal ensured better contact between CaO particles and CO₂ and improved the efficiency of CO₂ absorption.

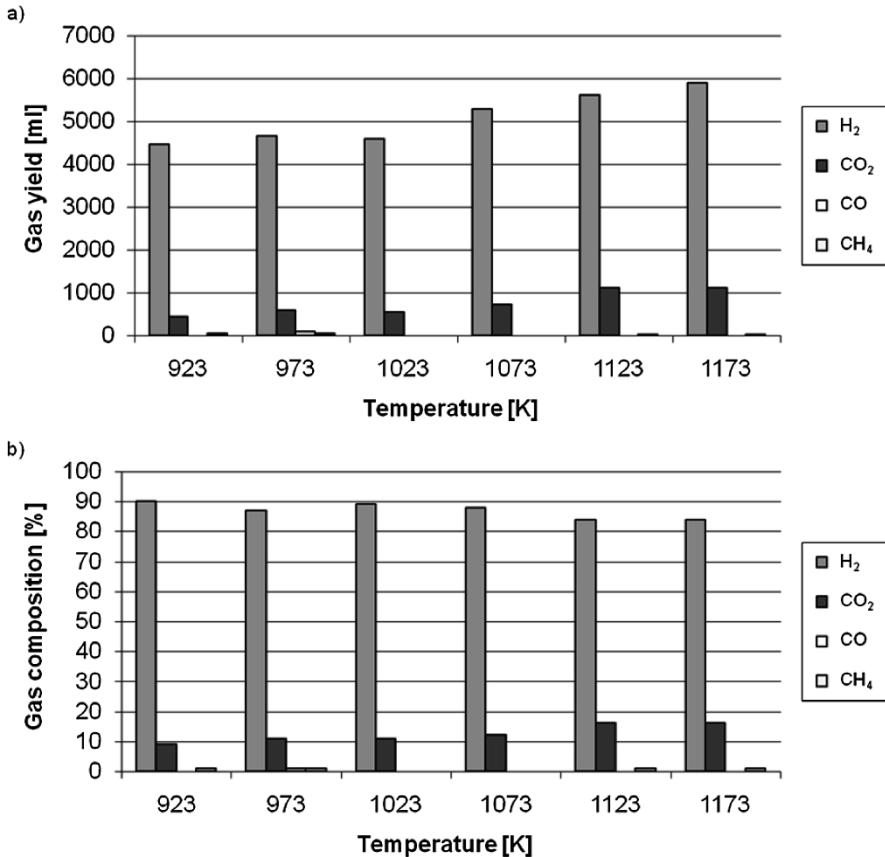


Fig. 17.6 (a) The total gas yield and (b) the gas composition obtained in 1 h tests of steam gasification with addition of Fe₂O₃ and CaO mixed with coal samples.

The process of CO₂ absorption was more effective at lower temperatures (923–1023 K). At the temperature of 923 K the CO₂ content was reduced to 16% and 9% in tests with additives layered and mixed, respectively. In the tests of steam gasification with Fe₂O₃ and CaO layered on coal samples the concentration of CO₂ increased to about 32, 43, and 39% at the temperatures of 973 K, 1023 K, and 1073 K, respectively. This was probably caused by CaO agglomeration (not sufficient amount of CaO available for absorption of CO₂) as this disadvantage

was overcome in tests with Fe_2O_3 and CaO mixed with a coal sample. In the latter cases the concentration of CO_2 was effectively reduced to 11–12% in a temperature range of 973–1073 K. At the temperatures of 1123 K and 1173 K an increase in CO_2 concentration was observed both in tests with additives layered and mixed with coal samples. It can be explained by the fact of CaCO_3 calcinations which, at higher temperatures, is favored over the carbonation of CaO .

17.5 Conclusions

- The presented results confirmed the feasibility of hydrogen-rich gas production in the process of steam gasification of coal combined with CO_2 capture.
- Fe_2O_3 added enhanced the conversion rate of CO to CO_2 , whereas CaO effectively absorbed the produced CO_2 (particularly when mixed with a coal sample).
- The total contents of 83% and 90% of hydrogen in the gaseous products mixture were achieved in the process of steam gasification of coal at the temperature of 923 K with addition of Fe_2O_3 and CaO in layers and mixed, respectively.
- The total yields of hydrogen produced in 1 h gasification tests increased with the temperature of the process and the highest ones were observed at the temperature of 1173 K (5295 ml and 5901 ml in case of additives of Fe_2O_3 and CaO layered and mixed, respectively).

References

- Bisio, A, Boots, S (1995) *Energy Technology and the Environment*. Vol. 3: New York: Wiley.
- Chiesa, P, Consonni, S, Kreutz, T, Williams, R (2005) Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology. Part A: Performance and emissions. *International Journal of Hydrogen Energy* 30: 747–767.
- Collot, A (2005) Matching gasification technologies to coal properties. *International Journal of Coal Geology* 65: 191–212.
- Cox, AW (2004) Hydrogen from coals. Prospects and challenges. *Energy World* 321: 10–11.
- Gambini, M, Vellini M (2005) Comparative analysis of H_2/O_2 cycle power plants based on different hydrogen production systems from fossil fuels. *International Journal of Hydrogen Energy* 30: 593–604.
- Göttlicher, G, Pruschek, R (1997) Comparison of CO_2 removal systems for fossil – fuelled power plant processes. *Energy Conversion and Management* 38: 173–178.
- Gray, D, Tomlinson, G (2002) Hydrogen from coal. Mitretek Technical Paper. MTR 2002-31.
- Hacker, V (2003) A novel process for stationary hydrogen production: the reformer sponge iron Cycle (RESC). *Journal of Power Sources* 118: 311–314.
- Hacker, V, Fankhauser, R, Faleschini, G, Fuchs, H, Friedrich, K, Muhr, M, Kordeschet, K (2000) Hydrogen production by steam iron process. *Journal of Power Sources* 86: 531–535.
- Hauserman, WB (1994) High yield hydrogen production by catalytic gasification of coal or biomass. *International Journal of Hydrogen Energy* 19: 413–419.
- Kreutz, T, Williams, R, Consonnia, S, Chiesa, P (2005) Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology. Part B: Economic analysis. *International Journal of Hydrogen Energy* 30: 769–784.

- Kuramoto, K, Fujimoto, S, Morita, A, Shibano, S, Suzuki, Y, Hatano, H, Lin, SY, Harada M, Takarada, T (2003) Repetitive carbonation-calcination of Ca-based sorbents for efficient CO₂ sorption at elevated temperatures and pressures. *Industrial and Engineering Chemistry Research* 42: 975–981.
- Lin, HY, Chen, YW, Li, Ch (2003) The mechanism of reduction of iron oxide by hydrogen. *Thermochimica Acta* 400: 61–67.
- Lin, SY, Harada, M, Suzuki, Y, Hatano, H (2005a) Process analysis for hydrogen production by reaction integrated novel gasification (HyPr-RING). *Energy Conversion and Management* 46: 869–880.
- Lin, SY, Harada, M, Suzuki, Y, Hatano, H (2005b) CO₂ separation during hydrocarbon gasification. *Energy* 30: 2186–2193.
- Lin, SY, Suzuki, Y, Hatano, H, Harada, M (2002a) Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons. *Energy Conversion and Management* 43: 1283–1290.
- Lin, S, Harada, M, Suzuki, Y, Hatano, H (2002b) Hydrogen production from coal by separating carbon dioxide during gasification. *Fuel* 81: 2079–2085.
- Rosen, MA, Scott, DS (1998) Comparative efficiency assessments for a range of hydrogen production processes. *International Journal of Hydrogen Energy* 23: 653–659.
- Mondal, K, Piotrowski, K, Dasgupta, D, Hippo, E, Wiltowski, T (2005) Hydrogen from coal in a single step. *Industrial and Engineering Chemistry Research* 44: 5508–5517.
- Smoliński, A (2007) Design and construction of a laboratory scale fixed bed reactor installation for testing of coal reactivity in a gasification process. *Mining and Environment* 1: 49–58.
- Smoliński, A, Stańczyk, K (2006) Catalysts in hydrogen production from coal, catalysis for environment: depollution. *Renewable Energy and Clean Fuels. Conference Proceedings* 115–122.
- Stiegel, GJ, Ramezan, M (2006) Hydrogen from coal gasification: An economical pathway to a sustainable energy future. *International Journal of Coal Geology* 65: 173–190.
- Takenaka, S, Sou, VTD, Otsuka, K (2004a) Storage and supply of pure hydrogen from methane mediated by modified iron oxides. *Energy and Fuels* 18: 820–829.
- Takenaka, S, Kaburagi, T, Yamada, C, Nomura, K, Otsuka, K (2004b) Storage and supply of hydrogen by means of the iron oxides modified with Mo and Rh species. *Journal of Catalysis* 228: 66–74.
- Tzimas, E, Peteves, SD (2005) The impact of carbon sequestration on the production cost of electricity and hydrogen from coal and natural gas technologies in Europe in the medium term. *Energy* 30: 2672–2689.
- Urasaki, K, Tanimoto, N, Hayashi, T, Sekine, Y, Kikuchi, E, Matsukata, M (2005) Hydrogen production via steam-iron reaction using iron oxide modified with very small amount of palladium and zirconia. *Applied Catalysis A. General* 228: 143–148.
- Yamashita, K, Barreto, L (2005) Energyplexes for the 21st century: Coal gasification for co-producing hydrogen, electricity and liquid fuels. *Energy* 30: 2453–2473.
- <http://www.eia.doe.gov/oiaf/archive/ieo06/index.html> (2008) International Energy Outlook, US, Department of Energy, Office of Integrated Analysis and Forecasting.

CO₂ Absorption in a Mini-module Membrane Contactor

G. Pantoleontos, S. P. Kaldis, D. Koutsonikolas, P. Grammelis,
and G. P. Sakellariopoulos

18.1 Introduction

Undesirable species such as CO₂ which is usually encountered in a coal upgrading process product gas is considered to be one of the major contributors to the global warming problem via the greenhouse effect. In fact, half of the anthropogenic CO₂ emissions are produced by fossil fuels in industry and power plants (Desideri and Paolucci, 1999). Unless major policy changes and technological innovations take place, future concentrations of CO₂ will continue to increase largely, mainly as a result of fossil fuel uses in transport, heating, and power generation (Wuebbles and Jain, 2001). Therefore, reduction of carbon dioxide (CO₂) emissions has become an international priority, requiring the introduction of efficient and flexible technologies, capable of operating over a wide range of concentration levels and volumetric flows.

Hollow fiber membrane contactors appear as a promising alternative to conventional equipment, such as packed columns, since they are flexible, modular, and energy-efficient devices with a high specific surface area (known a priori) (Mavroudi et al., 2003). Some possible applications for the use of membrane gas absorption are listed in Table 18.1 (Klaasen et al., 1998).

Membrane gas absorption is based on a gas–liquid contact across a hydrophobic membrane. In this manner, gas–liquid membrane contactors can also be effectively applied to carbonation of beverages, nitrogenation of beer to provide a dense foam head, oxygen removal in semiconductor industry for the production of ultra-pure water, and ozonation for water treatment (Drioli et al., 2005). The principle of these devices is that the membrane forms a permeable barrier between the liquid and the gas phase and does not act selectively for one gas species over the other. The gas preferentially fills the hydrophobic membrane pores and meets the liquid at the opposite side of the membrane. The liquid phase pressure should be slightly higher than that of the gas phase to prevent dispersion of gas bubbles into the liquid.

As long as the excess aqueous solution pressure is less than the breakthrough pressure of the membrane the solution does not penetrate the pores and the gas/liquid interface is immobilized at the pore mouth of the membrane on the solution side. As the membrane is non-selective, the chemistry of the separation is the same as for conventional equipment. The choice of a suitable combination of absorption liquid, membrane characteristics, and operation mode determines the selectivity of the process (Mavroudi et al., 2003).

Table 18.1 Applications for the use of membrane gas absorption (Klaasen et al., 1998).

SO ₂ , HCl, CO ₂ , NO _x	From flue gases
H ₂ O, H ₂ S, CO ₂ , Hg	From natural/landfill gas/biogas
O ₃ , SO ₂ , NO _x , VOC	From indoor air
NH ₃ , H ₂ S, CO ₂	From off-gases

18.2 Experimental

The membrane acts as a barrier between gas and liquid phases and does not add selectivity for one gas species over the other. The main reasons for gas dissolution into the liquid phase are the magnitude of gas solubility and whether a reaction takes place. In the case of physical absorption (CO₂ is dissolved into water) there is no reaction case, which otherwise would enhance mass transfer of the gas species. It may well be assumed that dissolution of nitrogen into water does not happen or it is negligible compared to that of CO₂, since the solubility of the latter is at least 30 times higher than that of N₂ at ambient conditions (For CO₂:29.6 mol/m³, for N₂:0.7 mol/m³).

Table 18.2 Contactor characteristics.

Cartridge configuration	Parallel flow
Maximum flow rates	500 ml/min
Overall length (with adapters)	22 cm
Membrane material	Polypropylene
Membrane porosity	40%
OD/ID	300 µm OD/220 µm ID
Number of fibers	2300
Active surface area (A _m)	0.18 m ²

In this study a Liqui-Cel Mini-Module 1 × 5.5 was used as a gas–liquid contactor. Mini-modules are increasingly gaining attention and were used in a number of cases (Rzechowicz and Pashley, 2006; Zhang et al., 2006; Jaenicke, 2005), but they were not extensively studied. The characteristics of the membrane contactor used are listed in Table 18.2.

The flow diagram of the unit designed and constructed for the gas–liquid absorption is shown in Fig. 18.1. The feed gas, namely a gas mixture containing 15% CO₂–85% N₂ (simulating a typical composition in major components of flue

gases from a coal combustion), is introduced directly from a gas cylinder to the fiber lumen of the module for minimum pressure drop, while the liquid (pure water or aqueous solutions of NaOH or KOH of 0.5 M, both) flows through the shell side at a pressure slightly higher than that of the gas. The feed gas flow is controlled and measured with a gas flow meter, while the liquid absorbent is pumped from the liquid storage tank by a gear pump (ISM446 BVP-Z Standard Gear Pump), so that pulseless flow is ensured. The composition of the gas streams is monitored by sampling a slip stream from the feed or exit line and diverting it into a Perkin–Elmer 8500 gas chromatograph with a thermal conductivity detector. The module was kept in an isothermal condition and experiments were carried out at 21–24°C. After each experiment the membrane was dried by passing nitrogen through the module overnight. This was done in order the liquid to be removed and evaporated from the contactor. Details for the drying procedure can be found in Liqui-Cel web site.

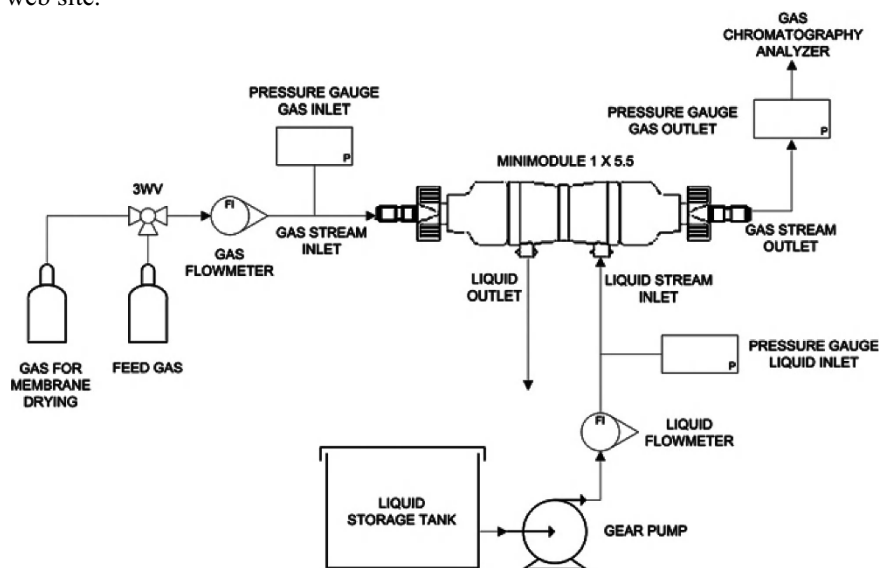


Fig. 18.1 Flow diagram of the hollow fiber membrane contactor unit.

18.3 Results and Discussion

For the case of physical absorption (pure water flowing in the shell side, gas mixture flowing in the lumen counter-currently to liquid flow) the membrane module reaches steady state in the first minutes of operation. In a period of 35 min the efficiency of the membrane module is kept constant to that of the first 5 min. However, the removal of CO₂ is very limited, due to the small ratio of liquid to gas flow rate (Q_l/Q_g), reaching 17% for Q_l/Q_g equaling 0.67. Increasing the liquid flow rate results in enhanced CO₂ removal: for a ratio of 30.74 the recovery of

CO₂ is almost complete when using pure water as the absorbent, as depicted in Fig. 18.2. However, the removal capacity of the membrane module does not vary linearly with the liquid to gas flow rate ratio, but rather there is retardation to absorption of CO₂ from the physical solvent (Fig. 18.3). The declining slope of CO₂ removal vs. Q_l/Q_g ratio indicates that the curve will reach a complete removal of CO₂ for very high ratios, thus leading to high amounts of liquid consumption. This is also the result of the absence of the chemical reaction enhancement, since the value of the equilibrium constant of the reaction between H₂O and CO₂ is very small.

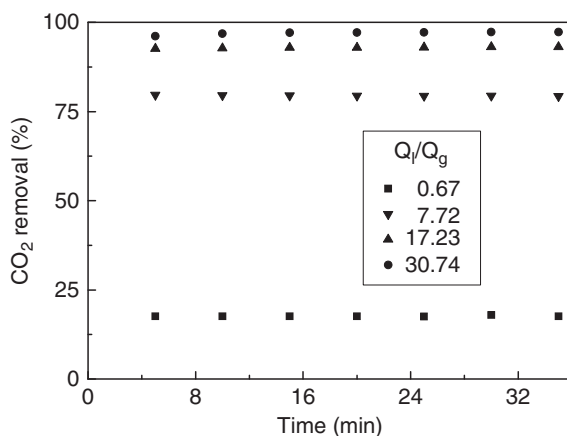


Fig. 18.2 CO₂ removal vs. time for various liquid to gas flow rate ratios using water as an absorbent (ambient temperature and pressure).

Using basic substances can enhance CO₂ absorption since the latter is a mild acid gas. Aqueous solutions of NaOH or KOH with a concentration of both being 0.5 M were prepared and used as solvents instead of pure water. Now the absorption is complete even when a very low Q_l/Q_g ratio was used. It is noted that for the same liquid to gas flow rate ratio of either NaOH or KOH (0.5 M) CO₂ removal remains the same as depicted in Fig. 18.4. For a ratio of 0.12 CO₂ removal reaches 95%, when using NaOH or KOH as the absorbent. For higher values, as 0.20, removal is complete, which is a big advancement for CO₂ removal, since the minimum liquid consumption is achieved. Compared to the corresponding ratio for physical absorption of CO₂, the consumption of the chemical solvent is 150 times lower.

A series of experiments with aqueous solutions of NaOH or KOH of 0.25 M was conducted, so that the most effective basic substance is identified. Figures 18.5 and 18.6 show the percentage removal of CO₂ using mild concentrations of NaOH or KOH. First, it is evident that the removal efficiency of the membrane contactor remains the same for identical ratios, but for different gas or liquid flow rates. This feature of the membrane device indicates that the removal efficiency is only dependent on the liquid to gas flow rate ratios regardless of the gas flow rate chosen. That is, it is advantageous to use the highest possible gas

flow rate without major decline in the removal efficiency. They also show that NaOH is a better reactant than KOH in treating CO₂. For the same liquid to gas flow rate ratios NaOH removes larger quantities of CO₂ than that with the use of KOH.

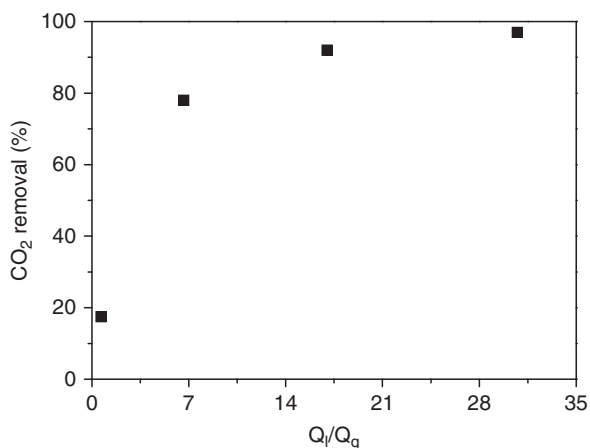


Fig. 18.3 CO₂ removal vs. Q_l/Q_g using water as absorbent (ambient temperature and pressure).

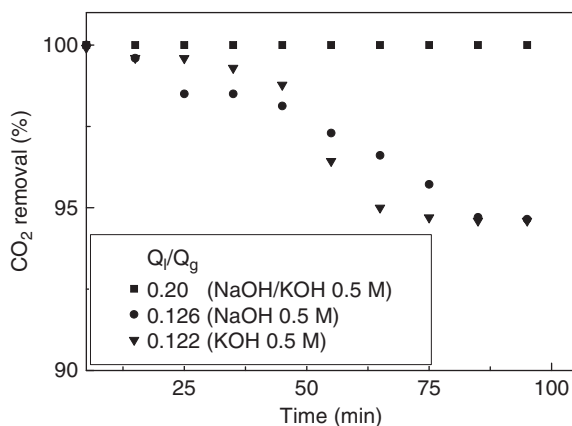


Fig. 18.4 CO₂ removal vs. time for different Q_l/Q_g ratios using NaOH or KOH (both of 0.5 M) as absorbents (ambient temperature and pressure).

In all cases considered CO₂ removal increases with the increase of the liquid to gas flow rate ratio. Keeping the gas flow rate constant the increase of the liquid flow rate leads to higher quantity of liquid to absorb the gas species. The increase of the gas flow rate (for constant liquid flow rate) leads likewise to higher CO₂ removal, since the concentration difference between the lumen and the shell side increases. Another aspect of the chemical absorption is the slight increase of

the removing capacity of CO_2 in the case of constant liquid flow rate compared to the constant gas flow rate case. This means that the increase of the liquid flow rate has higher impact to mass transfer than the increase of the gas flow rate: There is higher resistance to mass transfer in the bulk gas phase than that of the liquid one. The effect of the chemical reaction enhancement undermines the liquid phase resistance resulting to augmented CO_2 when the liquid flow rate increases.

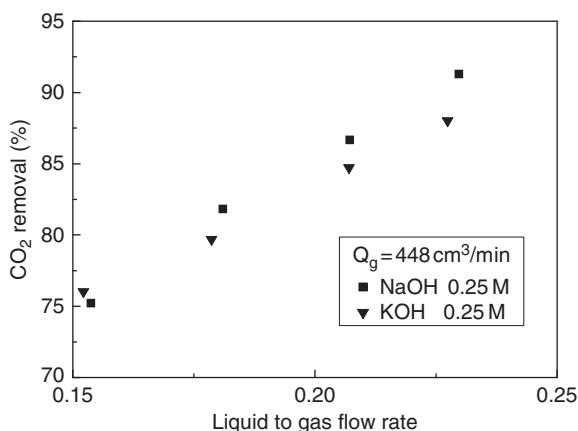


Fig. 18.5 CO_2 removal vs. liquid to gas flow rate ratio for constant gas flow rate.

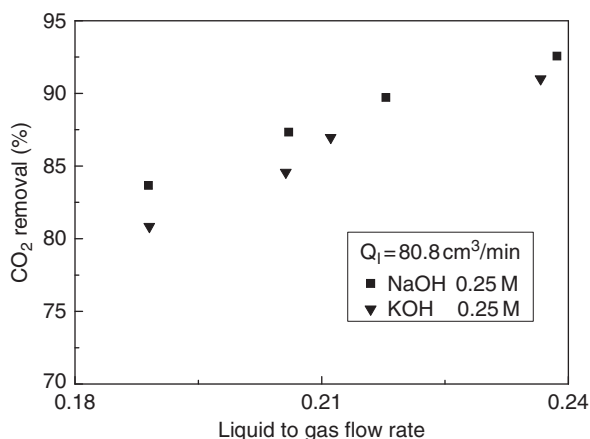


Fig. 18.6 CO_2 removal vs. liquid to gas flow rate ratio for constant liquid flow rate.

18.4 Conclusions

A series of experiments in a commercially available membrane mini-module was conducted in order to validate the capability of removing CO_2 from gas mixtures. Various liquid solvents were tested at different operating conditions, such as pure water and aqueous solutions of NaOH or KOH (0.5 and 0.25 M) concluding that

NaOH is a better reactant than KOH. In the case of chemical solvents the absorption of CO₂ is complete with very low consumption of the liquid compared to the physical absorption, which is likewise complete but with a higher liquid to gas flow rate ratio. The chemical reaction enhancement because of the presence of NaOH or KOH undermines the resistance of the liquid phase to mass transfer, thus making the gas phase the controlling stage of the absorption.

The mini-module is capable of removing undesirable species using rather mild solvents, showing very good behavior for every liquid and gas flow rate examined.

Acknowledgments

The experimental data were obtained within the framework of the European program HYDROSEP (contract RFCR-CT-2006-00003) and was partly funded by the European Commission. Liqui-cel web site is <http://www.liqui-cel.com> (Accessed on April 2008).

References

- Desideri, U, Paolucci, A (1999) Performance modelling of a carbon dioxide removal system for power plants. *Energy Convers. Manag.* 40: 1899–1915.
- Drioli, E, Curcio, E, Di Profio, G (2005) State of the art and recent progresses in membrane contactors. *Chem. Eng. Res. Des.* 83(A3): 223–233.
- Jaenicke, S (2005) Characterization of heterogeneous catalysts by use of test reactions. *Catal. Surv. Asia* 9: 173–185.
- Klaasen, R, Feron, PHM, Jansen, AE (1998) Flue gas treatment with membrane gas absorption. *Membr. Tech.* 102: 7–10.
- Mavroudi, M, Kaldis, SP, Sakellariopoulos, GP (2003) Reduction of CO₂ emissions by a membrane contacting process. *Fuel* 82: 2153–2159.
- Rzechowicz, M, Pashley, RM (2006) A membrane method for degassing nonaqueous liquids. *J. Coll. Interf. Sci.* 298: 321–326.
- Wuebbles, DJ, Jain, AK (2001) Concerns about climate change and the role of fossil fuel use. *Fuel Process. Tech.* 71: 99–119.
- Zhang, H-Y, Wang, R, Liang, DT, Tay, JH (2006) Modeling and experimental study of CO₂ absorption in a hollow fiber membrane contactor. *J. Membr. Sci.* 279: 301–310.

CO₂ Hydrogenation to Methanol on Cu–ZrO₂ Catalysts

Ferroudja Bali and Louise Jalowiecki-Duhamel

19.1 Introduction

The effective utilization of CO₂ is gaining great attention due to its environmental relevance. As a matter of fact, synthesis of methanol from syngas (CO + H₂) is very important in industry and synthesis of methanol from CO₂ + H₂ is one of the most economic processes. Therefore, it is important to develop new catalysts for this reaction with high activity and selectivity to methanol. Methanol synthesis is carried out at low temperature on copper-based catalysts, such as Cu/ZnO/Al₂O₃ and Cu/ZnO/Cr₂O₃ compounds, with various compositions (Klier et al., 1982). Besides, it has been shown that similar catalysts are also active for diene hydrogenation (Jalowiecki et al., 1987; 2006). Previously (Bali et al., 1995; 1996), we have shown that the Cu–Zr–O system prepared by coprecipitation is constituted after calcination of a zirconium and copper solid solution, in which Cu²⁺ cations are inserted into the zirconia lattice, in close contact with copper oxide. The size of the latter varies from crystallized grains to small particles and/or clusters depending on experimental conditions.

After activation in H₂, the solid solution is maintained and Cu²⁺ cations are partially reduced. The solids obtained are able to store hydrogen and are active toward isoprene hydrogenation reaction. Besides, some Cu- and Ni-based mixed oxides have already been found to be good hydrogenation catalysts related to their ability to store hydrogen (Wröbel et al., 1993). An active site modeling has been proposed based on the presence of coordinatively unsaturated sites (CUS) (Siegel, 1973), in agreement with some previous results reported by Siegel, considering that the most important parameter involved in the constitution of an active site is the number of coordinative unsaturations, whatever the nature of the cation (Jalowiecki et al., 1987). The purpose of this work was to synthesize a new catalyst based on copper which will be active in methanol synthesis and to understand its working during the catalytic process. Zirconia has been chosen as a support, because several studies have reported the interest of a Cu–Zr–O system for this

reaction. We report on CO₂ hydrogenation activity and selectivity of zirconium–copper oxides. Some physico-chemical characterizations are performed in order to explain the results obtained. Finally, we propose a modeling of the active site based on some results previously reported on Cu- or Ni- based mixed oxide catalysts (Wröbel et al., 1993).

19.2 Experimental

19.2.1 Catalysts preparation

The zirconium–copper mixed oxides were prepared by co-precipitation of hydroxides from mixtures of different salts, using NaOH or KOH as precipitating agent, as presented in Table 19.1. The solids have been dried at 100°C, calcined in air at 400°C (4 h), and in situ activated in H₂ (12 h) at a given treatment temperature.

19.2.2 XRD characterization

The structure of the oxides during reduction was analyzed in a Siemens D5000 diffractometer equipped with an Anton Paar HTK 10 chamber and connected to a gas introduction and purification line. A position-sensitive detector was used; the experimental conditions were similar to those adopted in Bali et al. (1995). Apart from the K α_2 contribution eliminated by computer post-processing, the patterns obtained were not subjected to further treatments. Owing to the use of a platinum holder, they show platinum diffraction peaks, the evolution of which with TR was taken into account in determining the exact position of the peaks of the solids analyzed.

19.2.3 XPS characterization

XPS were registered with a Leybold-hereaus LHS 10 spectrometer, using an Al anode (1486.6 eV) operated at 300 W in a chamber pressure of nearly 1.33×10^{-6} Pa. For calibration of the binding energy scale of the photoemission features, the C 1 s peak at 285 eV was taken as a reference. The reproducibility was ± 0.2 eV. The samples, pressed on a gold holder, were mounted on a sample rod that permitted reduction treatments (20% H₂ in N₂) up to 673 K, in a preparation chamber directly connected to the ultra-high vacuum analysis system. They were reduced for 16 h before analysis. The measurements were run at room temperature.

19.2.4 Catalytic isoprene hydrogenation

Measurement of the amount of hydrogen stored in the bulk and at the surface in the reduced oxides and the activities in isoprene hydrogenation is based on the ability of this class of solids to hydrogenate 2-methylbuta-1, 3 diene (isoprene) in the absence of gaseous hydrogen at atmospheric pressure, according to a dynamic method described previously (Jalowiecki et al., 1985). The solid is previously in-situ treated in H₂ at 250°C (12 h) and the reaction is studied in a temperature range between 80°C and 150°C. The mass of the catalyst is of 50 mg and the partial pressure of isoprene in He is of 19–20 torrs.

19.2.5 Catalytic CO₂ hydrogenation

The catalytic CO₂ + H₂ reaction was studied in a SOTHELEM RDP 830 apparatus. A stainless steel U tube reactor was placed into a tubular furnace. The catalyst was deposited as a slight layer on a fritted stainless steel disk within the reactor. The pressure of CO₂ + 3 H₂ was adjusted to the desired value by a system of capillars. This system permits to stabilize the pressure inside the reactor to 5 bars. The mass of catalyst is of 100 mg and the solid is analyzed after in situ reduction in H₂ at 250°C. The products analysis was done at the atmospheric pressure. The analysis of non-converted CO₂ and of the formed products (CO, CH₄, CH₃OH) was done by gas chromatography i) DELSI-type IGC 121 ML (TCD) for CO₂ and CO and ii) DELSI-type GC 121 DFL (FID) for CH₃OH, and CH₄, equipped with identical columns ($L=4$ m, $l = 1/8$ in.) Porapak R.

19.3 Results and Discussion

In previous studies, some characterizations of the studied catalysts have already been reported (Bali et al., 1995, 1996).

Thermal analysis in air and in H₂, metallic areas determination, in situ in H₂ XRD have allowed obtaining some information on the dried, calcined, and partially reduced states of the studied catalysts.

Table 19.1 Surface and metallic areas.

Catalyst	Cu/Zr	Salts	Surface area (m ² /g)	Metallic area (m ² /g)
(Cu/Zr0.5)K	0.5	CuCl ₂ +ZrOCl ₂	200	30.5
(Cu/Zr0.5)	0.5	Cu(NO ₃) ₂ +ZrO(NO ₃) ₂	89	13
(Cu/Zr1)	1	Cu(NO ₃) ₂ +ZrO(NO ₃) ₂	92	19
(Cu/Zr2)	2	Cu(NO ₃) ₂ +ZrO(NO ₃) ₂	94	6
(Cu/Zr0)	0	ZrO(NO ₃) ₂	93	–

In the oxidized state, a zirconia-like phase is evidenced in all the solids analyzed, while crystallized CuO appears for a specific copper content depending on the calcination temperature and/or the coprecipitation procedure. A solid solution of zirconium and copper is evidenced.

In H₂, the appearance of metallic copper depends on the same parameters as previously reported and also on the treatment temperature, meanwhile the crystallization of the zirconia phase increases with the temperature (for temperatures higher than 500°C) and some segregation phenomena occur. Metallic Cu⁰ is detected by XRD at 150°C for Cu/Zr1 and Cu/Zr2, at 200°C for Cu/Zr0.5, and at 400–500°C for (Cu/Zr0.5)K.

Moreover, for a given temperature, metallic copper appears at lower temperature when increasing the time of treatment in H₂. As a matter of fact, small quantities of metallic copper appear in (Cu/Zr0.5)K treated in H₂ at 150°C for several

hours. Figures 19.1 and 19.2 show the XRD patterns of the (Cu/Zr0.5)K and (Cu/Zr0.5) compounds treated in H_2 for 12 h.

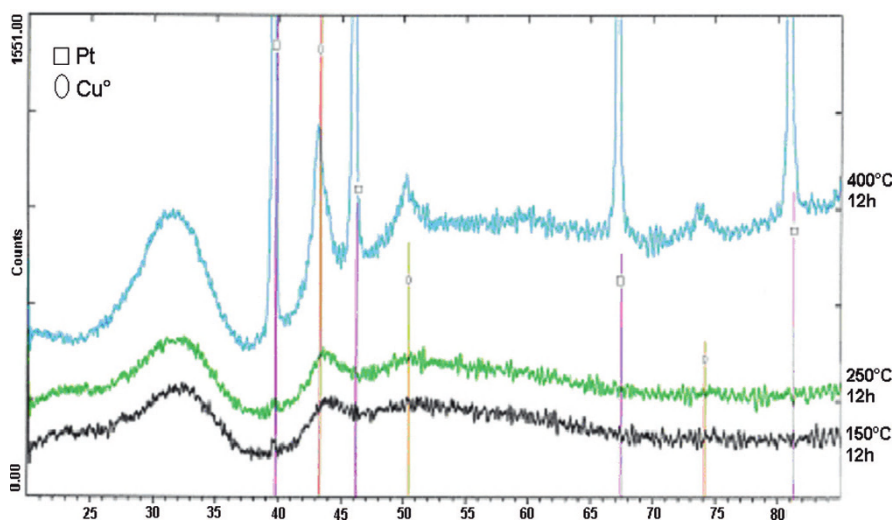


Fig. 19.1 XRD patterns of the (Cu/Zr0.5)K catalyst treated in H_2 versus time and treatment temperature.

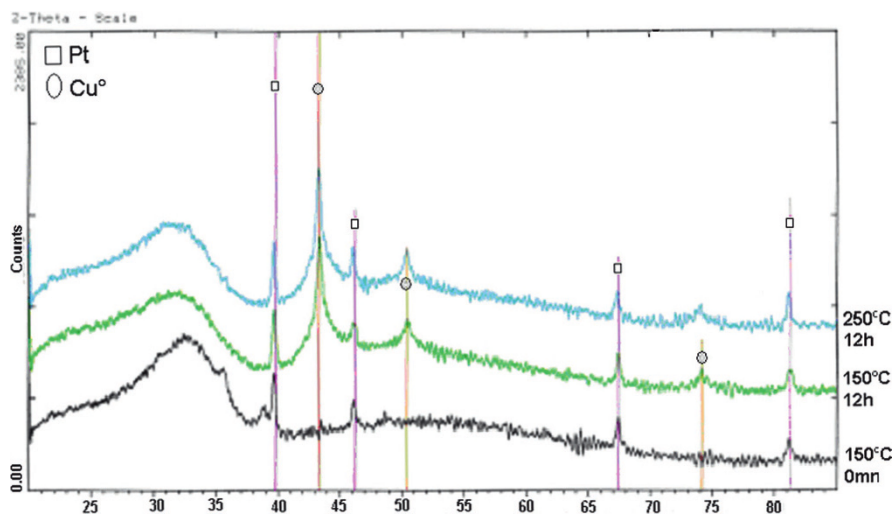


Fig. 19.2 XRD patterns of the (Cu/Zr0.5) catalyst treated in H_2 versus time and treatment.

In situ XPS and Auger analysis have been performed on the two Cu/Zr0.5 compounds in order to try to explain the differences observed by thermogravimetry and XRD, and on the Cu/Zr0 compound used as a reference. The reduction

temperatures range is between 100°C and 250°C with 12 h of treatment at each temperature. The Zr_{3d5/2} signal remains the same either zirconium is alone or with copper, in agreement with an oxidation state +4 of zirconium at the surface of the solid. The $n\text{O}/n\text{Zr}$ ratio is equal to 2.24 and the binding energy remains equal to 182.1 eV, identical to the one reported by Younes (Younes et al., 2000) and Katona (Katona and Molnar, 1995) for a Cu–Zr intermetallic compound. Besides this value is very different from those obtained by Yang (Yang et al., 1993) for a suboxide ZrOx and for Zr⁰ which are, respectively, equal to 183.9 and 179.9 eV. Table 19.2 shows the main characteristics of copper found in this study and compared to those reported in the literature for CuO, Cu₂O, and Cu⁰ compounds (Lide, 2002).

After treatment in H₂ at 100°C, the Cu_{2p3/2} line still shows the existence of two peaks typical of the Cu²⁺ species. The Sat/pp ratio is quite constant in the (Cu/Zr0.5)K sample (0.67–0.66%), while it is seriously decreasing on the (Cu/Zr0.5) solid from 0.60% to 0.55%, showing that the reaction has already started on this solid, in agreement with a huge variation of the kinetic energy reaching 917.1 eV, the typical value of the Cu⁺ species. This premature reduction may result in the reduction of big crystallites of copper oxide, which are visible by XRD for this compound.

At 150°C the reduction process is started for both compounds. However, the persistence of the satellite peak of the Cu_{2p3/2} line in the (Cu/Zr0.5)K spectra shows that Cu²⁺ species is still present and remains particularly well inserted. The Auger line of copper for this solid has been separated into three components with maxima at 915.6, 916.6, and 918.4 eV, corresponding to the three oxidation degrees of copper Cu⁺, Cu²⁺, and Cu⁰. In the spectra of the (Cu/Zr0.5) compound, the disappearance of the component corresponding to Cu²⁺ species is confirmed. It is important to notice that these values are sharply different from those obtained for Cu⁺ and Cu²⁺ species in pure Cu₂O and CuO. For instance, the component at 915.6 eV is much lower than that obtained for Cu⁺ in Cu₂O (916.2 eV), in favor of Cu⁺ species well inserted into the ZrO₂ matrix.

After treatment in H₂ at 250°C, the typical satellite peak of the Cu²⁺ species has totally disappeared from the spectra. The width of the Auger line can be attributed to the presence of Cu⁺ and Cu⁰ species, but the Cu⁺ binding energy is still low, assigned to Cu⁺ species located in the zirconia network.

Thus, XPS results are in good agreement with XRD and thermal reduction analysis. The peak observed at 130°C by thermal reduction (previous study) has been assigned to the reduction of very small particles of CuO that partly cover up the solid solution. Beyond 150°C, the reduction of very big crystallites visible by XRD is obtained on the (Cu/Zr0.5) solid. The reduction of the dissolved copper is slower and starts later, probably following the scheme Cu²⁺ → Cu⁺ → Cu⁰, the two steps being hard to distinguish with the used methods. The low Cu/Zr atomic ratio shows that the main part of copper cations is inserted into the bulk of the (Cu/Zr0.5)K solid. This ratio tends to the nominal value for the (Cu/Zr0.5) compound. So, for the analyzed depth (~20 Å), the different treatments do not really modify the distribution of copper in both solids. The quantity of surface oxygen

species drastically changes during the reducing treatment. On the other hand, the dispersion of the hydroxyl OH^- species around metallic cations must decrease because of the reduction of copper, which leads to the redistribution of the surface OH^- groups and their scattering at the surface of the network.

Table 19.2 XPS and Auger analysis.

	Compound	El (eV)	Ec (eV)	Sat/pp	Cu/Zr	Cu/Zr*
Calcined	(Cu/Zr0.5)K	934.7	916.7	0.67	0.30	0.49
	(Cu/Zr0.5)	934.5	916.7	0.60	0.57	0.55
Tr=100°C	(Cu/Zr0.5)K	934.6	916.4	0.66	0.28	—
	(Cu/Zr0.5)	934.4	917.1	0.55	0.55	—
			915.6			
	(Cu/Zr0.5)K	932.7	916.6	0.18	0.29	—
Tr=150°C			918.4			
	(Cu/Zr0.5)	932.7	915.6	—	0.59	—
Tr=250°C	(Cu/Zr0.5)K	932.3	918.8	—	0.31	—
	(Cu/Zr0.5)	932.4	918.8	—	0.57	—
			918.3			
	(Cu/Zr0.5)K	932.3	918.8	—	0.31	—
**	Cu^0	932.6	917.8	0		
**	Cu_2O	932.4	916.5	0		
**	CuO	933.6	917.6	55		

Cu/Zr* obtained by flame ionization analysis; ** according to (Wang et al., 1993).

Finally, after activation in H_2 , the (Cu/Zr0.5)K catalyst corresponds to a solid solution of copper and zirconium, Cu^{2+} cations replacing some Zr^{4+} cations in the quadratic zirconia phase, with a small quantity of metallic copper like clusters, located on the surface. For the other solids, the solid solution also exists, but zirconia is in a cubic phase, and when increasing copper content, surface metallic copper increases.

These observations lead us mainly to assume the existence of two kinds of sites: i) $\text{Cu}^+-\text{O}-\text{Zr}^{4+}$ sites due to the interaction between Cu^+ and Zr^{4+} cations either at the interface of small CuO clusters with the solid solution or in the copper and zirconium solid solution and ii) $\text{Cu}^+-\text{O}-\text{Cu}^+$ sites related to the interaction between Cu^+ cations in the solid solution or at the metal–solid solution interface. In the (Cu/Zr0.5)K catalyst, the $\text{Cu}^+-\text{O}-\text{Zr}^{4+}$ site is found in highest concentration, whereas the (Cu/Zr0.5) and (Cu/Zr1) catalysts present a great amount of $\text{Cu}^+-\text{O}-\text{Cu}^+$ sites with some $\text{Cu}^+-\text{O}-\text{Zr}^{4+}$ sites, as shown in Fig. 19.3.

19.3.1 Reactivity in isoprene hydrogenation in helium

The (Cu/Zr1), (Cu/Zr0.5)K, and (Cu/Zr0.5) catalysts present very good activities, respectively, equal to 38.0, 35.0, and $18.3 \times 10^{-3} \text{ mol g}^{-1}$. At 150°C, the isopentane

selectivity is almost similar to that obtained on industrial catalysts (Sene, 1992). Moreover, the isoprene hydrogenation product selectivity is analogous to that observed on some Cu–M–O catalysts. The existence of particular active sites, involving Cu⁺ cations of the solid, hydroxyl groups, anionic vacancies and hydrogen species of hydride nature have been proposed, such as ^xM⁺^yM' elementary ensembles (where *x* and *y* are the number of unsaturations, i.e., anionic vacancies, on each cation) (Jalowiecki et al., 1987). In particular, it has been shown that three coordinatively unsaturated sites (3 CUS or also noted ³M) are the prerequisite condition to obtain alkadiene hydrogenation activity, while the unsaturated second cation brings its contribution to selectivity. Thus, the production of isopentane could be associated with the ³M–³M' elementary ensemble while the ³M–²M' site leads to the formation of 2-methyl-but-2-ene. It has been shown that in helium, the migration of hydroxyl groups leads to an evolution of the surface active sites. The ³M–²M' site turns out to become an ³M–¹M' leading to the formation of 2-methyl-but-1-ene and 3-methyl-but-1-ene. This active site modeling can be applied to the solids studied here, the Zr⁴⁺ cation playing the role of the second cation, explained by its lower degree of coordinative unsaturations and its Lewis acidic sites, as it has been reported for Al³⁺ or Cr³⁺ (Hubaut et al., 1986). The ²M site has been proposed to be the prerequisite condition to observe isomerization reaction; therefore the ³Cu⁺–²Zr⁴⁺ site noted type I can be related to the formation of 2MB2. The big proportion of isopentane obtained is to be linked to the presence of a majority of ³Cu⁺–³M' sites, in other words mainly ³Cu⁺–³Zr⁴⁺ (Type III) in the (Cu/Zr0.5)K catalyst and ³Cu⁺–³Cu⁺ (Type II) in the (Cu/Zr 0.5) and (Cu/Zr1) catalysts. Table 19.3 presents the selectivity obtained at different reaction temperatures for the studied catalysts.

Table 19.3 Active sites and isoprene hydrogenation products distribution.

Products	Sites	(Cu/Zr0.5)K		(Cu/Zr0.5)	(Cu/Zr1)		(Cu/Zr2)	Cu ⁰
		80°C	150°C	150°C	80°C	150°C	150°C	150°C
2M1B	³ Cu ⁺ – ¹ Zr ⁴⁺	22	7.3	0.5	15	0.6	25.1	27
3M1B		8	0.2	0	7	0	0,3	7
2M2B	³ Cu ⁺ – ² Zr ⁴⁺	43.5	10	4.5	27	4	23.5	55.5
Isopentane	³ Cu ⁺ – ³ M ⁺	27	82.5	95	51	95.4	50.8	10

M' = Zr⁴⁺ and/or Cu⁺ depending on the catalyst.

According to the previous modeling, it can be proposed that at 80°C, the ³M²M' sites are more likely to be present in (Cu/Zr0.5)K catalyst, while (Cu/Zr1) compound presents a higher proportion of ³M³M' sites. For these two catalysts there is a sharp evolution between 80°C and 150°C, this means an increase of the surface dehydroxylation and then a creation of a higher proportion of ³M³M' sites. At 150°C the (Cu/Zr0.5) and (Cu/Zr1) catalysts have the same products

distribution. The (Cu/Zr2) catalyst acts like metallic copper and its products distribution at 150°C is similar to that of (Cu/Zr1) at 80°C, so the reaction temperature plays an important role in the constitution of the active sites.

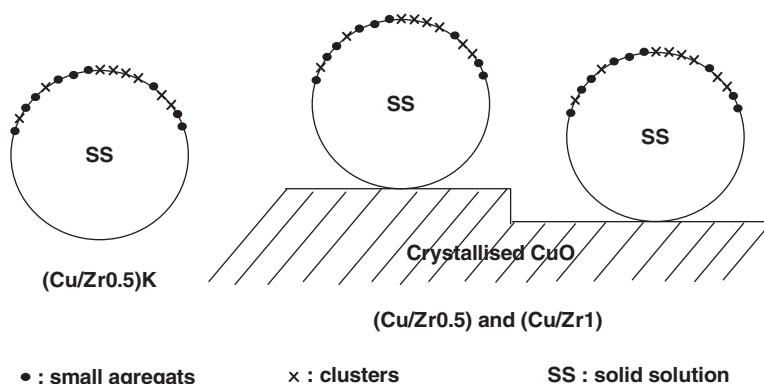


Fig. 19.3 Catalysts modeling.

19.3.2 Reactivity in CO₂ hydrogenation

Table 19.4 gives the results of the global CO₂ conversion and the selectivities in different products. As we can see, the activities are decreasing according to the following sequence: (Cu/Zr1) > (Cu/Zr0.5)K > (Cu/Zr0.5) > (Cu/Zr2). In our operating conditions ($T=250^{\circ}\text{C}$, $P=5\text{ atm}$), we comparatively get few methanol; CH₄ and CO are predominant for thermodynamic limits.

Table 19.4 Conversion and selectivities obtained in CO₂ hydrogenation.

	(Cu/Zr0.5)K	(Cu/Zr0.5)	(Cu/Zr1)	(Cu/Zr2)	(Cu/Zr0)
Conversion (%)	7.2	4.5	11.25	Traces	0
S. methanol (%)	9.54	3.55	4.00	//	0
S. CO (%)	89.13	64.38	72.00	//	0
S. CH ₄ (%)	1.32	32.01	24.00	//	0

19.3.3 Hydrogen species titration

This titration is performed on a catalyst previously in situ treated in H₂ at different temperatures. During the activation step in H₂, anionic vacancies created in the bulk and at the surface of the solid, by the loss of H₂O, are able to receive hydrogen in a hydride form according to a heterolytic dissociation ($\text{O}^{2-}\text{M}^{n+} + \text{H}_2 \rightarrow \text{OH}^- \text{M}^{n+} \text{H}^-$). The oxides become catalytic hydrogen reservoirs able to hydrogenate

isoprene in the absence of gaseous hydrogen. A chemical titration of these hydrogen species can be performed according to a method already published (Jalowiecki et al., 1985). As we can see in Table 19.5, there is no linear correlation between bulk and surface hydrogen storage. However, isoprene hydrogenation activity is directly proportional to surface hydrogen content. CO₂ hydrogenation depends on the Hs/S_{Cu} ratio in favor of the existence of a particular active site located at the metallic copper and solid solution interface (Bali et al., 1996).

Table 19.5 Bulk hydrogen (QH) and surface hydrogen [Hs] contents (mmol g⁻¹ of oxide) versus treatment temperature in H₂.

T red (°C)	(Cu/Zr0.5)K	(Cu/Zr0.5)	(Cu/Zr1)	(Cu/Zr2)
150	9.3 [0.3]	12.9 [1.0]	13.2 [1.2]	11.1 [0.3]
250	12.6 [1.3]	9.2 [0.6]	13.6 [1.3]	13.3 [0.6]
400	7.5 [0.35]	7.3 [0.2]	7.7 [0.6]	6.6 [0.1]

Several studies performed on catalytic systems based on copper have shown that different types of sites, necessary for dienes hydrogenation reactions, can be involved in other reactions, such as the hydrogenation of alpha beta carbonyl compounds and allylic alcohols. In a study on the hydrogenation activity obtained on these compounds, Hubaut et al. (1986) have shown that the activity is not linked to the presence of Cu⁰, but is directly proportional to the amount of Cu⁰ and H⁻ species, (Hubaut et al., 1991). Bechara has also presented a good correlation between activity and existence of Cu⁺–H⁻ sites in the methanol synthesis reaction from CO + H₂ (Bechara et al., 1992). Besides, it is generally admitted that methanol is not formed on copper alone; the addition of a second cation is needed. Several studies performed by in situ IR have evidenced an active ensemble constituted by two cations and have shown some adsorbed species on copper and/or on the second cation, each of these adsorbed species could lead to methanol (Gao et al., 2000, Kung et al., 2002, Ryczkowski, 2001). On the other hand, it is well known that methane can be obtained on catalysts containing a high proportion of copper (Sun and Sermon, 1994, Bartley and Burch, 1988, Gao et al., 2005).

In this study, for the two reactions, the activities are decreasing according to (Cu/Zr1) > (Cu/Zr0.5)K > (Cu/Zr0.5) > (Cu/Zr2). The (Cu/Zr0.5)K catalyst is the most selective toward methanol and the (Cu/Zr0.5) and (Cu/Zr1) catalysts give the highest proportion of methane. The methane selectivity could be explained by a high proportion of Cu⁰ in close contact with a solid solution, easily oxidized by CO₂. The very poor activity of (Cu/Zr2) can be due to the presence of large Cu⁰ crystallites covering the solid solution. As for the diene, the adsorption of CO₂ could be performed on the site presenting three CUS, the second cation being Zr⁴⁺ or Cu²⁺. The ³Cu⁺–²Zr⁴⁺ site is proposed for the formation of methanol and the ³Cu⁺–³Cu⁺ site, more unsaturated, for the formation of methane.

As it has been shown in the catalysts characterization section, the active site can belong to the solid solution (SS) or can be located at the interface of clusters

or small copper aggregates with the solid solution. Then there are three possibilities as shown in Fig. 19.4.

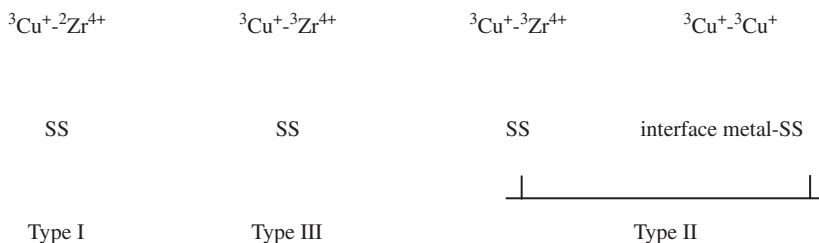


Fig. 19.4 Types of active sites.

In the case of the (Cu/Zr1) catalyst, the existence of a third type of site such as ${}^3\text{Cu}^{+}\text{-}{}^3\text{Zr}^{4+}$ in the solid solution could be considered. However, as it is also present in the (Cu/Zr0.5)K compound, it is unlikely that this kind of site can be greatly involved in the formation of methane. Conversely, the presence of type II sites is highly probable at the interface. This hypothesis is corroborated by an RPE study on Cu–Ce–O catalysts (Wröbel et al., 1996) which evidenced the interactions between copper species belonging to CuO entities of cluster types or small aggregates and the ceria network during reduction.

Differences exist between the two reactions: the hydrogenation of carbon dioxide takes place at 250°C; at this temperature it can be assumed that the surface is less hydroxylated, this could have an influence on the superficial anionic vacancies concentration. For this reaction, CO₂ can oxidize copper and particularly Cu⁰ species. This could be an argument to explain the good selectivity toward methane obtained on the (Cu/Zr1) catalyst which contains a higher proportion of metallic copper compared to the (Cu/Zr0.5)K catalyst. In a previous study, it has been shown that isoprene hydrogenation activity AH varies linearly with the amount of surface hydrogen H_S, while CO₂+H₂ conversion rather depends on the H_S/S_{Cu} ratio (Bali et al., 1996). This factor is therefore important and this result is in favor of an interaction between metallic copper and solid solution. As for the isoprene hydrogenation reaction, “elementary ensembles” corresponding to different structures of sites, constituted of a Cu⁺ cation inserted into the oxide matrix, a hydride species, and anionic vacancies (CUS) localized on the Cu²⁺ and Zr⁴⁺ cations, noted ${}^3\text{Cu}^{+}\text{-}{}^y\text{M}'$ (where *y* is the unsaturation degree of M' related to selectivity), are proposed for CO₂ hydrogenation reaction. The selectivity toward methanol and methane related to these sites has been discussed and the influence of the metallic area represented by the H_S/S_{Cu} ratio has been taken into account in order to localize the active sites for the formation of methane at the interface of the solid solution and the copper metal coming from the clusters. Finally, two mechanisms to methanol

and methane formation via bidental formats can be proposed as presented in Figs. 19.5 and 19.6.

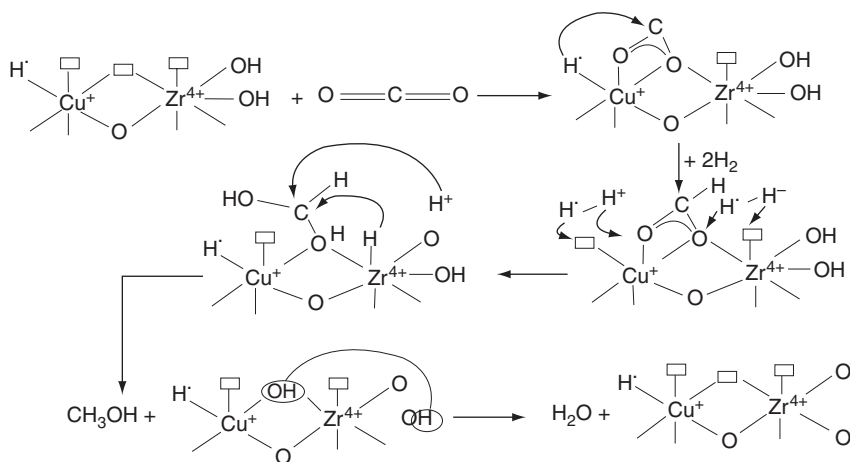


Fig. 19.5 CO₂ active site modeling for methanol synthesis mechanism on site I.

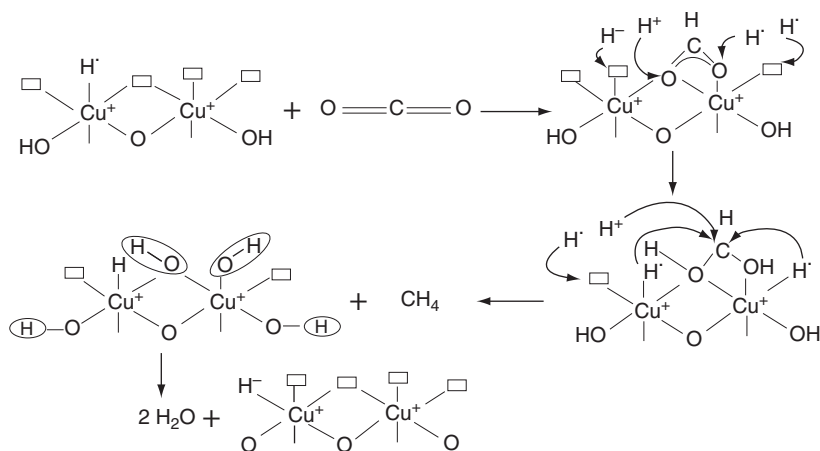


Fig. 19.6 CO₂ active site modeling for methanol synthesis mechanism on site II.

19.4 Conclusions

From this study we can extract the following remarks:

- In the oxidized state, the studied Cu–ZrO₂ system is formed of a hydroxylated solid solution of copper and zirconia and a variable amount of free CuO.

- In a partially reduced state, the solid solution is maintained until 250°C. Beyond this temperature, copper diffuses to the surface and a complete demixing of the solid solution is obtained between 550°C and 600°C with a clear crystallographic evolution of the ZrO_2 phase to cubic or quadratic form. Besides, metallic copper appears less or more rapidly according to the composition and the dimension of the copper oxide grains.
- During the activation step of the catalysts in H_2 (150°C or 250°C), Cu^+ species inserted in the zirconia network and Cu^0 are formed.
- The catalysts have been tested in isoprene and carbon dioxide hydrogenation reactions, in both cases solids showing the best activity are found to follow the decreasing order: $(\text{Cu}/\text{Zr1}) > (\text{Cu}/\text{Zr0.5})\text{K} > (\text{Cu}/\text{Zr0.5}) > (\text{Cu}/\text{Zr2}) > (\text{Cu}/\text{Zr0})$. Moreover, $(\text{Cu}/\text{Zr0.5})\text{K}$ presents a good selectivity to methanol while $(\text{Cu}/\text{Zr1})$ is more selective toward methane.

References

- Bali, F, Bettahar, MM, Wrobel, G, Bonnelle, JP (1995) Catalyseurs oxydes à base de cuivre et de zirconium. Caractérisation à l'état réduit et réactivité. *Journal de Chimie Physique* 92: 1405–1417.
- Bali, F, Bettahar, MM, Wrobel, G, Bonnelle, JP (1996) Préparation de catalyseurs Cu-Zr-O et caractérisation à l'état oxyde. *Colloque Acta on Catalysis* 2: 57–63.
- Bartley, JJ, Burch, R (1988) Support and Morphological Effects in the Synthesis of Methanol over Cu/ZnO, Cu/ZrO₂ and Cu/SiO₂ Catalysts. *Applied Catalysis* 43: 141–153.
- Bechara, R, Aboukais, A, Hubaut, R, Wrobel, G, D'Huysser, A, Bonnelle, JP (1992) Hydrogenation on copper chromite catalysts. Role of cuprous ions in the methanol synthesis from the syngas. *Journal de Chimie Physique* 89: 853–866.
- Gao, LZ, Li, JT, Au, CT (2000) Mechanistic studies of CO and CO₂ hydrogenation to methanol over 50 Cu/45 Zn/Al catalysts by in-situ FT-IR chemical trapping and isotope labelling methods. *Studies in Surface Science and Catalysis* 130: 3711–3716.
- Gao, LZ, Goeppert, A, Surya, GK (2005) CO₂ Hydrogenation to Methanol on a YBa₂Cu₃O₇ Catalyst. *Chemistry International* 44: 2636–2639.
- Hubaut R, Daage M, Bonnelle JP (1986) Selective hydrogenation on copper chromite catalysts. IV. Hydrogenation for α,β unsaturated aldehydes and ketones. *Applied Catalysis* 22: 231–241.
- Hubaut, R, Bonnelle, JP (1991) Reactions of unsaturated ethers on copper-chromium catalysts. *Studies in Surface Science and Catalysis* 59: 287–293.
- Jalowiecki, L, Daage, M, Tchen, AH, Bonnelle, JP (1985) Selective hydrogenation of dienes on copper chromite catalysts. I. catalytic role of occluded hydrogen species. *Applied Catalysis* 16: 1–14.
- Jalowiecki, L, Wrobel, G, Daage, M, Bonnelle, JP (1987) Structure of catalytic sites on hydrogen-treated copper-containing spinel catalysts. *Journal of Catalysis* 107: 375–392.
- Jaowiecki-Duhamel, L (2006) Hydrogen storage and induced properties in metallic catalytic materials. *International Journal Hydrogen Energy* 31: 191–195.
- Katona, T, Molnar, A (1995) Amorphous alloy catalysis: VII activation and surface characterization of an amorphous Cu-Ti alloy catalyst precursor in the dehydrogenation of 2-propanol and comparison with Cu-Zr. *Journal of Catalysis* 153: 333–343.

- Klier, K, Chatikavanij, V, Herman, RG, Simmons, GW (1982) Catalysis synthesis from CO/H₂. *Journal of Catalysis* 74: 343–360.
- Ryczkowski, J (2001) IR spectroscopy in catalysis. *Catalysis Today* 68: 263–381.
- Sun, Y, Sermon, PA (1994) Evidence of a metal-support interaction in sol-gel derived Cu-ZrO₂ catalysts for CO hydrogenation. *Catalysis Letter* 29: 361–369.
- Sene, A (1992) Formation et fonctionnement des sites actifs des catalyseurs d'hydrogenation Cu-Zn-O et Cu-Zn-Al-O. Thesis of University of Lille, France.
- Siegel, S (1973) Alkene hydrogenation and related reactions: A comparison of heterogeneous with homogeneous catalysts. *Journal of Catalysis* 30: 139–145.
- Wang, YM, Li, YS, Wong, PC, Mitchell, KAR (1993) XPS studies of stability and reactivity of thin films of oxidized zirconium. *Applied Surface Science* 72: 237–244.
- Lide, DR (2002) *Handbook of Chemistry and Physics* 83 ed. Boca Raton, 51–60.
- Wrobel, G, Sohier, MP, D'Huysser, A, Bonnelle, JP (1993) Hydrogenation catalysts based on nickel and rare earth oxides. Part II: XRD, electron microscopy and XPS studies of the cerium-nickel-oxygen-hydrogen system. *Applied Catalysis A General* 101: 73–93.
- Wröbel, G, Lamonier, C, Bennani, A, D'Huysser, A, Aboukais, A (1996) Effect of incorporation of copper or nickel on hydrogen storage in ceria. Mechanism of reduction. *Journal of Chemical Society Faraday Transient* 92(11): 2001–2009.
- Younes, MK, Ghorbel, A, Rives, A, Hubaut, R (2000) Catalysts and catalysis properties of aerogels sulphated zirconia. *Studies in Surface Science and Catalysis* 130: 3219–3224, Elsevier D 3219.

CO₂ and SO₂ Capture Capability of Two Greek Limestones

Panagiotis Basinas, Panagiotis Grammelis, John R. Grace, C. J. Lim, George Skodras and George P. Sakellariopoulos

20.1 Introduction

Carbon dioxide has been identified as the major greenhouse gas contributing to global climate change. As a result, various processes are being explored that would allow CO₂ to be captured and ultimately sequestered from processes, such as combustion, gasification, and steam methane reforming, where carbon dioxide is a major by-product. Use of amine solvents for CO₂ capture, while common in industry, is expensive and unlikely to be feasible on a large scale. Looping cycles involving calcium sorbents, where CO₂ is released at high temperature by calcinations and captured at lower temperature by carbonation, are of particular interest. However, evidence has shown that the ability of the sorbents to maintain their utilization over repeated cycles is quite limited.

One of the characteristics that influences the capture capability of limestones is the particle size distribution. Most previous studies report that particle size slightly affects the cyclic process and the performance of limestones (Sun et al., 2005; Li et al., 2005). Grasa and Abanades (2006) who focused on small particle fractions, of the order of 100–1000 μm , concluded that sorbent particle size did not influence the sorption capacity of the sorbents tested, instead only depending on the number of cycles performed. On the other hand, Ye et al. (1995) suggested that particles smaller than 5 μm be considered optional due to the increased cost of the milling.

Another experimental parameter that affects the sorption ability and the decay of the lime-based sorbents is the temperature of the reaction between CaO and CO₂. Typical temperatures in the carbonator exceed 600°C, while calcination requires higher temperatures. Grasa and Abanades (2006) proposed that the temperature of 950°C during the calcination stage could be beneficial for the sorbent cyclic performance. Sun et al. (2005) investigated sorbent performance at 850°C

and reported that lower temperatures (750°C) enhance the carbonation of the CaO during the first two cycles. The reaction time constitutes another crucial parameter affecting the sorption capability during continuous cycling of the sorbents. Previous research studies indicate that relatively brief sorption times result in decreased calcium utilization efficiencies, but in slightly increased reactivity, mostly for the few first cycles of the process.

In fluidized bed combustion (FBC) plants the presence of SO₂ is unavoidable. Therefore, the sulfation of the sorbents is of major importance as also shown from the numerous works performed on the behavior of sorbents under SO₂ (Adanez and Garcia-Labiano, 1993; Badin and Frazier, 1985; Cheng et al., 2004; Ghosh-Dastidar et al., 1996; Laursen et al., 2001, 2002; Stanmore and Gilot, 2005; Sun et al., 2007; Ye et al., 1995). Most of these studies claimed that sulfation mainly occurs on the surface of the particles forming a CaSO₄ layer, which impedes further sulfation and/or carbonation of the particle. Stanmore and Gilot (2004) reported that sulfite is also involved in the reaction scheme and concluded that the sulfation ability is reduced by the presence of the high proportions of O₂ and SO₂ in the gas stream. The sulfation extent is based on the Ca/S ratio. According to the chemical reaction the absorption of 1 mol of SO₂ requires 1 mol of Ca. Nevertheless, the utilization of Ca is most of the times higher. It is common notion that the pore structure strongly affects the sulfation process. Ghosh-Dastidar et al. (1996) underlined the existence of an optimum pore structure of the parent limestone, which after calcination will produce the optimum pore size for sulfation.

The aim of this study is to elucidate the factors leading to the deactivation of two individual limestone types. For this reason, two limestones originating from two different Greece locations are subjected to cyclic sorption/calcination investigations. The sorbents are characterized for their CO₂ caption ability under a specific number of carbonation/calcination cycles. The effect of particle size, reaction time, and reaction temperature on the CO₂ capture ability and the decay of the limestones is also investigated. Another purpose of the study reported here is to explore possible ways to diminish the sorbents deactivation. In practice, carbonation always occurs in the presence of SO₂, and therefore the comprehension of the interaction phenomena is of great importance. The durability of the limestones under simultaneous carbonation and sulfation is determined. Among the priorities of this work is to figure out the effect of SO₂ on the carbonation and simultaneously the effect of CO₂ on the sulfation process.

20.2 Experimental

20.2.1 Materials

Two limestones originating from Megalopolis (Southern Greece) and Florina (Northern Greece) areas were investigated for their CO₂ and SO₂ capture capability. Grinding and sieving were applied to provide a baseline particle size fraction between 150 and 250 µm and two other particle size fractions of 38–53 µm and

500–800 μm , for the investigation of the effect of granulometry on the cycling performance of the limestones.

20.2.2 Apparatus and procedure

The sorption and cyclic tests were conducted in a TA instruments Q600 thermogravimetric analyzer. The accuracy of this instrument is $\pm 1 \mu\text{g}$. Temperature is measured by a thermocouple located immediately below the sample holder. Each sample of $\sim 20 \text{ mg}$ is placed in an open alumina pan, which in turn is placed on a horizontal beam holder. The temperature and weight of the sample are recorded continuously. The same temperature was applied for both the sorption and the calcination stages. A schematic layout of the reactor is shown in Fig. 20.1. The initial calcination of the limestones, however, was performed under non-isothermal conditions, raising the temperature from 30°C to the sorption/calcination temperature with a heating rate of $20^\circ\text{C}/\text{min}$. The samples were then maintained at this temperature for 5 min to ensure complete calcination. The flow rate remained constant at 800 ml/min for both the sorption and calcination steps. Pure nitrogen was used for the calcination process in all cases, whereas carbonation of the samples was performed either with pure CO₂ or with a mixture containing 80% CO₂ and 20% N₂ by volume, respectively. A gas mixture composed of 80% CO₂, 2900 ppm SO₂, 3% O₂, and N₂ as the balance was used during the co-capture tests, whereas a mixture containing 2900 ppm SO₂ and 3% O₂ in N₂ was utilized for all the sulfation cycle tests.

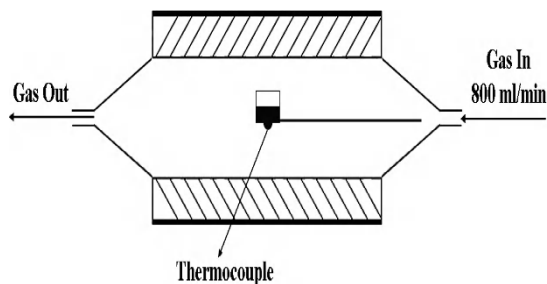


Fig. 20.1 Schematic diagram of the thermogravimetric analyzer at atmospheric pressure.

The sorption time plays an important role in determining the capture capability and performance of limestones. A fast carbonation stage is normally completed within 8 min. Therefore, a sorption time of 8 min was defined as the baseline for the tests performed. The effect of time on the sorption capability and performance of the samples was also investigated by tests with two alternative sorption times, 3 and 30 min. In all cases, the time for the calcination stage was maintained at 5 min. Two additional particle size fractions, 38–53 μm and 500–800 μm , were used to investigate the influence of sorbent granulometry on the carbonation behavior of the limestones. Moreover, the effect of the reaction temperature on the capture capability of the sorbents was studied by runs at two additional capture temperatures, 650°C and 750°C .

Chemical analyses of the limestone samples were conducted using inductively coupled plasma-atomic emission spectroscopy on an ICP-AES multi-element spectrophotometer (Perkin–Elmer). Various acid solutions (hydrochloric, hydrofluoric, etc.) were used to dissolve the samples and then to determine their elements. More details on the process are given elsewhere (Skodras et. al., 2007). A complete data set referring to the chemical analysis of both samples appears in Table 20.1.

Table 20.1 Chemical properties of the sorbents.

Samples	CaO (%wt)	MgO (%wt)	Al ₂ O ₃ (%wt)	Na ₂ O (%wt)	Fe ₂ O ₃ (%wt)	K ₂ O (%wt)	TiO ₂ (%wt)	Rest (%wt)
Megalopolis	45	0.48	0.03	0.01	0.02	0.00	0.00	54.46
Florina	58.1	0.36	1.33	1.42	0.22	0.55	0.06	37.96

20.3 Results and Discussion

20.3.1 Limestone properties

As shown in Table 20.1 both limestones mainly consist of calcite and small proportions of other impurities. Haji-Sulaiman and Scaroni (1990) considered any substances other than CaO as impurities and reported that natural limestones contain ~1–20% substances which are non-active during sorption. These additional substances include silica, quartz, and trace elements. The presence in high proportions of these impurities results in shrinkage of the limestones during calcination. ICP analysis revealed that Florina limestone had the highest percentage of CaO and at the same time the highest percentage of other substances, mainly Al and Na. As previously shown (Laursen et al., 2001), sodium can assist in the sorption of sulfur. Hence Florina limestone is the more promising candidate for the absorption of SO₂. On the other hand, these impurities result in lower surface areas for the limestones and their calcines. As indicated in a previous study (Haji-Sulaiman and Scaroni, 1990), the impurities content play a significant role in causing sintering during CO₂ capture and calcinations. It has been reported that concentrations of Fe₂O₃ beyond 0.5 wt.% contribute to the sintering of sorbents. In both Greek limestones, ferrous ions are present at low percentages, of the order of 0.02 wt.% and 0.22 wt.% for Megalopolis and Florina, respectively, so that its effect on sintering is expected to be limited. Na, which is also considered to favor sintering, is also present at a very low percentage in the Megalopolis sorbent.

According to Haji-Sulaiman and Scaroni (1990), impurities could be present in the limestone in one of two forms: (a) homogeneous, with the impurities well dispersed inside the sample particles and (b) heterogeneous, with the impurities concentrated between the crevices or strata. Cases where the impurities are not uniformly dispersed are also included in the second option.

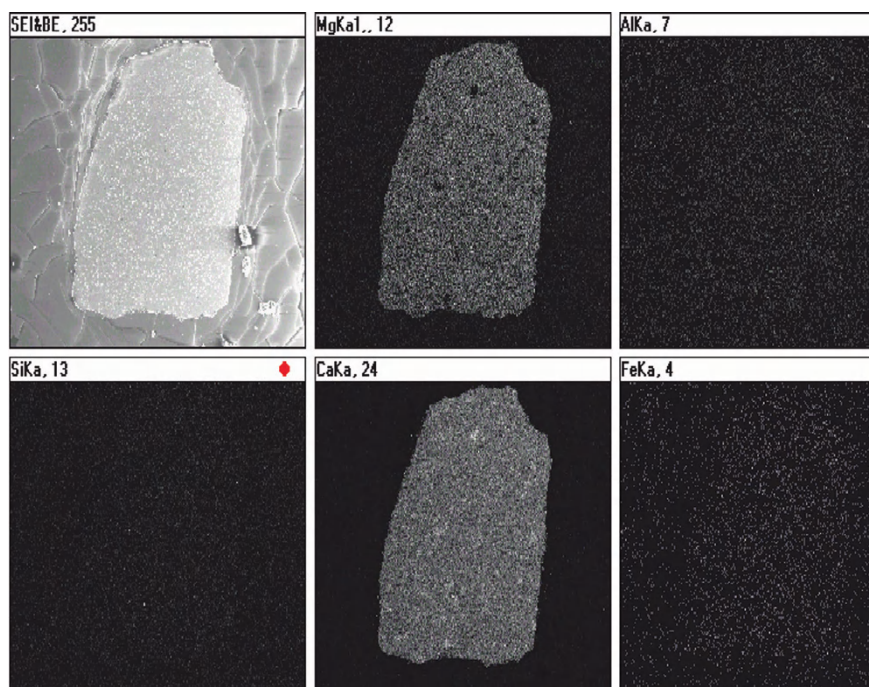


Fig. 20.2 X-ray mapping of epoxy-embedded as-received Megalopolis limestone.

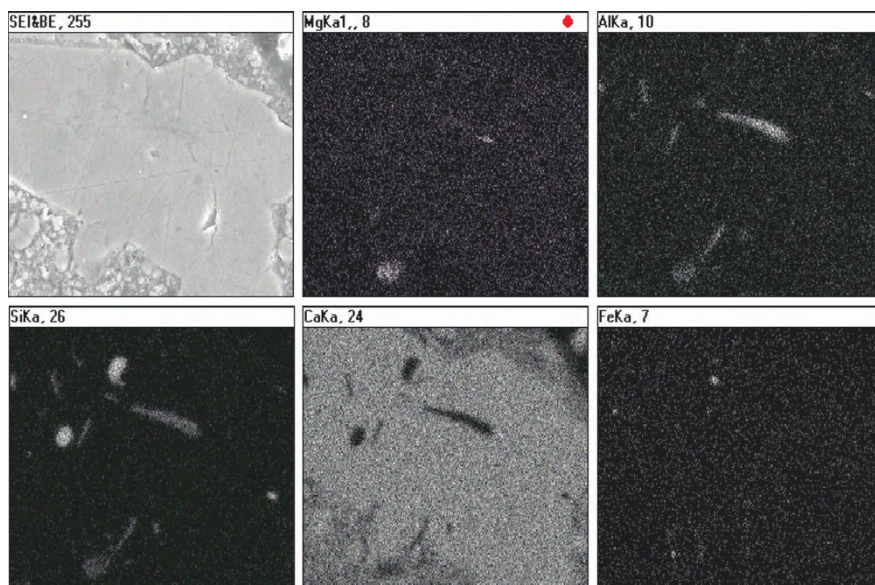


Fig. 20.3 X-ray mapping of epoxy-embedded as-received Florina limestone.

As can be seen from the SEM–X-ray images (Figs. 20.2 and 20.3), in the case of Florina limestone the silica content is concentrated in high proportions into crevices and is not dispersed in other places inside the particle. Aluminum, which together with silica constitutes the main impurities in Florina limestone, follows similar dispersion behavior. On the other hand, most of the Megalopolis limestone impurities are well dispersed inside the particles. Magnesium, the major impurity, is so well dispersed that it exhibits a similar profile as calcium. Four types of voids are presented in Ca-based sorbents – micro-pores, micro-fractures, macro-pores, and macro-fractures (Laursen, 2002; Cheng et al., 2004). These structural characteristics are also clearly visible in the SEM images. Megalopolis limestone exhibits a higher proportion of micro-pores and micro-structures, whereas Florina limestone presents a more stable structure with a higher number of macro-pores and macro-structures, as shown in Figs. 20.4 and 20.5.

20.3.2 Carbonation of the sorbents

The cyclic CO₂ capture capability for a pure CO₂ gas stream for both limestone samples is presented in Fig. 20.6. At the beginning of each carbonation cycle, the reaction between CaO and CO₂ is rapid, as indicated by the slope of the mass profile. This stage is governed by the gas–solid chemical reaction taking place on the surface of the particles. This reaction results in the formation of CaCO₃, which slowly obstructs the micro-pores and renders the internal CaO inaccessible to CO₂. This first stage is followed by a second slower stage, which is controlled by the diffusion of CO₂ in the CaCO₃ layer (Abanades, 2002; Abanades and Alvarez, 2003; Barker, 1973; Chrissafis et al., 2005; Grasa and Abanades, 2006; Mess et al., 1999; Silaban and Harrison, 1995; Sun et al., 2005). As can be seen from Fig. 20.6, the chemically controlled stage is completed in the first 2–3 min of the carbonation, and this time remained approximately constant for all the cycles performed. This indicates that the time for the chemically controlled stage is unaffected by the number of carbonation/calcination cycles. On the other hand, the conversion during the fast carbonation stage decreased as the number of cycles increased. For example, the time needed for calcination during the first three cycles was almost 5 min, whereas at elevated number cycle the calcination time was significantly reduced. Therefore, the calcination time seems to be affected by the cyclic process, in agreement with observations of previous studies (Grasa and Abanades, 2006; Ryu et al., 2006).

As depicted in Figs. 20.6 and 20.7, the CO₂ capture decreased during repeated cycles, meaning that part of the calcium was not able to be utilized as the cycle number increased. Even from the first cycle the carbonation capacity is limited to 89 wt.% and 86 wt.% for Megalopolis and Florina limestones, respectively. Similar values for the first carbonation of the limestones have also been reported in previous studies (Silaban et al., 1996).

Despite the fact that complete calcination was achieved in each cycle, the ability of CaO to react with CO₂ continuously declined. In all cases the reduction in CO₂ capture ability is considered to have resulted from textural transformations occurring after at least one carbonation/calcination cycle.

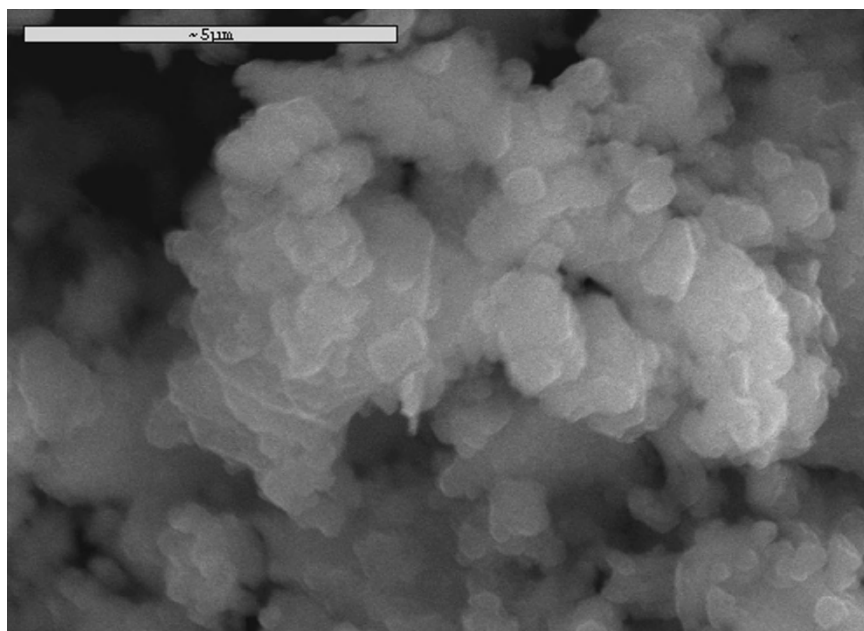


Fig. 20.4 High-resolution SEM image of as-received Megalopolis limestone.

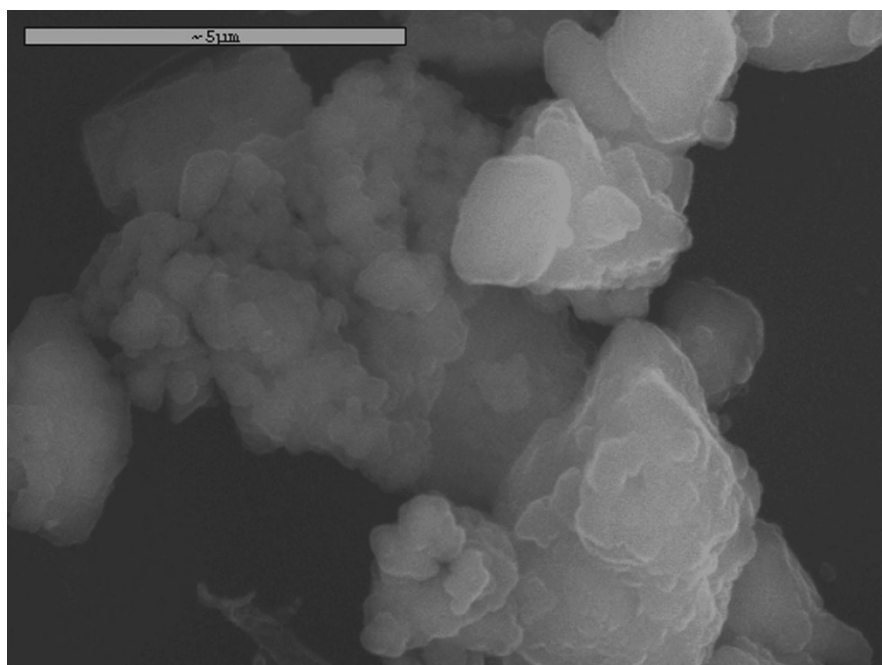


Fig. 20.5 High-resolution SEM image of as-received Florina limestone.

This reduction was highest in the first two cycles of the process. Munoz-Guillena et al. (1995) explained that the textural properties differ, even between the original limestone and the calcined CaO. Sun et al. (2005) attributed the continuously increasing failure of calcium carbonate to capture CO_2 to sintering effects during carbonation and to the lack of re-crystallization during calcination. During the successive carbonation/calcination cycles the voids between the grains are reduced due to formation of necks. These necks between the grains result in a decrease in the surface area and to the loss of porosity (Stanmore and Gilot, 2005). More specifically, sintering leads to the closure of micro-pores and simultaneously to the widening of the larger pores. As a result, the available CaO for CO_2 capture decreases continuously as the number of carbonation/calcination cycles increases.

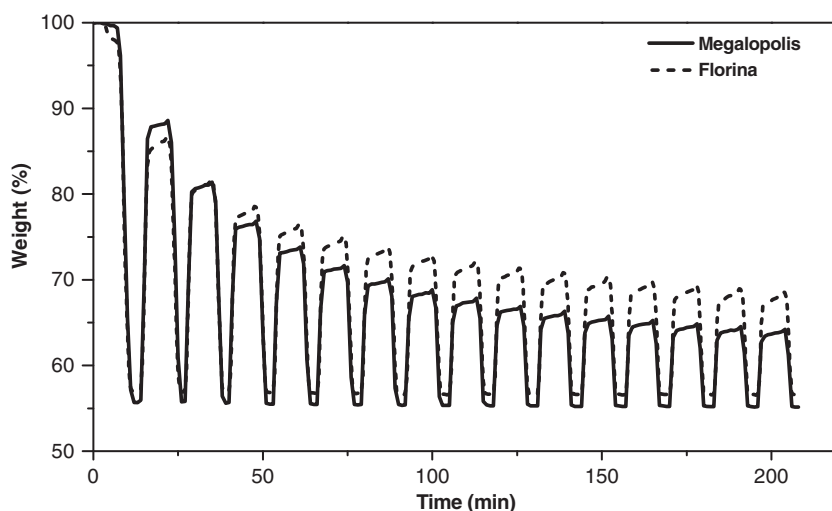


Fig. 20.6 Weight change during carbonation/calcination cycles, Carbonation–calcination at 850°C , 8 min, pure CO_2 , 15 cycles.

The CO_2 capture capability of Megalopolis limestone was higher for the first two cycles than for the Florina limestone, even though Megalopolis limestone has a lower Ca content than the Florina one. The most plausible explanation is that the calcium available for sorption is higher in the case of Megalopolis limestone, despite lower calcium concentration. Notwithstanding its initial higher capture, the decay for the Megalopolis limestone in the next cycles was higher from the 3rd cycle onward so that its capture capability became significantly lower than for the Florina sorbent. As noted above, the Megalopolis limestone structure has a greater number of micro-pores. Sintering causes closure of the micro-pores and therefore a rapid decrease in the capture capability. The number of micro-pores for Florina limestone is lower and thus its loss of capture ability was lesser than for the Megalopolis limestone. Hence the reduced capture capability of Florina limestone during the three initial cycles can be explained by the enhanced number of macro-pores during the early stages.

Abanades (2002) suggested an empirical equation to predict the decay of the limestone samples when subjected to continuous carbonation/calcination cycles:

$$X_{c,N} = f^{N+1} + b \quad (20.1)$$

where $X_{c,N}$ represents the CO₂ capture capacity, N is the number of cycles, while f and b are empirical constants with values $f = 0.782$ and $b = 0.174$. A schematic diagram of the empirical equation is depicted in Figs. 20.7 and 20.8 in comparison with the experimental results of the cyclic tests for both Megalopolis and Florina limestones. As can be seen from Fig. 20.7, there was excellent agreement between the correlation and the baseline test results. During the first five cycles the decay of Megalopolis limestone is higher than predicted by the correlation. From the 7th cycle onward the decay was below that indicated by Eq. (20.1). In both cases the deviation between the baseline and the correlation is minimal. On the other hand the deviation between the baseline corresponding to the capture capability of Florina limestone and the theoretical curve is higher both before the first five cycles and after the 7th cycle. Nevertheless, these deviations are relatively small.

a) Particle size effect

The conversion data for the Megalopolis and Florina limestones are compared in Figs. 20.7 and 20.8. For all the tests the particle size used is between 150 and 250 μm except where specified. The general trend is the same for all particle size ranges tested. The loss in capture capacity of the limestone is rapid during the first four cycles, especially for the first cycle. The rate of decay decreased during the following cycles. For the Megalopolis limestone, a reduction in the particle size resulted in increased capture capability and less decay for all cycles tested. Smaller particles result in higher external surface area and shorter penetration distances and thus lower decay during at least the first few cycles. However, the decay of the limestone was almost at the same level as that for the baseline during the following cycles. The capture capability during the successive cycles seems to have been unaffected by the increased particle size for Megalopolis limestone. The conversions for the 150–250 and 500–800 μm particle fractions were very similar in all cases.

As depicted in Fig. 20.8, during the first five cycles the capture capability of Florina limestone was almost identical for all the three particle sizes tested. From this cycle onward, the 150–250 μm particle fraction shows the best CO₂ capture ability, followed by the smallest particles (38–53 μm). The lowest CO₂ capture capability was for the largest particles (500–800 μm) for this limestone. The conversion deviations due to different particle sizes are of the order of 0.25. It is also notable that in all cases the conversion curves for all three particle size fractions investigated are higher than for Eq. (20.1).

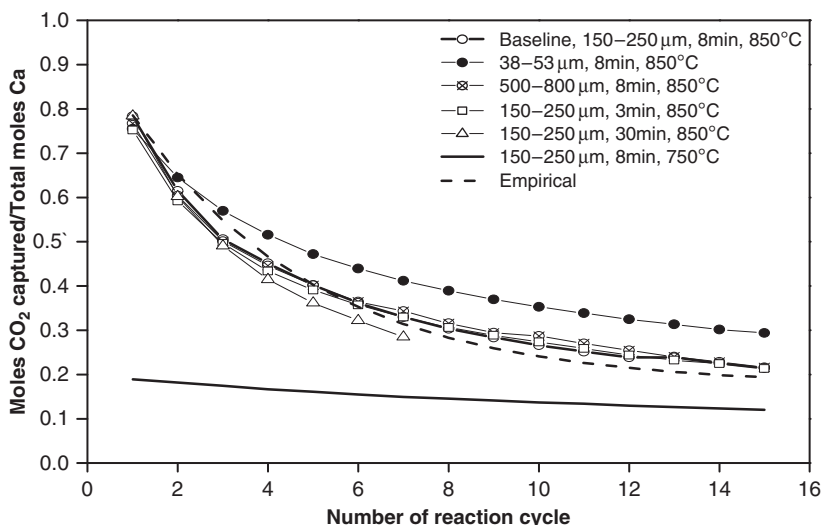


Fig. 20.7 Cyclic CO_2 capture ability of Megalopolis limestone in 80% v/v CO_2 –20% v/v N_2 . Calcination in N_2 .

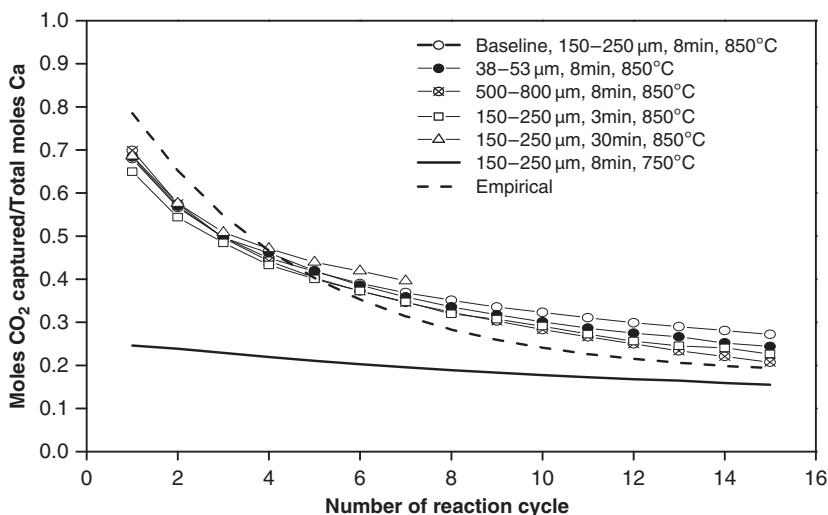


Fig. 20.8 Cyclic CO_2 capture ability of Florina limestone in 80% v/v CO_2 –20% v/v N_2 . Calcination in N_2 .

b) Effect of reaction time and temperature

As previously reported, the baseline tests were performed at a temperature 850°C and for a time of 8 min. The conversion profiles corresponding to the carbonation capacity of Megalopolis and Florina limestones at varying times (3 min and 30 min) are plotted in Figs. 20.7 and 20.8, respectively. It is seen that the reaction time affected the CO_2 capture capability quite differently for the two limestones. Megalopolis limestone seems to have been less affected by the variation in carbonation

times than the Florina limestone. Note that the 3-min time interval was long enough for the carbonation reaction. In previous studies (Grasa and Abanades, 2006; Sun et al., 2005) a reaction time of 3 min was considered to be too short to complete the reaction between CaO and CO₂. These differences in results probably reflect different experimental systems in each situation. In the present study, the experimental conditions such as the weight, the gas flow rate, and size of the furnace probably allow the reaction between the gas CO₂ and the solid sorbent to take place more quickly.

As shown in Fig. 20.7, Megalopolis carbonation was unaffected by a reduced reaction time, since the conversion profiles for the baseline (8 min) and the 3-min test almost coincide for every cycle. This behavior may be because the sintering of the limestone occurs to the same extent for 8 min as for 3 min of carbonation. The 30-min test showed that until the 3rd cycle, the carbonation capacity was not affected by the longer reaction times. As depicted in Fig. 20.7, for cycle number >3, the 30-min carbonation resulted in less CO₂ capture capacity for the Megalopolis limestone. The decay of the specific limestone also appeared to be greater for this elevated time interval, suggesting that the sintering effect was stronger for longer carbonation times. As reported previously (Stanmore and Gilot, 2005), various factors such as temperature, time, and the presence of CO₂ alter the sintering effect.

Different trends were observed for Florina limestone. As Fig. 20.8 illustrates, the carbonation efficiency in the 3-min tests was less than for the baseline. In fact, the conversion of Florina limestone was limited, even in the first cycle, with more than 3 min needed for calcium utilization of this limestone. The calcium utilization for the 30-min tests was similar to that of the baseline. However, the decay in the 3-min tests was unexpectedly lower, probably due to the morphological characteristics and the pore structure of the Florina limestone. Notwithstanding the sintering effect, the crevices and the larger pores in this sorbent provide pathways that allow CO₂ to reach the calcium available in the interior. This, in conjunction with the high reaction time, leads to the absorption of higher quantities of CO₂.

Carbonation temperature constitutes another parameter that affects the CO₂ capture capability of the Ca-based sorbents. Carbonation is an exothermic reaction, while calcination is endothermic. Therefore, the latter is favored by higher temperatures, whereas the carbonation reaction is favored by lower temperatures around 750°C at atmospheric pressure (Li et al., 2005). In the present study a temperature of 850°C was used as the baseline for both the carbonation and calcination stages. As shown in Figs. 20.7 and 20.8, the CO₂ capture capacity was significantly lower for the tests performed at 750°C and a reaction time of 8 min for both limestones. In the case of Megalopolis sorbent, the calcium utilized for sorption was only 25.3% of the calcium utilized at 850°C. The corresponding value for Florina limestone was somewhat higher (35%). Note that the decay of the limestones varies throughout the entire cycling test. In effect, only part of the calcium was utilized and underwent sintering, and therefore most of it was available for the following carbonation cycles. The tests performed at calcination and

carbonation temperature of 650°C showed even worse CO₂ capture profiles for both the limestones tested.

20.3.3 Sulfation of the sorbents

Figure 20.9 shows results of sulfation tests on 150–250 µm particles performed with 2900 ppm SO₂ without CO₂ being present for 2 h. It is seen that the Florina limestone had a higher sulfation efficiency than Megalopolis, with the calcium utilization in the latter case being almost 13%, whereas the corresponding value for Florina limestone was almost 26% after 2 h of continuous operation. As depicted in Fig. 20.9, the lime utilization could continue after 2 h. According to previous research (Stanmore and Gilot, 2005), the total calcium utilization for SO₂ capture has the potential to continue to increase, reaching conversions up to 95% after extended reaction times. Fundamental studies on the sulfation of Ca-based sorbents (Laursen, et al., 2002; Ryu et al., 2006) have reported three different sulfation modes: unreacted core, uniform, and network sulfation. The mode in a given case depends on the morphological characteristics of the limestones after sulfation. These studies found that the unreacted core sulfated particles exhibited higher SO₂ sorption capacity than the uniform and the network sulfated particles. The uniformly sulfated particles should contain a large fraction of micro-pores, and their sulfation should occur in a homogeneous manner. Although the quantity of SO₂ absorbed by unreacted core particles is higher, the CaSO₄ layer produced at the rim of the particles is thicker than for the uniformly sulfated particles. Taking into account these general characteristics, Florina limestone seems to follow an unreacted core mode, while Megalopolis is subject to the uniform sulfation mode.

Another important finding is that the sulfation of the samples took place in two clearly distinguished stages. In the first stage, the sulfation rate increased almost linearly with time, whereas in the second, the sulfation proceeded at a significantly slower rate. These observations are consistent with the findings of Ye et al. (1995), who claimed that sulfation is divided into two different stages, the first accompanied by pore filling by gaseous SO₂ considered to be the rate-limiting step. As illustrated in Fig. 20.8, this step lasted for ~50 min for Florina limestone. For the Megalopolis limestone, this step required a shorter time interval (30 min). As previously mentioned, the reaction between CaO and SO₂, which mainly occurs on the outer surface and inside the pores of the sorbent particles, results in the formation of an outer CaSO₄ layer, which obstructs SO₂ from reaching the available CaO. However, some SO₂ permeates through this layer to gain access to the interior calcium. Therefore, sulfation of the limestone continues slowly in the second reaction stage. In the case of Megalopolis limestone, the contribution of the second stage to the overall sulfation of the limestone is low, accounting for only 15% for a reaction time of 2 h. The second stage contributes more to the sulfation of Florina limestone, accounting for almost 26% of the overall sulfation.

The effect of calcination on the sulfation of the limestones was investigated with experiments, which include a number of sulfation/calcination cycles at 850°C and a constant reaction time of 8 min. The results are also presented in Fig. 20.9. It is well known that the SO₂ absorbed by CaO cannot be desorbed upon calcination.

It is clear that the calcination affected the sulfation of both limestones, but to a different extent. The sulfation of Megalopolis limestone followed behavior similar to the continuous sulfation pattern, until the first reaction stage was complete. During the second sulfation stage, SO₂ absorption was higher for the cyclic sulfation/calcination process. The sulfation utilization of Florina limestone also increased with implementation of the sulfation/calcination cycles. This enhancement in sulfation capacity accounts for 1.5% of the 2 h continuous sulfation for both limestones. As in previous research (Laursen et al., 2002), the unreacted core sulfated particles tended to be regenerated, whereas the uniformly sulfated particles showed very little regeneration. The different effects of calcination on the two limestones are probably related to the different sulfation modes. It is also notable that for the Florina limestone, the times for each of the reaction stages were transformed. As shown in Fig. 20.9, the reaction-limited stage (first stage) extended to 80 min, while the second stage shortened to 40 min. A plausible explanation could be that the calcination cycles prevented the CaSO₄ layer from forming, resulting in longer reaction-limited and shortened diffusion-limited stages. Consequently, calcination cycles during the sulfation are beneficial to achieve higher sulfation efficiencies.

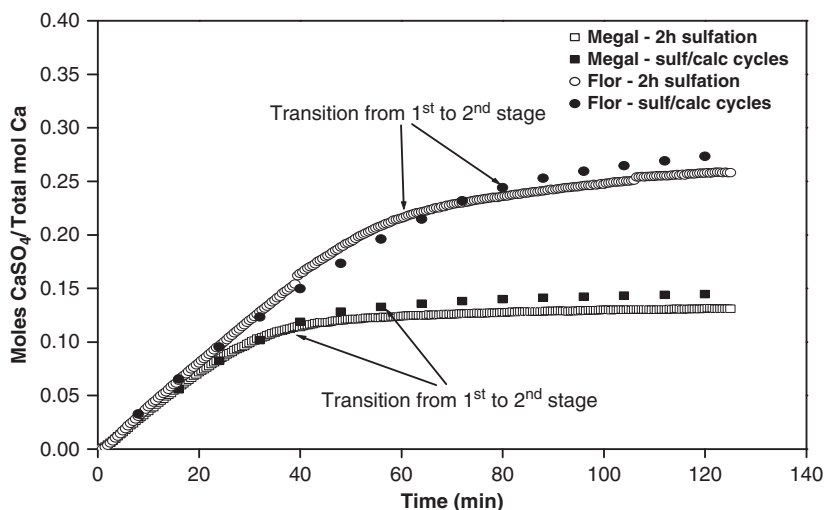


Fig. 20.9 Sulfation profiles for Megalopolis and Florina limestones in no CO₂ – 2900 ppm SO₂ – 3% v/v O₂ – balance N₂. Calcination in N₂.

20.3.4 Co-capture capability of the sorbents

The sorption capacity and performance of the limestone samples when both CO₂ and SO₂ are present is of significant importance in fluidized bed combustion. Therefore, simultaneous carbonation and sulfation behavior of the Greek limestones was investigated with a gas mixture containing 80% CO₂, 2900 ppm SO₂, 3% O₂, and the balance N₂. In every cycle, the quantities of CO₂ and SO₂ captured were calculated from the thermogravimetric curves. The main consideration is that

the entire quantity of SO_2 captured in each cycle remains absorbed in the sorbent after calcination. A schematic diagram of the proportion of the CO_2 captured, in conjunction with the total available calcium in each cycle, is depicted in Fig. 20.10. During simultaneous CO_2/SO_2 capture a portion of the available CaO is utilized to absorb CO_2 , while another part participates in the absorption of SO_2 . This results in reduced CO_2 capture capacity compared to carbonation alone. The reactions between the sorbent and the gases along with a detailed analysis are presented by Sun et al. (2005).

As shown in Fig. 20.10, the falloff in CO_2 capture capability, during the 10–12 cycles is similar to that for the carbonation tests. This observation creates the perception that for the first 10–12 cycles the reduced availability of CaO during co-capture results in the same deterioration in CO_2 capture as due to the sintering effect during carbonation. Nevertheless, the falloff in CO_2 capture capability of both the Greek limestones increased after the 12th cycle. As the number of cycles increased, both sulfation and direct sulfation resulted in formation of a thick CaSO_4 layer on the surface of the sorbent particles. From the 12th cycle onward, a major portion of the available CaO was utilized for SO_2 absorption, and together with the sintering effect caused by the CO_2 absorption, resulted in a rapid decay in the CO_2 capture capability.

As for the carbonation of the sorbents, each cycle of the simultaneous CO_2/SO_2 capture is characterized by a rapid sorption stage, followed by a second much slower stage. For the first cycle, the fast sorption stage lasted for about 4 min. As the number of cycles increased, the time needed for the fast sorption stage continuously decreased and the second stage became dominant. During the final sorption cycle, the first stage lasted for less than 1 min. These results are consistent with the observations of Ryu et al. (2006), who ascribed this behavior to the reduced capture capability of the limestones. It is obvious that the first effective sorption stage involves carbonation of the available calcium. As previously mentioned, sulfation is also present during this stage. Therefore, after a sufficient period of sorption, the products of both reactions prevent CO_2 from reaching the available calcium, causing a reduction of reaction rate. The slow reaction stage which follows is characterized by the diffusion of CO_2 through the product layers. As the number of cycles increases, the thickness of the CaSO_4 layer also increases. As a result, the fast reaction time is limited and the slow reaction stage becomes dominant.

Another important aspect of the results is the effect of CO_2 in co-capture tests on the sulfation of the limestones. The presence of CO_2 in the gas stream initially reduces the available calcium for SO_2 absorption and consequently the SO_2 sorption is expected to be reduced. In fact as the number of cycles increases the SO_2 capture is also increased at a slow but constant rate. Taking into account that SO_2 captured in each cycle remains absorbed during calcination, the sulfation of the limestone is expected to increase. Therefore, sulfation could be extended to higher conversions than carbonation. In the meantime, the CaCO_3 produced during each cycle could be converted to CaSO_4 due to direct sulfation reaction (Stanmore and Gilot, 2005; Sun et al. 2007).

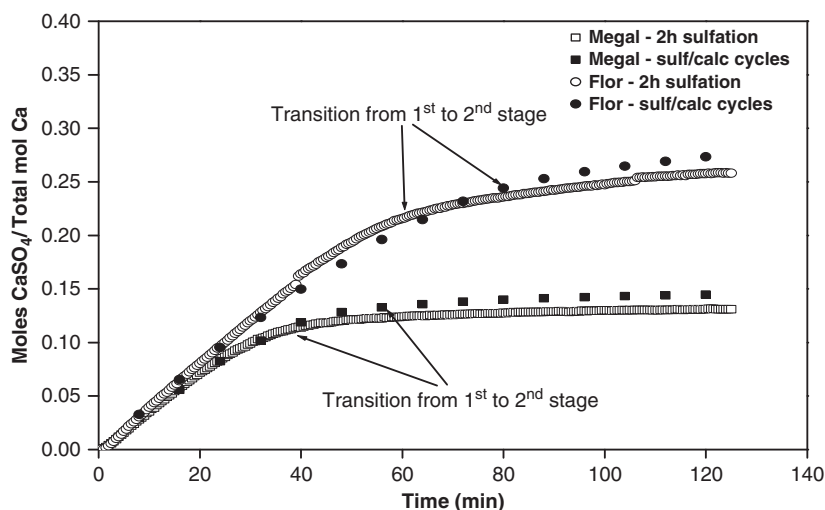


Fig. 20.10 Cyclic CO₂/SO₂ sorption ability of Megalopolis and Florina limestones in 80% v/v CO₂ – 2900 ppm SO₂ – 3% v/v O₂ – balance N₂. Calcination in N₂.

20.3.5 Sequential carbonation and sulfation

Two sets of consecutive carbonation/sulfation experiments were performed in an effort to elucidate the partial effects of sulfation and carbonation on the performance of the limestones. During the first experiments, the samples were initially calcined and subjected to a single carbonation cycle. The second cycle included sulfation of the product calcine in a gas mixture containing 2900 ppm SO₂, 3% O₂ in N₂, and then calcination. The sample was then subjected to 15 carbonation/calcination cycles. The second experimental set included 21 cycles, with one sulfation for every four carbonation/calcination cycles. Each carbonation, sulfation, or calcination step lasted for 8 min. The results appear in Fig. 20.11 and 20.12 for the Megalopolis and Florina limestones, respectively. The baseline curves are also included for comparison.

As expected, the CO₂ capture capability of both Megalopolis and Florina limestones was reduced after one sulfation cycle is presented. However, the decay of both limestones after the sulfation cycle followed the same trend as for the baseline test. This behavior indicates that the formation of a CaSO₄ layer constrains the available CaO, but does not affect the decay mechanism of the sorbents during carbonation/calcination cycles. The slope of the thermogravimetric curves during carbonation cycles, which follow the sulfation, remains the same as for the carbonation/calcination tests. On the other hand, the sulfation rate was slightly affected by the carbonation/calcination cycles. Li et al. (2005) affirmed that the sulfation rate increased when a carbonation/calcination cycle was inserted between the initial calcination and the sulfation of the limestone.

Another important aspect of the results is the increased decay in CO₂ capture for the Megalopolis limestone exposed to one sulfation, compared to the

corresponding behavior of the Florina limestone. As already noted, Florina limestone follows an unreacted core pattern when exposed to sulfation conditions, and therefore a CaSO_4 layer formed on the surface of the sorbent particles. CO_2 molecules are able to penetrate this layer and reach the CaO available on the interior. CaCO_3 results in the formation of crevices on the CaSO_4 layer. Therefore, the decrease in the ability to capture CO_2 occurs due to sintering during carbonation/calcination cycles. The same is also true for the uniformly sulfated Megalopolis limestone. As previously mentioned, sintering affects the CO_2 capture capability of Florina limestone to a lesser extent, and this could be the reason for the greater decay of Megalopolis limestone when subjected to calcination and sulfation followed by sequential carbonation/sulfation cycles.

The four-sulfation tests showed that the decay of each limestone strongly depended on the number of sulfation cycles interspersed with the carbonation cycles. After each sulfation cycle, a sharp decay was observed in the sorbent performance, indicating loss of an additional portion of the available CaO . However, the previously noted independence between the sulfation and the rate of decay is again relevant. This finding suggests that the decay mechanism remains unaffected, whether the number of sulfation stages is one or much higher. It is also worth emphasizing the decreased effect of each sulfation stage on the Florina limestone compared to the Megalopolis sorbent. In the one-sulfation tests, the decay in CO_2 capture capability of the Florina limestone was less than for the limestone from the Megalopolis one. The sulfation and re-carbonation mechanisms previously described seem to have also applied to the four-sulfation tests. Consequently, Florina limestone presents increased sulfation tolerance compared to the Megalopolis limestone.

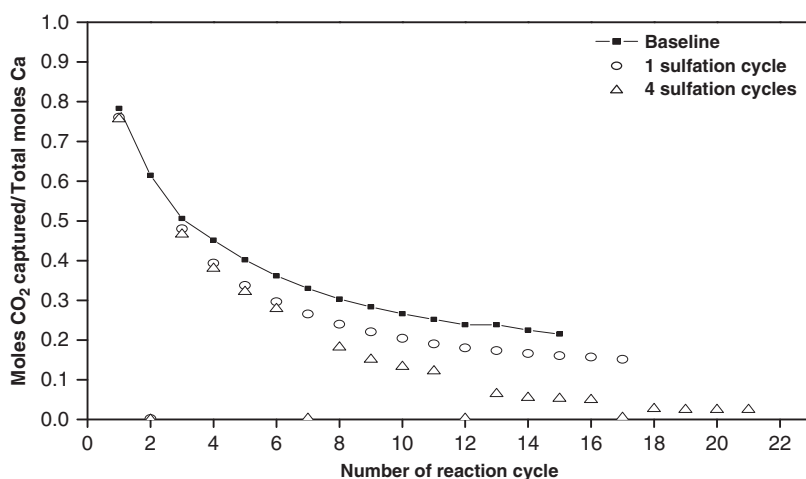


Fig. 20.11 Sequential CO_2/SO_2 capture capability of Megalopolis limestone. Carbonation in 80% v/v CO_2 – 20% v/v N_2 , sulfation in no CO_2 – 2900 ppm SO_2 – 3% v/v O_2 – balance N_2 . Calcination in N_2 .

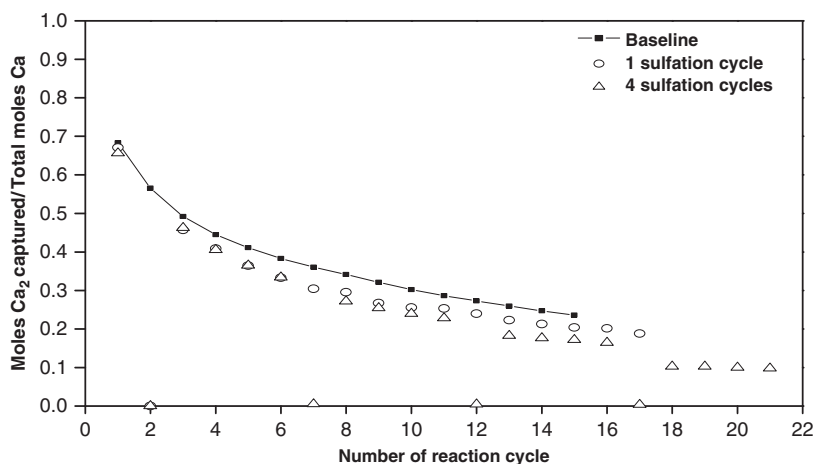


Fig. 20.12 Sequential CO₂/SO₂ capture capability of Florina limestone. Carbonation in 80% v/v CO₂ – 20% v/v N₂, sulfation in no CO₂ – 2900 ppm SO₂ – 3% v/v O₂ – balance N₂. Calcination in N₂.

20.4 Conclusions

The cyclic sorption ability of two Greek limestones for CO₂ and SO₂ was investigated aided by thermogravimetric analysis. Effects of CO₂ on the sulfation and of SO₂ on carbonation were also determined by simultaneous sulfation and carbonation.

The time required for the chemically controlled CO₂ capture stage was unaffected by the number of carbonation/calcination cycles. On the other hand, the time needed to calcine the samples decreased with an increase in the number of cycles. Increasing the particle size resulted in a reduction in the CO₂-sorption capacity of both limestones. Reducing the reaction temperatures caused a reduction in the capture capability of the limestones due to the reduced calcium utilization.

Florina limestone sulfated according to an unreacted core sulfation mode, whereas Megalopolis limestone followed a uniform sulfation mode. Periods of calcination during sulfation resulted in higher SO₂ capture efficiencies than continuous sulfation of the limestone. Simultaneous carbonation/sulfation tests showed that each one of these processes is affected by the other. The CO₂ capture capacity of the limestones was significantly reduced by the presence of SO₂, whereas SO₂ capture can be increased by slow carbonation, and sulfation remains unaffected by the presence of CO₂ for longer time periods. Florina limestone presents increased tolerance to sulfation compared with Megalopolis limestone. Overall the Florina limestone is superior to the Megalopolis limestone.

References

- Abanades, JC (2002) The maximum capture efficiency of CO₂ using a carbonation/calcination cycle of CaO/CaCO₃. *Chem. Eng. J.* 90: 303–306.
- Abanades, JC, Alvarez, D (2003) Conversion limits in the reaction of CO₂ with lime. *Energy Fuels* 17: 308–315.
- Adanez, J, Garcia-Labiano, F (1993) Factors affecting the thermogravimetric technique in the characterization of sorbents for AFBC. *Thermochimica Acta* 217: 99–113.
- Badin, EJ, Frazier, GC (1985) Sorbents for fluidized-bed combustion. *Environ. Sci. Technol.* 19 (10): 894–901.
- Barker, R (1973) The reversibility of the reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. *J. Appl. Chem. Biotechnol.* 23: 733–742.
- Cheng, L, Chen, B, Liu, N, Luo, Z, Cen, K (2004) Effect of characteristic of sorbents on their sulfur capture capability at a fluidized bed condition. *Fuel* 83: 925–932.
- Chrissafis, K, Dagounaki, C, Paraskevopoulos, KM (2005) The effects of procedural variables on the maximum capture efficiency of CO₂ using a carbonation/calcination cycle of carbonated rocks. *Thermochimica Acta* 428: 193–198.
- Ghosh-Dastidar, A, Mahuli, SK, Agnihotri, R, Fan, LS (1996) Investigation of high-reactivity calcium carbonate sorbent for enhanced SO₂ capture. *Ind. Eng. Chem. Res.* 35: 598–606.
- Grasa, GS, Abanades, JC (2006) CO₂ capture capacity of CaO in long series of carbonation/calcination cycles. *Ind. Eng. Chem. Res.* 45: 8846–8851.
- Haji-Sulaiman, MZ, Scaroni, AW (1990) The calcination and sulphation behavior of sorbents in fluidized bed combustion. *Fuel* 70: 169–176.
- Laursen, K, Duo, W, Grace, JR, Lim, CJ (2001) Characterisation of steam reactivation mechanisms in limestones and spent calcium sorbents. *Fuel* 80: 1293–1306.
- Laursen, K, Duo, W, Grace, JR, Lim, J (2002) Sulfation and reactivation characteristics of nine limestones. *Fuel* 79: 153–163.
- Li, Y, Buchi, S, Grace, JR, Lim, CJ (2005) SO₂ removal and CO₂ capture by limestone resulting from calcination/sulfation/carbonation cycles. *Energy Fuels* 19: 1927–1934.
- Mess, D, Sarofim, AF, Longwell, JP (1999) Product layer diffusion during the reaction of calcium oxide with carbon dioxide. *Chem. Eng. J.* 90: 999–1005.
- Munoz-Guillena, MJ, Linares-Solano, A, Salinas-Martinez de Lecea, C (1995) A new parameter to characterize limestones as SO₂ sorbents. *Applied Surface Science* 89: 197–203.
- Ryu, HJ, Grace, JR, Lim, CJ (2006) Simultaneous CO₂/SO₂ characteristics of three limestones in a fluidized-bed reactor. *Energy Fuels* 20: 1621–1628.
- Silaban, A, Harrison, DP (1995) High temperature capture of carbon dioxide: characteristics of the reversible reaction between CaO(s) and CO₂(g). *Chem. Eng. Commun.* 137 (1): 177–190.
- Silaban, A, Narcida, M, Harrison, DP (1996) Characteristics of the reversible reaction between CO₂(g) and calcined dolomite. *Chem. Eng. Commun.* 146: 149–162.
- Skodras, G, Grammelis, P, Basinas, P, Kaldis, S, Sakellariopoulos, GP (2007) A kinetic study on the devolatilisation of animal derived byproducts. *Fuel Process. Technol.* 88: 787–794.
- Stanmore, BR, Gilot, P (2005) Review-calcination and carbonation of limestone during thermal cycling for CO₂ sequestration. *Fuel Process. Technol.* 86: 1707–1743.
- Sun, P, Grace, JR, Lim, CJ, Anthony, EJ (2005) Simultaneous CO₂ and SO₂ capture at fluidized bed combustion temperatures. *Proceedings of the 18th International Conference on Fluidized Bed Combustion*, 22–25 May 2005, Toronto, Ontario, Canada.
- Sun, P, Grace, JR, Lim, CJ, Anthony, EJ (2007) Removal of CO₂ by calcium-based sorbents in the presence of SO₂. *Energy Fuels* 21: 163–170.
- Ye, Z, Wang, W, Zhong, Q, Bjerle, I (1995). High temperature desulfurisation using fine sorbent particles under boiler injection conditions. *Fuel* 74: 743–750.

Effect of Oxidative Medium on Removal of Sulfur and Mineral Matter from the Can Lignites

Jale Gulen

21.1 Introduction

Environmental problems associated with energy use consist of an increasing spectrum of pollutants, hazards, accidents, and degradation of environmental quality and natural ecology (Dincer, 1998). Climate change is threatening human beings on the world. Earthquakes, typhoons, cyclones, floods are the common natural disasters for all of us because of the seasonal variations. The industrialized countries are mainly responsible for air pollution, ozone depletion, and carbon emissions due to the small contribution of developing countries (Dincer, 1998). Increased emissions of greenhouse gases from human activities are the main reason for this situation. In these days, acid rains, energy requirement, greenhouse gas effect, etc., are global problems for human beings.

Energy can be supplied from fossil or renewable ones. It is predicted that fossil fuels will be the primary source of energy for the coming several decades (Dincer, 2001a). Fossil fuels must be used by increasing the fuel quality because of the risk of depleting those natural resources. Besides, environmental problems are closely associated with the usage of these low grade fossil fuels (Dincer, 2001b).

Demineralization can be managed by applying acidic, basic agents, or some solutions like H_2O_2 (Kusakebe et al., 1989).

In this study, some acidic solutions were chosen for decreasing undesired parts of H_2O_2 -treated lignite.

21.2 Background

Mineral matters of fossils may cause many problems in the utilization problems such as combustion, gasification, carbonization (Shirazi et al., 1995). Demineralization of coal can be achieved by using acidic solutions such as HCl, HF, H_2SO_4 and basic solutions such as NaOH, $Ca(OH)_2$, or some solutions like H_2O_2 . With

applying chemicals, first of all, the carbonaceous materials were separated from the structure. Later ash minerals were soluble and finally some elements in the organic structure such as Ca, K, Na were extracted (Yang et al., 1985). Karaca et al. (1997) studied the leaching effect of H_2O_2 on Turkish lignites of Beypazari and Tuncbilek. Maximum demineralization ranged from 30 to 70% in ash according to lignite type (Karaca and Ceylan, 1997). A high volatile UK coal was treated with aqueous HF followed by aqueous HNO_3 by Steel and Patrick (2001a). They reported that the ash level could be reduced from 7.90 to 2.6% using HF alone and from 2.8 to 0.6% by treating the sample with 3.51 HF and then 1.26 M HNO_3 (Steel and Patrick, 2001a). Steel et al. (2001b) applied hydrochloric and hydrofluoric acids for leaching mineral matter in Australian black coal. The results show that HCl could dissolve simple compounds such as phosphates and carbonates, but HF could react with almost every minerals especially siliceous except pyrite in the mineral matter (Steel et al., 2001b). Wu and Steel (2007) studied the two-stage leaching of UK bituminous coal using HF and $\text{Fe}(\text{NO}_3)_3$ ions. The ash amount decreased in Harworth coal from 5.30% to 990 ppm (Wu and Steel, 2007). Gulen et al. (2005) studied the various aqueous acidic solutions on the demineralization effect of Silopi Harput asphaltite. HCl was the most effective one among the other acids such as H_2SO_4 , HNO_3 , and HF (Gulen et al., 2005). Gulen studied to identify some mineral groups in Nallihaman lignite with polishing treatments after applying some acidic solutions such as HCl, H_2SO_4 , HNO_3 , and HF of 5% (Gulen, 2007). In this study, the effects of aqueous H_2O_2 and some acidic solutions are investigated.

21.3 Experimental Study

Turkey has huge lignite deposits although most of them are of low quality. The total reserve of Can lignite is 79,000,000 tonnes (Kahriman et al., 2000). The proximate analysis results of Can lignite are given in Table 21.1.

Table 21.1 Proximate analyses (%) of Can lignite.

Fixed carbon	64.81
Volatile matter	28.08
Sulfur	3.80
Ash	7.11
Moisture	10.70
Calorific value	22,402 kJ/kg

H_2O_2 solution was chosen as an oxidative medium for decreasing sulfur and mineral matter of Can lignite. At the beginning, the sample was ground, sieved to pass 0.250 μm . It was stirred with 50 ml H_2O_2 of 5% for 20 minutes. Then, that sample was washed with distilled water and dried in the autoclave at 105°C. Later, it was treated with 50 ml aquatic acidic solutions of HNO_3 , HCl, H_2SO_4 , H_3PO_4 , HCOOH , and HF of 5% for 20 minutes, separately. The solution

was filtered through the blue ribbon filter and dried in the autoclave at 105°C. The sulfur and ash analyses of these demineralized samples were done according to ASTM standards (ASTM, 1983).

As seen from Table 21.1, the sulfur ratio of Can lignite is too high. In order to utilize this natural source, some pretreatments were applied for. For this purpose, some acidic solutions were chosen for decreasing sulfur and mineral parts of lignite treated after 5% H₂O₂ solution. The total sulfur results of demineralized Can lignite are given in Table 21.2.

Table 21.2 Total sulfur % values of Can lignite and other 5% chemical-treated samples.

Sample	5% H ₂ O ₂	Decrease in sulfur amount	Sulfur removal %
Can (A)	3.56	0.24	6.32
(A)+HNO ₃	3.46	0.34	8.95
(A)+H ₃ PO ₄	3.08	0.72	18.95
(A)+H ₂ SO ₄	3.06	0.74	19.47
(A)+HCOOH	2.94	0.86	22.63
(A)+HF	2.83	0.97	25.53
(A)+HCl	2.43	1.37	36.05

The calculations are shown below. Decrease in sulfur amount was determined as follows: $3.80 - 3.56\% = 0.24\%$; Sulfur removal % was determined as follows: $0.24/3.80 \times 100 = 6.32\%$.

Table 21.3 shows the mineral matter ratios of Can lignite and chemical-treated samples according to the leaching process which was applied to them.

Table 21.3 Ash and demineralization variation % of Can lignite and 5% chemical-treated samples.

Sample	5% H ₂ O ₂	Ash reduction %	Demineralization %
Can (A)	5.98	1.13	15.89
(A)+H ₃ PO ₄	5.03	2.08	29.35
(A)+HCOOH	4.70	2.41	30.89
(A)+HNO ₃	4.70	2.41	33.89
(A)+HCl	4.64	2.47	34.74
(A)+H ₂ SO ₄	3.99	3.12	43.88
(A)+HF	3.69	3.42	48.10

The calculations are done as follows:

$$7.11 - 5.98\% = 1.13\%$$

$$1.13/7.11 \times 100 = 15.89\%$$

The calorific values were determined with IKA C4000 bomb calorimeter. The variation in calorific values of Can lignite after applying for those chemicals to original lignite and chemical-treated samples is given in Table 21.4. The calorific values are high heating values. Those variations of calorific values were found at the following: $(24\,106.9 - 22\,401.6) / 22\,401.6 = 7.61\%$. The calorific value was increased after H_2O_2 plus HCl application as 7.61%.

Table 21.4 Calorific values of Can lignite and 5% chemical-treated samples.

Sample	5% H_2O_2 kJ/kg	Variation in calorific value %
Can (A)	22 401.6	–
(A)+HF	22 273.9	(–) 0.57
(A)+HCl	24 106.9	(+) 7.61
(A)+ HNO_3	24 163.3	(+) 7.86
(A)+ H_2SO_4	24 281.9	(+) 8.39
(A)+ HCOOH	24 280.2	(+) 8.39
(A)+ H_3PO_4	24 374.3	(+) 8.81

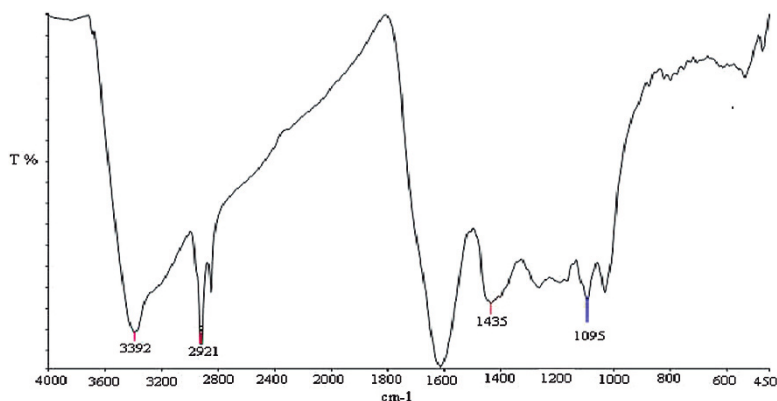


Fig. 21.1 FTIR spectrum of Can lignite treated after 5% H_2O_2 solution (X scale wave number cm^{-1} and Y scale transmittance %).

FTIR spectrum was taken with Perkin–Elmer spectrometer for observing the leaching process effects. Figure 21.1 shows the FTIR spectrum of Can lignite treated with 50 ml, 5% H_2O_2 as follows:

Wave numbers (cm^{-1})	Bond properties
1095	C–O stretching
1435	C=C and C=O groups
2921	Aliphatic C–H groups
3392	Aliphatic C–H groups

Figure 21.2 shows the FTIR spectrum of Can lignite treated with 5% H_2O_2 plus 5% H_2SO_4 solutions. The peaks were originated because of those defined groups.

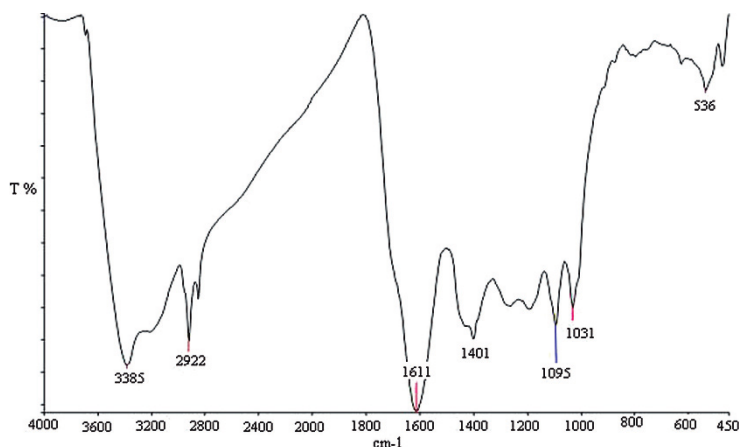


Fig. 21.2 FTIR spectrum of Can lignite treated with 5% H_2O_2 and later 5% H_2SO_4 solutions with the following:

Wave numbers (cm^{-1})	Bond properties
536	Mineral matter
1031	C—O stretching
1095	C—O stretching
1401	Asymmetric symmetric carboxyl groups
1611	Asymmetric symmetric carboxyl groups
2922	Aliphatic C—H groups
3385	Aliphatic C—H groups

Figure 21.3 shows the FTIR spectrum of Can lignite treated with 5% H_2O_2 , later 5% HF solutions. Those peaks belong to these groups in the body.

Figure 21.4 shows the X-ray spectrum of original Can lignite. X-ray spectra were taken with Rigaku-X-ray spectrometer between 2θ ($0-70^\circ$)

The peaks at $2\theta = 23.962, 33.162, 40.858, 43.436, 49.498, 54.158, 62.522$ show hematite (Fe_2O_3) groups in the body. The peaks seen at $2\theta = 24.521, 31.338, 38.582, 52.352, 57.717$ are due to anhydrite (CaSO_4) groups. Figures 21.5 and 21.6 show the X-ray spectrums of Can lignite treated with 5% H_2O_2 solution and 5% H_2O_2 plus H_2SO_4 solutions, respectively.

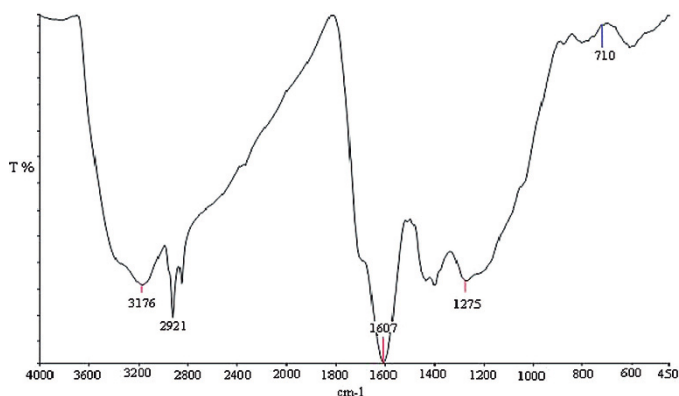


Fig. 21.3 FTIR spectrum of Can lignite treated with 5% H_2O_2 plus 5% HF solutions with the following:

Wave numbers (cm^{-1})	Bond properties
710	Mineral matter
1275	C—O stretching
1607	Asymmetric symmetric carboxyl groups
2921	Aliphatic C—H groups
3176	Aliphatic C—H groups

The peaks seen in Figure 21.5 at $2\Theta = 20.781, 31.025, 31.871, 36.606$ and $2\Theta = 24.179, 33.218, 40.935, 49.500, 62.577, 64.056$ are due to anhydride and hematite groups, respectively.

Figure 21.6 shows the X-ray spectrum of Can lignite treated with 5% H_2O_2 and later 5% H_2SO_4 solutions. The peaks shown at $2\Theta = 20.882, 26.661, 39.517, 40.438, 42.556, 45.837, 50.194, 59.998, 64.201, 67.877, 68.342, 75.654$ and $2\Theta = 24.184, 33.181, 35.682, 40.960, 43.537, 49.557, 54.178, 57.701, 62.514$ are quartz (SiO_2) and hematite (Fe_2O_3) groups left in the body at the end of the experiment.

Figure 21.7 shows the X-ray spectrum of Can Lignite treated with 5% H_2O_2 and later 5% HF solutions. Quartz and hematite groups give peaks at $2\Theta = 20.839, 26.640, 39.518, 60.104, 67.718$ and $2\Theta = 22.953, 25.422, 31.375, 38.660, 40.839, 48.796, 49.220, 52.298$, respectively.

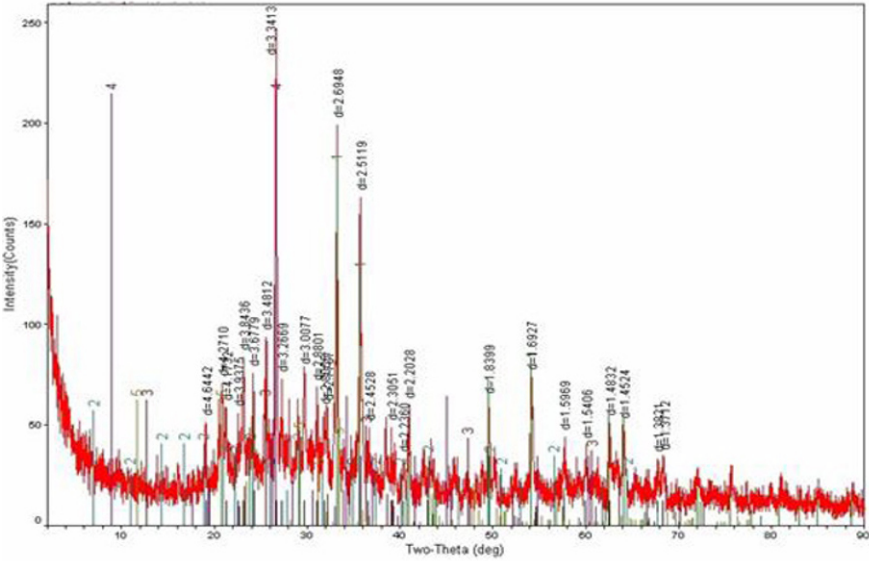


Fig. 21.4 X-ray spectrum of Can lignite.

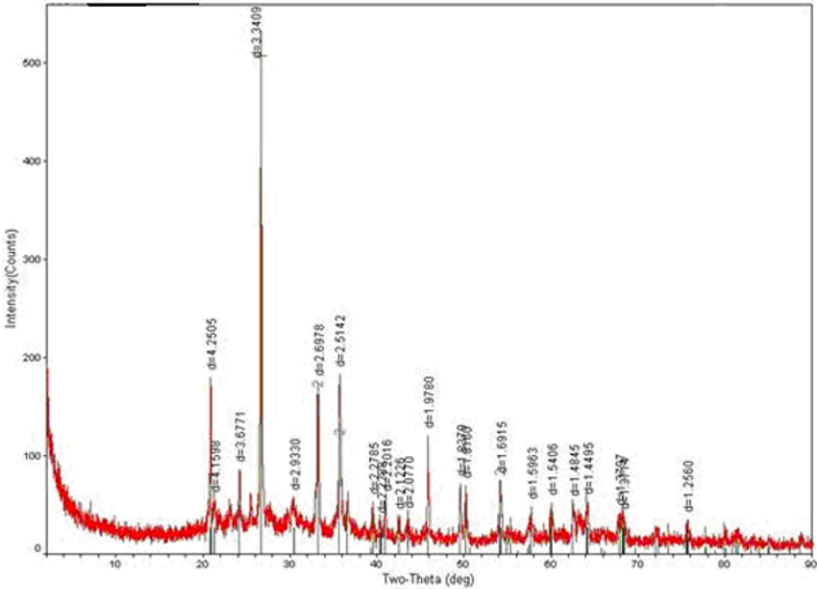


Fig. 21.5 X-ray spectrum of Can lignite treated with 5% H₂O₂ solution.

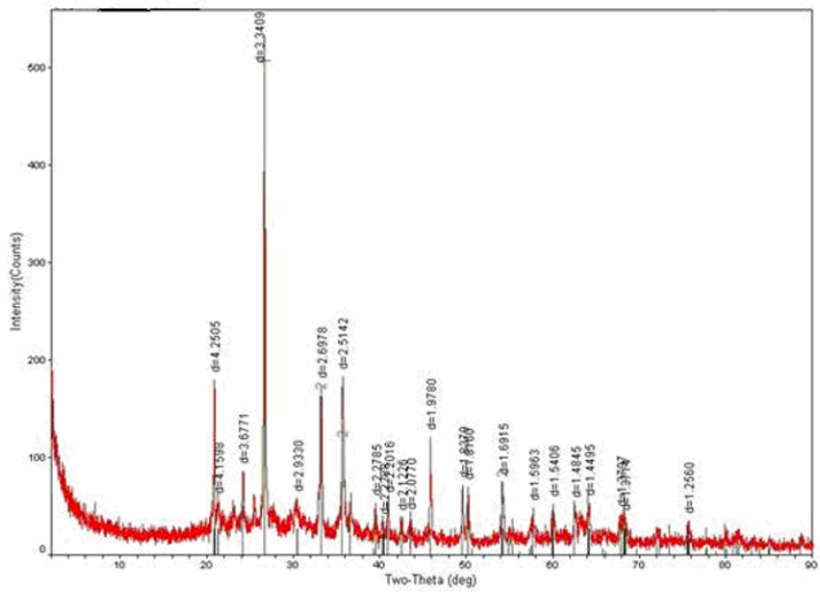


Fig. 21.6 X-ray spectrum of Can lignite treated with 5% H_2O_2 plus 5% H_2SO_4 solutions.

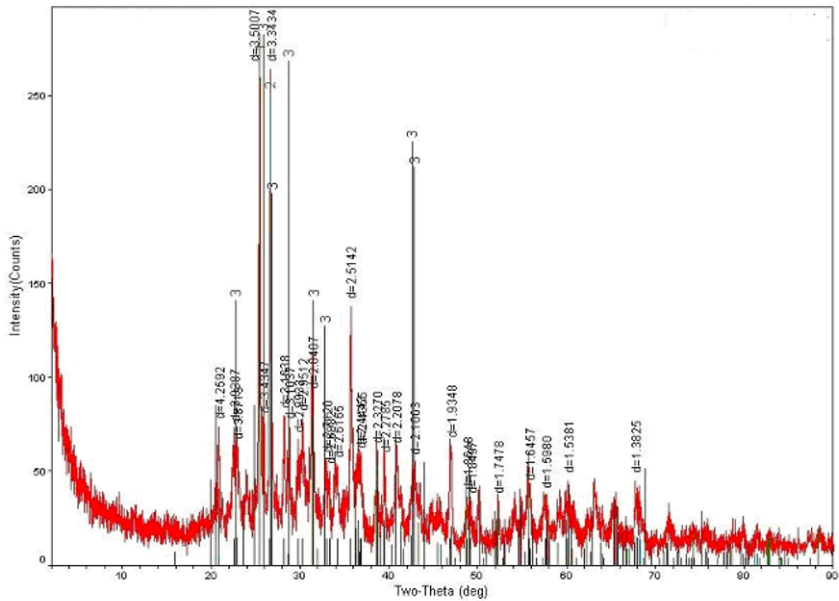


Fig. 21.7 X-ray spectrum of Can lignite treated with 5% H_2O_2 plus 5% HF solutions.

21.4 Conclusions

Acidic medium was effective for decreasing the high amount of sulfur ratio of Can lignite. The most effective medium was $\text{H}_2\text{O}_2 + \text{HCl}$ solution. With this treatment sulfur ratio was removed by the order of 36%, and HF was also effective for decreasing sulfur from 3.8 to 2.83% of giving 26% yield. These treatments were also effective for decreasing mineral parts of Can lignite. The highest ash reduction was accomplished with $\text{H}_2\text{O}_2 + \text{HF}$ solution which was given approximately 48% demineralization yield. HF could react almost with every minerals especially siliceous ones in the mineral matter.

References

- American Society for Testing and Materials (1983) Annual book of ASTM Standards. Part 26 (Methods D 2015, D 2072, D 3174 and D 3177). Philadelphia, PA, USA.
- Dincer, I (1998) Energy and environmental impacts: Present and future perspectives. *Energy Source* 20: 427–453.
- Dincer, I (2001a) Environmental Issues I -Energy Utilization. *Energy Source* 23: 69–81.
- Dincer, I (2001b) Environmental issues II - Potential solutions. *Energy Source* 23: 83–92.
- Gulen, J, Doymaz, I, Piskin, S, Toprak, S (2005) Removal of mineral matter from Silopi Harput asphaltite by acid treatment. *Energy Sources* 27: 1457–1464.
- Gülen, J (2007) Mineral matter identification in Nallihan lignite by leaching with mineral acids. *Energy Sources-Part A* 29: 231–237.
- Kahriman, A, Ipekoglu, B, Kesinel, A, Zemcen, G, Karadogan, A, Gorgun, S (2000) Rezerv calculation and evaluation of Can lignites for the power plant. Turkey 12. Komur Kongresi, 23–26 Mayıs, Zonguldak, Turkey.
- Karaca, H, Ceylan, K (1997) Chemical cleaning of Turkish lignites by leaching with aqueous hydrogen peroxide. *Fuel Processing Technology* 50: 19–33.
- Kusakebe, K, Orita, M, Kato, K, Morooka, S, Kato, Y, Kusunaki, K (1989) Simultaneous desulphurization and demineralization of coal. *Fuel* 68: 396–399.
- Shirazi, AR, Bortin, O, Eklund, L, Lindquist, O (1995) The impact of mineral matter in coal on its combustion. A new approach to the determination of the calorific value of coal. *Fuel* 74 (2): 247–251.
- Steel, KM, Patrick, SW (2001a) The production of ultra clean coal by chemical demineralization. *Fuel* 80: 2019–2023.
- Steel, KM, Besida, J, O'Donnell, TA, Wood, DG (2001b) Production of ultra clean coal Part I-Dissolution behavior of mineral matter in black coal toward hydrochloric and hydrofluoric acids. *Fuel Processing Technology* 70: 171–192.
- Wu, Z, Steel, KM (2007) Demineralization of a UK bituminous coal using HF and ferric ions. *Fuel* 86: 2194–2200.
- Yang, RT, Subho, KD, Tsai, BMC (1985) Coal demineralization using sodium hydroxide and acid solutions. *Fuel* 64: 735–742.

Biogenic Emission and Essential Oils of Some *Eucalyptus* Species: A Comparison Study

Yazid Foudil-Cherif, Noureddine Yassaa and Brahim Y. Meklati

22.1 Introduction

The eucalyptus genus includes more than 800 species. Native of Australia and nearby regions, it is now spread all over the world. *Eucalyptus* oil represents an important raw material for pharmaceutical, confectionery, and cosmetic industries. The main substance of medicinal oil is 1,8-cineole, and its amount has a great importance in defining the quality of the oil. Some pharmacopeias, such as British and United States, require a 1,8-cineole content to be higher than 70% together with the absence of phellandrene. Numerous authors (Ahmadouche et al., 1985; Boland et al., 1991; Dellacassa et al., 1995; Bignell et al., 1996) have extensively studied the oils of different *Eucalyptus* species with a special emphasis on the determination of the chemical composition of *E. globulus* (Chenoufi et al., 1980; Barton et al., 1989; Zrira et al., 1992).

Apart from their pharmaceutical and industrial benefits, plants produce a great variety of organic compounds, most of them being volatile. They emit into the atmosphere about 400 non-methane hydrocarbons (NMHC), including aldehydes, ketones, organic acids, alcohols, C₂–C₄ alkenes and alkenes, isoprene, and the C₁₀–C₄₀ terpenes (Olivera et al., 1972; Singh et al., 1986; Bignell et al., 1997). These natural hydrocarbon compounds play an important role in the formation of photochemical oxidants such as ozone and peroxy acetylnitrates (Lelieveld et al., 2008). They are a significant part of the global carbon cycle and contribute by the way of organic acids to acidic deposition in rural and urban areas (Lelieveld et al., 2008). On regional and global scales, these biogenic non-methane organic compound emissions may dominate over anthropogenic emissions (Guenther et al., 1995). Among the variety of organic species, only isoprene and monoterpenes from forests, crops, and pastures have been studied in detail with reference to their high reactivity which controls the OH and NO₃ mixing ratio.

In this chapter the analysis of organic compounds was performed both in the essential oils and in the atmospheric emissions of some eucalyptus species growing in Algeria. The results obtained are discussed in the context of plant–atmosphere interactions.

22.2 Materials and Methods

22.2.1 Essential oils

Plant Materials: The adult leaves of the eleven Eucalyptus species (*E. punctata* DC, *E. sideroxylon* Cunn., *E. saligna* Smith, *E. cladocalyx* F. Muell., *E. albens* Miq.ex Benth., *E. ovata* Labill., *E. leucoxylon* F. Muell., *E. Blakelyi* A. Cunn, *E. microcorys* F. Muell. *camaldulensis* DC., and *E. globulus* Labill) were collected from the trees located in Bainem forest (16 km to the west of Algiers). Two or three trees of each species were taken randomly. Voucher specimens were cut off and housed in the arboretum of the Institute National de la Recherche Forestière (INRF). The oils were isolated from the fresh leaves by steam distillation.

- **Oil isolation:** The oils were isolated from the fresh leaves by steam distillation for 2.5 hours using a modified cleverger-type apparatus and stored at low temperature. The oil yield of each species was calculated. The following analyses were conducted on the oils: specific gravity (20°C), refractive index (20°C), optical rotation (20°C), ester value and acid value, GC, GC-MS, and GC-FTIR.
- **Physicochemical indices:** The physicochemical indices of the oils were determined following the ISO regulation. ISO 279:1981 for the specific gravity, ISO 280:1976 for the refractive index, ISO 592:1981 for the optical rotation, ISO 709: 1980 for the ester value and ISO 1242: 1973 for the acid value.
- **GC analysis:** Each oil was analyzed by GC on a Carlo Erba Gas Chromatograph 5160 using the following experimental conditions: fused silica SE52 column, 30 m × 0.32 mm; column temperature 45°C (6 min) to 250°C at 3°C/min; injection mode split; detector FID; injector and detector temperature, 280°C; carrier gas He 100 KPa; injected volume 1 µl of solution 1/100 in pentane of the oil.
- **GC-MS analysis:** Samples were analyzed by GC/MS (EI) on a Fison MD 800 system equipped with Adams' library (15). Two different columns were used: DB5 (30 m × 0.25 mm) and Carbowax 20 M (30 m × 0.32 mm) fused silica columns. The GC condition for the two columns: 60°C (6 min) to 240°C at 3°C/min; injector temperature 250°C; injection mode split, split ratio 1/30; volume injected 1 µl of solution 1/100 in pentane of the oil; carrier gas He 90 KPa; interface temperature 250°C; detector 1.5 kV; and acquisition mass 41–300 amu.
- **GC-FTIR analysis:** Samples were analyzed on Nicolet 20SXC system equipped by a MCT detector. The interface GCIR was a light pipe of 100 µl and 1 mm diameter. The chromatograph was a Perkin–Elmer 8500 equipped with a FID detector and a BP1 fused silica column (50 m × 0.32 mm). GC conditions: 60–250°C at 2°C/min.

The identification of components was established by combining the comparison of mass spectra of components with the published spectra (Adams, 1995) and the retention indices with the published index data (Jennings et al., 1980). The quantitative composition was obtained by peak area normalization, the response factor for each component was supposed to be equal to one. For the GC-FTIR, the

identification of components was achieved by combining the comparison of spectrum of components with Aldrich-vapor phase (Library spectrum) and a spectrum of condensed compound in a literature especially for the sesquiterpenes. The quantitative composition was obtained by peak area normalization, the response factor for each component was supposed to be equal to one.

22.2.2 Atmospheric emission

Biogenic VOCs emitted from *E. globulus* were collected using static branch cuvettes. They were made by Tedlar bags, 3 L in volume, equipped with inlet and outlet lines for air circulation. Samples were collected 5 min after branch enclosure to prevent heat stress to the plant leaves. All experiments were carried out under light saturation conditions ($\text{PAR} > 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) with leaf temperatures ranging from 27 to 30°C.

Air emission samples from the tree were enriched on glass tubes (15 cm $\times$ 0.3 cm I.D.) filled with a bed of Carboxen 100 (0.034 g) and Carbograph 1 (0.17 g), set in series. Flow rates ranging from 200 to 330 ml were used for sample collection. After sample collection, traps were wrapped in aluminum foil and stored at room temperature until they were subjected to chemical determinations. After removing oxygen and the excess of water from the adsorbents by a back-flushing step, traps were thermally desorbed at 250°C and VOCs cryofocused in an empty liner kept at -120°C. Injection into the capillary column was achieved by fast heating the liner from -150 to +150°C in 10 s.

The separation of desorbed VOCs was performed on a Cyclodex-B capillary column, 30 m $\times$ 0.256 mm I.D., 0.25 μm film thickness supplied by J & W Scientific (CA, USA). Mass spectrometric determinations were performed using a HP 5890 gas chromatograph coupled with a HP 5970B mass-selective detector (Hewlett Packard Instruments, Palo Alto, CA, USA). Thermal desorption of sampled tubes, cryofocusing of released vapors, and their injection into the capillary column were performed with a TCT/PT1 CP4001 unit supplied by Chrompack (Middleburg, The Netherlands).

For peak identification the mass spectrometer was operated in scan conditions by collecting all ions from 20 to 250 m/z. A scan frequency of 3 scans s^{-1} was used for generating the mass chromatogram. Positive identification was obtained by combining the mass spectral information with the elution sequence obtained through the analysis of pure compounds.

22.3 Results and Discussion

Table 22.1 reports the yield and physicochemical indices of the oils. Different oil yield was found for each sample: the lowest value was obtained for *E. leucosylon* (0.15%) and *E. ovata* (0.17%); the opposite resulted for *E. punctata* (1.41%) and *E. blakelyi* (1.42%). Differences of these yields with those reported in literature could be attributed to many factors (age of the tree, climate, nature of the soil, mode of extraction, method of analysis).

Table 22.1 Yields and physicochemical indices of different *Eucalyptus* essential oils.

	Yields (% w/w)	Specific gravity (20°C)	Refractive index (20°C)	Optical rotation (20°C)	Acid value	Ester value
<i>E. punctata</i>	1.41	0.9235	1.4524	—	1.21	14.21
<i>E. leucoxylon</i>	0.15	0.9263	1.4624	+3°	2.80	4.20
<i>E. cladocalyx</i>	0.49	—	—	—	—	—
<i>E. blakelyi</i>	1.42	0.8820	1.4846	−17.5°	3.51	17.53
<i>E. ovata</i>	0.17	0.8670	1.4756	—	5.61	29.45
<i>E. microcorys</i>	0.32	0.8790	1.4806	−25.0°	2.1	18.93
<i>E. saligna</i>	1.16	0.8980	1.4896	—	3.51	3.50
<i>E. sideroxylon</i>	0.77	0.9160	1.4636	+5.0°	2.10	18.93
<i>E. albens</i>	0.56	0.9080	1.4946	—	2.80	46.28
<i>E. globulus</i>	0.69	0.9265	1.4617	+4°95	4.38	9.80
<i>E. camaldulensis</i>	0.33	—	—	—	—	—

Table 22.2 reports the composition as single components and Table 22.3 the percentage composition of various classes of compounds for the analyzed *Eucalyptus* oils. On the whole, 100 components were identified. In *E. punctata*, *E. leucoxylon*, *E. ovata*, *E. microcorys*, *E. sideroxylon*, and *E. globulus*, the main compound was 1,8-cineole (from 26.6 to 77.1%); otherwise, *p*-cymene prevailed in *E. blakelyi* (29.3%) and *E. camaldulensis* (18.8%), benzaldehyde in *E. cladocalyx* (32.3%), β -phellandrene in *E. saligna* (16.8%), and spathulenol in *E. albens* (20.9%). It is interesting to note that Moroccan *E. cladocalyx* oil (Zrira et al., 1992) was free of benzaldehyde compared with the Algerian and the Uruguayan (34.20%) oils (Dellacassa et al., 1990). In opposite the Algerian *E. globulus* was free of phellandrene compared with the Moroccan (Zrira et al., 1992) or the Uruguayan (Dellacassa et al., 1990) species.

Table 22.2 Comparative percent composition of different *Eucalyptus* essential oils.

Compounds	A	B	C	D	E	F	G	H	I	J	K
Tricyclene	tr	tr	tr	tr	—	tr	—	tr	—	—	—
α -Thujene	0.1	tr	1.1	0.4	0.1	0.9	1.5	0.1	0.3	—	—
α -Pinene	7.7	9.9	6.7	1.3	7.8	7.9	10.9	2.0	1.0	9.0	3.3
α -Fenchene	0.1	tr	tr	tr	tr	tr	—	—	tr	tr	tr
Camphene	0.1	0.1	tr	0.1	tr	0.2	0.1	tr	0.1	0.1	tr
Thuja 2,4 (10) diene	0.2	tr	0.1	0.1	tr	tr	0.1	tr	tr	—	—
Benzaldehyde	tr	tr	32.3	tr	tr	—	tr	tr	0.1	—	—
Sabinene	tr	tr	0.6	0.2	tr	Tr	0.8	tr	0.1	tr	tr
β -Pinene	4.1	0.5	0.2	0.1	0.4	0.9	0.4	0.2	0.1	0.2	tr
6- Méthyl-5-hepten-2-one	tr	tr	—	—	tr	—	tr	—	—	—	—
Myrcene	0.1	0.4	0.7	0.3	0.5	0.6	0.9	0.1	0.1	tr	—
Dehydro -1,8-cineole	tr	—	—	—	—	—	—	tr	tr	—	—
δ -2-Carene	—	—	—	—	—	—	tr	—	—	—	—
α -Phellandrene	0.1	0.3	4.1	2.4	2.1	4.4	3.2	0.4	0.1	—	tr
α -Terpinene	0.1	tr	0.1	0.2	0.2	0.2	0.3	tr	0.1	—	Tr
<i>p</i> -Cymene	8.8	1.9	9.0	29.3	2.9	15.7	14.5	1.9	19.9	0.5	18.8

Limonene	tr	tr	tr	tr	tr	tr	tr	tr	1.6	0.5	tr
β -Phellandrene	tr	tr	12.1	6.5	tr	10.9	16.8	tr	tr	–	tr
1,8-Cineole	58.2	74.4	14.9	21.2	51.2	26.6	1.0	77.1	5.2	74.1	17.6
(Z)- β -Ocimene	tr	0.3	0.1	tr	4.7	0.1	tr	0.1	tr	tr	–
(E)- β -Ocimene	tr	tr	tr	0.1	0.5	0.1	0.1	tr	tr	–	–
γ -Terpinene	0.1	0.3	0.3	0.2	0.1	0.2	0.4	0.1	0.1	tr	tr
<i>cis</i> -Sabinene hydrate	0.1	–	tr	–	tr	tr	0.1	tr	0.1	–	–
<i>cis</i> -Linalool	–	tr	tr	0.1	–	tr	–	–	0.1	tr	0.1
Oxide <furanoid>	–	–	–	–	–	–	–	–	tr	tr	0.1
<i>trans</i> Linalool ox- ide<furanoid>	–	–	–	–	–	–	–	–	tr	tr	0.1
Terpinolene	0.2	0.1	0.2	0.5	0.1	0.5	0.3	tr	0.3	tr	tr
α , <i>p</i> -Dimethylstyrene	–	–	–	–	–	tr	–	tr	–	tr	0.1
α -Pinene oxide	tr	–	–	–	–	–	–	–	–	0.1	0.2
Linalool	0.1	0.1	0.5	0.1	2.2	tr	1.9	0.1	0.9	tr	tr
Nonanal	tr	0.1	–	0.1	–	–	–	–	0.2	–	–
Isoamyl 2-methylbutyrate	0.1	0.1	tr	–	0.4	0.1	–	0.3	–	–	–
Isoamyl isovalerate	–	–	–	–	–	–	–	tr	–	–	–
β -Thujone	–	–	0.1	0.2	tr	–	0.1	0.1	0.1	–	0.3
β -Fenchol	0.2	0.1	–	–	–	0.3	–	–	–	tr	0.1
<i>cis</i> - <i>p</i> -Menth-2-en-1-ol	0.2	0.1	0.1	0.8	0.2	0.4	1.0	–	1.0	–	–
α -Campholenal	0.2	tr	0.1	0.2	–	0.1	0.3	–	0.2	–	–
<i>trans</i> -Pinocarveol	2.8	2.0	1.5	0.8	0.5	1.6	1.4	0.6	0.2	2.7	6.8
<i>trans</i> - <i>p</i> -Menth-2-en-1-ol	–	–	0.4	0.5	0.1	0.3	0.3	–	0.7	–	–
<i>cis</i> -Verbenol	0.1	tr	0.2	–	–	–	–	–	–	–	–
Nerol oxide	–	–	–	–	–	–	~	tr	–	–	–
Camphene hydrate	tr	tr	–	–	–	tr	–	–	–	tr	tr
Pinocarvone	1.1	0.8	0.4	0.2	0.1	0.6	0.2	0.1	0.1	–	–
Isomenthone	–	–	–	–	–	–	–	–	0.1	–	–
borneol	–	0.1	–	–	–	0.6	–	–	–	2.7	tr
Terpinen-4-ol	0.7	0.4	1.5	1.2	0.5	2.4	3.0	0.5	5.0	0.1	0.6
<i>p</i> -Cymen-8-ol +?	2.5	0.3	2.5	14.0	–	0.9	7.0	0.8	14.7	0.1	1.8
α -Terpineol	1.6	1.0	0.6	0.3	10.3	1.6	2.8	1.3	1.6	0.7	0.9
Myrtenal	1.5	0.1	0.2	0.3	0.1	0.2	0.5	0.1	0.3	tr	0.3
<i>cis</i> -Piperitol	–	–	tr	–	–	–	–	–	–	–	0.1
Verbenone	0.2	–	–	–	–	tr	0.6	–	–	–	1.6
Trans-piperitol	–	tr	0.3	0.3	0.1	0.2	–	–	0.4	–	–
Trans-carveol	0.3	0.1	0.1	0.3	0.1	0.1	0.2	0.2	0.2	0.1	0.5
Citronellol	–	–	–	–	–	–	–	–	tr	–	–
<i>cis</i> -Carveol	0.3	0.1	0.2	0.4	0.1	–	0.2	0.2	0.8	tr	tr
Cuminaldehyde	0.7	–	0.7	3.2	–	0.1	1.2	–	4.1	–	–
Carvone	0.2	tr	tr	–	0.2	tr	0.1	0.1	–	tr	0.3
Carvotanacetone	–	tr	–	–	–	tr	–	–	–	tr	–
Piperitone	0.1	tr	0.3	1.6	0.1	0.2	0.3	0.1	0.4	–	tr
Geraniol	–	0.1	–	–	–	–	–	–	–	–	–
Geranial	–	tr	tr	–	tr	–	tr	–	0.1	–	–
<i>p</i> -Mentha-1,3-diene-7-al	tr	–	0.1	0.1	–	tr	0.2	–	tr	–	–
Thymol	0.2	tr	0.1	0.6	tr	tr	0.4	tr	1.2	–	tr
Carvacrol	0.2	tr	0.1	0.4	tr	0.5	0.5	0.1	0.8	–	0.6

6-Hydroxy-carvotanacetone	tr	—	—	0.1	—	—	tr	—	tr	—	—
α -Terpenyl acetate	tr	—	0.1	0.1	—	—	—	2.1	tr	0.9	—
Citronellyl acetate	—	—	tr	—	—	—	—	—	—	—	—
β -Elemene	—	—	—	—	—	—	tr	tr	—	—	—
<i>cis</i> -Jasmone	tr	—	—	—	—	—	—	—	—	—	—
α -Gurjunene	—	—	—	—	—	—	0.1	tr	—	—	—
β -Caryophyllene	tr	—	0.2	0.1	—	0.1	0.4	0.2	—	—	—
β -Gurjunene	—	—	—	—	tr	—	—	—	—	—	—
Aromadendrene	0.1	0.2	tr	tr	0.7	tr	tr	0.1	0.1	0.3	tr
α -Humulene	—	0.1	tr	—	—	—	0.1	tr	0.1	—	—
Allo-aromadendrene	tr	tr	0.1	0.1	0.2	tr	0.4	0.1	0.3	tr	—
β -Ionone	—	tr	—	—	—	—	—	—	—	—	—
Germacrene D	—	—	—	0.1	—	—	—	—	—	—	—
2-Phenethyl-isovalerate	tr	tr	0.1	—	0.2	—	—	—	—	—	—
Bicyclogermacrene	—	—	0.1	0.3	—	0.2	0.8	1.0	—	—	—
α -Muurolene	—	—	tr	—	—	—	—	—	—	—	—
γ -Cadinene	—	—	tr	—	—	—	—	—	—	—	—
δ -Cadinene	tr	—	0.2	—	tr	—	tr	—	—	—	—
<i>trans</i> -Calamenene	tr	—	—	—	—	tr	—	—	—	—	—
Elemol	—	—	tr	—	—	—	—	—	—	—	—
(E)-nerolidol	—	tr	—	—	—	—	—	—	—	—	—
Ledol	tr	0.2	—	0.1	0.5	0.8	tr	0.5	tr	tr	tr
Spathulenol	0.8	0.2	0.7	3.7	0.3	6.2	9.5	0.9	20.9	tr	0.4
Caryophyllene oxide	1.7	—	0.7	1.2	6.7	2.8	1.9	1.9	0.9	—	1.0
Globulol	—	3.0	—	—	—	—	—	—	—	0.8	0.5
Viridiflorol	0.1	0.6	tr	tr	1.1	2.8	0.2	1.7	0.1	0.1	tr
Humulene epoxide II	0.1	—	tr	—	—	—	—	—	—	—	tr
γ -Eudesmol	—	tr	—	—	—	—	—	—	tr	—	—
1-Epi-cubenol	tr	—	tr	—	—	—	—	—	—	—	—
α -Muurolol	—	—	—	—	—	tr	—	—	—	—	—
α -Eudesmol	0.3	0.1	—	—	tr	—	—	0.2	—	—	—
α -Cadinol	—	—	tr	—	—	0.4	—	—	—	—	—
(E,E)-Farnesol	—	—	—	—	—	—	—	0.1	—	—	—
(E,Z)-Farnesol	—	—	—	—	—	—	0.5	—	—	—	—

A: *E. punctata*; **B:** *E. leucoxylo*; **C:** *E. cladocalyx*; **D:** *E. blakelyi*; **E:** *E. ovata*; **F:** *E. microcorys*; **G:** *E. saligna*; **H:** *E. sideroxylo*; **I:** *E. albens*; **J:** *E. globulus*; **K:** *E. camaldulensis*.

With regard to the monoterpene hydrocarbons, *E. cladocalyx*, *E. microcorys*, *E. blakelyi*, and *E. saligna* showed the highest amount of the main component *p*-cymene. Moreover, α -pinene prevails in *E. leucoxylo* and *E. ovata* while α -pinene and *p*-cymene showed similar values in *E. punctata* and *E. sideroxylo*. Furthermore, the following hydrocarbons were present in significant amounts: β -pinene (4.1%) in *E. punctata*; (Z)- β -ocimene (4.7%) in *E. ovata*; α -phellandrene (2.1% – 4.4%) in *E. cladocalyx*, *E. blakelyi*, *E. ovata*, *E. microcorys*, and

E. saligna; β -phellandrene (6.5–16.8%) in *E. blakelyi*, *E. cladocalyx*, *E. microcorys*, and *E. saligna*.

Alcohols content was found different in the different samples analyzed (from 7.1% to 48.6%), the most abundant constituents being *trans*-pinocarveol, terpinen-4-ol, α -terpineol, spathulenol, linalool, and viridiflorol. Sesquiterpene hydrocarbons were present in low amounts (0.2–1.6%). The components present in all the oils analyzed were aromadendrene (<0.1–0.7%), allo-aromadendrene (<0.1–0.4%), bicyclogermacrene (<0.1–1.0%), β -caryophyllene (<0.1–0.4%) and α -humulene (<0.1–0.1%).

Table 22.3 Percent composition of various classes of compounds of the different *Eucalyptus* essential oils.

Classes	A	B	C	D	E	F	G	H	I	J	K
Monoterpene hydrocarbons	21.5	13.8	35.1	41.5	19.4	42.6	50.2	4.9	23.8	10.2	22.1
Sesquiterpene hydrocarbons	0.1	0.3	0.6	0.6	0.9	0.3	1.6	1.4	0.4	0.3	0.0
Alcohols	10.5	8.5	8.8	25.6	16.0	19.1	28.4	6.7	48.6	4.8	12.2
Aldehydes	2.4	0.2	33.4	3.9	0.1	0.4	2.2	0.1	5.0	0.0	0.6
Ketones	1.6	0.8	0.8	2.0	0.4	0.8	1.3	0.4	0.7	0.6	32.7
Esters	0.1	0.1	0.3	0.3	0.6	0.1	0.1	2.4	0.1	0.9	0.0
Oxides	60.0	74.4	15.6	22.6	57.9	29.4	2.9	79.0	6.2	74.3	18.8
Other classes	0.2	0.0	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.2
Total I identified	96.4	98.1	94.7	96.6	95.3	92.7	86.8	94.9	84.8	91.1	86.6
Unknown	3.6	1.9	5.3	3.4	4.7	7.3	13.2	5.1	15.2	8.9	13.4

A: *E. punctata*; **B:** *E. leucoxylon*; **C:** *E. cladocalyx*; **D:** *E. blakelyi*; **E:** *E. ovata*; **F:** *E. microcorys*; **G:** *E. saligna*; **H:** *E. sideroxylon*; **I:** *E. albens*; **J:** *E. globulus*; **K:** *E. camaldulensis*.

The percent composition of monoterpenes present in the emission of *E. globulus* is reported in Table 22.4. Most organic compounds present in the plant emission are also contained in the essential oils of the same plant species. Worth noting is the large predominance of 1,8-cineole both in the essential oil and in the emission of *E. globulus*. This interesting finding implies that the emitted organic compounds and those containing essential oils are produced from the same photosynthesis pathway. These results should be developed and extended to several plants in field or in laboratory conditions by measuring their emission rates using sensitive sampling technique and analysis with chiral capillary columns. Further studies are needed to confirm the chiral behavior of these compounds and to explain whether or not the enantiomeric distribution of monoterpenes could be related to the metabolic pathway of terpenes emissions. As the monoterpenes are believed to play ecological roles such as chemical defense or pollinator attraction, the discrimination in enantiomeric reactions or attractions would be taken into account for further investigations.

Table 22.4 Percent composition of biogenic volatile organic compounds in the emission of *E. globulus*.

Compounds	%	Compounds	%
α -Thujene	0.03	<i>p</i> -Cymene	3.5
(-)- α -Pinene	1.5	<i>trans</i> - β -Ocimene	1.9
(+)- α -Pinene	33.7	(+)- β -Phellandrene	n.d.
Myrcene	0.38	(-)- β -Phellandrene	n.d.
Tricyclene	n.d.	γ -Terpinene	n.d.
(+)-Sabinene	n.d.	α -Terpinolene	n.d.
(-)-Sabinene	n.d.	1,8-Cineole	53.1
(+)-Camphene	n.d.	(-)-Linalool	n.d.
(-)-Camphene	n.d.	(+)-Linalool	n.d.
(+)- δ -3-Carene	n.d.	(-)-4-Terpineol	0.10
(-)- δ -3-Carene	n.d.	(+)-4-Terpineol	0.08
(+)- β -Pinene	0.22	(+)- α -Terpineol	n.d.
(-)- β -Pinene	0.46	(-)- α -Terpineol	n.d.
<i>cis</i> - β -Ocimene	0.46	(+)- γ -Terpineol	0.07
(-)-Limonene	1.1	(-)- γ -Terpineol	0.25
(+)-Limonene	3.1		

n.d.: not detected.

22.4 Conclusions

More than 60 compounds were identified in the essential oils of 11 *Eucalyptus* species, namely *E. leucoxylon* F. Muell; *E. punctata* DC; *E. sideroxylon* Cunn; *E. saligna* Smith; *E. cladocalyx* F. Muell; *E. blakelyi* A.Cunn; *E. ovata* Labill; *E. albens* Miq.ex Benth; *E. camaldulensis* DC., and *E. globulus* Labill. The major compounds were 1,8-cineole, α -pinene, *p*-cymene, spathulenol, and benzaldehyde.

Interestingly, the major volatile organic compound, 1,8-cineole, was also the predominant one in the atmospheric emission of *E. globulus* Labill. This result could provide an important insight about the origin of 1150 TgC ($T_g=10^{12}$ g) of biogenic volatile organic compounds emitted each year into our atmosphere (Guenther et al., 1995) by terrestrial trees.

References

- Adams, RP (1995) Identification of essential oils components by gas chromatography/mass spectrometry. Allured Publishing Corporation, Carol Stream, Illinois, U.S.A.
- Ahmadouche, A, Bellakdar, J, Berrada, M, Denier, C, Pinel, R (1985) Analyse chimique des huiles essentielles de cinq espèces d'*Eucalyptus* acclimatées au Maroc. *Fitoterapia*, 56 (4): 209–220.
- Barton, AFM, Tjandra, J, Nicholas, PG (1989) Chemical evaluation of volatile oils in *Eucalyptus* species. *J. Agric. Food Chem.*, 37: 1253–1257.
- Bignell, CM, Dunlop, PJ, Brophy, JJ, Jackson, JF (1996) Volatile leaf oils of some South-western and Southern Australian species of the genus *Eucalyptus*. Part VII Subgenus *Symphomyrtus*, Section *Exsertaria*. *Flav. Fragr. J.*, 11: 35–41.

- Bignel, CM, Dunlop, PJ, Brophy, JJ, Jackson, JJ (1997) Volatile leaf oils of some Queensland and Northern Australian Species of the genus *Eucalyptus*. (Series II) Part I. Subgenus *Symphyomyrtus*, Section *Adnataria*: (a) Series *Oliganthae*, (b) Series *Ochrophloiae*, (c) Series *Moluccanae*, (d) Series *Polyanthemae*, (e) Series *Paniculatae*, (f) Series *Melliodorae* and (g) Series *Porantheroideae*. *Flav. Fragr. J.* 12: 19–27.
- Boland, DJ, Brophy, JJ, House, APN (1991) *Eucalyptus Leaf Oils. Use, Chemistry, Distillation and Marketing*. Inkata Press, Melbourne, Sydney.
- Chenoufi, R, Morizur, JP, Richard, H, Sandret, F (1980) Etude des huiles essentielles d'*Eucalyptus globulus* du Maroc (Feuilles de jeunesse et feuilles adultes). *Rivista Ital. EPPOS*, 7: 353–357.
- Dellacassa, E, Menendez, P, Moyna, P, Soler, E (1990) Chemical composition of *Eucalyptus* essential oils grown in Uruguay. *Flav. Fragr. J.*, 5: 91–95.
- Guenther, A, Hewitt, CN, Erickson, D, Fall, R, Geron, C, Graedel, T, Harley, P, Klinger, L, Lerdau, M, McKay, W, Pierce, T, Scholes, B, Steinbrecher, R, Tallamraju, R, Taylor, J, Zimmerman, P (1995) A global-model of natural volatile organic compound emissions. *J. Geophys. Res.* 100: 8873–8892.
- Jennings, W, Shibamoto, T (1980) *Qualitative analysis of flavor and fragrance volatiles by glass capillary chromatography*. Academic Press, New York.
- Lelieveld, J (2008) Atmospheric oxidation capacity sustained by a tropical forest. *Nature* 452: 737–740.
- Olivera, JS (1972) *Oleos essenciais de eucalipto*. Garcia de Orta, 1(1): 1–20.
- Singh, AK, Bhattacharya, AK, Singh, K, Diwedi, BN (1986) Evaluation of essential oil in *Eucalyptus* varieties grown in Kumaon Hills (Ranikhet), Uttar Pradesh for Timber. *Indian For.* 112 (3): 223–228.
- Zrira, SS, Benjilali, BB, Fechtal, MM, Richard, HH (1992) Essential oils of twenty-seven *Eucalyptus* species grown in Morocco. *J. Essent. Oil Res.* 4: 259–264.

Embodied Carbon: The Concealed Impact of Residential Construction

Geoffrey P. Hammond and Craig I. Jones

23.1 Introduction

Modern society is underpinned by a complex web of economic and social activities; commerce, transport, and leisure interweave providing support to not only sustain, but also enhance our way of life. In doing so we have created unprecedented environmental impacts and a burden that must be carried by our planet and our planet alone. Much of this burden is associated with cities, which appear to ‘sustain’ immense populations and satisfy the consumption activities of its many inhabitants. Unfortunately such activities normally require a quantity of natural resources well beyond the bio-capacity of its locality. For example, the ‘Georgian’ city of Bath, in the UK, has been estimated to have an environmental footprint 20 times larger than that of the neighboring land in the area (Doughty and Hammond, 2004). In modern times such trends in over-consumption are not uncommon. Urban immigration is expected to continue, and it is estimated that by the year 2025 three-quarters of the world’s population will be living in a city (Rogers, 1997). This places greater burden on existing city infrastructure and potentially hinders progress toward true sustainability. It is therefore clear that widespread change is required, and without which we will quickly deplete the carrying capacity of our planet. It has already been estimated that we are currently exceeding the carry capacity of our planet by 20% (Loh, 2002). Clearly concerted action must be taken not only to limit but also to reverse potential long-term damage, and thus ensuring that we live on this planet in a sustainable manner.

Sustainable development can be defined as “Meeting the needs of the present without compromising the ability of future generations to meet their own needs” (Brundtland, 1987). Such aspirations require broad sweeping actions in order to ensure economic and social development, while securing environmental protection, across each sector of the economy. Each sector has its own part to

play, and the building sector is a large energy-consuming and carbon-releasing sector, that is responsible for almost half of the UK's total energy consumption and carbon emissions (Brown et al., 2006). However, the additional embodied impact of construction must be considered. The construction industry requires the extraction of vast quantities of materials, resulting in the consumption of energy resources and the release of deleterious pollutant emissions to the biosphere. Each material has to be extracted from the Earth, then processed, and finally transported to its place of use. The energy consumed during these activities is therefore critically important for human development, but they also put at risk the quality and longer-term viability of the biosphere as a result of unwanted or 'second'-order effects. Many of these side effects of energy production and consumption give rise to resource uncertainties and potential environmental hazards on a local, regional, or national scale (Hammond, 2000). Energy and pollutant emissions, such as carbon dioxide (CO₂), may be regarded as being 'embodied' or associated with materials. Here embodied energy is viewed as the quantity of energy required to process and supply to the construction site the material under consideration. In order to determine the magnitude of this embodied energy, an accounting methodology is required that sums the total of the energy consumed over the major part of the material supply chain or life cycle. In the present context, this is taken to include raw material extraction, processing, and transportation to the construction site: a 'cradle-to-site' approach. Likewise the emission of energy-related pollutants, like CO₂ that is a concern in the context of global warming and climate change, may be viewed over their life cycle. This gives rise to the notion of embodied carbon. Embodied impacts are often forgotten and apparently concealed from view. With estimates of 7.6 to 10.8 million new dwellings to be constructed in the UK by the year 2050 (Palmer et al., 2006), the embodied or 'concealed' impact of such residential construction must be considered.

23.2 Method

23.2.1 Energy analysis

Energy analysis may be used to estimate the embodied energy of a product. Several differing methods of energy analysis have been developed (Boustead and Hancock, 1979; Champan, 1976; Hammond and Jones, 2008a; Slessor, 1978), the most significant being statistical analysis, input-output (I-O) analysis, process analysis, and hybrid analysis. The latter method bridges elements of I-O and process analyses in an attempt to remove some of the downfalls of each individual method (see for example Treloar et al., 2000). The analysis of a product over its life cycle is a complex and involved activity. It requires the consideration of a large number of processes, and as such gaps often appear in the data. Studies often have different boundary conditions or cut-off points. In 1974 the International Federation of Institutes for Advanced Study (IFIAS) described the concept of 'level of regression' for analysis (IFIAS, 1974), which is a structured method of pruning a data tree. Figure. 23.1 displays this concept, indicating the relative

contribution (in many cases) of each level to the total life cycle energy (the area of the triangle).

A first level of analysis includes only the direct energy consumption. It is normally expected that the results of a first-level regression will represent the majority of the life cycle energy. This does not, however, imply that a first-level analysis is sufficient on its own, as this is rarely the case. A second level of regression additionally considers energy that was required to manufacture feedstock materials (material production energy). It has been estimated that in many cases a second order of analysis can account for 90% of the total life cycle energy (Slessor, 1978). This is, however, merely a guideline, and deviation from this 'rule' does occur. While this may hold true for many building materials there will be many systems and activities that fall outside of this 'rule of thumb.' Analysis beyond this level is time consuming and hence studies of this order and above are rare. A third level of regression includes energy consumed while manufacturing capital equipment (energy required to manufacture machines). And finally the machines from the third level of analysis were themselves manufactured from other machines. As such a fourth level of regression exists.

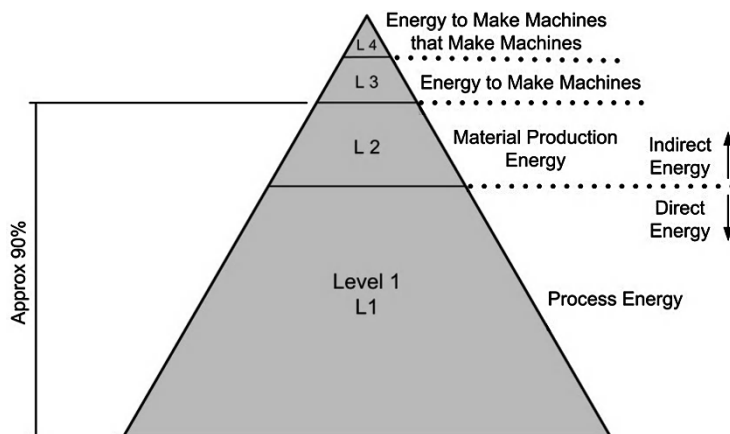


Fig. 23.1 Pyramid of representation.

In the case of steel production a first level of regression would include the energy consumed in direct production processes. This includes energy consumed directly in the blast furnace and fabrication processes. The second level of analysis would include energy that was consumed during the quarrying and mining of feedstock materials, such as the iron ore consumed during the steelmaking process. A third level of regression would include energy that was required to manufacture the blast furnace (capital equipment). And a fourth level would consider the energy that was required to manufacture the machines that manufactured the blast furnace. The contribution from a fourth level of analysis is usually minor and very time consuming to determine. However, if a fourth level of analysis was never undertaken its 'insignificance' could never be concluded with absolute

certainty. As such in the first investigation of a system it is desirable to complete an energy analysis to the highest attainable level of regression that is possible.

23.2.2 Life cycle thinking

Energy analysis preceded environmental life cycle assessment (LCA) and it shares much of the same fundamental methodology (Hammond and Jones, 2008a). It is widely recognized that in order to evaluate the environmental consequences of a product or activity the impact resulting from each stage of its life cycle must be considered. This has led to the development of ecotoxicology, a study of the harmful effects of releasing chemicals into the environment, and a range of analytical techniques that now come under the 'umbrella' of environmental LCA. In a full LCA, the energy and materials used and pollutants or wastes released into the environment as a consequence of a product or activity are quantified over the whole life cycle, 'from cradle-to-grave.' The aim of the LCA is often to identify opportunities for environmental improvement by detecting the areas with the most significant impacts. In the case of non-energy-consuming products, for example, buildings materials, the energy result of an environmental life cycle assessment can often be taken to be its 'embodied energy.' The latter is often confined within the boundaries of cradle to site to separate it from the operational energy. However, end-of-life impacts are inevitable and as such are often integrated into the boundaries of embodied energy studies. An LCA should ideally conform to international standards (ISO 14040, 2006a; ISO 14044, 2006b).

Determination of a product's life cycle is invariably difficult; it requires the elementary understanding of material, energy, and emission flows across a broad spectrum. It is complicated by the fact that many such contributions are apparently hidden or 'concealed' from view. For example, if a consumer were to estimate the full impact of its activities they would need to consider a significant number of 'concealed' activities. It may be considered that many consumers live in a 'virtual world' in which they interact directly. This bears the bulk of their considerations. But what lies outside this world is an unavoidable and essential web of ancillary activities. The consumer is rarely exposed to such activities and as such they have little awareness of the resulting impacts. The marriage of the two worlds leads to the real, 'actual world,' as represented by Fig. 23.2. In the case of driving a car, as illustrated in Fig. 23.2, a consumer believes that he/she achieve 50 miles to the gallon (mpg) fuel economy (5.65 liters per 100 km). However, this does not bear the full environmental impact. There is an entire web of ancillary activities that must be considered, which includes each process leading up to the delivery of fuel into their vehicle in a usable format and at a convenient location. Progression up the production tree would reveal such activities as fuel pumping, delivery, refining, shipping, storage, oil well operations, drilling, and exploration activities. Once the impact of such activities is accounted for the actual (or 'true') fuel economy may be only 45 mpg (6.28 liters per 100 km). In reality the consumer may have only a modest direct influence on such ancillary activities. But were they to start considering them from a consequential point of view, then they might exhibit wider environmental concern than just taking into account

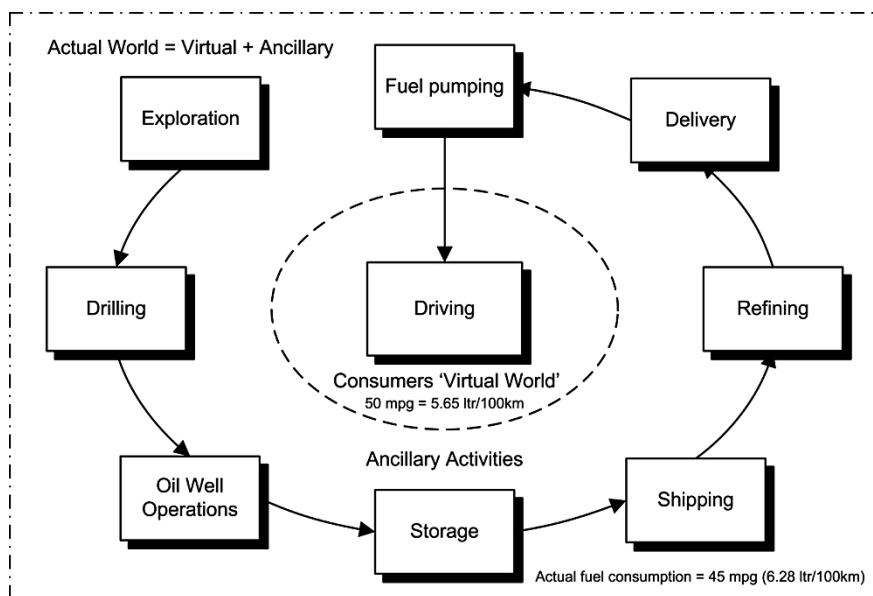


Fig. 23.2 Consumers' 'virtual world' versus the 'actual world' Adapted from: Hammond and Jones 2007.

the burden of their virtual world (i.e., their own interactions). Thus, they may become impelled to think about not only conserving energy, but conserving all that they undertake and consume.

23.2.3 The Inventory of Carbon and Energy (ICE)

In order to enable the determination of embodied energy and embodied carbon of buildings a robust, reliable, and transparent database is required. Initial research proved that finding such a database in the public domain would be difficult, this was especially true for embodied carbon (embodied carbon coefficients naturally carry a higher uncertainty than embodied energy as a result of variations in fuel mixes, electricity generation technologies, and process technologies). For these reasons the present authors at the University of Bath decided to develop their own database for a wide range of materials. This resulted in the creation of '*The Inventory of Carbon and Energy*' (ICE) (Hammond and Jones, 2008a and 2008b). This inventory contains the embodied energy and carbon of approximately 200 materials and has been released freely into the public domain. The ideal data would involve undertaking complete environmental LCA for each individual material, but with a likely material inventory amounting into the hundreds, and each LCA requiring up to 9 months to undertake, this was not considered feasible. For such reasons the data were sourced from the literature and may be considered to be a summary of the current knowledge base.

During the creation of ICE it was quickly discovered that estimating the embodied carbon from literature sources would present difficulties, even more so than any difficulties experienced for embodied energy. In the first instance it was determined that only 20% of the collected data was usable for estimating embodied carbon. The ideal resource was to obtain embodied carbon from a full-scale environmental LCA. But these were not normally available. For the majority of materials the embodied carbon was therefore estimated through calculation. When considering a material list in the region of 200 materials it is vital that an efficient and reliable method be applied in the conversion of embodied energy to embodied carbon. A generic emissions factor would be the quickest way to achieve this, and such methods are available in practice. However, there are a number of reasons for avoiding such methods. Application of a generic emissions factor (i.e., the average UK emissions per unit energy consumed) may offer acceptable results for a large number of materials. There are many cases when errors are induced. Possible causes of such errors include:

- A generic emissions factor neglects to consider that certain industries have fuel mixes that differ significantly from the average. As an example, world-wide aluminum production is known to utilize a high percentage of hydro-electricity. The net effect of this is to reduce the embodied carbon below that based on national emissions factors. Despite this the absolute embodied carbon of aluminum per kilogram remains high.
- Generic factors do not account for non-fuel-related emissions of individual materials (process emissions). Such emissions play an important role for several key building materials. In the manufacture of cement, for example, carbon dioxide is released into the atmosphere as a result of material processing. In this case it contributes in the region of 60% to the total embodied carbon; the remaining 40% is attributable to fuel-related carbon dioxide (Hammond and Jones, 2008a and 2008b). Cement is the largest process-related carbon dioxide emitter. Other materials that experience non-fuel-related emissions are glass and ceramics, the latter including clay and bricks.

Further errors may be induced as a result of the following:

- Embodied energy is a measure of primary energy and as such it is vital that the correct emissions factors are applied. Emissions factors for delivered electricity differ by an approximate factor of 3 with those converted into its primary energy equivalent.
- It is important to understand what the data include. Many of the traditional energy analysis studies are calculated via the gross calorific value (also known as the higher heating value). Environmental LCA results are often (although certainly not exclusively) calculated by net calorific value (also known as the lower heating value). In the case of embodied energy this could result in a 5–11% difference, although this should in theory have no effect on the embodied carbon results unless errors subject to the above misinterpretations have been induced. For example if carbon emissions factors for gross

calorific values were applied to embodied energy calculated by its net calorific value.

There is additionally the complication of organic materials, materials such as timber which absorbs carbon dioxide during the growth phase of trees. Whether to include or exclude this factor is not a simple matter. The authors of this chapter prefer to exclude the sequestered carbon dioxide from their data until such a time that timber demonstrates to be operating in a globally sustainable manner (see Amato, 1996; Eaton and Amato, 1998; Hammond and Jones, 2008a). At present this is not the case, and consequently global tree populations are in decline.

After consideration of the above matters, a methodology for converting embodied energy to embodied carbon was developed. The method has proven to be effective and reliable. It represents a large improvement over industry-wide (generic) emissions factors and is displayed in Fig. 23.3 below.

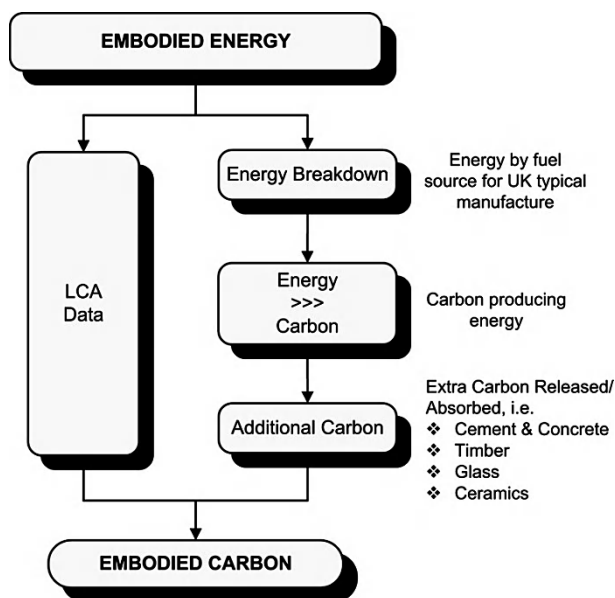


Fig. 23.3 Embodied energy to embodied carbon.

Once the embodied energy has been determined the process of converting to embodied carbon begins. In the absence of LCA results containing embodied carbon the present method was applied (see Fig. 23.3). First it was necessary to estimate the embodied energy breakdown by fuel type. To achieve this, the fuel mix used in the most relevant industrial sector was applied. Appropriate emissions factors were then applied to obtain the fuel-related carbon dioxide emissions. Once the additional carbon dioxide release has been determined the total embodied carbon had been estimated from the sum of these and fuel-based emissions.

23.2.4 System boundaries

The system boundaries for this study were adopted as appropriate for ‘cradle-to-site’ studies. Feedstock energy was included only if it represented a permanent loss of valuable resources, such as fossil fuel use. Thus, fossil fuels utilized as feedstock for the petro-chemicals used in the production of plastics were included (although identified separately). However, the calorific value of timber has been excluded. This approach is consistent with a number of published studies and methodologies, including the BRE methodology for environmental profiles (Howard et al., 1999). The effects of carbon sequestration (for example, in the case of timber) were considered, but not integrated into the data. Non-fuel-related carbon emissions have been accounted for (process-related emissions) and a recycled content, or cut-off approach, was preferred for the handling of recycling (i.e., metals).

23.3 Results

23.3.1 ICE domestic building model

The ICE database (Hammond and Jones, 2008a and 2008b) has been applied to real-world applications. A number of case study buildings were collected from both domestic (Hammond and Jones, 2007) and non-domestic building sectors, not only from the literature-based resources but also utilizing primary case studies. It was not always possible to determine a sufficient specification of the buildings under analysis. However, building specification has profound effects upon results of embodied energy and carbon. Therefore, to enable embodied estimates for bespoke buildings to be determined, an ICE Domestic Building Model was developed. The model operates with the following variable parameters:

- Building type: detached, semi-detached, terraced, bungalow, or low-rise apartment
- Fabric reconstruction: a range of predetermined walls, floors, and roofs allow a building to be reconstructed to specified thermal standards
- Total floor area and height of each floor
- Window type and area
- Finishes: floor finishes (carpets, vinyl, laminate, timber floorboards), wall finishes (paint, wallpaper, tiles), and window furnishes (a range of curtains and blinds)
- Garage (single, double) and driveway (concrete, gravel, brick, tarmac)
- Housing development impact (connecting roads, pathways, walls, etc.)
- Conservatory (small, medium, large)
- Grid electricity carbon coefficient and electricity generation efficiency

The model utilized flow charts, one of which is displayed as a schematic in Fig. 23.4. This flow chart may be used along with appropriate coefficients to estimate the output of the ICE Domestic Building Model. Figure 23.4 depicts the simplified representation of a semi-detached building. In contrast, the full ICE

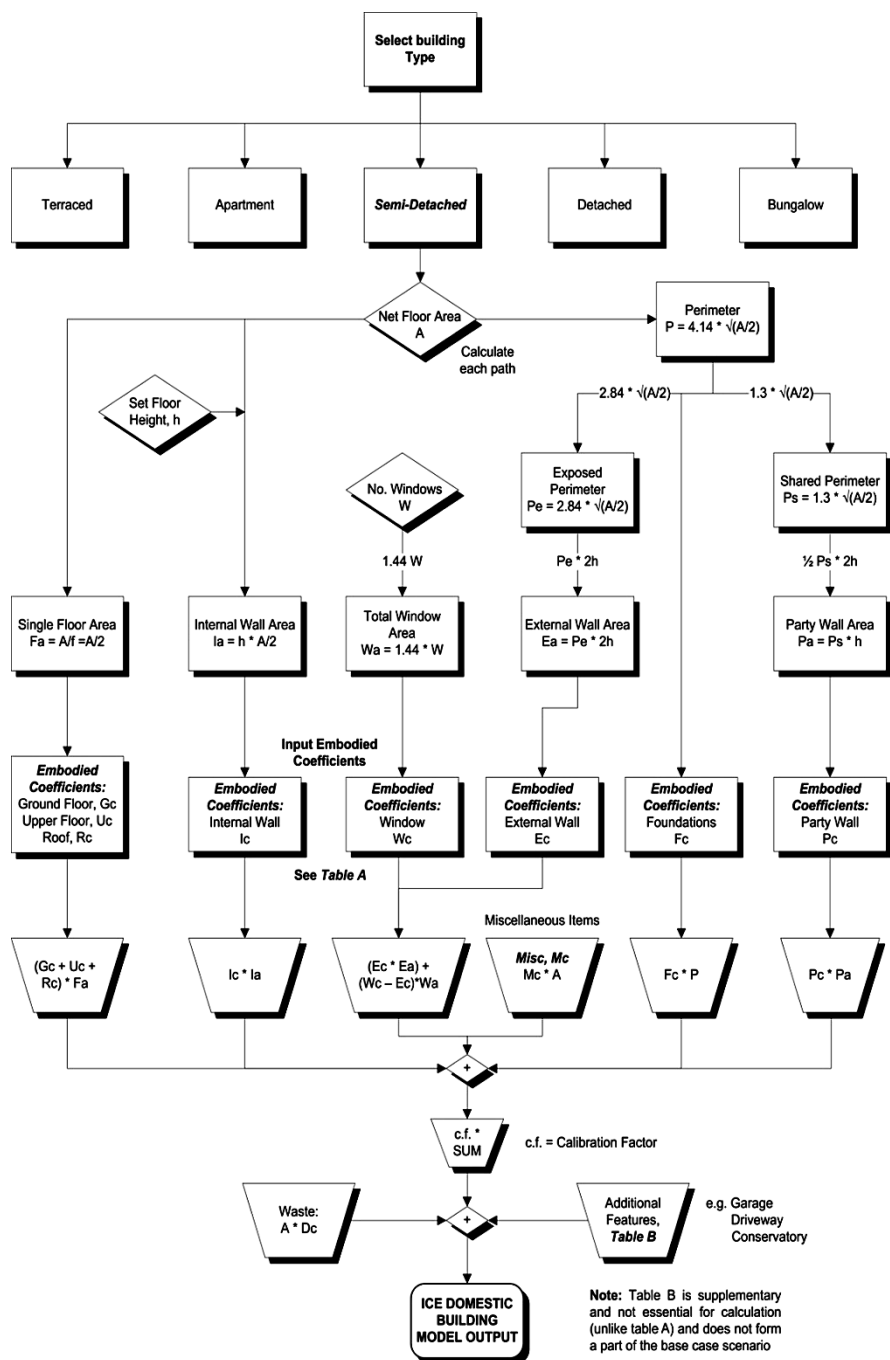


Fig. 23.4 Schematic of the ICE Domestic Building Model.

Domestic Building Model retains higher detail, ease of use, and dynamic assumptions, although the simplified ICE Flow Charts produce results with good proximity of the full ICE Domestic Building Model. The full model is tied into the generation efficiency and the carbon coefficient of electricity as a variable parameter. To calculate the embodied energy and embodied carbon it is required to run through the flow chart twice, once for embodied energy and once for embodied carbon. Two tables accompany the flow charts (not included in whole herein); 'Table A' contains embodied energy and embodied carbon coefficients for construction elements, such as walls, floors, and roofs and a miscellaneous addition (which accounts for kitchens, bathrooms, and toilets as a function of floor area). A sample of embodied coefficients (from 'Table A') is shown in Table 23.1. These coefficients have been selected for a building that meets the 2006 (Part L) UK building regulations. 'Table B' contains embodied energy and carbon coefficients of extra building features, for example, driveway, garage, conservatory, energy to construct a housing development (i.e., connecting roads and pathways, etc.). 'Table A' is integral and must be applied, whereas 'Table B' is optional but is required to model the impacts of additional features such as a garage, driveway, and conservatory. Application of Table 23.1 to the flowchart (in place of 'Table A') allows an example building to be analyzed. In the case of a 100 m² semi-detached building with a floor height of 2.5 m and 14 windows (1.2m × 1.2m), for example, the embodied energy was estimated at 533 GJ and embodied carbon at 39.6 tonnes CO₂.

Table 23.1 Sample coefficients of embodied energy and embodied carbon.

Construction element	Embodied energy (– MJ/m²)	Embodied carbon (–kgCO₂/m²)
Ground floor, Gc	781	86.0
Upper floor, Uc	453	23.3
Roof, Rc	554	37.1
Internal wall, Ic	290	26.3
uPVC window, Wc	2,300	112.2
External wall, Ec	782	64.4
Foundations, Fc	867	103.0
Party wall, Pc	483	45.2
Miscellaneous, Mc	350	25.0
Waste, Dc	1,200	76.0
Calibration factor, c.f.	1.3	1.3

23.3.2 Benchmark results

Hammond and Jones (2007) analyzed semi-detached houses and provided benchmark results by building floor area for this single building type only. Results from the ICE Domestic Building Model have been analyzed to create benchmarks of embodied energy and embodied carbon for a broader range of dwelling types. The work has now been extended to include detached and terraced houses, bungalows

(detached), and apartments (three storey blocks and four storey blocks). The results may be used to estimate the embodied impacts of residential buildings by floor area and building type. It is hoped that these results may be used by building professionals to determine a baseline, and therefore offer benchmarks for future carbon mitigation strategies.

The base case buildings were assumed to have a basic building specification. Each property conforms to 2006 UK building regulations with uPVC double-glazed windows. There were no additional features such as garages, driveways, or conservatories. The benchmarks therefore only estimate the embodied energy and carbon of the building itself and include no external additions. They allow the total embodied energy and total embodied carbon to be estimated based on the floor area and property type. Figure 23.5 shows the benchmark results for embodied energy and Fig. 23.6 for embodied carbon in the form of contour charts or plots.

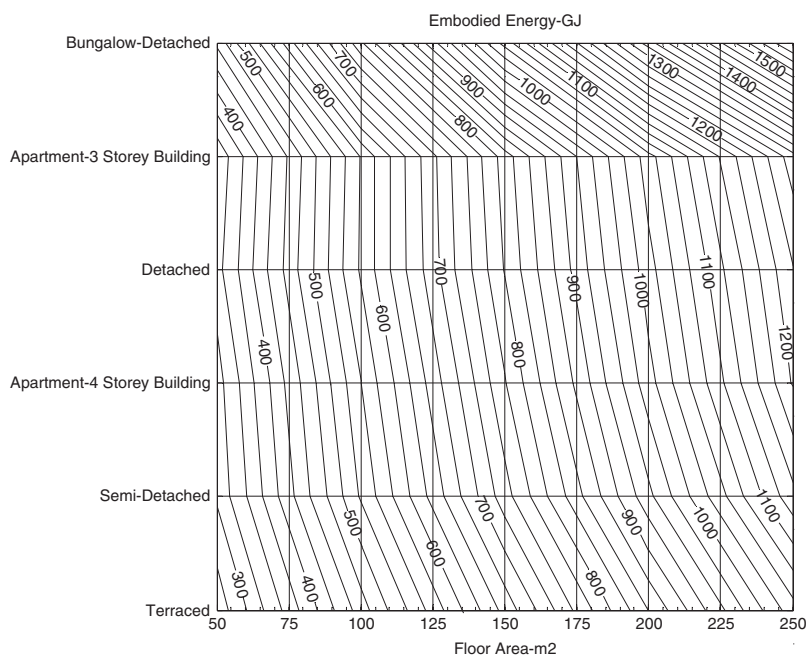


Fig. 23.5 Embodied energy guidelines for domestic buildings.

The uncertainty associated with these benchmarks was estimated to be $\pm 30\%$. Using these charts a detached house of 150 m² was predicted to have an embodied energy of 800 GJ (see Fig. 23.5) and an embodied carbon of 59 tonnes CO₂ (see Fig. 23.6). Likewise a 100 m² semi-detached property was estimated at 530 GJ and 39.5 tonnes CO₂, which is comparable to the previous estimate (from the flow chart). These results may be used to estimate the embodied impacts of average

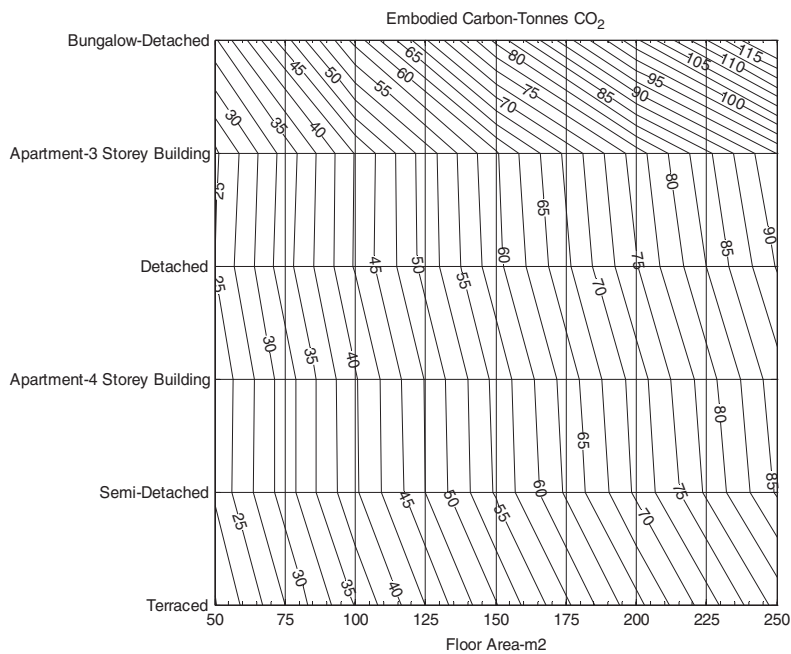


Fig. 23.6 Embodied carbon guidelines for domestic buildings.

UK dwellings. To do this the average floor area of each building type would be required. For English buildings (UK-wide data are not available) the average floor area of each newly built property type was obtained (ODPM, 2001). The benchmark results were then applied to the average floor areas to determine the typical embodied energy and carbon of each building type. These results are displayed in Table 23.2.

The weighted average embodied energy of a newly built property in the UK was estimated to be 480 GJ and its embodied carbon 36 tonnes CO₂ (Table 23.2). Average apartments and terraced properties were estimated to have similar impacts and were the lowest impact options; however, comparatively the terraced building was larger with an additional 18 m² floor area. An average semi-detached property was estimated to have a 30–35% higher impact than an average terraced or apartment building, but was only 7% larger in floor area than the former. Bungalows were determined to have a particularly high impact per unit floor area, especially in comparison to the alternative options. An average bungalow of 76 m² was estimated to have an embodied energy only 10% lower than an average detached house of 125 m², although the latter benefits from a 65% larger floor area. These results demonstrate the importance of both floor area and building type in terms of total embodied energy and carbon. It is interesting to compare these

building types by how well (environmentally) they perform to provide a set floor area. The results from Table 23.2 were therefore normalized to per unit floor area, as are displayed in Table 23.3. The results in Table 23.3 suggest that (detached) bungalows have the largest impact per unit living area and by a fair margin. In the case of a bungalow this was mainly attributed to the property having a single floor at ground level. Such buildings require a larger area of foundations and roofing than any other building type, consequentially resulting in a high embodied energy. Low-rise apartment blocks were, additionally, considered to have a high impact per unit floor area. But there are two other factors working in favor of apartment-style buildings. First of all the floor area is defined as the total floor area enclosed by the walls of the property. Low-rise apartment blocks in the UK require a level of communal space, such as stairways or hallways, which is dependent on the size of the building and not included in the floor area of the apartment. However, the embodied energy and carbon were estimated for the entire building and therefore each property takes its share of these burden. This implies that an apartment of area 80 m² is in effect more ‘spacious’ than a semi-detached or detached building of the same floor area. While this seems implausible, it is the absence of internal stairways and (possibly) reduced hallways that increases the comparative spaciousness of these properties. Furthermore it can be expected that a property arranged over a single level would utilize space more efficiently than one over multiple levels.

Table 23.2 Embodied energy and carbon of typical newly built English dwellings.

Building type	Percentage of new properties	Average floor area (m²)	Embodied energy (GJ)	Embodied carbon (tonnes CO₂)
<i>Apartment</i> (three storey building)	24	50	330	24
<i>Apartment</i> (four storey building)			315	23
<i>Terraced</i>	20	68	330	25
<i>Semi-detached</i>	15	73	410	31
<i>Bungalow (detached)</i>	11	76	620	47
<i>Detached</i>	31	125	690	51
<i>Weighted average</i>	100	83	480	36

The second factor is from the reduced physical footprint of the building. These buildings take up less space, not only of the building, but normally the surrounding landscape. Semi-detached, detached, and bungalows are likely to have their own gardens, driveways, and pathways, they may have a garage and further landscaping. In comparison apartment-style buildings could have communal gardens and perhaps individual garages, although a block of garages is considered to be a more efficient arrangement than the same quantity of separate garages. The

combined effect may be to save embodied energy and carbon of these ‘external features’ whilst offering a more ‘spacious’ property for the same floor area. That said, low-rise apartment-style buildings which are well spaced apart (not within a single block), and with spacious surroundings (gardens), may negate any expected external works savings. The external works include the impacts from excavation and filling, concrete, walls, paving, kerbs, roads, fences, gates, painting, storm drainage, and other duct works (see Hammond and Jones, 2008a).

Table 23.3 Normalized embodied energy and carbon of typical newly built UK dwellings by floor area

Building type	Average floor area (m^2)	Embodied energy (GJ/m^2)	Embodied carbon (kgCO_2/m^2)
<i>Apartment</i> (three storey building)	50	6.6	480
<i>Apartment</i> (four storey building)		6.3	460
<i>Terraced</i>	68	4.9	370
<i>Semi-detached</i>	73	5.6	425
<i>Bungalow</i> (detached)	76	8.2	620
<i>Detached</i>	125	5.5	410
<i>Weighted average</i>	83	5.8	435

External works were estimated to be within the embodied energy range 1844–2230 MJ/m^2 (habitable floor area) and embodied carbon range 135–177 kgCO_2/m^2 . However, with only two data points, it was difficult to estimate the accuracy of such results. In comparison with Table 23.3 external works represent a significant extra impact. When applied to the average semi-detached house the embodied carbon would increase from 425 to 581 kgCO_2/m^2 . Given its floor area of 73 m^2 , the embodied carbon increases from 31 tonnes CO_2 to 42 tonnes kgCO_2 , representing an increase of over 35%. For a complete and fair analysis, the impact of external works must obviously be considered on a case-by-case basis. However, these results indicate that further analysis of external works would be desirable.

23.4 Discussion

While it is important to consider the embodied impacts of new building designs this must not be the sole factor for selection. A full analysis of operational energy should be completed. Energy in operation presently has the largest impact over the lifetime of a property. With the current benchmarks it was estimated that the energy in operation would overtake the initial embodied energy within 7 years and the carbon would take almost 12 years (see Hammond and Jones, 2007 and 2008a). It was also discovered that the inclusion of a single garage, a driveway, a

conservatory, and the contribution of a housing development would increase this to 12 years for energy and 19 years for carbon. This is a significant duration, especially considering the design life of such a house which may be 60 years, and over this time it will require further embodied energy and carbon inputs during refurbishment and routine maintenance. It is expected that this duration will increase over time as UK building regulations become more energy efficient and lower carbon. It is anticipated that by the year 2016 all newly built English dwellings will be zero carbon in operation. If this occurs embodied carbon will become the predominant life cycle impact.

These results demonstrate that the time required for the energy in operation to overtake the embodied energy is quicker than for embodied carbon, the climate change marker. This was mainly attributed to the release of non-fuel-related carbon into the atmosphere (as a result of manufacturing processes); cement is the key material with this additional release. The carbon in operation has originated from predominantly natural gas and electricity, which do not experience the same additional carbon releases. The net effect of this is to increase the relative size of the embodied carbon in comparison with operational carbon. This extends the duration for the operational carbon to overtake the embodied carbon. While it may be expected that organic materials, such as timber may negate this effect on a whole building, the chosen methodology did not allow for such carbon sequestration. The authors choose to neglect the effects of timber carbon sequestration until such a time that timber is utilized in a globally sustainable manner (consumption equals replenishment) and that the science of carbon pools and the carbon cycle is better understood.

Normalized results per unit floor area may appear particularly attractive as benchmarks: they are simple to apply and easy to understand. However, it must be noted that the relationship of embodied carbon to floor area is not linear, and therefore buildings of different sizes (but same type) normalize to give very different results. For example, the 'typical' semi-detached building in Table 23.3 was estimated to require $425 \text{ kgCO}_2/\text{m}^2$ based on its 73 m^2 floor area. However, using the same benchmarks, a semi-detached property of 125 m^2 is estimated to have an embodied carbon of 47.5 tonnes CO_2 in total (Fig. 23.6). This normalizes to $380 \text{ kgCO}_2/\text{m}^2$, which is a significantly different (lower) value. Normalized results may therefore be unsuitable for domestic benchmarks. It would be preferential, and is recommended, that a model or formulae be applied (such as the results from Figs. 23.5 and 23.6, or the use of an equation [as in Hammond and Jones, 2007]). Normalized results of embodied energy and carbon may be particularly unsuitable for environmental policy making and legislation. The above analysis suggests that larger properties experience lower embodied carbon per unit floor area. If legislation required all semi-detached buildings to have an embodied carbon (per unit floor area) below a set threshold the easiest way to achieve this would be to increase its total floor area. This is naturally counterproductive and would increase the total embodied carbon of the property as a result of the larger floor area. In light of this, it is recommended that any environmental policy or legislation should set absolute benchmarks of embodied energy and carbon (such as Table 23.2,

Fig. 23.5, or Fig. 23.6) rather than normalized benchmarks (such as Table 23.3). Despite this recommendation valuable lessons can still be learnt from normalized embodied carbon results.

The study of a product or building over its life cycle is often geographically diverse; that is, the material inputs to a product may be drawn from any continent or geo-political region of the world. This unfortunately makes the improvement process complex, in that many businesses and economies are involved in the manufacture of a product. Therefore to achieve low or zero environmental burdens will require concerted efforts over a wide domain. Each business, nation, and individual must contribute in an altruistic manner, through acts of selfless wellbeing, rather than the current trend of egoism. Invariably such action may be too idealistic and is therefore unlikely to be achieved. But it may be encouraged with accepted international regulation and frameworks, providing examples of good practice and sustainable development.

23.5 Conclusions

The construction industry requires the extraction of vast quantities of materials, resulting in the consumption of energy resources and the release of deleterious pollutant emissions to the biosphere. Energy and pollutant emissions, such as carbon dioxide (CO_2), may be regarded as being ‘embodied’ or associated with materials. Here the embodied energy was viewed as the quantity of energy required to extract, process, and supply the material under consideration. Likewise the emission of energy-related pollutants, like CO_2 that is a concern in the context of global warming and climate change, may be viewed over their life cycle. This gives rise to the notion of embodied carbon. With an estimated 7.6–10.8 million new dwellings to be constructed in the UK by the year 2050 (Palmer et al., 2006), the embodied impact of such construction must be considered.

The ICE database (Hammond and Jones, 2008a and 2008b) has been applied to both domestic and non-domestic buildings. Forty case study buildings were collected for domestic buildings (Hammond and Jones, 2007). These were primarily extracted from a variety of literature resource, including several primary case studies. These resources did not always contain sufficient detail on the building specification and therefore the *ICE Domestic Building Model* was created. The model operates in a bottom-up manner; therefore allowing buildings to be reconstructed through the selection of walls, floors, roofs, etc. Application of this model and comparison with the case study results allowed initial embodied energy and carbon benchmarks to be created for semi-detached, detached, terraced, bungalow (detached), and apartment (three storey block and four storey block) dwellings. Benchmarks were created for ‘typical’ English buildings of each classification. The average detached property was determined to have the highest embodied impact; however, they also had by far the largest floor area (125 m^2). An average newly built (detached) bungalow was estimated to have a slightly lower impact but with a much reduced floor area (76 m^2) they were determined to be an inefficient method of construction. Semi-detached buildings (73 m^2) have significantly

lower embodied impact and terraced buildings (68 m²) lowest yet. Apartments were determined to have the lowest impact, but only provided an average floor area of 50 m².

Normalized results per unit floor area may appear particularly attractive to apply as benchmarks, they are simple to apply and easy to understand. However, it must be noted that the relationship of embodied carbon to floor area is not linear, and therefore buildings of different sizes (but same type) normalize to give very different results. Normalized results of embodied energy and carbon may be particularly unsuitable for environmental policy making and legislation. Analysis suggested that larger properties experience lower embodied carbon per unit floor area. Therefore if regulation required all semi-detached buildings (for example) to have an embodied carbon below a specified threshold (per unit floor area) the easiest way to achieve this would be to increase its total floor area. This would, however, increase the total embodied carbon of the property. In light of this it was recommended that any environmental policy or legislation should set absolute benchmarks of embodied energy and carbon (such as Fig. 23.5, Fig 23.6, or Table 23.2) rather than normalized benchmarks (such as Table 23.3). Such regulation would allow society to reduce the total (embodied plus operational) energy and carbon impact of residential construction, thereby minimizing 'concealed' impacts.

Acknowledgments

The research leading to the development of the ICE inventory was principally supported via a UK research grant awarded by the Carbon Trust and the Engineering and Physical Sciences Research Council (EPSRC) [Grant GR/S94292/01, as part of the '*Carbon Vision Buildings*' (Building Market Transformation (BMT)) Programme] awarded to the first author (GPH). Both authors are grateful to the BMT consortia co-ordinators: Dr Brenda Boardman and Dr Mark Hinnells of the Environmental Change Institute, University of Oxford. Dr Boardman was succeeded in her post by Dr Nick Eyre on October 1, 2007. The corresponding author (CIJ) is at present partially funded via a strategic partnership between E.ON UK (the electricity generator) and the EPSRC to study the role of electricity within the context of 'Transition Pathways to a Low Carbon Economy' [under Grant EP/F022832/1]. Here the ICE database is being used to aid the determination of the embodied energy and carbon associated with various types of power generation plant. Prof. Hammond is the co-leader of this large consortium of university partners (jointly with Prof. Peter Pearson, an energy economist from Imperial College London). The authors greatly appreciate the interchange with Peter Pearson and the other main UK partners at E.ON Engineering and at the Universities of East Anglia (Prof. Jacque Burgess), Leeds (Dr Timothy Foxon), Loughborough (Dr Murray Thomson), Surrey (Prof. Matthew Leach), and Strathclyde (Dr Graham Ault and Prof. David Infield), as well as at Imperial College London (Prof. Goran Strbac) and Kings College London (Dr Neil Strachan). The authors have also benefited from a discourse with colleagues in the Sustainable Energy Research Team (SERT) at Bath. However, the views expressed are those of the authors alone and should not necessarily be attributed to the collaborators or funding bodies.

References

- Amato, A., 1996. *A Comparative Environmental Appraisal of Alternative Framing Systems for Offices*. PhD thesis, Oxford Brookes University.
- Boustead, I. and Hancock, G.F., 1979. *Handbook of Industrial Energy Analysis*. Ellis Horwood, Chichester.
- Brown, A.I., Hammond, G.P., Jones, C.I. and Rogers, F.J., 2006. Greening the UK building stock: historic trends and low carbon futures 1970–2050. *Proc. Second International Green Energy Conference (IGEC-2)*. 25–29 June 2006, Oshawa, Canada, p423–435.
- Brundtland. 1987. *Our Common Future*, Report of the World Commission on Environment and Development. World Commission on Environment and Development.
- Chapman, P., 1976. Methods of energy analysis. In *Aspects of Energy Conversion* (Blair I.M., Jones B.D. and Van Horn A.J. (eds.)). Pergamon, Oxford, 739–757.
- Doughty, M.R.C. and Hammond, G.P., 2004. Sustainability and the built environment at and beyond the city scale, *Building and Environment*, 39(10): 1223–1233.
- Eaton, K.J. and Amato, A., 1998. *A Comparative Environmental Life Cycle Assessment of Modern Office Buildings*. The Steel Construction Institute, Berkshire. SCI Publication 182.
- Hammond, G.P., 2000. Energy, environment and sustainable development: a UK perspective. *Trans IChemE Part B: Process Safety and Environmental Protection* 78: 304–323.
- Hammond, G.P. and Jones, C.I., 2007. Benchmarks for embodied energy & carbon: domestic buildings. *Proc. of the International Conference of the Society for Sustainability and Environmental Engineering 07 (SSEE 07)*, 31 October–2 November, Perth, Australia.
- Hammond, G.P. and Jones, C.I., 2008a. Embodied energy and carbon in construction materials, *Proc. Instn Civil Engrs: Energy*, 161 (2): 87–98. [DOI:10.1680/ener.2008.161.2.87].
- Hammond, G.P. and Jones, C.I., 2008b. 'Inventory of Carbon and Energy' (ICE), Version 1.6a, Sustainable Energy Research Team (SERT), Department of Mechanical Engineering, University of Bath, Available from: www.bath.ac.uk/mech-eng/sert/embodied/.
- Howard, N., Edwards, S. and Anderson, J., 1999. *BRE Methodology for Environmental Profiles of Construction Materials, Components and Buildings*. Report BR370, CRC, London.
- IFIAS. 1974. *Report of Workshop on Energy Analysis*, International Federation of Institutes of Advanced Studies, Stockholm.
- ISO. 2006a. *Environmental management – Life Cycle Assessment – Principles and Framework*. EN ISO 14040, International Standards Organization, Geneva, Second Edition.
- ISO. 2006b. *Environmental Management – Life Cycle Assessment – Requirements and Guidelines*. EN ISO 14044, International Standards Organization, Geneva.
- Loh, J. 2002. *Living Planet Report 2002*. WWF International, Gland, Switzerland.
- ODPM, 2001. *English House Condition Survey*. Office of the Deputy Prime Minister, London, UK.
- Palmer, J., Boardman, B., Bottrill, C., Darby, S., Hinnells, M., Killip, G., Layberry, R. and Lovell, H., 2006. *Reducing the Environmental Impact of Housing. Final Report*. Consultancy study in support of the Royal Commission on Environmental Pollution's 26th Report on the Urban Environment. Environmental Change Institute, Oxford.
- Rogers, R. 1997. *Cities for a Small Planet*, Faber and Faber, London.
- Slessor, M. 1978. *Energy in the Economy*, Macmillan Press, London.
- Treloar, G.J., Love, P.E.D., Faniran, O.O. and Iyer-Raniga, U., 2000. A hybrid life cycle assessment method for construction, *Construction Management and Economics* 18 (1): 5–9.

Sustainable Construction Practices in Malaysia

Nazirah Zainul Abidin

24.1 Introduction

A building occupies land, alters the ground and vegetation, prevents the percolation of rainwater into the ground, interrupts the flow of wildlife through the area, and consumes resources, labor, materials, and fuel. The design of the building has an enormous impact on the environment, both present and future. Once completed, the building continues to use finite resources to power, heat, cool, and maintain the building for about 100 years (Lee, 2007). However, to not build is not a solution. Buildings and structures enabled mankind to meet their social needs for shelter, to meet economic needs for investment, and to satisfy corporate objectives. It changes people's lifestyle, improves people's standard of living, and modernized a community. The construction industry is regarded as an essential and highly visible contributor to the process of growth of one country. Nevertheless, the adverse impacts to the environment lead to a growing realization and acceptance throughout the world that there is a need for a more responsible approach to the environment. The opportunity for improvement arrived when a new philosophy called 'sustainable development' was introduced in 1987 in Brundtland Report. Since that, many progressive world events had taken place to increase the awareness on environment and sustainability agendas such as Rio Earth Summit 1992, Maastricht Treaty 1992, Kyoto Conference on Global Warming 1997, Johannesburg Earth Summit 2002, and Washington Earth Observation Summit 2003 (Zainul Abidin, 2005). The ideas and strategies initiated by these world events have prompted positive actions and plans by many countries to implement and absorb this philosophy within their industries. Subset to this philosophy is sustainable construction, which described the responsibility of the construction industry to attain sustainability. Formulating a robust strategy to improve sustainable construction knowledge and acceptance is a significant milestone in the construction industry to becoming more socially and environmentally responsible, not only for each construction project, but also for its stakeholders. It creates a framework within which the industry can make a strong contribution to a better future.

Building sustainably has many merits but applying this concept is not easy as it requires changes to the old ways. Delivering sustainable construction requires action from all engaged in constructing and maintaining the structure or building including those providing design, consulting, and construction services. To increase the consideration to sustainability, the construction practitioners must be willing to change their behavior in exploring new territory and willing to adopt new products, ideas, and practices. Because of the merits and the growing interest on building sustainably, the race is now on for researchers and construction practitioners worldwide to put their best foot forward and initiate actions to reduce the negative impacts of development and sharpen their competitive edge. As global interest on sustainability is steadily blooming, Malaysia should not fall short in its attitude on sustainability and sustainable construction. Malaysia needs to demonstrate that it can abide by this new interest and can compete in the global market.

This chapter delves into the actions undertaken by the Malaysian government, non-government organizations, and construction players in promoting sustainability in construction. Through extensive literature review, this chapter will discuss the commitment of the Malaysian government on sustainability agenda and the progress so far in the construction industry. This chapter will also discuss the findings from a survey conducted to investigate the awareness of the developers regarding this issue and whether those developers have absorbed the concept of sustainable construction in their current practices.

24.2 Sustainability in Construction

Construction industry must inevitably change its historic methods of operating with little regard for environmental impacts to a new mode that makes environmental concerns a centerpiece of its efforts. Previously, the concern on environment was relatively a small part of most construction development. However, with the growing awareness on environmental protection due to the depletion of non-renewable resources, global warming, and extremity of destruction to ecology and biodiversity impact, this issue has gained wider attention by the construction practitioners worldwide. Many efforts are being directed to build sustainably in the construction world. The direction of the industry is now shifting from developing with environmental concern as a small part of the process into having the development process being integrated within the wider context of environmental agenda. Thus, the activities of construction industry must work and comply with the needs to protect and sustain the environment. This shift of ideology is illustrated in Fig. 24.1. Sustainable construction, which has inevitably been dubbed 'green construction,' describes the responsibility of the construction industry in attaining sustainability. Sustainable construction aims to produce structures that enhance the quality of life and protect the environment efficiently and profitably. Sustainable construction is all about maintaining a balance between the human need for buildings for shelter and business operations and infrastructure for higher quality of

well-being on the one hand, and preserving natural resources and ecosystems, on which we and future generations depend on the other hand, as shown in Fig. 24.2.

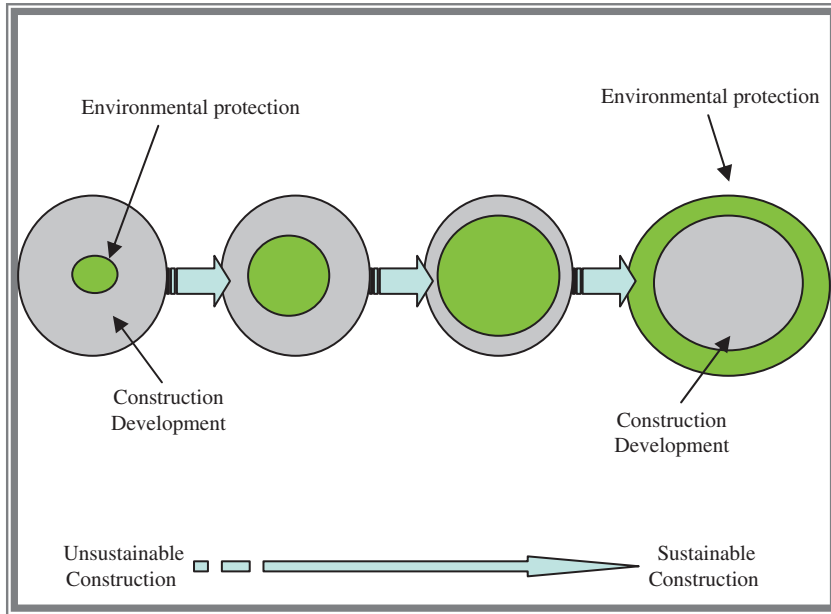


Fig. 24.1 The movement of concern for sustainable construction.

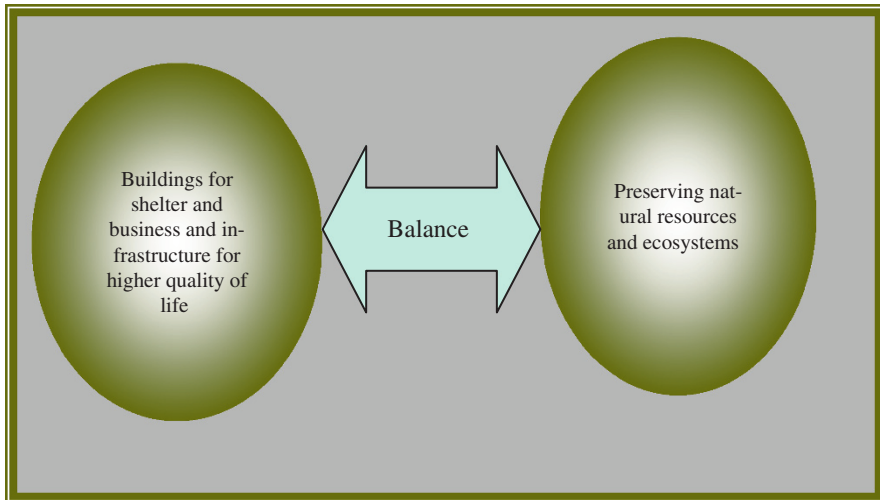


Fig. 24.2 Achieving balance of sustainable construction.

Kibert (2007) has introduced seven principles of sustainable construction as encapsulated in Table 24.1. The first principle (conserve) is of utmost importance because it contrasts the major problem that forces us to address sustainability in the first place – over consumption. It leads us to use passive measures to provide heating, cooling, ventilation, and lighting and forces us to consider high-efficiency system and durable materials that require low maintenance. Second principle (reuse) refers to the desire of reusing resources that we have extracted with minimal reprocessing. Third principle (renew/recycle) refers to items that are in essence reduced to raw materials and used as new products. Resources that are recyclable, that have recycled content, or that are from renewable resources must be given priority over non-recyclable/non-renewable resources. Principle 4 concerns exercising environmental stewardship and restoring the nature where possible. The fifth principle (non-toxics) in a practical sense is the elimination of toxics in the indoor and exterior built environment. Principle 6 is about the economic side of construction which has direct consequences on the environment. By including the life cycle costing as early as possible in the project process and embedded this consideration in the development of project design, it will have a positive impact on the level of pollution produced, energy usage and frequency of maintenance during the occupation of the building. Last but not least, Principle 7 is about quality of life which can be achieved through excellence in design, workmanships in producing the outcome, planning for communities at large, management and selection of materials, etc.

Table 24.1 The seven principles of sustainable construction.

Principle 1 – Minimize resource consumption (<i>conserve</i>)
Principle 2 – Maximize resource reuse (<i>reuse</i>)
Principle 3 – Use renewable or recyclable resources (<i>renew/recycle</i>)
Principle 4 – Protect the natural environment (<i>protect nature</i>)
Principle 5 – Create a healthy, non-toxic environment (<i>non-toxics</i>)
Principle 6 – Apply life cycle cost analysis and true cost (<i>economics</i>)
Principle 7 – Pursue quality in creating the built environment (<i>quality</i>)

Source: Kibert (2007)

Construction practitioners worldwide are beginning to appreciate sustainability and acknowledge the advantages of sustainable building. For example, the concept of green building costs lower than conventional method and saves energy as demonstrated by Hydes and Creech (2000). This was further supported by Heerwagen (2000), Bartlett and Howard (2000), and Pettifer (2004), who added that sustainable buildings will contribute positively to better quality of life, work efficiency, and healthy work environment. Yates (2001) explored the business benefits of sustainability and concluded that the benefits are diverse and potentially very significant. The approach of sustainable construction with its underlying principles provides a comprehensive guide to enable the construction players to be more responsible to the environmental protection needs without neglecting the social and economic needs in striving for a better living.

24.3 Moving Toward Sustainable Construction in Malaysia

As a developing country, Malaysia realized that the construction industry plays a significant role in its economic growth. Over the last 20 years, the industry has been consistently contributing between 3% and 5% of the national GDP (Construction Industry Development Board (CIDB), 2000). However, the industry is not without weaknesses. Challenges have been in the areas of productivity, quality, safety, technology, and unproductive practices. The government is now striving to upgrade the country, including its construction industry, by committing toward Vision 2020, which calls for a comprehensive quantum leap toward a knowledge-based society. The book 'Malaysia's Vision 2020' published in 1993 defined national ambitions and future opportunities for us and to consider long-term strategies to assist the achievement of national goals. One of the basic visions that emerged is for the country to be ecologically sustainable. This basic vision has become an impetus toward sustainability agenda in the country. The issue of sustainable development has emerged as one of the top issues in the Eight Malaysia Plan (2001–2005). According to the plan, the government gave high priority to research and development as one of their strategy for sustainable development (Eight Malaysia Plan, 2001). Section 19 of the plan was devoted to integrate environmental consideration into development planning. During that period, concerted efforts were expected to intensify in order to improve energy efficiency, forestry, waste and environmental management.

The Construction Industry Development Board Malaysia (CIDB), which is a body corporate established with the main function of developing, improving, and expanding the Malaysian construction industry, has identified the environment and other sustainability-related issues as one of the top issues of the construction industry (CIDB, 2000). CIDB calls upon the researchers and construction practitioners to reassess the process of construction to develop good construction planning and management to safeguard the environment. To initiate research in this field, they have formed many focus groups in research and development. One of the focus group focuses on environment and sustainability, which is presently involved in research in waste minimization, environmental management plan, water management, and construction hazard identification (CIDB, 2006). Other institutions in Malaysia such as INSPEN (National Institution of Valuation, Malaysia) (INSPEN, 2006) and MASTIC (Malaysian Science and Technology Information Centre) (Under Ministry of Science, Technology and Innovation) (MASTIC, 2006) are among the leading institutions for research and development and they have also identified sustainability and environment as one of the areas for research. The subject of sustainability continues to be one of the important agenda of the government since it has been identified as one of the five key thrusts in the Ninth Malaysia Plan, which was unveiled on March 31, 2006 (Star Special, 2006).

Apart from these government and non-governmental organizations, the local universities such as Science University of Malaysia (USM), University Technology of Mara (UiTM), and National University of Malaysia (UKM) have also shown interest in this field by offering funding for more research. These universities

have also been involved in organizing many symposiums and conferences to raise the awareness on sustainable development and to exchange knowledge in this field. Holcim Malaysia has founded a Foundation for Sustainable Construction to promote innovative approaches to sustainable construction and to recognize outstanding achievements through competition and international forum awards (Holcim, 2006). At present, there are several sustainable projects that are being or have been constructed in Malaysia. One of the examples is project Tanarimba at Janda Baik, Pahang. Tanarimba is a sustainable housing project that blends man-made and natural elements in an exciting concept of ecologically sensitive community development and also introduces the world to eco-tourism opportunities in Malaysian highlands. The project has been dubbed as the forefront of the ecological movement in construction (Tanarimba, 2006). Another example is the DDC Project (Demonstration and Documentation Centre for Sustainable Urban Household Energy Usage), launched in 2004 by the Centre for Environment, Technology and Development, Malaysia (CETDEM). This project pioneered the construction of urban energy saving house (CETDEM, 2006). Malaysia Energy Centre (PTM) has also embarked on energy-efficiency building by constructing a zero energy office building (ZEO) at Bandar Baru Bangi, Selangor (PTM, 2006). The Planning and National Development Doctrine (DPPS), which stresses development that is balanced and sustainable from the economic, social, spiritual, and environmental aspects, served as the foundation for the planning and development of Putrajaya and Cyberjaya. A total of 32 physical planning guidelines were established by the Town and Country Planning Department (TCPD) to ensure sustainable development of areas such as coastal areas, islands, open space, housing, retention ponds, solid waste disposal areas, conservation of trees and for environmentally sensitive areas (Eight Malaysia Plan, 2001).

The initiatives by the government and others have shown positive signs as people are becoming more conscious in their responsibilities toward environment, and sustainable projects are being built in Malaysia. However, projects on sustainability in Malaysia are mostly at the pioneering stage, indicating that Malaysia construction industry is still at infancy when dealing with sustainability matters. With the promotion from the government and non-governmental institutions on sustainability, it is hoped that the awareness on sustainability among the construction practitioners will improved exponentially in the near future.

24.4 The Survey

From the literature review, it is clear that with the encouragement from the government, sustainable concept is beginning to settle in the construction industry. However, referencing several projects does not represent the wider scenario. To understand how far this concept has penetrated the industry, a survey was conducted among construction developers in Malaysia focusing on their understanding on this subject matter and whether they have incorporated this knowledge within their current and past projects. This survey focused on developers of building

construction such as property and commercial building located in the area of Kuala Lumpur (capital city of Malaysia) and Selangor. These areas were selected because many construction developers, who have projects throughout Malaysia, are based there. All construction development companies from these areas were approached when conducting the postal survey. The list of the companies was obtained from the Real Estate and Housing Developers' Association (REHDA). A total of 271 respondents were approached and 35 questionnaires were returned for analysis. The data gathered were analyzed qualitatively and quantitatively. Software called Statistical Packages for Social Sciences (SPSS) was used to analyze the data quantitatively. This software enabled the data to be transferred automatically from spreadsheet to graphic to present the data in a more attractive manner. The averaging statistical analysis was also used to calculate straightforward totals, percentages, and averages. Qualitative technique was applied to make sense of meanings. Contextualizing strategy was used to connect statements, opinion, and comments to provide a coherent picture. The results are discussed next.

24.5 Result and Discussion

A total of 35 construction developers had responded to this survey. These developers have been active in the industry between 4 and 36 years. The majority of them have been involved with more than 20 projects with project cost within the range of Ringgit Malaysia RM10 to more than RM100 millions. Their range of project profiles varied from landed property to shop, houses, and others. The progress in Malaysia is discussed under several subheadings:

- a) the level of knowledge and awareness of construction developers on the concept of sustainability and sustainable construction;
- b) the application of sustainable concept in past and current projects; and
- c) the future outlook of this application in the construction industry.

To articulate the level of knowledge among project developers with regard to sustainability concept, the respondents were asked to rate their knowledge on this subject matter and what they perceived, based on their experience, the general population of project developers' level of understanding on this subject. From Fig. 24.3, most of the respondents considered themselves to have moderate or good knowledge on sustainable concept. The mean level is 3.43 (moderate) out of 5 rating system. The respondents also perceived that overall developers' knowledge on sustainable concept was between low and moderate level (mean of 2.80). Although they believed their knowledge was above moderate, they seemed to think that overall, the knowledge was still below average.

To investigate further what the respondents understand about the concept of sustainable construction, they were asked to select issues that match their understanding about the concept of sustainable construction. Issues that are related to environmental aspect of sustainability received highest percentage: effective protection of the environment (88.6%), effective environmental planning, management and control (80%), and prudent use of natural resources (68.6%). Issues that

related to social aspects of sustainability received moderate percentage: enhance the quality of life and customers' satisfaction (71.4%) and social progress which recognizes the need of everyone (42.9%). Lastly, the issues that related to the economic aspect of sustainability received lowest percentage: generating profit without compromising future needs (42.6%) and maintenance of high and stable level of economic growth (48.6%). From this result, it is deduced that the majority of the respondents understand that sustainability is about protecting the environment but many are still unaware that sustainability is also about balancing social and economical aspects of construction.

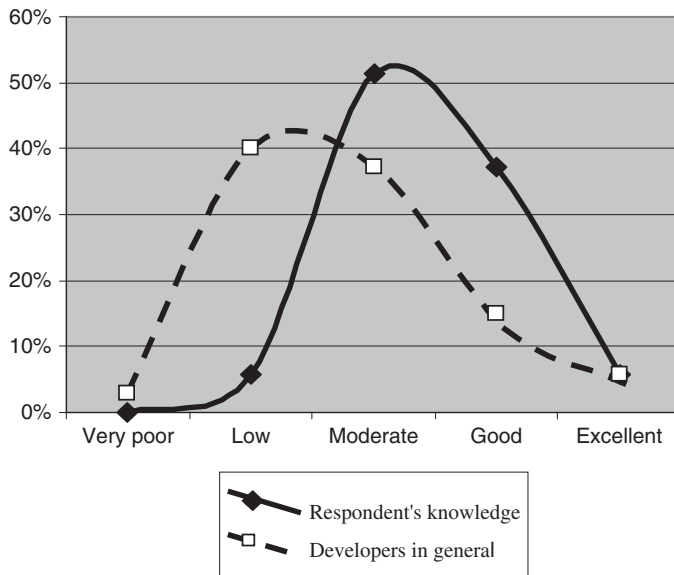


Fig. 24.3 Level of understanding on sustainability concept.

The majority of respondents rely on written materials (journals, proceedings, newspapers, web site) to improve their knowledge about sustainable construction. Other sources of knowledge are through education and higher learning; seminars and conferences; and experience with sustainable projects. In-house learning was given a relatively low percentage indicating that most of the companies do not promote this concept within their organizations and project, thus giving small window of opportunity for the employees to learn about this concept internally.

Aligned with the level of knowledge revealed by the respondents, the level of implementation is also at moderate level, as shown in Fig. 24.4. None of the respondents believed that the implementation of sustainable practices is excellent. Majority believed that the implementation is at low level, followed by moderate level.

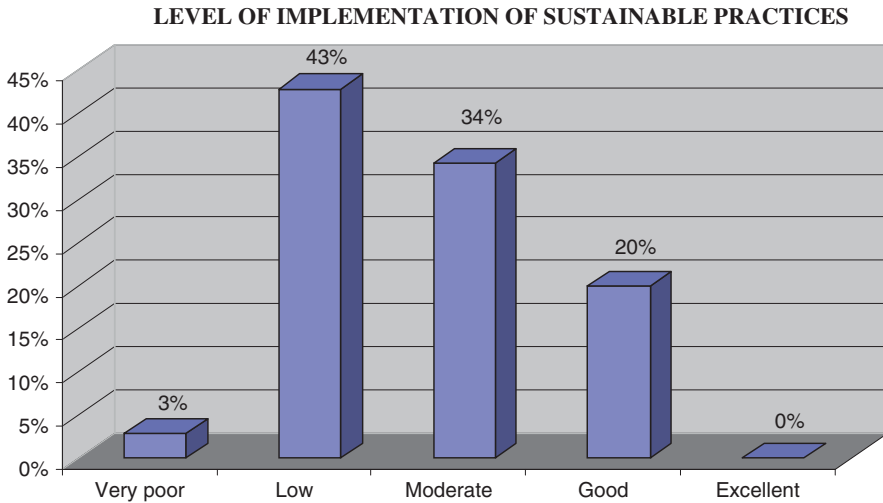


Fig. 24.4 Level of implementation of sustainability practices.

The reasons for the current level of implementation can be clustered under several headings.

1. **Lack of enforcement** – There are many respondents that stress the need for enforcement through law and legislation. Although there are several acts which focus on environment, such as Environmental Protection Act, due to lack of monitoring and enforcement, people just do not really care much about it.
2. **Government intervention** – Some of the respondents believed that the government should play a bigger role in promoting sustainable construction, through actions such as strong enforcement of legislation, devising new policy, or giving incentives to developers who want to pursue sustainability in their projects.
3. **Pointing fingers** – Some of the respondents believed that the role of ‘promoting’ and ‘encouraging’ sustainable practices lies on other shoulders too as well, such as designers and contractors. The respondents also highlighted that there are too many players in the construction industry and who mostly are not professionally qualified. The implementation can be improved if various construction players including engineers, architects, and QS play their role in advising the developers on the merits of pursuing sustainable practices. If the consultants can come up with a good design within the project budget that can sustain the environment and give a good business return, then the developers will be inclined to accept the proposal.
4. **Urgency factor** – Some of the respondents stated that people are indirectly aware of this issue. However, they do not feel the need to incorporate this issue in their projects. This issue is not in their top list. One of the respondents even stated that Malaysia has abundant of natural resources such as water, oil,

- and energy. Thus, there is general lack of urgency on this issue. The respondents also felt that this issue lack's publicity which could speed up people's interest on the matter.
5. Education vs. experience – Many of the respondents stated that developers have poor knowledge about sustainability and sustainable construction. A decade ago, environmental issue was not pertinent and was not given a priority in education. Many developers are still trying to balance the three pillars within their means. It is hard to break from their norm in practice. The young generation, however, have been exposed to sustainable construction in their higher education level but, due to their lack of experience in the real world, they have problem disseminating their theoretical understanding of sustainability knowledge into practice.
 6. Cost factor – Many respondents believed that the main factor that impedes implementation of this concept in the Malaysian construction industry is the financial constraint. A few respondents stated that sustainable construction is believed by many to be economically non-viable. Sustainable practices are believed to increase project cost because they need to have higher capital upfront. Higher cost means higher price. If they pursue sustainability in the projects, they need to know that there is a market for it because technically, the cost will be transferred to the buyers/end users.
 7. Passive culture – There are a few respondents who believed that sustainability is an academic pursuit. It is often used in the intellectual circle but seldom known outside leading to non-practice.

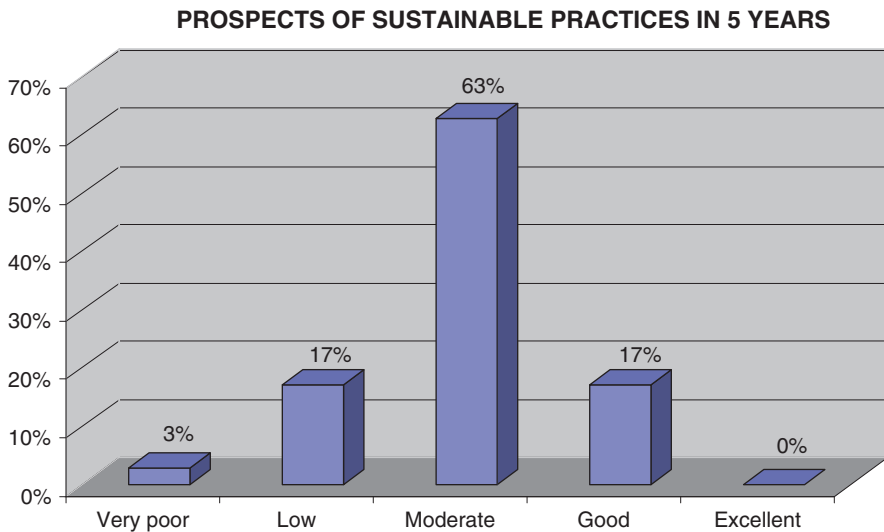


Fig. 24.5 Prospect of sustainable practices in 5 years.

Finally, the respondents were requested to give their opinion on the prospect of sustainable construction application in Malaysia in the next 5 years. From Fig. 24.5, it is clearly shown that 63% of the respondents believed that in 5 years, not much will change and the level is still moderate. About 17% of respondents believed that it will get better (good) and equally on the opposite site, 17% believed that it will still be low. There are a few people (3%) who think that the future of sustainable construction is very bleak.

From the comment given, these are the reasons behind the 'low' and 'moderate' opinion:

- As long as there is no by-law or new regulation by the government, the players in the industry will not care less. There is also lack of enforcement on existing legislation.
- Developers must be convinced that sustainability issues will add value to its development and the public is prepared to pay a higher entry cost to enjoy such privilege.
- Cost is still the main priority of any development. Sustainable construction increases project cost which makes this option less favorable.
- Need more construction players to get involved for improvement.
- Lack of awareness. No political will.
- Speed is the issue. Our country is moving too fast without building a strong base of culture itself. The success of a sustainable project is very dependable of the soul of the project, that is, every individual' that is involved in the project.
- Sustainable construction still lack's of understanding by industry.

These are the reasons for a brighter prospect in sustainable construction:

- The trend is going toward it and eventually, the Malaysian construction players will follow it.
- There is a gradual improvement by all parties involved in the industry about this concept. Many people are becoming aware of this new concept; even though the application is still weak, the knowledge is improving.
- Developers and local authorities are improving such sustainable construction including preparation of EIA report, slope protection, and river protection. However, such evolution does take time to improve.
- The rise of building material costs would force developers/contractors to seek more sustainable construction application.
- Various universities with various courses offer student's awareness for the above issues. New employees will bring in new attitude.
- Awareness on sustainable development at the national or global basis is increasing at an encouraging pace which is beneficial.
- The players in construction will improve their ability and know-how about the sustainable construction application from their experience.
- Awareness among citizens is increasing. Environmental-friendly concept is being planted either at education level or through media report.

The evidence of several sustainable projects being built in Malaysia from literature review shows positive signs that the concept of sustainable construction has begun to settle within the industry. However, the survey revealed that the concept of sustainability has not been widely applied in many projects. This strengthens the argument that the industry is still at its infancy in this field. The findings indicated that generally, the respondents believed the level of knowledge on sustainability is still below average. Perhaps, this perception is derived from the lack of implementation of this concept in the construction industry. Other developers may have good knowledge on sustainable concept, but because they did not put it in practice or incorporate it in their projects, others will tend to believe that knowledge is not apparent. Knowing but not practicing is another major problem in sustainable concept implementation. A lot more efforts are necessary to enhance the level of environmental awareness and civic consciousness among the people to build sustainably in the future. It is recommended to improve the understanding and awareness on this concept and initiate actions to enable this concept be applied efficiently in future construction projects. There are many ways to do this such as educating the construction players through conferences, trainings, seminars, workshops. Since this concept is viewed as academic pursuit, perhaps, the academician should play a more active role in reaching to the construction players through collaboration and consultations works. Education should not be limited to the construction players only. As the industry's supply is closely influenced by the demand for it, the education should be expanded to the wider stakeholders, which includes the potential buyers as well. Raising buyers demand for sustainable houses, for example, will push the housing developers to improve the specification of their houses which include certain sustainable elements to attract buyers. Government has a major role to play in encouraging sustainable construction. Their support and incentives will prompt interest among construction players. It is also recommended for a full-length study on the weakness of present legislation implementation to alleviate the problem of 'lack of enforcement.'

As this subject is a new territory in Malaysia, there are many angles in which research can be extended. Knowledge on present application, weaknesses, and potentials can open avenues for further action toward performance improvement. Apart from that, producing guidelines to highlight the aspects of sustainability within construction process would be useful to enable those aspects be managed effectively and efficiently. Last but not least, the challenges to build sustainably need to be critically analyzed and surmounted. Various techniques and tools existed that in the construction industry should be utilized to enhance the appreciation on sustainability in construction processes.

24.6 Conclusions

The construction industry has been singled out as the focus of special attention, since creating and running our built environment accounts for about half of all energy used, has high potential to pollute rivers and ground, generate unacceptable noise and emission to the air, producing construction waste and debris, and damaging beyond repair our rich diversity and ecology. Although construction is re-

garded as an essential and highly visible contributor to the process of growth of one country, the adverse impacts to the environment lead to a growing realization and acceptance throughout the world that there is a need for a more responsible approach to the environment. The agenda for a more environmentally responsible construction industry is captured under the concept of sustainable construction. Delivering more sustainable construction requires action from all engaged in constructing and maintaining the built environment including those providing design, consulting, and construction services.

The advantages of building sustainably have been revealed through much research and case studies conducted abroad. In Malaysia, the active promotion of sustainable development by the government, non-governmental organizations, and education institutions in the past 5 years has shown some encouraging progress in this field such as

- a) more research and development in this field by non-governmental organization and education institution;
- b) introduction of several guidelines for environmental protection (for different types of land/area) by government agencies;
- c) increase in number of pioneer projects initiated by construction players (developers and contractors);
- d) increase in number of seminars/symposiums/conferences which focus on improving the awareness of construction players on the issues related to sustainable construction and development.

A survey was conducted among construction developers in Malaysia focusing on their understanding on this subject matter and whether they have incorporated this knowledge within their current and past projects. From the survey, it is concluded that

- a) There is a slow permeation of this concept among the construction practitioners. Many construction developers believed that the implementation of this concept is at low level. Factors that have been identified as impeding the active implementation are lack of knowledge, poor enforcement of legislation, education vs. experience, and passive culture.
- b) It is believed that with current pace, this situation will not change much in 5 years. This is due to the lack of enforcement on existing legislation, budget constraints, and lack of awareness. But there is a glimpse of hope as several respondents argued that once the knowledge and awareness are raised, the situation will gradually be improved.

This research has unveiled the level of knowledge among developers with regard to sustainable construction. The positive moves by the government and non-governmental agencies to raise the awareness of environmental issues among construction players and to encourage the interest to pursue sustainability in the construction projects do bear some fruit as the knowledge among developers is within moderate level, with a few respondents admitted to have good and excellent knowledge of sustainability concept (none is very poor). The implementation, however, is between poor and moderate. It is expected that this situation is most likely to remain the same, if not slightly better, in the next 5 years. With this

finding, the government, non-governmental agencies, and professional bodies need to step up their momentum to ensure that the awareness of sustainable construction is not only raised but also implemented. More strategies and actions should be pursued actively to speed up the process in creating a sustainable-oriented construction industry. By effective implementation, this concept will become a norm and perhaps, the 5-year prediction will shift from moderate to good or excellent. Only then, the advantages of sustainable practices can be firmly seized and enjoyed by everyone, construction players and end users alike.

Acknowledgment

The author acknowledges the financial support provided by the Science University of Malaysia (USM) in Penang, Malaysia.

References

- Bartlett, E, Howard, N (2000) Informing the decision makers on the cost and value of green building. *Building Research and Information* 28 (5/6): 315–324.
- Centre for Environment, Technology and Development, Malaysia (CETDEM) (2006) DDC project – demonstration and documentation centre for sustainable urban household energy usage. http://www.cetdem.org.my/sustainable_energy/ddc.html.
- Construction Industry Development Board (CIDB) (2000) Malaysian construction industry: Technology foresight report. CIDB Malaysia and APEC Technology Foresight Center. Bangkok.
- Construction Industry Development Board (CIDB) (2006) <http://www.cidb.gov.my>.
- Eight Malaysia Plan (2001) Eight Malaysia Plan 2001–2005. Kuala Lumpur: Percetakan Nasional Malaysia.
- Heerwagen, J (2000) Green building, organizational success and occupant productivity. *Building Research and Information* 28(5/6): 353–367.
- Holcim Foundation for Sustainable Construction (2006) <http://www.holcim.com.my>.
- Hydes, K, Creech, L (2000) Reducing mechanical equipment cost: the economics of green design. *Building Research and Information* 28(5/6): 403–407.
- Kibert, CJ (1994) Establishing principles and a model for sustainable construction. Proceedings of the First International Conference of CIB Task Group 16 on Sustainable Construction. Tampa, FL, 6–9 November, Final Session, pp. 3–12.
- Malaysia Energy Centre (PTM) (2006) A Zero Energy Office (ZEO) Building. http://www.ptm.org.my/PTM_Building/Index.htm, Accessed on 5/3/2006.
- Malaysian Science and Technology Information Centre (MASTIC) (2006) <http://www.mastic.gov.my>.
- National Institute of Valuation, Malaysia (INSPEN) (2006) <http://www.inspen.gov.my>.
- Pettifer, G (2004) Gifford studios – A case study in commercial green construction. CIBSE National Conference on Delivering Sustainable Construction. 29–30 September., London.
- Star Special (2006) 9th Malaysia Plan 2006 – 2010. The Star. page SP 2, 1st April 2006
- Tanarimba Development (2006) <http://tanarimba.com.my>.
- Yates, A (2001) Quantifying the business benefits of sustainable buildings – Summary of existing research finds (Extract) (Draft for discussion). Centre for Sustainable Construction. London: BRE.
- Zainul Abidin, N (2005) Using value management to improve the consideration of sustainability within construction, Ph.D. Thesis, Loughborough University, UK.

Emission Market at the End of the Commitment Period

Ryosuke Ishii and Haruo Imai

25.1 Introduction

We have several emission trading schemes at work currently and one eminent market among them is the one for GHG emissions under Kyoto Protocol starting 2009. For emissions to be tradable, property right must be securely set. Especially monitoring has to be reliable and timely, and leakage must be taken care of adequately. But this in turn implies that there is a discrepancy between the period where the amount of emission is ascertained and the period during which trading is supposedly bringing efficiency to the emission reduction. For instance, EU-ETS ended its first trading period at the end of 2007, but the emission level becomes available only after several months passed. Therefore, the so-called trueup period is necessary so that trading has to go on until the emission data are finalized. In the case of EU-ETS, the emission until 2007 can be traded till April 2008, and similar trueup period is set aside for the first commitment period of Kyoto Protocol. One of the concern arising from the earlier period over the discussion of the details of Kyoto Protocol was the possible frenziness of the market in this trueup period. Because some surprise is possible as to the extent of emission, one of the Annex B (ratifying Kyoto Protocol) may find it in a severe shortage of the emission amount in the registry and has no possibility left to reduce actual emission but to purchase emission amount from the market. Upon foreseeing such a possibility, some seller nation or private brokers may find a profit taking opportunity.

There could be a multitude of issues concerning trueup period. And it fits to the game theoretical modeling of financial markets. However, the basic tool for such analysis has not been fully developed yet. There is a literature in finance known as the execution problem. There is the optimal strategy for one agent holding financial securities who has to sell off given amount of securities until a certain date in the market. For example, see Bertsimas and Lo (1998), Almgren and Chriss (2000), Huberman and Stanzl (2000), Almgren

(2003), and Obizhaeva and Wang (2005). All who behave strategically is the very agent in their models, which are partial equilibrium analyses. Ishii (2008) introduces small traders similar to market makers in Kyle (1985), and extends the model to a general equilibrium model. In many aspects, trueup period problem fits to this problem. A further extension of the execution problem to multiagents with visible and invisible but many rational agents together with noise traders were made possible in Ishii (2008). Below, we show one attempt of such adaptation.

Let us suppose there are n Annex B nations falling short of the assigned amount. Other Annex B nations are already safe in the sense that they are sure to achieve the assigned amount and leftover emissions can be carried to become emissions for the next commitment period (provided that such period exists), called banking. Still there are many other market participants. If an Annex B party's holding of emissions falls short of the assigned amount, then the penalty is of 30% more of the shortage being subtracted from the assigned amount of the next commitment period. If the other party holds the emission at the end period, we assume that it is treated as if it is a part of emission belonging to the nation to which they belong to.

25.2 Presumptions

We try to utilize and extend Ishii's (2008) result to our case, so that the scope of our analysis is limited to much extent by that result. In particular, we have to assume the following:

1. There are enough participants in the emission market in the trueup period, both rational and erratical participants. This can be justified by the fact that many CDM credits are available so that they can choose to enter into the market for each commitment periods which overlaps.
2. Near the final stage of the trueup period, the emission amount of each nations in the past becomes common knowledge. This is somewhat a simplification, because some exact statistics would only be available very late. But approximately, this would hold.
3. Except for the nations under consideration who have to purchase emission from the market, all the other agents who have emission at hand in the beginning of the periods analyzed are not rational or moving randomly. This is somewhat heroic assumption necessitated by the earlier analysis. And we list it again explicitly.
4. For the market participants who are not nations, they can bank the emission they hold even after the trueup period. This is an assumption which could differ from the actual rule. Thus, elimination of this assumption would be the most desirable.

25.3 Model

There are three types of traders in our emissions trading market: N nations, a lot of small investors, and one noise trader. They can trade at times $t=1, 2$. Every nation $i=1,2,\dots, N$ has to buy $W_{i,1}$ units of emissions over this time period. Those who have one unit of emission obtain a banked value $\bar{F}$ at time $t=3$.

$$\bar{F} = F + \varepsilon, \quad (25.1)$$

where F is observed by all traders at the beginning of $t=1$. ε follows a normal distribution that has a mean 0 and a variance σ_F^2 at $t=3$.

Each nation i places a market order $S_{i,t}$ at time $t=1,2$. We require $S_{i,1} + S_{i,2} = W_{i,1}$. We define $W_{i,2} = W_{i,1} - S_{i,1}$. The utility of a nation i is

$$U_i^N (S_i, S_{-i}; P_1, P_2, \bar{F}) = -\exp \left[-\lambda_i (\bar{W}_i - P_1 S_{i,1} - P_2 S_{i,2}) \right], \quad (25.2)$$

for constant values $\lambda_i > 0$, $\bar{W}_i$.

There are infinitely many small investors. They are uniformly distributed over $[0,1]$. The measure of each small investor is 0. They have no position at $t=0$. They can borrow some money or emission credits and place limit orders at $t=1,2$. They face no liquidity constraint. The interest rate is 0 for simplicity. We denote the quantity possessed by a representative small investor at the end of t ($t=1,2$) as B_t . His utility is

$$U^P (B_1, B_2; P_1, P_2, \bar{F}) = -\exp \left[-\rho \left((P_2 - P_1) B_1 + (\bar{F} - P_2) B_2 \right) \right], \quad (25.3)$$

for a constant value $\rho > 0$. The trading volume of the representative small investor at t is $MB_t = \psi B_t - \psi B_{t-1}$ ($B_{-1} = 0$)

The noise trader randomly places a market order n_t at $t=1,2$. n_t follows a normal distribution that has a mean 0 and a variance $\sigma_{n_t}^2$ independently of each other and of ε .

The price P_t is determined to conform the amount of all buy order's to all sell order's at every $t=1,2$:

$$\sum_{i=1}^N S_{i,t} + MB_t + n_t = 0. \quad (25.4)$$

At the end of period t , all traders observe the price P_t .

We define some notations. $E_1 [\cdot]$ and $Var_1 [\cdot]$ are an expectation and a variance, respectively, conditional on events that the small investors can observe by the end of the time 1. Furthermore, we define

$$\sigma_{P_{t+1}}^2 = Var_t [P_{t+1}]. \quad (25.5)$$

25.4 Equilibrium

25.4.1 Decision making of private brokers

The conditional expectation and the conditional variance that the representative private brokers have are

$$\begin{aligned} E_1 \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] &= (E_1 [P_2] - P_1) B_1 + (F - E_1 [P_2]) B_2 \\ E_2 \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] &= (P_2 - P_1) B_1 + (F - P_2) B_2, \\ Var_1 \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] &= \sigma_{P_2}^2 B_1^2 + Var_1 \left[(\tilde{F} - P_2) B_2 \right], \text{ and} \\ Var_2 \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] &= \sigma_{\tilde{F}}^2 B_2^2. \end{aligned} \quad (25.6)$$

We consider a linear equilibrium in the following. Since a linear combination of variables that follow normal distributions also follows normal distributions, the equilibrium prices follow normal distributions.

The utility of the representative private broker at $t=1,2$ is

$$E_t [U^P] = -\exp \left(-\rho E_t \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] - \frac{\rho^2}{2} Var_t \left[(P_2 - P_1) B_1 + (\tilde{F} - P_2) B_2 \right] \right). \quad (25.7)$$

The first-order condition is

$$\begin{aligned}
\frac{\partial E_1[U]}{\partial B_1} &= -\rho (E_1[P_2] - P_1 - \rho\sigma_{P_2}^2 B_1) E_1[U] = 0 \\
&\Rightarrow B_1 = \frac{E_1[P_1] - P_1}{\rho\sigma_{P_2}^2}, \text{ and} \\
\frac{\partial E_2[U]}{\partial B_2} &= -\rho (F - P_2 - \rho\sigma_F^2 B_2) E_1[U] = 0 \\
&\Rightarrow B_2 = \frac{F - P_2}{\rho\sigma_F^2}.
\end{aligned} \tag{25.8}$$

25.4.2 Decision making of nations

25.4.2.1 Time 2

By the sellout constraint of each nation i $S_{i,2} = W_{i,2}$ and by the market clearing condition $\sum_{i=1}^N S_{i,2} + MB_2 + n_2 = 0$,

$$P_2 = F + \rho\sigma_F^2 \left(\sum_{i=1}^N W_{i,2} + n_2 \right) - \frac{\sigma_F^2}{\sigma_{P_2}^2} (E_1[P_2] - P_1). \tag{25.9}$$

The variance conditional on the events by the time 1 is equal to

$$\sigma_{P_2}^2 = (\rho\sigma_F^2)^2 \sigma_{n_2}^2.$$

Take the expectation of both sides conditional on the events by the time 1, and obtain

$$\begin{aligned}
E_1[P_2] &= F + \rho\sigma_F^2 \sum_{i=1}^N W_{i,2} - \frac{\sigma_F^2}{\sigma_{P_2}^2} (E_1[P_2] - P_1) \\
&\Leftrightarrow E_1[P_2] - P_1 = \frac{\sigma_{P_2}^2}{\sigma_F^2 + \sigma_{P_2}^2} \left(F + \rho\sigma_F^2 \sum_{i=1}^N W_{i,2} - P_1 \right).
\end{aligned} \tag{25.10}$$

Substituting (25.10) in to (25.9), we obtain

$$P_2 = \frac{\sigma_{P_2}^2}{\sigma_F^2 + \sigma_{P_2}^2} \left(F + \rho\sigma_F^2 \sum_{i=1}^N W_{i,2} \right) + \frac{\sigma_F^2}{\sigma_F^2 + \sigma_{P_2}^2} P_1 + \rho\sigma_F^2 n_2. \tag{25.11}$$

25.4.2.2 Time 1

By the market clearing condition $\sum_{i=1}^N S_{i,1} + B_1 + n_1 = 0$,

$$P_1 = E_1 [P_2] + \rho \sigma_{P_2}^2 \left(\sum_{i=1}^N S_{i,1} + n_1 \right). \quad (25.12)$$

Substituting (25.12) in to (25.11), we obtain

$$P_1 = F + \rho \sigma_F^2 \sum_{i=1}^N W_{i,1} + \rho \sigma_{P_2}^2 \sum_{i=1}^N S_{i,1} + \rho (\sigma_F^2 + \sigma_{P_2}^2) n_1.$$

In the case where nation i buys $S_{i,1}$ emission credits at time 1, the cost of nation is

$$\begin{aligned} P_1 S_{i,1} + P_2 S_{i,2} &= \left[\rho \sigma_{P_2}^2 \sum_{i=1}^N S_{i,1} + \rho \sigma_{P_2}^2 n_1 - \rho \sigma_F^2 n_2 \right] S_{i,1} \\ &\quad + \left(F + \rho \sigma_F^2 \sum_{i=1}^N W_{i,1} + \rho \sigma_F^2 n_1 + \rho \sigma_F^2 n_2 \right) W_{i,1}. \end{aligned}$$

The expectation and the variance are

$$\begin{aligned} E [P_1 S_{i,1} + P_2 S_{i,2}] &= \rho \sigma_{P_2}^2 S_{i,1} \sum_{j=1}^N S_{j,1} + \left(F + \rho \sigma_F^2 \sum_{j=1}^N W_{j,1} \right) W_{i,1}, \text{ and} \\ Var [P_1 S_{i,1} + P_2 S_{i,2}] &= \sigma_{n_1}^2 (\rho \sigma_{P_2}^2 S_{i,1} + \rho \sigma_F^2 W_{i,1})^2 + \sigma_{P_2}^2 (S_{i,1} - W_{i,1})^2 + \sigma_F^2 W_{i,1}^2. \end{aligned}$$

The substantial cost minimizing problem of a nation i is

$$\min_{S_{i,1}} E [P_1 S_{i,1} + P_2 S_{i,2}] + \frac{\lambda_i}{2} Var [P_1 S_{i,1} + P_2 S_{i,2}].$$

We have the first-order condition for $i=1,2,\dots, N$:

$$\rho \sigma_{P_2}^2 S_{i,1} + \rho \sigma_{P_2}^2 \sum_{j=1}^N S_{j,1} + \lambda_i \{ (\rho \sigma_{P_2}^2) \sigma_{n_1}^2 (\rho \sigma_{P_2}^2 S_{i,1} + \rho \sigma_F^2 W_{i,1}) + \sigma_{P_2}^2 (S_{i,1} - W_{i,1}) \} = 0.$$

We obtain

$$S_{i,1} = \frac{\lambda_i (1 - \rho^2 \sigma_{n_1}^2 \sigma_F^2)}{\rho + \rho \sum_{j=1}^N \frac{\rho + \lambda_i \rho^2 \sigma_{n_1}^2 \sigma_{P_2}^2 + \lambda_i}{\rho + \lambda_j \rho^2 \sigma_{n_1}^2 \sigma_{P_2}^2 + \lambda_j} + \lambda_i \rho^2 \sigma_{n_1}^2 \sigma_{P_2}^2 + \lambda_i} \cdot \left\{ W_{i,1} + \sum_{j=1}^N \frac{\rho}{\rho + \lambda_j \rho^2 \sigma_{n_1}^2 \sigma_{P_2}^2 + \lambda_j} \left(W_{i,1} - \frac{\lambda_j}{\lambda_i} W_{j,1} \right) \right\}.$$

25.5 Numerical Examples

25.5.1 $N=2, \lambda_1, \lambda_2 \rightarrow 0$

The results are as follows:

$$\begin{aligned} S_{1,1} = S_{2,1} = 0, \quad S_{1,2} = W_{1,1}, \quad S_{2,2} = W_{2,1}, \\ P_1 = F + \rho \sigma_F^2 (W_{1,1} + W_{2,1}) + \rho (\sigma_F^2 + \sigma_{P_2}^2) n_1, \\ P_2 = \frac{\sigma_{P_2}^2}{\sigma_F^2 + \sigma_{P_2}^2} \{ F + \rho \sigma_F^2 (W_{1,1} + W_{2,1}) \} + \frac{\sigma_F^2}{\sigma_F^2 + \sigma_{P_2}^2} P_1 + \rho \sigma_F^2 n_2. \end{aligned}$$

The ex ante expected prices at $t=1,2$ are the same:

$$E[P_1] = E[P_2] = F + \rho \sigma_F^2 (W_{1,1} + W_{2,1}).$$

The market impact at time 2 is smaller than the one at $t=1$:

$$\rho (\sigma_F^2 + \sigma_{P_2}^2) > \rho \sigma_F^2.$$

Therefore, it is best for the nations that want to minimize the expected costs to trade only at $t=2$. The trading partner of the small traders is the noise trader at $t=1$.

The price at time 1 has an impact on the price at time 2. This is because the private brokers are risk averse and hate buildup of inventory. In the case where there is heavy selling at time 1, the price at time 1 becomes low and small traders are long inventory by a large margin. Then they will prefer to sell in order to avoid the inventory risk, and place lower price at time 2.

25.5.2 $N=2, \lambda_1=\lambda_2=\rho=\sigma_F^2=\sigma_{n_1}^2=1, \sigma_{n_2}^2=6, W_{i,1}=W_{j,1}=W$

The results are as follows:

$$\begin{aligned}
S_{1,1} &= S_{2,1} = -\frac{1}{2}W, \\
P_1 &= F + W + 2n_1, \\
P_2 &= \frac{1}{2}(F + 3W + P_1) + n_2.
\end{aligned}$$

The price at time 1 has an impact on the price at time 2. The market impact at time 2 is smaller than the one at $t=1$, as in the first example. The nations dare to sell at time 1, drive down the price, and make the price at time 2. The ex ante expectation and the variance of the cost of a nation on the equilibrium are $WF+(5/2)W^2$ and $((15)/4)W^2$, respectively. If the nations do not trade at time 1, fixing the behaviors of the small traders, the ex ante expectation and the variance of the cost are $WF+2W^2$ and $7W^2$, respectively. That is, the expected cost of the nations become larger and the variance smaller, compared to the case of risk neutrality.

25.6 Conclusions

We have established that the trade concentration at the end period indeed takes place as is expected. Looking at this from another viewpoint, market frenzy does not occur, although this fact is mostly due to the fact that there are a lot of CDM credits available at each moment. As is stressed, this is a mere example based on several assumptions imposed for the sake of convenience. One can make up an enormous list of assumptions to be removed and situations to be considered. Besides, actual data are piling up everyday, which would suggest the future agenda of research. As is mentioned in the beginning, this is meant to be an attempt to show the possibility of research.

References

- Almgren, Robert, and Neil Criss, 2000, Optimal execution of portfolio transactions, *Journal of Risk*, 3, 5–39.
- Almgren, Robert, 2003, Optimal execution with nonlinear impact functions and trading-enhanced risk, *Applied Mathematical Finance*, 10, 1–18.
- Bertsimas, Dimitris, and Andrew W. Lo, 1998, Optimal control of execution costs, *Journal of Financial Markets*, 1, 1–50.
- Ryosuke Ishii, 2008, Optimal Execution in a Market with Small Investors, KIER discussion paper series, Kyoto Institute of Economic Research, Discussion Paper No.653.
- Albert S. Kyle, 1985, Continuous Auctions and Insider Trading, *Econometrica*, Vol. 53, No. 6, 1315–1336.
- Huberman, Gur, and Werner Stanzl, 2000, Optimal liquidity trading, Yale ICF Working Paper No. 00–21.
- Obizhaeva, Anna, and Jiang Wang, 2005, Optimal trading strategy and supply/demand dynamics, AFA 2006 Boston Meetings Paper.

Game Analysis of Kyoto and Post-Kyoto Schemes

Haruo Imai

26.1 Introduction

Game theory is a tool utilized in economics to analyze the consequences of interaction among rational agents. It has been found to be especially useful for evaluating the workings of economic schemes at the theoretical level and also designing a possible mechanism to improve the economic system. In environmental economics, the use of game theory is most prominent in the analysis of IEAs (international environmental agreements), and the current negotiations on post-Kyoto (or post-2012) present a potential interesting application of game theory. Furthermore, such studies inspire further use of game theoretical tools in the study of such issues. In this chapter, we examine game theory analysis in this context and suggest some further directions of study with an emphasis on the role played by one particular mechanism under the Kyoto protocol (KP) called the CDM (clean development mechanism).

Kyoto mechanisms are supplementary measures included in the Kyoto protocol (adopted in 1997 and entered into force in 2005) under the United Nations Framework Convention on Climate Change (UNFCCC), so that Annex B nations (nations listed in Annex B of KP, which essentially coincide with nations listed in Annex I of UNFCCC) can achieve their emission targets in a cost-effective manner. There are three measures involved that will be made operational during the first commitment period (between 2008 and 2012).

After 2013, no concrete scheme has been determined yet, and this is the issue discussed through several channels currently and is referred to as the post-Kyoto (or post-2012) negotiation.

Below, we first consider the so-called Kyoto mechanisms (flexibility mechanisms included in Kyoto protocol) from the viewpoint of possible game theoretical appraisal. Then, in the next section, we examine the current post-Kyoto negotiation along with a game theoretical analysis of the IEAs by making use of a

simple example, and then we attempt to list the problems related to game theory that are occurring in the course of that negotiation and also the practice of the Kyoto mechanisms.

26.2 Kyoto Mechanisms

Here, we shall discuss each flexibility mechanism in the KP and examine the design features and incentive issues involved.

26.2.1 Emission trading (ET)

The idea of ET as a resolution to environmental problems has already been put in practice in several areas. For greenhouse-effect gases (GHG) emissions, the EU started the EU emission trade system (EU-ETS) in 2005. ET is a widely accepted concept in economics and has been well tested.

Let us introduce a simple model often utilized for this issue. There are n Annex B nations ratifying the KP. Their GHG emission levels (for the entire 5-year commitment period of the KP or annual) are denoted by x_i while the assigned amount is a_i : By the economic activity level associated with x_i , country i enjoys benefits $R_i(x_i)$ and incurs costs $C_i(x_i)$ to achieve that emission level, and let us denote the net benefit by $B_i(x_i)$, which we assume is continuously differentiable, strictly increasing, and strictly concave. Note that, even though the KP requires that $\sum a_i = \sum x_i$, x_i could be more than a_i because country i can purchase emission permits from the market of the amount $x_i - a_i$ at the going price p .

The efficient emission level (x_i^*) given quota $(a_i)_{i=1}^n$ is a solution to

$$\max \sum B_i(x_i) \text{ s.t. } \sum a_i = \sum x_i$$

and characterized by $m_i(x_i^*) = m_j(x_j^*)$ for each i, j , with $\sum a_i = \sum x_i$, where $m_i(x_i^*) = B'_i(x_i)$ is the marginal net benefit, which is usually referred to as the marginal emission reduction costs. We assume that the condition for the existence of the interior solution, i.e., $x_i^* > 0$ is satisfied for all i .

In a competitive equilibrium, each country chooses x_i so that the net benefit with market revenue, $B_i(x_i) + p(a_i - x_i)$, is maximized given a price p . Given an arbitrary p , the corresponding emission level $x_i(p)$'s does not necessarily satisfy the market clearing condition $\sum a_i = \sum x_i(p)$. When this condition is met, we call the price an equilibrium price p^* . It can be easily seen that $p^* = m_i(x_i^*)$ for each i .

This competitive analysis alone is classified as market analysis but there are many related issues where game theoretic analysis can be useful. Some of these issues are

- (i) initial allocation of a_i 's
- (ii) noncompetitive behavior
- (iii) compliance
- (vi) dynamic issues

As for (i), one can see that the final payoff depends on the initial allocation of the quota and in fact, given the prospect of a continuation of Kyoto-style schemes, it would be a central issue in negotiation. We shall discuss it in the subsequent section. Emission trading works only if these quotas are firmly enforced, and so the issue could be viewed as one that precedes the emission trading. Issue (ii) is also an important issue as, once some agents start exerting market power, the efficiency property as outlined above no longer holds. People are also worried that Russia may become a single significant supplier. (One analysis accounting for such a possibility is Bernard et al. (2008) which combines computable general equilibrium (CGE) analysis and dynamic games.) Russia has been very slow in participating in ET, and its intention is not clear yet.

Issue (iii) is a fundamental issue for the entire mechanism. Emission trading is carried out over a fixed duration of time. Emissions are like other durable commodities that can be consumed or stored. But, unlike other commodities, there are entities that might have to purchase a certain amount of emission reduction units from the market (irrespective of its past trade position in emission trading) at the end of the period. Otherwise, they are deemed to be in a state of noncompliance. The immediate costs of noncompliance under the KP are a reduction in the emission cap in the next commitment period by an amount that is more than the actual excess emission in the current commitment period. (Actually, one is not sure whether the next commitment period exists so it is uncertain whether such a penalty is effective or not, and so there is a non-negligible probability that one gets away with this noncompliance penalty. Barrett (2005) views this loose compliance as the fatal defect of the KP. Of course, besides the “real” penalty, not delivering on its past promise harms the government’s reputation, which is often of considerable importance in ensuring that nations abide by treaties in international relation theory.)

Besides, there is a lot of uncertainty (and rules yet to be determined) with regard to the dynamic aspect of the emission trading market, but an important issue in emission trading is the fact that only a few months after the end of the commitment period does the nation discover its own emission level and, here, issue (iv) becomes relevant. To accommodate this time lag, an additional 3-year time period is allowed. This creates an interesting end-period problem for this type of market. (In fact, no rule has been specified for this transition phase.) Ishii and Imai (2008) apply an extension of existing literature on execution strategy to the game situation, to this end-period problem. The number of applicable situations is limited and so there are only a few nations whose emissions may exceed the assigned amount together with a small number of speculators, and the emission quantity held by the third party is uncertain. The obtained result confirms the earlier assumption that speculators and the country under consideration wait until the last moment to execute their transactions.

26.2.2 Joint implementation (JI)

JI is a somewhat superfluous mechanism because there seems no need to award a special status to an emission-reducing project taking place inside Annex B nations because that reduction is a part of the emission reduction achieved within that nation

and, to that effect, if the credit is obtained by the entities belonging to the other nation, it is nothing but one form of ET, provided that those entities are allowed to participate in ET. Therefore, except for the case where the national inventory system is discredited so that the nation is excluded from ET, JI has little to offer.

Noting this fact, the JI supervisory committee (JISC) offered two options to choose from for the proponents of a project: one without any special registration and monitoring system and one that parallels that of the CDM. In fact, for investing entities, there could be merit to choosing the second option, as they are assured of obtaining credits (called ERU (emission reduction units)) once the project is approved by the government of the host country, without further intervention.

Still, there arises several points of interest that might deserve further investigation. One is that of a possible switch from a non-Annex B nation to an Annex B nation and, concomitantly, a formerly CDM project would become a JI project. The Russian proposal at SB 25 and COP13 in 2007 turned such a possibility into a reality. Would such a shift create an incentive problem? Analysis of this problem would be potentially interesting and important. A related study of a non-Annex B nation's incentive given its future switch of status is given in Akita (2003).

Another problem would be the governmental incentive for engaging in JI concerning entities belonging to that nation. This is also a fruitful future research topic.

26.2.3 Clean development mechanism

The CDM is one innovative mechanism introduced into the KP, and it has already produced credits (called CER: certified emission reduction) before the first commitment period started. The UN announced that the amount of credits from the projects (including those in the pipeline) reached 2 billion tons (equivalent of CO₂) which, according to some estimates, would be more than sufficient to fill the gap between the demand and supply of the emissions among Annex B nations ratifying the KP for the first commitment period. (According to the World Bank's 2008 report on market outlook, there is still a gap between demand and supply. See *State and Trend of Carbon Markets* issued annually.) This in turn implies that there would be no emission reduction for those nations if the marginal cost of the reduction is above those in non-Annex B nations. Thus, the overall environmental effect of the CDM is subtle, as the emission reduction in non-Annex B nations is used up by Annex B nations. The anticipated by-product, the technology transfer through the CDM, seems to have been unsuccessful (because of the prevalence of a unilateral CDM, which marks some distinction from JI). Partly because of this fact, the EB (executive board) of the CDM is rather rigid (by following the Marrakech Accord) in the approval of methodologies and credits in some instances.

26.2.3.1 Issues concerning baseline setting methods and additionality

The KP requires the CDM credits to be those emission reductions that are additional, i.e., those reductions occurring only because the project is undertaken

because it is registered as a CDM project. Consequently, one must choose a baseline emission level so that the difference between the baseline and the actual emission level is the credited emission level. To determine the baseline, the applicant must select from the list of approved methodologies. For those familiar with counterfactual estimation in statistics, it should be well understood that reaching a reasonable estimate of the baseline is difficult. Therefore, skeptics have cast substantial doubt on this part of the mechanism. In fact, the methodology remains one of the major issues for the EB even now.

One issue concerns the basic principle of setting a baseline. The Marrakech Accord 2001 prepared three such approaches, which we may term (1) historical baseline, (2) industrial average baseline, and (3) technologically estimated baseline. Fischer (2005) evaluated these three approaches from an incentives viewpoint.

Apart from the choice of data source determining the baseline scenario, there is another issue concerning the baseline emission level. The easiest example is the case of a manufacturing firm undergoing an energy improvement project under the CDM. To produce an output level x_0 , one had to emit $e_0 x_0$ before the project whereas, after the project, the emission level associated with an output level x_0 is $e x_0$ with $e < e_0$. However, suppose the output level changes to x after the project. Thus, the emission level after the project is $e x$. Suppose simplistically, no technological progress was foreseen and so the historical baseline is appropriate. This implies that, to reach the baseline emission level, using the old emission coefficient e_0 is appropriate. Still, the question remains whether the baseline emission level is based on the old output level or the current output level. We call the former method the *ex ante* baseline and the latter method the *ex post* baseline. (Other authors use names such as absolute vs relative, and level-based vs rate-based.) Note that the *ex ante* baseline emission level is deterministic at the start of the project whereas the *ex post* baseline emission level is uncertain as it depends on the actual output level.

Laurikka (2002) and Imai and Akita (2003) compare these two methods from a risk perspective. All these analyses fall into the category of individual decision making. Imai, Akita, and Niizawa (2008a) assume that the CDM firm is operating in an imperfectly competitive industry. Under such circumstances, one firm's decision to adopt a CDM project may well affect another firm's performance and, hence, incentive via the change in the relative cost advantages. In that paper, we compare not only the simplistic *ex ante* and *ex post* baselines but also other methods representing the industry average baseline and a conservative baseline, that is, an *ex post* baseline with an upper bound on the baseline emission level. In an analysis utilizing the Cournot competition game, we show that the impact of the incentive effect of baseline methods tends to be mitigated by the existence of other firms in the industry.

Consideration of the CDM by a firm interacting with other firms motivates one to study the incentive effect of the adoption of the CDM in a

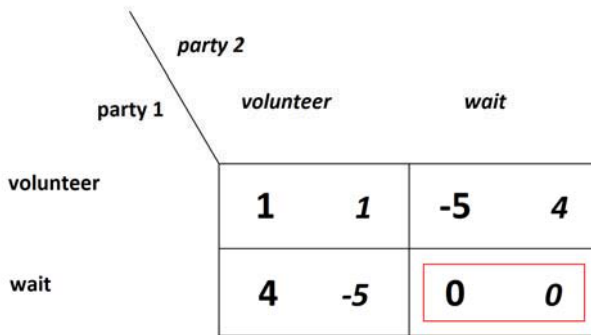
dynamic setting. In Imai, Akita, and Niizawa (2008b), the possibility of one firm adopting a CDM project may trigger adoptions by other firms. In general, this needs a special assumption of complementarity of their products and some sort of imperfection of knowledge. Given a related goods oligopoly model under several different settings, this possibility is established.

26.2.3.2 Bottom-up method

Most complaints regarding the current mechanism are about the management of the CDM. The basic issue is the role and functioning of the CDM-EB, which critics consider too centralized and slow, and too inconsistent over time with political views. However, at least some of these problems originate from the principle of the “bottom-up” method that was adopted in its inception. This method has a typical game theoretical problem and we shall briefly describe this below.

The bottom-up method implies that the UNFCCC office or the EB does not provide any prototype of methodologies usable for projects at the inception. Thus, the first project proposer has to draft up a methodology as well or it has to wait until somebody else develops a suitable methodology that is approved by the EB. To get a methodology approved is a costly procedure, apart from the writing of the project design document. Thus, the bottom-up method poses a typical collective-action problem of Olson. As this problem typically indicates, the initial pace of application for new methodology approval was slow and the coverage of approved methodologies remained quite incomplete for some time, so that solicitation for methodology applications was made in particular areas by the EB. A resolution for this would be some sort of coordination among the potential beneficiaries. One of the costs in those days was the cost of drafting a methodology where few templates existed and there is also uncertainty regarding whether the project can be registered, even though the methodology was approved. In contrast, the delay involved in waiting for others to submit a usable methodology is also costly, but other costs may be substantially reduced. Consequently, there could be incentives for all prospective proposers to wait, which would result in an all-wait equilibrium if the cost is too large for one entity to bear (cf. Fig. 26.1). If no one applies for approval of a new methodology, then nothing happens and if applying alone is profitable, or the agent has a motivation other than profits, then that agent may initiate. However, if there are two such agents, again a coordinating issue arises in the form of competition for the position of a free-rider.

One resolution for “nobody volunteers” or potential coordination failure would be a public coordination. In fact, there has been a request for the EB to provide a template. Furthermore, to help the EB process many requests, donations were made by beneficiary firms so that the EB can meet more frequently and employ more staff.



		party 2	
		volunteer	wait
party 1	volunteer	1 1	-5 4
	wait	4 -5	0 0

Fig. 26.1 Prisoners dilemma in bottom-up method (regardless of the opponent's, five choice of actions, each party finds it better to choose "wait").

26.3 Post-Kyoto

26.3.1 Post-Kyoto and coalition formation theory

Negotiation over the post-Kyoto (or post-2012) scheme is occurring currently, as the Bali roadmap set 2009 as the deadline for a conclusion to be reached and carried out through several levels including an AWG (ad hoc working group) of the CMP (conference of parties serving as meeting of parties) of KP and the COP (conference of parties) of UNFCCC, and G7 (or G8). Several proposals have been made by several parties, ranging from an expansion of the current Kyoto scheme to reinstituting a new scheme that completely replaces the Kyoto schemes, and also there are several intermediate proposals such as sector by sector methods and the addition of regional schemes to current frameworks. One of the biggest disagreements, between the EU and USA, stems from the differing priority regarding adaptation vs mitigation. Yet another big issue is how to make developing countries become involved with the stricter international arrangement.

The extent of the size of cooperating nations is a classical issue studied by the branch of game theory called coalition formation, and there is a vast literature even for international environmental agreements alone (for a general overview, see Barrett (2005), for example, and also see the references in Rubio and Ulph (2007), which consider this problem from a dynamic perspective). One conclusion frequently reached is that there is not much hope of having many countries join a cooperative ring. Several devices to enlarge the extent of cooperation have been examined and proposed, but the sovereignty and limited commitment ability of nations severely restricts such a possibility.

As an illustration, let us go back to the model described earlier in which we show a simple example of a two-stage analysis (initiated by Barrett (1994) and Carraro and Siniscalco (1993). Now, we separate out the term representing the benefit from the world emission reduction, $V_i(X)$, where $X = \sum x_i$ is now a variable determined by each nation. Accordingly, the rest of the net benefit is

written as $K_i(x_i)$, so that $V_i(X) - K_i(x_i) = B_i(x_i)$. In addition, we adopt a specific functional form: linear public benefit and quadratic costs and assume that each nation is symmetric to each other. That is, we assume that $V_i(X) = \hat{X} - X$ and $K_i(x_i) = (\hat{x}_i - x_i)^2 / 2$, where $\hat{X} = \sum \hat{x}_i$, and $\hat{x}_i$ is the natural level of emission, which is the emission level if no benefit from the total emission reduction is reflected, i.e., $K'_i(\hat{x}_i) = 0$. It would be more convenient to express things in terms of emission reduction $y_i = \hat{x}_i - x_i$ and $Y = \sum y_i$. Then, the benefit from the total reduction is Y and the individual abatement cost for i is $k_i(y_i) = y_i^2 / 2$. Given an emission reduction of other nations, the best emission reduction level is given by $1 = k_i(y_i)$ or $y_i = 1$, which is the dominant strategy. Without coordination, each nation reduces its own emission by 1 and the total reduction is N . The situation is inefficient because, if each nation reduces by one more unit, then the total benefit increases by N^2 while the total cost of doing so would be $N^2 / 2$, meaning that such an attempt is beneficial for every nation.

Cooperative game theory considers the possibility of making binding agreements among a subset of players called a coalition. If s players agree to form a coalition S and decide on the best actions for them to take, then, from the maximization of $\sum_{i \in S} (Y - k_i(y_i)) = s \sum y_i - \sum_{i \in S} \sum (y_i^2 / 2)$ in terms of $(y_i)_{i \in S}$, one obtains $y_i = s$. Thus, their target increases by forming a coalition or they agree to internalize their parts of the externalities. Obviously, forming a grand coalition including all members and reducing emissions by N each would be the optimal solution yielding a net benefit of $N^2 / 2$ each.

Coalition formation theory, however, predicts that the chance of forming a grand coalition is not that great in many instances. In the above example, suppose that N equals 4. If one nation leaves the coalition and changes its reduction level to just one unit, while the other three nations remain in the coalition, the departing nation obtains a net benefit of $9.5 > 8$, where 8 is the net benefit level when it joined the grand coalition. Thus, there is an incentive to leave the grand coalition. At the other extreme, when no genuine coalition (consisting of at least two nations) exists, each nation's net benefit is $4 - 0.5 = 3.5$, whereas, by joining with one nation to form a coalition of size 2, a nation's net benefit becomes 4, and hence there is an incentive to form a coalition. Supposing that there is at most one coalition, one finds that coalitions of 2 and 3 are "stable" in the sense that no insider wishes to leave and, at the same time, no outsider wishes to join (except for the case that they are indifferent between the two options), and this fact holds regardless of N , in this example (cf. Fig. 26.2). Thus, it indicates that a relatively small coalition forms, and many remain as free-riders.

The above observation seems to parallel the process leading to the current configuration of the KP, in that only a limited number of nations are accepting the emission quota. Remedies for this situation to increase the size

of the coalition have been investigated, such as linking environmental issues with other policy issues (Russia was said to be induced to ratify the KP in return for the EU's support for Russia joining the WTO), providing a side payment as an inducement to recruit new participants, and creating other commitment devices such as a minimum participation requirement (55% requirement in terms of emission levels among Annex B nations in the case of the KP). (For references, see the literature cited in Carraro, Eyckmans, and Finus (2006), for example.)

Among these options, the use of transfers (interpreted broadly to include changes of rules in favor of new participants, etc.) seems to be of wider use, especially for the negotiation within the framework of the CMP of the KP or the COP of UNFCCC. Funding and technology transfer are discussed at the meetings in parallel to discussions on the scheme after 2012 (although developing countries constantly claim that those discussions should not be combined with the involvement of those countries in the quota scheme).

The above example is too simple in many respects. One important element is that of asymmetry among nations, which affects the composition of members of the coalition to form and the identification of necessary inducement to expand a coalition becomes more player specific.

Another important element is the fact that both climate problems and international cooperation together with its negotiation are dynamic issues. In fact, formulating the problem dynamically expands the possibility of cooperation substantially. The basic logic is that the possibility of future failure of cooperation would prevent countries from not cooperating. Such "sanction" is within the ordinary policy choice rather than a new action created to force other nations to obey an international agreement or to participate in a treaty, which would have grave consequences in the international relations.

Following Barrett (1999), researchers focused on equilibria that satisfy dynamic rationality conditions called subgame perfectness and renegotiation proofness. The former condition yields many outcomes whereas the latter condition can reduce the number of solutions. Renegotiation proofness is appropriate in this context because, in the international negotiation, it would be difficult to implement inefficient sanctions for a long time and also any agreement reached has a time limit and so renegotiation actually takes place similar to the KP. However, requiring this condition in terms of efficiency in any event so that there is no room to renegotiate is too strong and a weaker criterion is utilized. For more details, refer to Weikard and Dellink (2008) where finitely many periods with a prefixed allocation for each potential coalition is examined, Asheim et al. (2006) where it is shown that multiple coalitions can attain better allocations, and also Rubio and Ulph (2007) and De Zeeuw (2008) which examine the effects of stock pollutants utilizing dynamic programming methods, and references therein.

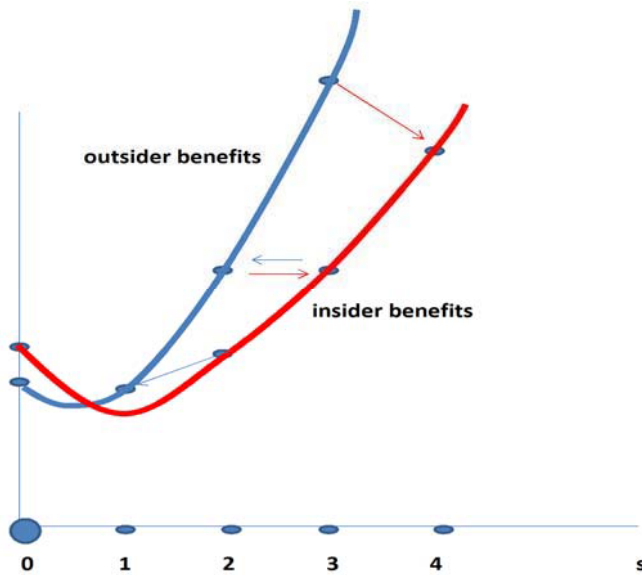


Fig. 26.2 Benefits from five-person agreement (at $s = 2$ or 3 , any insider does not wish to leave and any outsider wishes to join the coalition).

26.3.2 Negotiation

As shown in the examples of analyses in the papers listed above, game theory can serve as a device to simulate the negotiation process as well as to evaluate options to be proposed in the course of negotiation. As mentioned above, several proposals have been made for a scheme after 2012, some of which were proposals proposed before the KP was adopted or before the KP entered into force. These range from a simple expansion of the Kyoto regime with tighter targets to diverse alternative schemes including fragmentizing the Kyoto approach by sectors or regions, voluntary commitment schemes, world carbon taxes, establishing global technological standards, and setting emission intensity targets. Many agree that the key factors are uncertainty and enhancement of the chance of technological breakthrough. Beyond that, there seems to remain a big gap in the ranking of policy alternatives. This discrepancy in subjective beliefs, together with the Kyoto mechanism being in a position of quasi status quo, seems to make agreement among broader participants very difficult.

To illustrate the issue, take the simple case of negotiation between two countries. They can agree on some scheme so that both become better off, whereas, if they fail to reach agreement, they are left with the “status quo.” This setup is known as a two-person pure bargaining problem. If the two people disagree on the best option, possibly because of future probabilities of events and future costs and benefits, then agreement would become harder. (In general, a discrepancy in subjective probability helps agreement when contingent payments based on future events, probabilities of which the parties disagree on, is possible.) However, in the post-2012 negotiation, it seems that adoption of one scheme (e.g., starting

mitigation now) may change the likelihood of one event (technological breakthrough) occurring. Under common expectations (and complete information) and when the number of potential cooperators is known and fixed, bargaining theory provides the solution as a predictor or a focal point for negotiation. Under the possibility of each player joining or leaving a coalition, the analysis is slightly more complicated, but the resulting outcome often corresponds to solutions in cooperative game theory.

One focal solution concept is the Nash bargaining solution. To illustrate these points, consider the model discussed earlier with the membership of signatory nations fixed and a world quota A as given but its breakdown yet to be determined. Each nation i expects the given allocation of assignments $a = (a_i)_{i=1}^N$, with an associated competitive allocation $\bar{x}(a) = (\bar{x}_i(a))_{i=1}^N$, where the equilibrium is as above and denoted by the induced level of net benefit as $B_i(a)$. Furthermore, assume that there is a benefit level B_0 corresponding to the case where each nation chooses its environment policy without an assigned quota (for this, we have to assume that each government is aware of the public good aspect of its own emission and chooses its policy from that point of view). The Nash bargaining solution approach assumes that a is chosen so that $\prod_{i=1}^N (B_i(a) - B_i^0)$ is maximized provided that each term inside the multiplication operator is positive. This is a typical cooperative game solution, although there are many other solutions proposed.

Many modifications are necessary before applying this type of solution to the ongoing negotiation. For instance, one may question the validity of taking a *laissez faire* allocation of net benefits as the reference point of the solution and the equal weights given to each nation's net benefit, which means that bargaining power is equal. Another more serious need to modify the theory stems from the recognition of the moral or emotional factor. In particular, the historical process that led to today's position of each nation is not accounted for. In the ongoing negotiation, some claim that those who were eager to advance environmental regulation much earlier than other nations deserve consideration. Furthermore, the spirit in the UNFCCC is that some of the nations that emitted much more in the past should be given different obligations from those who need more emissions to catch up. These claims are often made in the political negotiation, and several proposals account for some of those data (cf. Brazilian proposal of COP8 (FCCC/SBSTA/2002/INF.14)). This would be an interesting topic to study from the viewpoints of both game theory and political science. (See references in Böhlinger and Helm (2008), for example.)

When one considers a process prior to the above negotiation so that the world community first agrees on the total emission quota A in a manner similar to the negotiation over individual quotas, with an expectation that the subsequent negotiation would be resolved as predicted by the Nash bargaining solution or any cooperative game solution, then there would be a trap that the overall choice of the quota a may turn out to be inefficient. The reason is that each nation considers only its share in the final outcome and would not take into account the entire gain

for the world community. This sort of negotiation procedure is very common but involves a danger known as the problem posed by incomplete contracts, as pointed out by Tadenuma (2004) particularly for the emission quota problem.

One could go one step further and attempt to capture the fact that a nation is not a single objective maximizer. We have seen several policy changes following election results; from Democrat to Republican in 2000 leading to US secession from the KP, the Canadian election in 2005 resulting in the new government declaring intentional noncompliance, and the Australian election in 2007 was followed by an immediate ratification of the KP at the last minute.

This phenomenon cannot be accounted for even if one models the governmental policy position as a consequence of the Downsian voting game, which essentially points to the median voter theorem so that policy change becomes continuous. (Applications of the Downsian model are common in the discipline. See Roelfsema (2007), for example.) Recent developments in political economics introduced the probabilistic voting model, which has some chance of accommodating such discontinuous randomness in voters' preferences. Parties face uncertainty in voter's preference along with some policy-ideology dimension. Assume that the parties cannot choose their ideological traits themselves, and so they mostly compete with each other along a more deterministic policy dimension. After they chose their policy positions, uncertainty over the ideological dimension of voters' preferences is resolved. (It is assumed that the rate of substitution of ideology with the other policy is common across voters.) Then, the power is given to the party whose ideological position is closer to the realized position. One can create policy change with respect to the KP listed above or alike in this sort of model. Obviously, one needs more information on how the preference over environmental policy is affected, but this seems to be one plausible research agenda.

26.3.3 Role of CDM

In the same way that the agreement on the KP in 1997 was a surprise to some observers, we cannot predict the consequence of current negotiations with much confidence. At least because the time left is short and many parties have vested interests in the current scheme, a modification of the Kyoto scheme (with possibly a smaller number of participants) or a return to no scheme at all may have some chance. In this situation, the role of the CDM seems to be of growing importance. Even among those who propose different schemes to the Kyoto scheme, some seem to agree to retaining the CDM as a device to keep developing countries in the framework. In this regard, CDM reform continues to be an important agenda.

In view of bargaining theory, the CDM could be part of the "status quo" if the Kyoto scheme is supposed to last. By contrast, if the Kyoto scheme is discontinued, the value of CDM credits may depreciate significantly. Hence, the status quo payoff for non-Annex B countries would decrease too. In other words, non-Annex B countries have a stake in the current scheme and so, to gain their support, something at least as attractive as their current expected payoff must be assured. At the same time, they have something to lose if the negotiation of the Kyoto scheme breaks down completely.

In addition, the detailed decision of the COP (UNFCCC) and CMP (KP) on the coverage of the CDM project matters. In fact, there is a chance that the type of “project” eligible as a CDM project may be widened by the CMP. Programmable CDM is one such example. Notable are policy CDMs that are not admitted currently, which would widen the category of eligible projects substantially and hence raise the future value of countries retaining non-Annex B status while reducing the value of CDM credits (compared with the case if a policy CDM were not admitted, other things being equal) because of an increase in the supply of credits.

This suggests that, in the end, a CDM treating emission reduction by one developing country as a whole can be constructed. If this is the case, non-Annex B countries are effectively given a one-sided incentive to cut their emissions relative to the “business as usual” (BAU) level. There is no penalty for excessive emissions but, by reducing emissions, they obtain benefit in the form of credits, provided that there is a market that values the credits. This seems to be a politically viable option to get non-Annex B countries involved and, indeed, guarantees participation incentives, on the one hand. On the other hand, making their current expected growth paths equal to its future quota on emissions would increase the prospective payoff for non-Annex B countries greatly, which would make their incentives to change their status very low. The restraint posed by such a CDM with respect to BAU could be too lenient and potential emissions could be so large that mitigation cannot be achieved. Moreover, administration of the CDM becomes too much of a political problem and exceeds the capacity of the CDM-EB.

The San Paulo proposal (a report prepared under the Basic project (<http://www.basicproject.net/data/.nal/Paper17Sao%20Paulo%20Agreement%20on%20Future%20International%20Climate%85.pdf>) contains a mechanism to get non-Annex B countries to choose to enjoy such nationwide CDMs while, at the same time, making them declare the amount of total credits they produce under this proposal so that, if the amount of credits they produce exceeds that level, they must change their status into Annex B. This is one example of an innovative scheme that accounts for incentives well.

For the evaluation of the schemes involving CDM in this post-Kyoto context, one could repeat the arguments made for smaller CDM projects, including baseline methods. Furthermore, the impact of the CDM defined for one nation as a whole may not be small compared with the size of the market, and thus a broader scope of analysis may be required. (One relevant point would be that raised in Imai and Akita (2003) that a juxtaposition of the cap on the one hand and a CDM with an ex post baseline scheme on the other hand may skew the distribution of risk bearing with respect to environmental risk in the world community.)

Another possibility, as mentioned above, is a replacement of the Kyoto-type scheme with another scheme without a quota on emissions (including the case of ending up with no scheme at all), and so the value of CDM projects falls substantially. If no alternative compensation scheme for CDMs is instituted at the same time, this would imply scraping constructed machineries such as DOEs

(designated operational entities) and DNAs (designated national authorities) and possibly damage the adaptation fund. Thus, this possibility works as a threat to non-Annex B countries but there seems to be enormous costs and vested interests on the rest of the world as well.

All these suggest the importance of CDMs in this negotiation and it seems that an improvement in the organization to handle CDMs is quite important. At the same time, it should be kept in mind that any decision on the CDM would have some effect on the current negotiation over the post-2012 scheme, and game theoretical thinking can help evaluate such an effect.

26.4 Concluding Remarks

We have briefly reviewed the use of game theory and potential game theoretical problems in the analysis of negotiation occurring at the UNFCCC and KP, with an emphasis on the role played by the CDM. At this moment, the future of the international scheme after 2012 is not clear, and the course of negotiation itself is a challenge to game theory. However, as many incentive issues are involved in both the negotiation process and current or proposed mechanisms, the use of game theory can contribute to the better functioning of the international effort to cope with the current global environmental problems.

Acknowledgments

We appreciate comments made at the first World Congress of global warming and, in particular, to the anonymous referees who provided information not contained in the earlier version. Furthermore, financial aid from the Grants in Aid (20330037) of the Japanese Society for Promotion of Science and Sumitomo Foundation is gratefully acknowledged.

References

- Akita, J. (2003). A simple model of CDM low-hanging fruits, in T. Sawa (ed.) *International Frameworks and Technological Strategies to Prevent Climate Change*, Tokyo, Springer Verlag, 66–96.
- Asheim, G. B., C. B. Froyen, J. Hovi, and F. C. Menz (2006). Regional versus global cooperation for climate control, *Journal of Environmental Economics and Management*, 51, 93–109.
- Barrett, S. (1994). Self Enforcing International Environmental Agreement., *Oxford Economic Papers*, 46, 878–94.
- Barrett, S. (1999). A Theory of full international cooperation, *Journal of Theoretical Politics*, 11, 519–41.
- Barrett, S. (2005). *Environment and Statecraft*, Oxford University Press.
- Bernard, A., A. Haurie, M. Vielle, and L. Vigui r (2008). A two-level dynamic game of carbon emission trading between Russia, China, and annex B countries, *Journal of Economic Dynamics and Control*, 32, 1830–56.
- Bohlinger, C. and C. Helm (2008). On the fair division of greenhouse gas abatement cost, *Resource and Energy Economics*, 30, 260–76.

- Carraro, C. and D. Siniscalco (1993). Strategies for the international protection of environment, *Journal of Public Economics*, 52, 309–328.
- Carraro, C., J. Eyckmans, and M. Finus (2006). Optimal transfers and participation decisions in international environmental agreements., *Review of International Organization*, 1, 379–396.
- Fischer, C. (2005). Project based mechanisms for emission reductions: balancing trade-offs with baselines, *Energy Policy*, 33, 1807–23.
- Imai, H. and J. Akita (2003). On the incentive consequences of alternative CDM baseline schemes, in T. Sawa (ed.) *International Frameworks and Technological Strategies to Prevent Climate Change*, Tokyo: Springer Verlag, 110–126.
- Imai, H., J. Akita and H. Niizawa (2008a). Effects of alternative CDM baseline schemes under imperfectly competitive market structure, in A. Dinar, J. Albiac, and J. S. Soriano (eds.) *Game Theory and Policy Making in Natural Resources and the Environment*, Routledge, 307–333.
- Imai, H., J. Akita and H. Niizawa (2008b). CDM domino, in L. Petrosjan and N. Zenkevich (eds.) *Contributions to Game Theory and Management*, Graduate School of Management, St. Petersburg State University, 177–88.
- Ishii, R. and H. Imai (2008). Emission Trading at the End of Commitment Period, *Proceedings of the World Congress of Global Warming*, 1295–302.
- Laurikka, H. (2002). Absolute or relative baselines for JI/CDM projects in the energy sector?, *Climate Policy*, 2, 19–33.
- Roelfsema, H. (2007). Strategic delegation of environmental policy making., *Journal of Environmental Economics and Management*, 53, 270–5.
- Rubio, S. and A. Ulph (2007). An infinite-horizon model of dynamic membership of international environmental agreements, *Journal of Environmental Economics and Management*, 54, 296–310.
- Tadenuma, K. (2004). Possibility and Optimality of Agreements in International Negotiations on Climate Change, Hitotsubashi University, mimeo.
- Weikard, H.-P. and R. Dellink (2008). Sticks and Carrots for the design of climate agreements with renegotiations, FEEM, working paper 26.
- Zeeuw, A. de (2008). Dynamic effects on the stability of international environmental agreements, *Journal of Environmental Economics and Management*, 55, 163–74.

Enterprise Risk Management Perspective

Ayşe Kucuk Yilmaz and T. Hikmet Karakoc

27.1 Introduction

Global warming has become a highly concerned issue in enterprise risk management (ERM) and corporate sustainability practices in the business management. Enterprise risk management and corporate sustainability are directly linked with climate change and global warming. Global warming-based results are affected by business risks and their handling priorities. Because risks are verified and increased by global warming, they impact both our world and the business. Also, global warming-based impacts can have effect on corporate sustainability. In this concept, global warming should be considered as part of enterprise risk management issue and sustainability practices. The consequences of the global warming-based risks are threats for sustainability of our world. In this study, enterprise risk management-based framework has been developed to support managing-related risks and promote corporate sustainability risk efforts in the business management. Implementation of such models and getting results takes as much as 5 or 6 years in optimum period. For this reason, basic framework is given in this study. Further work is planned for implementation of this model in specific business sector as a real world situation. Also, this model based on ‘enterprise risk model to corporate sustainability model’ has been developed by Kucuk Yilmaz and Yilmaz (2008).

Global warming is threatening sustainability of the world. Impacts of global warming create important negative results to social, economic, and environmental systems.

In the context of global warming factor assessment, uncertainty arises because we do not know exactly the magnitude of the global warming and its associated impacts, and in some subjects it is not clear. Also, uncertainty may arise because decision makers do not know the threshold at which global warming impacts have a particular level of consequence for organization.

Global warming/climate change risks are developing into one of the critical risk areas of the 21st century. These risks are part of a larger set of sustainability

risks, which emanate from the environmental and corporate social responsibility areas. Sustainability risks need to be incorporated into corporate Enterprise Risk Management (ERM) systems (Anderson, 2007).

During the last decade, concerns have grown continuously in anthropogenic GHGs and the associated risks of climate change. Enterprises, as a major contributor to global GHGs emissions, will need to play a significant role in helping countries to achieve the goal of reduction under the Kyoto Protocol. The enterprise risk is fundamental to firms and is inherent in their operations. This type of risk sometimes is identified as operating risk that can be technological, distributional, or informational. And enterprises can use operating risks as resource of competitive advantages (Chen et al., 2007).

While risk management and sustainability risks are not necessarily new, it is only recently that their impacts are being felt by businesses. Environmental and social risk costs, which for years were externalized, are increasingly internalized to the firm (Anderson, 2007).

In recent years, global warming and its consequences have become a key international issue for both industrialized and developing countries. The global warming risk looks to be a serious threat to our species and all living beings on the earth. Its consequences are numerous and varied. As is obvious by its name, global warming is a global phenomenon with a number of effects on the global level. Global warming has various effects, ranging from the effects to the atmosphere to the economical, environmental as well as the health of human beings. There are also a number of effects to the nature and atmosphere. One of the most serious effects of global warming that humans have to think about is the effects on the health of individuals, nations, and therefore civilizations (D'Silva, 2008).

This chapter presents a suggestion to integrating global warming risk and its impacts on risk management and other strategic planning activities in public and private sector organizations. The study is aimed to support current risk management efforts about sustainability and global warming in the world. This study is also aimed to contribute to risk management literature regarding the sustainable development and global warming subjects. It also includes four main sections. The following section describes enterprise risk management and related strategies. In the third section, the methodology of research: risk management process is given. Overall conclusion is given in the last section.

27.2 Enterprise Risk Management (ERM) and Related Strategies

ERM enables an organization to deal effectively with uncertainty and associated risk. ERM is a systematic approach for identifying and managing the business risks of an organization. ERM offers a proven method to align risk appetite with strategic goals, deploys resources more effectively, reduces operational surprises and losses, and improves risk response (PricewaterhouseCoopers, 2007).

ERM is the most important support to balancing approach to assessing products, services and business activities using the following criteria as indicators to essence of sustainability (The Dictionary of Sustainable Management, 2009):

(1) Financial criteria

- Economically sustainable
- Technologically feasible
- Operationally viable

(2) Environmental criteria

- Environmentally robust
- Generational sensitive
- Capable of continuous learning

(3) Social criteria

- Socially desirable
- Culturally acceptable

The business impacts of climate change may require companies to initiate adaptation strategies and risk management actions even for companies that produce relatively few greenhouse gas emissions and have little if any need to reduce such emissions. Some industries and companies will be more concerned with adaptation issues, others with mitigation. Adaptation involves taking action to minimize and respond to the effects of climate change on the business. These effects may be readily apparent or may take time to develop and may be cumulative. Mitigation refers to actions required to reduce greenhouse gas emissions, sooner or later (CICA, 2005).

Sustainability risks impact businesses, but also society as a whole. When we start considering the viability of the water we drink, the air we breathe, and the land upon which we live, we may be contemplating the ultimate risk management challenge. We need to manage risks that impact the planetary ecosystems, on which we all depend. ERM deals with risks emanating from the environmental and corporate social responsibility areas. A few examples illustrate the nature and scope of sustainability risks (Anderson, 2007):

- Increasing ocean temperatures as the result of global warming are producing stronger hurricanes and greater property damages.
- Island states are considering litigation against certain industries, like the oil industry, and countries, like the United States for producing global warming, which is threatening the existence as a society.
- Numerous companies, like Nike, ExxonMobil, Citigroup, Shell, Nestle, have suffered financial and reputation damages from boycotts against their operations, which harm the environment and/or workers and the public.
- Several corporations have paid sizeable settlements following suits brought by female employees alleging gender discrimination.
- As water sources are contaminated and depleted, many corporations face litigation for injuries and damages.

- Multinational corporations operating in the European Union face a myriad of environmental regulations, including the Kyoto Protocol, the Waste Electrical and Electronic Equipment Directive (WEEE), the Restriction of Hazardous Substances Directive (RoHS), and the Registration, Evaluation, and Authorization of Chemicals framework (REACH).
- At current deforestation rates, the Amazon Rainforest could be gone before the end of the century.
- A study in *Nature* reported that industrial-scale commercial ocean fishing has reduced the world's populations of large predatory fishes by 90% over the last 50 years.
- Directors and officers face penalties and litigation for failure to effectively manage sustainability risks.

Increasingly climate change can be expected to impact many strategic factors and key performance drivers such as availability of and access to resources, raw material and production costs, supply chain arrangements, and market demand for products. For companies with longer operating or investment cycles, it will be important to help investors understand the impact of structural changes in markets arising from climate change adaptation and mitigation issues (CICA 2005).

Nowadays, business management systems and risk management frameworks reshaped and improved as including climate change and global warming-based impacts. Risk management strategies categorized global warming into 2 dimensions, 6 aspects, and 28 strategies by Chen, Yu-Ling and colleagues as shown in Fig. 27.1 This adapted figure can be useful to understand relationship between global warming, ERM, and business management concept.

Dimensions	Aspects		Strategies
ENTERPRISE RISK MANAGEMENT (ERM)	Command risk information	1	Establish targets for reducing risks
		2	Fully understand corporate risks
		3	Efficiently manage corporate risks
		4	Cooperate and communicate operating risks with other agencies
		5	Use common risk language to discuss with environmental risks
		6	Support and participate in related research plans
	Have tools and technology of risk management	1	Fully understand and use tools to reduce risk
		2	Promote rate of energy use by innovate and improve technology
		3	Use and purchase renewable energy to save costs
		4	Establish environmental risk management system

		5	Insure related environmental insurance
	Implement greenhouse gas inventory and reduction	1	Establish target to greenhouse gas reduction
		2	Implement greenhouse gas inventory to provide valuable information from emission
		3	Establish risk management standards by greenhouse gas inventory
		4	Use greenhouse gas inventorial report to be information from manage risks and opportunities
		5	Conform to related environmental laws and regulations
		6	Implement voluntarily greenhouse gas reduction
CORPORATE SOCIAL RESPONSIBILITY	Communicate with stakeholders	1	Continued increase value for stakeholders in risk management strategies
		2	Communicate operating risks with stakeholders
		3	Explain operating risks to employees
		4	Take responsibility for rights and interests to stakeholders
		5	Increase knowledge and awareness for employees by risk train courses
	Cooperate and integrate for corporate	1	Learn the different management strategies from other groups
		2	Integrate related risk information to gain the optimum management effects
		3	Participate international environmental organizations to increase corporate image
	Corporate information disclose	1	Disclose related greenhouse gas reports
		2	Promise and ensure to investors
		3	According information include related greenhouse gas data

Fig. 27.1 Enterprise risk management strategies and strategy categorization (Chen et al. 2007).

27.3 The Risks–Reward Paradigm

Risk may have positive or negative outcomes, resulting in either an opportunity or a loss for a business. Risk management is the way in which adverse effects from risk are managed and potential opportunities are realized. Therefore, risk management involves (Global Risk Alliance Pty, 2005)

- minimizing those things that may negatively impact upon a business;
- identifying and harnessing those things that will help to achieve the goals and objectives of a business.

Risk is the chance of something happening that will have an impact on objectives (The Australian Greenhouse office, 2006):

1. A risk is often specified in terms of an event or circumstance and the consequences that may flow from it.
2. Risk is measured in terms of a combination of the consequences of an event and their likelihoods.
3. Risk may have a positive or negative impact.

Figure 27.2 illustrates the components of each step of the basic integrated risk management process and illustrates the cyclical nature of the process.

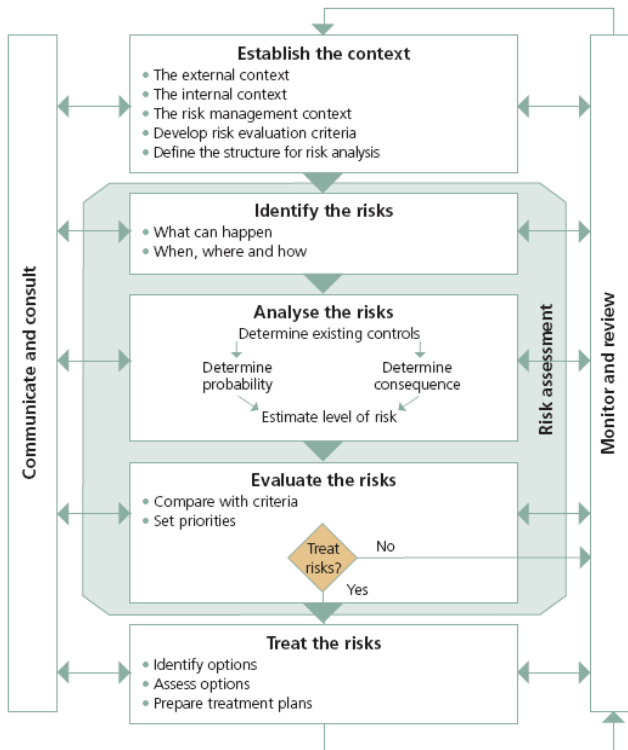


Fig. 27.2 Details of the risk management process.

The current best ERM frameworks and process (such as AS/NZS 4360:2004) can shape and improve according to the climate change and global warming-based factors. ERM can be considered an integral part of sustainable development process as seen in Fig. 27.3.

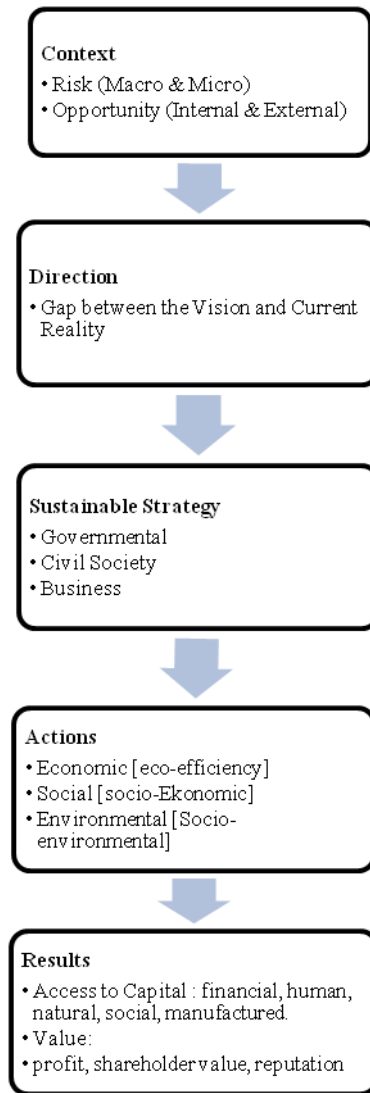


Fig. 27.3 Sustainable development process (Hutton et al. 2006).

In the context of global warming risk assessment, uncertainty arises because we do not know for certain the magnitude of the global warming and its associated impacts, and in some subjects it is not clear. Also, uncertainty may arise because decision makers do not know the threshold at which global warming impacts have a particular level of consequence for organization.

Risk management, in the environmental, health, and safety functions, is important to any organization, but especially to the sustainability of the world. Sea level rise, heat waves, and increased intensity and frequency of prolonged droughts, floods, storms, and wildfires are already triggering increased financial losses. These physical changes affect a broad range of sectors, including real estate, agriculture, tourism, health care, insurance, fisheries, and forestry, as well as any company with offshore or coastal facilities. Oil producers and other businesses along the US Gulf Coast, for example, suffered billions of dollars of infrastructure damage from Hurricane Ike this past summer. The increasing threat of water scarcity, which will likely be exacerbated by climate change in the many parts of the world, will impact many sectors, including the agriculture, electric power, industrial, beverage, and food sectors. But embedded in the risk of climate change are numerous opportunities for innovation. In anticipation of a carbon-constrained world, DuPont has developed carbon-free refrigerants, more energy-efficient home insulation products, and bio-based fuels. The company expects to realize additional revenues of US\$6 billion or more by 2015 from products that reduce greenhouse gas emissions, cut water consumption, or provide other environmental benefits. DuPont has reduced its own greenhouse gas emissions by more than 70% over the past 15 years, saving US\$3 billion on its energy bills in the process. General Electric's often mentioned Ecomagination initiative is another example of wise business planning in the face of climate change. Predictably, both companies have key board members who are keenly aware of the risk-reward paradigm represented by global warming (Lubber, 2008).

Global warming risk is managed by holistic risk management and provides sustainability. For this reason, risk management is key factor between global warming and sustainability (see Fig. 27.4).



Fig. 27.4 Link between global warming, sustainability, and risk management.

Risk management is the process that the systematic application of management policies, procedures, and practices to the tasks of communicating, establishing the context, identifying, analyzing, evaluating, treating, monitoring, and reviewing risk (The Australian Greenhouse office, 2006). Sustainability-

based ERM deals with risks emanating from the environmental and social justice areas (Anderson, 2006). It includes both climate change and global warming issue.

The risk management approach allows companies to save money by anticipating and avoiding expenditures arising from global warming. In addition, operating costs can be reduced through waste minimization, pollution prevention, and the elimination of health and safety hazards (BSD Global, 2008).

27.4 The Risk Management Process

Every year, the economists who meet in Davos at the World Economic Forum present an updated estimate of the major risks facing the business world and the global economy. They do this using a grid that shows the two dimensions of risk (Polard and Stephen 2008):

- the likelihood or probability of the risk occurring (expressed as a percentage)
- the severity or consequences if the risk does occur (expressed in monetary units)

The risks that are most closely connected to environmental sustainability and to climate change are marked in red. Many of these risks are interconnected, and a major crisis of one type could trigger a series of related crises, a domino effect. It is unwise, then, to attempt to assess any of these risks in isolation from the others (Polard and Stephen 2008).

ERM can apply into global warming-based business strategies and management subjects. Integrating global warming into risk management requires a systematic approach, commitment leadership, team work, and a systems approach that enables establishment and management strategy and its implementation to best managing of global warming risk. The new Cwg model provides direction and guidance to help managers and decision makers to integrate global warming into their daily decisions and to better understand and manage social, environmental responsibilities and corporate performance. Sustainability-based ERM is required to understanding the sustainable development context truly.

ERM can apply to global warming-based business strategies and management subjects. Integrating global warming into risk management requires a systematic approach, commitment leadership, team work and a systems approach that enables establishment and management strategy and its implementation to best management of global warming risk. This new Cwg model provides direction and guidance to help managers and decision makers integrate global warming into their daily decisions and to better understand and manage social, environmental responsibilities and corporate performance. Sustainability-based enterprise risk management is required for understanding the sustainable development context in the best way.

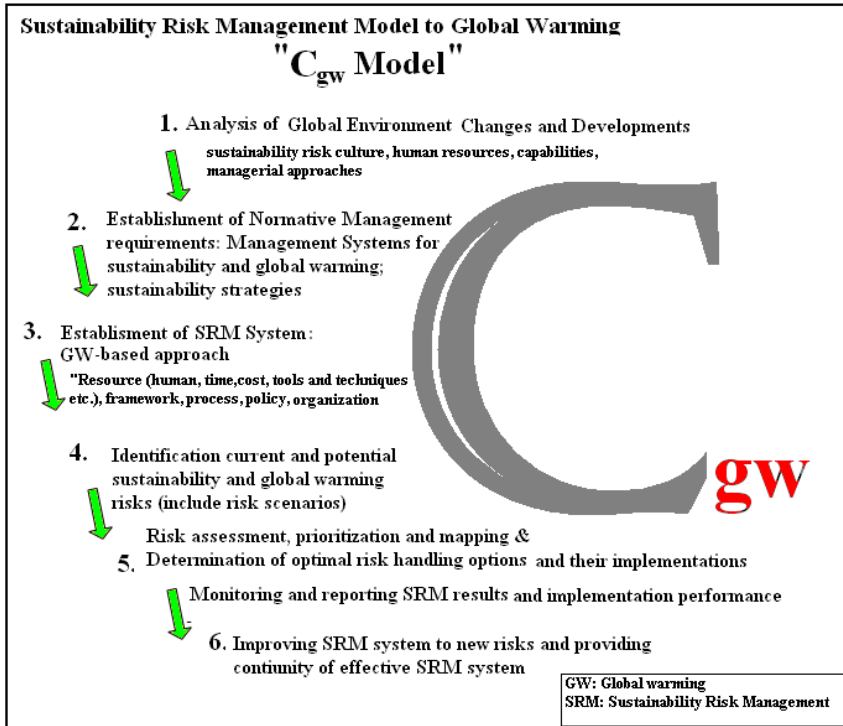


Fig. 27.5 Sustainability risk management model to global warming: Cgw model.

Fundamentals and aims of sustainability development and ERM are considered for the determination of the steps of Cwg model. Basically, the new model is offered for the best global warming-related risk management practice. The model provides a reasonable assurance for achieving sustainability objectives. The model is basically based on 'C Model' (Kucuk Yilmaz and Yilmaz, 2008). Details of 'enterprise risk management model for corporate sustainability' are given in this book. Cwg model has been developed by authors according to this model which is designed as the six key components and their sub-components (see Fig. 27.5). The detail of components is not given here. Cwg model is shaped according to the sustainability fundamentals, requirements, and related efforts.

The Cgw model process consists of a series of steps that, when undertaken in sequence, enable continual improvement in decision making. Communication and consultation will be reflected in each step of the process. Monitor and review are the essential and integral steps in the risk management process. The basic model steps are as follows:

- i. Analysis of global environment
- ii. Establishment of normative management requirements
- iii. Establishment of SRM System: GW-based approach
- iv. Risk identification (threat and opportunities; includes risk scenarios)

- v. Establishment of data flow and feedback systems; analysis of ERM implementation performance
 - vi. Providing the continuity of the ERM system for corporate sustainability
- Also, Cgw model encompasses:
- Enhancing sustainability and global warming risk response decisions via combination of both the proactive and reactive approach
 - Reducing impact severity of global warming threats
 - Seizing opportunities (renewable energy, new technology, etc.)

The context for Cgw model sets up a framework for identifying, assessment, and prioritization risks. It places the assessment on a clear foundation so that everyone works from a common understanding of the scope of the exercise, how risks are to be rated, and how the analysis is to be approached. Establishing the context consists of five main parts (The Australian Greenhouse office, 2006):

1. Global warming and its impacts scenarios
2. Scope: Defining the scope of the assessment including activities to be covered, geographic boundaries, and the time horizon.
3. Stakeholders: Determining whose views need to be taken into account, who can contribute to the analysis, and who needs to know its outcomes.
4. Evaluation framework: Defining how risks will be evaluated by clarifying the objectives and success criteria for the organization and establishing scales for measuring consequences, likelihoods, and risk priorities.
5. Key elements: Creating a framework that will assist in identifying risks by breaking down the organization's concerns into a number of areas of focus and relating them to the global warming scenarios.

To manage the risks of global warming, it is necessary to define how global warming is projected to change in the future. This is achieved by using global warming scenarios. Global warming scenarios provide a plausible summary of the global warming variables that could apply in your geographical region and timescale of interest. Scenarios can provide a consistent and efficient basis for assessing global warming-related risks across different organizations without affecting the integrity of the analysis.

Growing environmental concerns, coupled with public pressure and stricter regulations, are changing the way people do business across the world. Industry is on a three-stage journey from environmental compliance, through environmental risk management, to long-term sustainable development strategies (BSD Global, 2008).

There are samples given to global warming risks. Global warming-based risks are identified in the threats and opportunity categories by the authors. These threat risks are identified with current research about global warming issue worldwide. Cwg model has been adapted and developed from the book entitled *Auto Wars* by Kucuk Yilmaz and Yilmaz (2008). There are few samples showing important impacts of global warming:

Threats

Risk considers both threat and the opportunity by Holistic ERM concept. This has shown difference and dominance of risk management managerial approach. There are some threats which are identified as the following:

- Threats to cultures
- Reduction in sea ice
- Increasing yields
- Decreased snowpack
- Severe storms
- Water shortages
- Species losses
- Reduced tourism
- Heat waves
- Reduced growing seasons
- Increased diseases
- Receding glaciers
- Unsustainable development
- Populations at risk
- Species extinction
- Changes in precipitation
- Flooding
- Drought
- Changing range of decrease
- Loss of biodiversity
- Changing forests
- Rising sea levels
- Temperature changes
- Changes in the frequency and intensity of extreme weather events
- Economic adverse impacts

Opportunities

There are some opportunities identified according to the global warming issue. These are presented as opportunities to the sustainable world:

- Cooperation among people, nations, and companies for sustainability
- Increasing of health, safety, and environmental awareness
- Development of environmental management system
- Sustainable energy resources with new technologies
- Developing renewable energy resources such as wind, sun, and geothermal developed renewable energy projects
- Production of the environmental friendly products
- Respect for the human being and the environment
- Common goals for success and a peaceful world

- More rational and fair sharing of scarce and limited resources
- Setting of the best international communication
- Investment in human resources, sustainable economy, renewable energy, green technologies, environment protection, technology transfer, etc.

Our civilization can seize opportunities for a universal and peaceable world. Hence, our civilization and culture will rise. Global peace and global sharing are important opportunities, which can and should be provided by global warming to all of us. Otherwise, we may face with new and important threats in the history of human kind. The sharing of scarce resources can be a new reason for war. Increase in the risk is emerging since some countries are going into war to get control of or managing scarce resources. This is not a humanistic and civilized attitude.

Nations, companies, and everyone have environmental responsibility. All of us are responsible toward our world. We should develop our sustainable risk culture for a peaceful world. 'Everyone is risk manager for managing the global warming, protection, and saving our world.'

Natural disaster losses have been increasing at an alarming rate, and it is prudent to consider what practical steps can be taken today. The following are some suggestions (Mills, 1998):

Educate: Risk managers and insurers should educate themselves and their customers alike on the climate change issues and options to help minimize potential exposures. They may choose to participate in the public policy process with other industry groups.

Articulate a policy: Many firms have published policy statements concerning environmental issues. For example, General Accident's Statement of Environmental Principles asserts: 'As a successful commercial business, we consider minimizing resource use, energy use and waste production to be integral for good business practice.'

Lead by example: Many companies have initiated efforts to manage energy in their own buildings. Swiss Re (see sidebar), Storebrand, and other insurers have adopted environmental criteria for purchasing office products and equipment. The voluntary Energy Star and Rebuild America programs offered by the US Environmental Protection Agency and Department of Energy are open to risk managers seeking technical assistance in this realm.

Mobile disaster preparedness technology and planning: Many of the losses sustained during natural disasters stem from inadequate building codes or poor compliance. The IBHS has advanced a major initiative that includes special training for code officials and working with ISO to implement a community-level code rating system. In another example of fostering disaster preparedness, Arkwright has recently provided weather-warning radios to its client. Also, the tendency to locate buildings and populations in high-risk areas must be addressed.

Support climate monitoring and research: While on one hand, climate research is arguably not the domain of insurers and risk managers, Mr. Nutter has noted that 'it is incumbent upon us to assimilate our knowledge of the natural sciences with the actuarial sciences.' To this end, 13 insurers formed the Risk Prediction Initiative in Bermuda in 1993. The members collectively funded a \$1.3

million annual research program aimed at understanding the risks posed by hurricanes. Some insurers are also hiring staff climatologists.

Make green investments: It helps to invest in environmentally sound ventures.

Capitalize on energy efficiency and renewable energy: Energy consumption is the largest contributor to human-induced greenhouse gas emissions. Fortunately, there is a class of energy-efficient and renewable energy technologies that also helps mitigate insurance risks. For example, efficient refrigeration equipment minimizes the likelihood of food or pharmaceutical spoilage following power outages and solar energy systems can help keep lights on following natural disasters. Risk managers should encourage their insurance providers to assist them in implementing such technologies.

27.5 Conclusions

Companies face many significant risks continuously. Issues and concerns around climate change have heightened the need for enterprise-wide risk management efforts. Treating climate change risks in an isolated or one-off manner can result in flawed decisions that cost a company dearly in both financial and reputation terms. ERM is applied in a risk intelligent manner and is well suited to dealing comprehensively and effectively with climate change risks in this study. It is an effective approach for handling complex, correlated risks, and it offers a meaningful structure for identifying, measuring, prioritizing, and responding to these additional risks. Global warming is and will have high-level impact on organizations. It includes both risk mitigation and creates new opportunities to develop new markets and business strategies.

ERM for climate change and global warming issues will give the organization the right information at the right time to support key decisions and ultimately create enhanced shareholder value (Curtis and Concessi, 2008). ERM may provide effective solution to sustainable development and global warming issue. Proactive Cwg model presents fresh approach to best managing of sustainability and global warming risks by ERM perspective. ERM perspective and Cwg model can be considered a systematic way to save our world to fight against global warming-based threats. Cwg model can be useful to capture global warming-based opportunities along sustainable world, too.

References

- Anderson, DR (2007) Sustainability risk management as a critical component of enterprise risk management: global warming – climate change risks. International Insurance Society, ISS 2007 Berlin, Seminatr, <http://www.iisonline.org/berlin2007/> 2008.08.14.
- The Australian Greenhouse office (AGO) (2006) Climate Change Impacts & Risk Management, A Guide for Business and Government, The Australian Greenhouse office, in the Department of the Environment and Heritage. P. 72, <http://www.climatechange.gov.au/impacts/pubs/risk-management.pdf>, 2009.08.17.
- Canadian Institute of Chartered Accountants (2005) Building a better MD&A climate change disclosures: 9, www.cica.ca 2008.06.12.

- Chen Yu-Ling, Hu, Tseng Chao-Heng AH (2007) Corporate risk management strategies under threats of global warming-Taiwan's experience. International Society for Environmental Information Sciences Environmental Informatics archives, EIA07-003 Volume 5: 18–26.
- Curtis, PC, Concessi, P (2008) The risk intelligent energy company: weathering the storm of climate change. Oil & Gas Financial Journal Online, Vol. 5, No. 1, http://www.ogfj.com/display_article/318054/82/ARCHI/none/none/1/The-risk-intelligent-energy-company:-weathering-the-storm-of-climate-change/ 2008.06.12.
- D'Silva, R (2008) The effects and consequences of global warming. <http://www.buzzle.com/articles/effects-consequences-global-warming.html>, 2008.07.21
- Union of Concerned Scientists (2008) Common sense on climate change: practical solutions to global warming. http://www.ucsusa.org/global_warming/solutions/common-sense-on-climate-change-practical-solutions-to-global-warming.html 2008.07.21.
- Global Risk Alliance Pty Ltd NSW Department of State and Regional Development (2005) Risk management guide for small business, 9.
- Hutton, RB, Cox, DB, Clouse, ML, Gaensbaur, JB (2006) The role of sustainable development in risk assessment and management for multinational corporations. Georgia Tech Center for International Business Education and Research Working Paper Series 2007–2008, Working Paper 001-07/08:17.
- Kucuk Yilmaz, A, Karakoc, TH (2008) Sustainability management based approach to global warming. Journal of Management Research, Vol. 1, No. 1: e 5:3, www.macrothink.org/jmr.
- Kucuk Yilmaz, A, Yilmaz, M (2008) Auto Wars: Enterprise Risk Management Model for Corporate Sustainability in the Automotive Business. VDM Verlag Dr. Müller, Germany
- Lubber, MS (2008) Climate change and the dangers of undisclosed risk, Financial Risk, Finance, www.climateactionprogramme.org, 2009.08.16.
- Mills, E (1998) The coming storm global warming & risk management. Risk Management Magazine, May iss. 20–27. <http://eetd.lbl.gov/EMills/PUBS/comingstorm.html> 2008.07.21
- Polard D, Stephen DW (2008) Sustainability, Risk and Opportunity: A Holistic Approach, Accounting for Sustainability, Toronto, November 2008, <http://www.accountingforsustainability.org/files/pdf/CICA%20%20A%20Holistic%20Approach%20Report.pdf>, 2009.08.17.
- PricewaterhouseCoopers (PwC) (2007) Enterprise risk management methodology. Overview/Baseline, version 1.2 PricewaterhouseCoopers Inc., <http://www.pwc.com/us/en/retail-consumer/reporting-risks-compliance-controls.jhtml>, retrieved on 2009.08.17
- Standards Australia (2004) AS/NZS 4360:2004 Standard. Third edition: 28.
- The Dictionary of Sustainable Management (2009) Sustainability, <http://www.sustainabilitydictionary.com/s/sustainability.php>, 2009.08.17.

Environmental Assessment of Solar Heating and Cooling Systems in Kuwait Climate

Adel A. Ghoneim, Kandil M. Kandil, Adel M. Mohammedein and Ibrahim M. Kadam

28.1 Introduction

Solar energy is a clean and renewable energy source, which produces neither greenhouse effect gases nor hazardous wastes through its utilization. Wide installation of renewable energy systems helps to keep our environment clean and healthy. World energy demand has been significantly increased in the last years due to the world economic growth and population increase, especially in developing countries. Conventional methods of generating electricity can produce pollutants such as carbon dioxide, the main gas responsible for global warming. The potential for reduction of greenhouse gases' emissions is an important issue for the wide spread of renewable energy systems. Greenhouse gases (GHG) that are most relevant to global warming are carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). The carbon dioxide (CO₂) emissions resulted from fossil fuel resources need to be reduced substantially to prevent global warming. Conventional energy sources can damage air, climate, water, land and wildlife, landscape, as well as raising the levels of harmful radiation. As a consequence, there will be a need for development of large scale of a range of new technologies for conversion, storage, and efficient use of energy.

It is necessary to have air conditioning systems in hot climate areas like Kuwait. One does not feel comfortable if the temperature and humidity level is too high. A large amount of the operating costs of a building is determined by the energy requirements and the fuel consumption of its heating, ventilation, and air conditioning system (HVAC system). Active solar heating systems are now widely used in many applications, while active solar cooling systems are not. Numerous publications studied the performance of the solar heating systems (Lunde, 1978; Garg, 1987; Ghoneim et al., 1993; Bo Nordell and Hellström 2000; Mathioulakis and Belessiotis 2002; Thür et al., 2006; Oliveira, 2007). On the other hand, there are fewer publications discussing the performance of solar cooling and air conditioning systems.

Absorption chiller systems are considered as the most suitable option for solar cooling because they are compact, reliable, and can be easily integrated into different building energy systems. An absorption air conditioner or refrigerator does not use an electric compressor to mechanically pressurize the refrigerant. Instead, the absorption device uses a heat source, such as natural gas or a solar collector, to evaporate the already-pressurized refrigerant from an absorbent/refrigerant mixture. Although absorption coolers require electricity for pumping the refrigerant, the amount is small compared to that consumed by a compressor in a conventional electric air conditioner or refrigerator. It is more economical to use a solar system for both heating and cooling purposes, because implementing solar space cooling systems alone is quite expensive. Significant space heating and/or water heating can be accomplished with the same equipment used for the solar cooling system.

Lof and Tybout (1974) made an extensive study of solar heating and cooling systems for eight cities in the USA. The system has been optimized to minimize the annual energy cost. The performance of solar heating and cooling system has been studied by Nakahara et al. (1977). Their results showed that the system was able to provide all the required heating energy in the winter and 70% of the energy needed to drive an absorption chiller on a typical summer day. In Saudi Arabia, a 3.5 ton lithium bromide–water absorption chiller ($\text{LiBr-H}_2\text{O}$) system with flat plate collectors was installed and tested by Sayigh and Khoshaim (1981). Van Hattem and Dato (1981) conducted an experimental study of a solar-powered cooling system in Ispra, Italy. The overall cooling efficiency (the ratio of cooling load to total solar energy) was found to be around 11%. The feasibility of utilizing solar energy for comfort cooling in Hong Kong has been studied by Yeung et al. (1992). The system has an overall efficiency of approximately 8% and an average solar fraction of 55%.

Bruno et al. (1996) integrated an absorption chiller in a combined heat and power plant. They concluded that the absorption chiller is economically viable with the gas turbine when the chiller is used to cool the inlet air to the turbine to increase generator capacity. The half-effect absorption unit can also be used in applications where the heat source temperature is too low to be used to fire a single-effect unit (Bruno et al., 1996). Furthermore, natural night ventilation appears to be much more effective than an earth-to-air heat exchanger to improve comfort. Gordon and Choon (2000) claimed that solar mini-dish systems are able to realize net COPs of around 1.0. A further boost in net COP to around 1.4 can be achieved by modifying the conventional scheme to a thermodynamic cascade that takes maximal advantage of high-temperature input heat. The compactness and modularity of solar mini-dish systems opens the possibility for small-scale ultra-high-performance solar cooling systems.

Ciampi et al. (2003) presented an analytical method for the calculation of the energy saving achievable by using ventilated facades in which the air flow inside the air duct is due to stack effect. The influence of the variation of some quantities necessary for calculation on the energy performance of ventilated facades is investigated. In particular, the energy performance of such facades

results to be strongly influenced by the air duct width, the insulating material distribution, the solar radiation intensity, the wall outer surface thermal resistance, and the roughness of the slabs delimiting the air duct.

Breesch et al. (2005) studied passive cooling in a low-energy office building in Belgium in which natural night ventilation and an earth-to-air heat exchanger are applied. The overall thermal comfort in the office building is evaluated by means of measuring and simulation results. The evaluation shows that passive cooling has an important impact on the thermal summer comfort in the building.

A mathematical and numerical models were developed by Mesquita et al. (2006) for internally cooled liquid-desiccant dehumidifiers, using three different approaches. The variable thickness model results closely matched the experimental data available in the literature. Belarbi et al. (2006) proposed a cellular approach in which the spray is considered as a pile of rigid spheres of equal size; each sphere has multiple layers and contains a drop in its center. Their parametric studies showed the influence of each variable on the evaporation time of the droplets. The model can be used for sizing passive evaporative cooling systems and towers for buildings using the passive evaporative.

The first goal of this study is to investigate the thermal performance and the feasibility of solar system designed for space heating, domestic water heating, and cooling requirements of a typical house in Kuwait. The single-effect lithium bromide–water ($\text{LiBr-H}_2\text{O}$) absorption chiller model is based on a commercially available $\text{LiBr-H}_2\text{O}$ absorption chiller, Arkla model WF-36. The Arkla chiller has a nominal cooling capacity of 3 ton (37,980 kJ/h). In this work, transient simulation program, TRNSYS (1993) is adapted to simulate the thermal performance of different solar heating and cooling system components. The economic calculations for this study are based on life cycle savings (LCS) method (Duffie and Beckman 1991). The second purpose of this work is to assess the environmental impact of the solar heating and cooling system in Kuwait climate. The environmental impact is assessed by evaluating the annual avoided CO_2 emission attained and the reduction cost achieved when the conventional energy sources are replaced by solar heating and cooling systems.

28.2 System Description and Control Strategy

A schematic diagram of the system studied is represented in Fig. 28.1. The system consists of a solar collector, a storage tank, an absorption chiller, heat exchanger, and auxiliary units. The system operates in four different modes. When solar energy is available for collection and there is a load demand, heat is supplied directly from the collector to the heating or cooling unit. When solar energy is available for collection and there is no heat or cooling demand, heat is stored in the storage unit. On the other hand, if solar energy is not available for collection and there is a load demand, storage then supplies heat to the heating or cooling

unit. However, if storage temperature is not sufficient, the heating or cooling load is supplied by the auxiliary source.

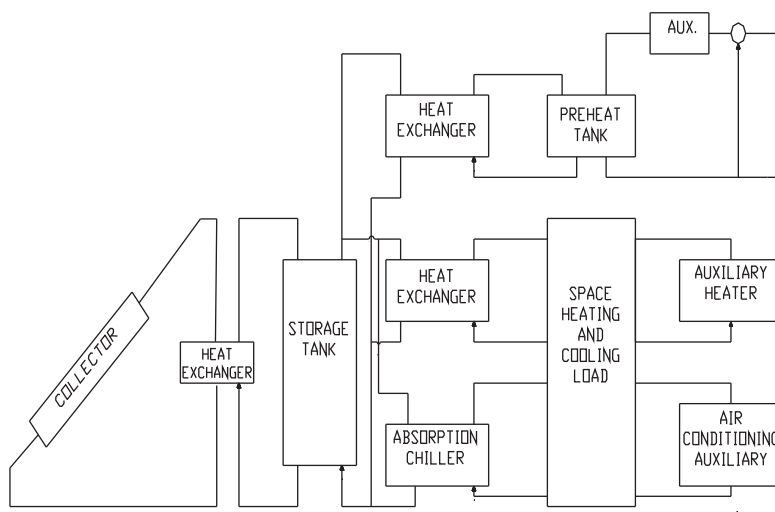


Fig. 28.1 Schematic diagram of the solar heating and cooling system.

Figure 28.2 shows a schematic of the single-effect lithium bromide water absorption chiller. The main components of the absorption unit are generator, condenser, evaporator, absorber, and low-temperature heat exchanger. The lithium bromide solution is pumped from the absorber to the generator where the water is boiled off. The heat source is passed in a counter-flow arrangement through the generator to boil off water vapor from the $\text{LiBr-H}_2\text{O}$ solution. A cooling water loop is needed to condense the water vapor boiled off from the generator and to aid in the absorption of water vapor back into the $\text{LiBr-H}_2\text{O}$ solution. This cooling water is passed first through the absorber and then through the condenser. The evaporator takes in low-pressure cold water and produces a cooling effect by evaporating the water and passing it to the absorber. The chiller model is based on a commercially available $\text{LiBr-H}_2\text{O}$ absorption chiller system, Arkla model WF-36. The Arkla chiller has a nominal cooling capacity of 3 ton (37,980 kJ/h). Units of different capacity are approximated by scaling the Arkla performance. Hot water is supplied to the air conditioner at a temperature of 87°C (minimum), 93°C (maximum), and leaves this unit 10°C cooler than the supply and returns to the storage (or to the auxiliary heater if storage is below 77°C). Whenever hot water from storage is cooler than 87°C , the auxiliary heat is supplied to raise its temperature to 87°C . When storage is cooler than 77°C , it is not used, and the auxiliary heater carries the full cooling load. The performance of air conditioning systems is expressed by their coefficient of performance (COP). COP determines how many units of cooling/heating one gets for every unit of energy he puts.

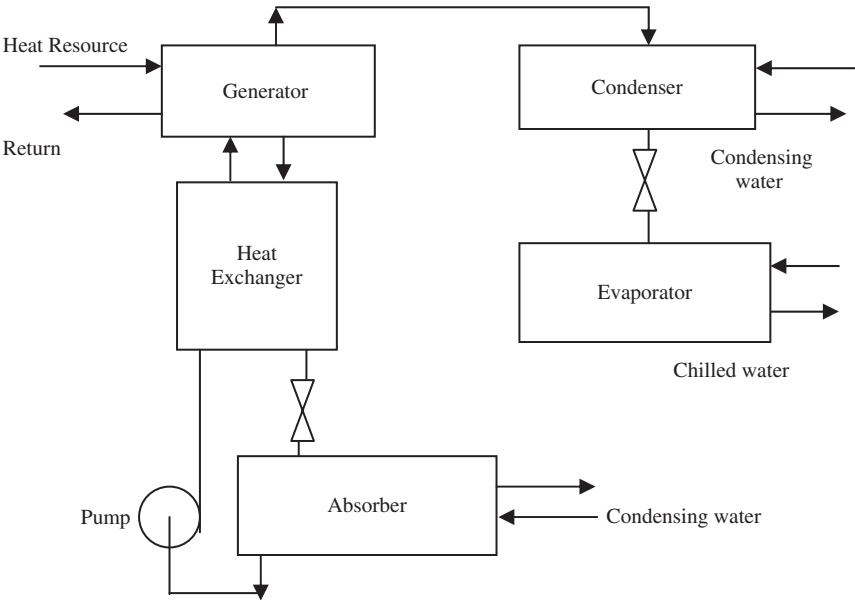


Fig. 28.2 Schematic diagram of the single-effect lithium bromide–water absorption chiller.

Table 28.1 Control Strategy for Room Thermostat.

	On-temperature (°C)	Off-temperature (°C)
Solar AC	$T_R > 24.9$	$T_R < 24.1$
Auxiliary I AC	$T_R > 25.5$	$T_R < 25.0$
Auxiliary II AC	$T_R > 26.6$	$T_R < 26.0$
Solar heat	$T_R > 19.7$	$T_R < 21.2$
Auxiliary heat	$T_R > 18.2$	$T_R < 19.6$

The coefficient of performance (COP) and the ratio of actual cooling capacity to the rated capacity (f) depend on the generator temperature and the condensing water inlet temperature. Both COP and f are found from curve fits to the Arkla WF-36 performance. The cooling tower is modeled using a constant approach to ambient wet bulb temperature. In addition, a constant COP model of a vapor compression air conditioner is included as a secondary cooling auxiliary so that the energy required to meet space cooling is provided even if the absorption machine cannot meet the full load. The control strategy and the multistage room thermostat used is shown in Table 28.1.

28.3 Theoretical Analysis

The collector efficiency, η_c , can be expressed using the well-known formula:

$$\eta_c = \frac{Q_u}{A_c G} = F_R (\tau\alpha) - F_R U_L \frac{(T_i - T_a)}{G} \quad (28.1)$$

where Q_u is the useful energy rate gained by the collector, A_c is the collector area, G is the incident radiation on horizontal surface, F_R is the heat removal factor, $(\tau\alpha)$ is the transmittance-absorbance product, U_L is the collector overall heat transfer loss coefficient, T_i is the inlet collector temperature, and T_a is the ambient temperature. The storage tank is modeled as a stratified tank (Duffie et al., 1991). The energy balance of the water in the storage tank accounts for energy gain from the collector, energy removed by the load, and energy lost to the surroundings. The equation describing these quantities is given by

$$M_s c_p \frac{dT_s}{dt} = m_c c_p (T_o - T_s) + (m_L + m_F) c_p (T_{RN} - T_s) + U_{LS} A_s (T_a - T_s) \quad (28.2)$$

of water to the service hot water system, m_F is the mass flow rate of water to the air conditioner or air heater, T_{RN} is the temperature of the combined stream of water returning from the air conditioner or air heater, and service hot water systems, U_{LS} is the storage tank heat transfer loss coefficient, and A_s is the storage tank surface area.

28.4 Economic Analysis

The cost of the conventional fuel energy is the the most important factor affecting the economic feasibility of the solar system. The economic calculations for this study are based on life cycle savings (LCS) method (Duffie and Beckman 1991). There are two variables which characterize the life cycle savings method: the duration of the analysis and the discount rate. The discount rate is defined as the rate of return which can be obtained from the best alternative investment. The life cycle savings of a solar system (LCS) over a conventional system can be defined as the difference between the reduction in fuel costs and the increase in expenses resulting from the additional investment for the solar system and is given by the following equation:

$$LCS = P_1 C_F L F_i - P_2 (C_A A_c + C_E) \quad (28.3)$$

where P_1 is the factor relating life cycle fuel cost to first-year fuel cost savings, P_2 is the factor relating life cycle by additional capital investment to initial investment, C_A is the solar energy investment cost which is directly proportional to collector area, C_E is the solar energy investment cost which is independent of collector area, C_F is the unit cost of delivered conventional energy for the first year of analysis, L is the total load, and F_i is the total solar fraction of the solar system. For a particular

locality and set of economic conditions, the economic analysis can be used to evaluate the economic feasibility of the solar system in terms of the life cycle savings. For example, optimization is made with respect to collector area to obtain the maximum life cycle savings for a given locality and a set of collector parameters. However, when two parameters were considered simultaneously, optimization was made in terms of the life cycle cost and not the life cycle savings.

A subroutine type compatible with TRNSYS is developed to calculate money savings due to using solar heating and cooling systems. The price of kW h generated by utility is constant and is equal to the tariff of Kuwait, which is subsidized by the government. It is supplied to the program on an hourly basis. The hourly load is assumed to be repeated each day and the inputs to the program are load in W and power generation. The hourly load values are read from a separate file and the output of the program is the life cycle solar savings (LCS). Life cycle solar savings is the money savings due to the use of solar heating and cooling systems. A FORTRAN program is developed based on the method proposed by Duffie and Beckman (1991) to evaluate the payback time of a solar system. The energy payback time is the minimum time it takes to recover investment costs. So, the number of years that a solar investment takes to pay off (N_p) is given by the following expression:

$$N_p = \frac{\ln \left[\frac{C_s(F-D)}{C_E - C_M} + 1 \right]}{\ln \left[\frac{F+1}{D+1} \right]} \quad \text{for } F \neq D \quad (28.4)$$

$$N_p = C_s \left[\frac{F+1}{C_E - C_M} \right] \quad \text{for } F=D \quad (28.5)$$

where C_s is the system cost, C_E is the electrical saving, and C_M is the annual operation and maintenance cost.

The gains or losses for the space heating and cooling system after a period of N years is given by

$$P = \left(\frac{1}{(D-F)} \left\{ 1 - \left[\frac{1+F}{1+D} \right]^N \right\} (C_E - C_M) \right) - C_s \quad \text{for } F \neq D \quad (28.6)$$

$$P = \left[\frac{N}{1+F} (C_E - C_M) \right] - C_s \quad \text{for } F=D \quad (28.7)$$

A positive value of P means a profit; on the other hand a negative result indicates a loss. The electrical load data are the electrical energy consumption over a period equal to the time step of TRNSYS simulation, which is at 15-min interval.

28.5 Environmental Life Cycle Assessment

Greenhouse gases that are most relevant to energy system analysis are carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O); however, CO₂ is considered the main contributor to global warming. For this reason, CO₂ emission effects are only considered in the present analysis. The amount of fossil carbon emission avoided by using a renewable resource instead of a fossil fuel power generation technology depends on the fossil fuel type that is avoided and on the conversion technology that would have been used to make the power from that fossil fuel. Replacing a higher CO₂ emitting plant with a lower or non-CO₂ emitting plant results in decreased CO₂ addition to the environment. This difference in the amount of CO₂ emitted is referred to as CO₂ avoided emission. The CO₂ emission reduction or CO₂ emission avoided is generally defined as the difference between emissions generated by conventional systems and emissions generated in the production of the solar system over the lifetime of the system (25 years). A theoretical model is developed to calculate the CO₂ avoided emission achieved by using solar heating and cooling system.

The energy generation cost (E_g) of the solar heating and cooling system in \$/kW h is calculated from the following equation:

$$E_g = \frac{C_{hc}}{P_g} \quad (28.8)$$

where C_{hc} is the annual expenses of the solar heating and cooling system (\$/year) and P_g is the annual power generation in kW h.

In the present analysis, avoided CO₂ emission (E_A) in (tonne CO₂) is mainly the CO₂ emissions which generated by conventional systems and can be expressed by the following expression:

$$E_A = P_g \times F_E \quad (28.9)$$

where P_g is the power generation (kW h) and F_E is the plant emission factor (tonne CO₂/kW h).

The cost of CO₂ gas mitigation using renewable energy technologies depends on both the difference between the generation costs of the renewable energy systems and the costs of conventional energy generation and the carbon emissions that are displaced by the renewable energy generation. The mitigation costs are usually expressed in units of the cost per unit fossil carbon emissions that are avoided.

The present model also calculates the annual reduction in CO₂ emissions estimated to occur if the proposed solar heating and cooling system is implemented instead of alternative conventional energy systems assuming that each kW h generated by solar system substitutes 1 kW h produced by the conventional energy systems. To perform CO₂ emission reduction analysis for the solar system, one needs to define the baseline (also called base case or reference case) electricity system. Often this will simply imply defining a conventional

system and its associated fuel (oil, natural gas, coal). The default emission factors and conversion efficiencies of various fuel types (Energy Information Administration, 1999) are input to the model in each case. The model can calculate the CO₂ emission reduction for each reference fuel type.

The cost associated with CO₂ emission reduction is generally expressed in \$/tonne of CO₂ avoided. The CO₂ avoided cost or reduction cost (C_R) is calculated as follows (Narula, 2002):

$$C_R = \frac{C_C - C_{hc}}{E_C - E_{hc}} \quad (28.10)$$

where C_C is the cost of kW h generated using conventional electricity system, C_{hc} is the cost of kW h generated using solar heating and cooling system, E_C is CO₂ emissions in tonne/kW h from conventional system, E_{hc} is CO₂ emissions in tonne/kW h from solar heating and cooling system. In another way around, CO₂ emission reduction cost can be calculated by dividing the annual life cycle savings of the solar heating and cooling system by the net CO₂ emission reduction per year, averaged over the system life.

28.6 System Parameters and Data

Table 28.2 shows the system parameters for the different system components.

Table 28.2 Solar system parameters.

<u>House</u>	
UA house	600 W/K
House capacitance	7000 W/K
<u>Hot water load</u>	
Daily hot water demand	210 kg/day
Demand temperature	50°C
Inlet temperature	25°C
Volume of preheat tank	0.28 m ³
<u>Flat plate collector</u>	
$F_R(\tau\alpha)$	0.68
$F_R U_L$	7.78
<u>Storage Tank</u>	
Volume	0.07 m ³ /m ²
U_{LS}	0.65 W/m ² K
<u>Solar source space heating</u>	
Mass flow rate of water	0.016 kg/s m ²
Mass flow rate of air	0.024 kg/s m ²

Auxiliary space heating

Max. rate at which heat can be provided	14,000 W
Max. temp. at which air is returned to the load	48°C

Absorption chiller with auxiliary I

Chiller cooling capacity	37980 kJ/h
Cooling tower approach	10°C
Max. useful solar source temp	75°C

Auxiliary energy to generator

Temp. of firing water delivered	92°C
Series auxiliary if solar source temp.	>85°C
Parallel auxiliary if solar source temp.	<85°C

Air conditioner auxiliary II

Capacity	7000 kJ/h
COP	2.2

Economic parameters

Cost per unit area (FPC)	\$300/m ²
Cost of transparent insulation material	\$150/m ²
Area independent cost	\$4000
Cost of conventional fuel in first year	\$0.05/kW h
Annual increase in fuel cost	6%
Period of economic analysis	25 years

28.7 Results and Discussion

The solar heating and cooling system is designed to satisfy the needs of space heating, water heating, and air conditioning loads for a family in a typical Kuwaiti house. The weather data file for Kuwait is provided by Kuwait Institute for Scientific Research (2006). The weather file contains monthly average values of daily radiation on horizontal surface, clearness index, ambient temperature, and wind speed. The weather data generator subroutine included in TRNSYS package is used to generate hourly data from the available average monthly data for Kuwait.

The thermal performance of a solar system is usually measured by the solar fraction (F). Solar fraction is defined as the fraction of load met by solar energy. Figure 28.3 shows the variation of the solar fraction of space heating (F_s), domestic water heating (F_D), and cooling load (F_{Ac}) as well as the total solar fraction (F_t) with collector area. As seen from the figure, a significant portion of the solar fraction for space heating and domestic water heating is satisfied at areas around 38 m². Conversely, the space cooling requires much greater areas.

The variation of total solar fraction, life cycle savings, and overall system efficiency (ratio of solar energy provided to the total incident radiation) with collector area is presented in Fig. 28.4. This typical figure shows the choice of optimum collector area which is approximately equal to 38 m² in this case. It is

clear from this figure that this optimum area neither corresponds to maximum system efficiency nor to the maximum solar fraction.

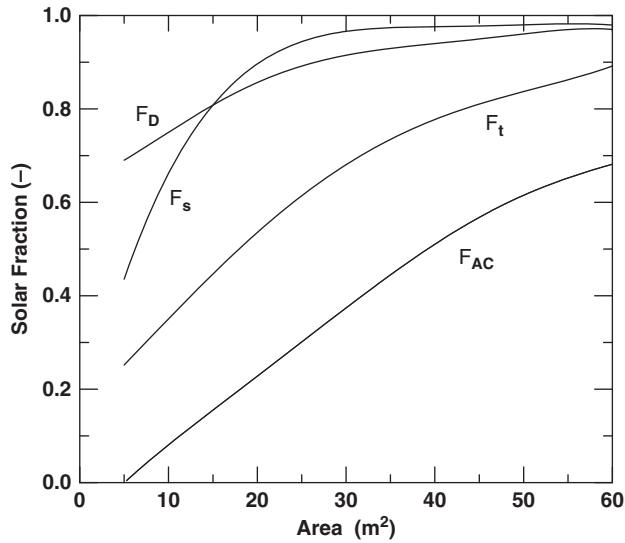


Fig. 28.3 Solar fraction variation with collector area.

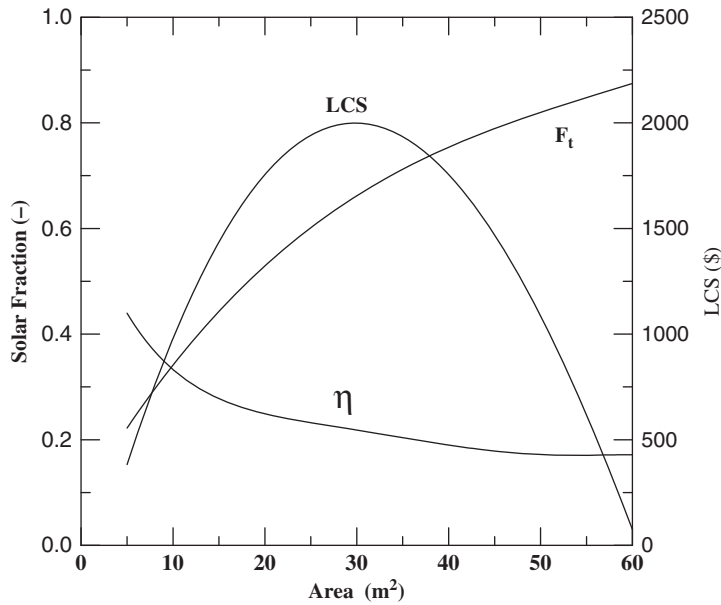


Fig. 28.4 Variation of system parameters with collector area.

Also, the total solar fraction (F_t) for flat plate solar collector satisfies a great portions of the load about 0.76. The collector efficiency (η_c) behaves the same as the system efficiency with slightly higher numerical values. Finally, the coefficient of performance (COP) of the absorption chiller is approximately 0.64 which is within the accepted practical values of the conventional lithium bromide system. The life cycle cost of the conventional and the solar system varies significantly due to the corresponding variation of the total load. The value of life cycle savings (LCS) is found to be \$1900 per year for the optimum conditions. In this study, the cost of unit energy provided by solar heating and cooling system, i.e., the cost of 1 kW h provided by the proposed solar system is about \$0.017/kW h which represents 68% of the value provided by the conventional fuel system (\$0.025/kW h). These results prove the feasibility of the solar heating and cooling systems in Kuwait climate.

The variation of annual avoided CO₂ emission with collector area is presented in Fig. 28.5. The figure again illustrates that the optimum area which maximizes the avoided CO₂ emission is 38 m². At this optimum area, the avoided CO₂ emission has been found to be approximately equal to 9.7 ton/year. This corresponds to a reduction cost of \$10.3/ton which is comparable to the values reported in the literature (Narula et al., 2002).

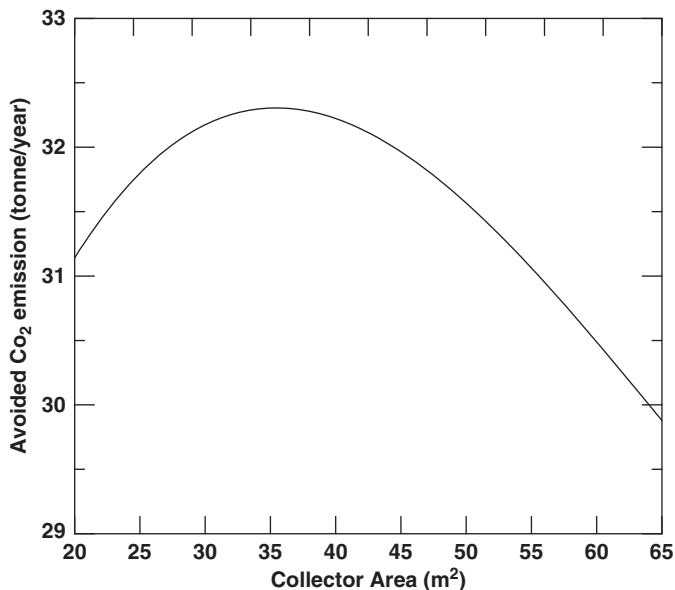


Fig. 28.5 Avoided CO₂ emission variation with collector area (azimuth angle=0).

In addition, the costs due to the application of the Kyoto Protocol, which penalizes the emissions of greenhouse effect gases, fundamentally CO₂, should be added to the costs of conventional energy resources. In spite of the fact that Kyoto Protocol is not currently applied in Kuwait, however, considering application of

this protocol will enhance the economical and environmental aspects of solar heating and cooling systems much more. Application of Kyoto Protocol will force various productive sectors specially electrical and industrial sectors to pay for CO₂ emissions making solar heating and cooling systems more feasible in Kuwait climate.

The present results should encourage governments for wide installation of solar heating and cooling systems in different applications which will reduce energy consumption of conventional fuel as proved by the results of this analysis. In addition, wide utilization of solar energy systems will help in reducing environmental pollution.

28.8 Conclusions

- Great portions of the total heating and cooling loads are satisfied by solar energy at the optimum conditions and the overall system efficiency is within the previously published results.
- The cost of unit energy for solar heating and cooling systems approximately equals to 68% of the corresponding cost of the conventional fuel at the current prices. This maximum energy is attained with a solar collector area of 38 m².
- An annual solar savings of about \$1900 is achieved at these optimum conditions which confirms the feasibility of solar heating and cooling systems in Kuwait climate.
- The avoided CO₂ emission has been found to be equal to 9.7 tonne/year corresponding to a reduction cost of \$10.3/tonne.
- The results of this study should encourage wide utilization of solar energy systems which will help in keeping our environment healthy and clean.

Nomenclature

A_c	Collector area (m ²)
A_s	Storage tank surface area (m ²)
c_p	Specific heat of the water (J/kg K)
C_A	Solar energy investment cost which is directly proportional to collector area (\$)
C_C	Cost of kW h generated using conventional electricity system (\$)
C_E	Solar energy investment cost which is independent of collector area (\$)
C_F	Unit cost of delivered conventional energy for the first year of analysis (\$)
C_{hc}	Cost of kW h generated using solar heating and cooling system (\$)
C_R	Avoided cost or reduction cost (\$)

D	Discount rate (%)
E_A	Avoided CO ₂ emission (tonne CO ₂)
E_C	CO ₂ emissions from conventional system (tonne/kW h)
E_g	Energy generation cost of the solar heating and cooling system (\$/kW h)
E_{hc}	CO ₂ emissions from solar heating and cooling system (tonne/kW h)
F_{AC}	Solar fraction of space cooling
F_D	Solar fraction of domestic water heating
F_E	Plant emission factor (tonne CO ₂ /kW h)
F_s	Solar fraction of space heating
F_t	Total solar fraction
F_R	Heat removal factor
G	Incident radiation on horizontal surface (W/m ²)
K_T	Clearness index
L	Total load (kJ)
L_{CS}	Life cycle savings (\$)
M_S	Mass of the water in the storage tank (kg)
P_1	Factor relating life cycle fuel cost to first-year fuel cost savings
P_2	Factor relating life cycle by additional capital investment to initial investmet
P_g	Annual power generation (kW)
Q_u	Useful energy rate gained by the collector (W)
T_a	Ambient temperature (°C)
T_i	Inlet collector temperature (°C)
T_o	Outlet collector temperature (°C)
T_{RN}	Temperature of the combined stream of water returning from the air conditioner (°C)
T_S	Temperature of water in the energy storage tank (°C)
U_L	Collector overall heat loss coefficient (W/m ² K)
U_{LS}	Storage tank heat transfer loss coefficient (W/m ² K)
m_C	Mass flow rate of water to the collector (kg/s)
m_F	Mass flow rate of water to the air conditioner or air heater (kg/s)
m_L	Mass flow rate of water to the service hot water system (kg/s)
w_s	Wind speed (m/s)

η_{AC}	Space cooling efficiency
η_c	Collector efficiency
η_D	Domestic water heating efficiency
η_s	Space heating efficiency
η_t	Total system efficiency
$(\tau\alpha)$	Transmittance–absorbance product

References

- Belarbi, R, Ghiaus, C, Allard, F (2006) Modeling of water spray evaporation: Application to passive cooling of buildings. *Solar Energy* 80: 1540–1552.
- Bo Nordell, B, Hellström, G (2000) High temperature solar heated seasonal storage system for low temperature heating of buildings. *Solar Energy* 69: 511–523.
- Breesch, H, Bossaer, A, Janssens, A (2005) Passive cooling in a low-energy office building. *Solar Energy* 79: 682–696.
- Bruno, JC, Fernandez, F, Castells, F (1996) Absorption chillers integration in a combined heat and power. *Solar Energy* 2: 759–767.
- Ciampi, M, Leccese, F, Tuoni, G (2003) Ventilated facades energy performance in summer cooling of buildings. *Solar Energy* 75: 491–502.
- Duffie, JA, Beckman, WA (1991) *Solar Engineering of Thermal Process*. Wiley Interscience, New York.
- Energy Information Administration (1999) Emissions of Greenhouse Gases in the United States 1998" Chapter 2, "Carbon Dioxide Emissions," DOE/EIA-0573 (98), Washington, DC.
- Garg, HP (1987) *Advances in Solar Energy Technology*. D. Reidel Publishing Company, Holland.
- Ghoneim, AA, Fisch, N, Ammar, AS, Hahne, E (1993) Design of a Solar Heating System for Alexandria, Egypt. *Renewable Energy* 3: 577–583.
- Gordon, JM, Choon, K (2000) High-efficiency solar cooling. *Solar Energy* 68: 23–31.
- Herold, KE, Rademacher, R, Klein, SA (1996) *Absorption Chillers and Heat Pumps*. CRC Press. Inc., ISBN 0-08493-9427-9
- Klein, SA, et al. (1993) TRNSYS, A Transient Simulation Program, University of Wisconsin-Madison, version 13.1.
- Kuwait Institute for Scientific Research (2006) Personal Communication.
- Lof, GOG, Tybout, RA (1974) The design and cost of optimized systems for residential heating and cooling by solar energy. *Solar Energy* 16: 9–18.
- Lunde, PJ (1978) Prediction of monthly and annual performance of solar heating systems. *Solar Energy* 20: 283–287.
- Mathioulakis, E, Belessiotis, V (2002) A new heat-pipe type solar domestic hot water system. *Solar Energy* 72: 13–20.
- Mesquita, LCS, Harrison, SJ, Thomey, D (2006) Modeling of heat and mass transfer in parallel plate liquid-desiccant dehumidifiers. *Solar Energy* 80: 1475–1482.
- Nakahara, N, Miyakawa, Y, Yamamoto, M (1977) Experimental study on house cooling and heating with solar hnergy using flat plate collector. *Solar Energy* 19: 657–662.

Narula, RG, Wen, H, Himes, K (2002) Incremental cost of CO₂ Reduction in Power Plants. Proceedings of IGTI, ASME TURBO EXPO 2002, June 3–6, Amsterdam, The Netherlands.

Oliveira, AC (2007) A new look at the long-term performance of general solar thermal systems. *Solar Energy* 81: 1361–1368.

Sayigh, MAA, Khoshaim, BH (1981) Three and a half ton solar absorption air conditioner's performance in Riyadh, Saudi Arabi. *Solar Cooling and Dehumidifying* Pergamon Press, Oxford.

Thür, A, Furbo, S, Shah, LJ (2006) Energy savings for solar heating systems. *Solar Energy* 80: 1463–1474.

Van Hattem, D, Dato, PA (1981) Description and Performance of an Active Solar Cooling System Using an LiBr-H₂O absorption machine. *Energy and Buildings* 3: 169–196.

Yeung, MR, Yuen, PK, Dunn, A, Cornish, LS (1992) Performance of a Solar Powered Air Conditioning System in Hong Kong. *Solar Energy* 48: 309–319.

Steam Network Optimization by Utilizing Biomass and Solar Energy Sources in an Oil Refinery

M. Hassan Panjeshahi, Lena Ahmadi and Simon Perry

29.1 Introduction

Greenhouse gases (GHG) emissions from fossil fuel combustion in industrial processes contribute significantly to global warming. A reduction in GHG emissions can only be achieved by a conversion to renewable energy sources and a simultaneous increase in energy efficiency; therefore, the application of renewable energies for evaluating the site utility systems and environmental aspects should be considered. Site utility systems involve complex interactions. For improving the systems, a structured approach is needed. Steam generators are important components of site utility systems that affect the thermal performance of chemical and petrochemical industry processes.

In an oil refinery, steam is available at different pressures and temperatures. Some processes use steam while others generate steam. There are interactions between the processes and the utility system via steam use and generation. There are also interactions between the processes on the site through the steam mains (Smith, 2005). Heat demands of the plant for generating steam are generally extremely high. The steam is usually supplied by two sources, the boiler station and the power plant which are generally fed by fossil fuels. However, using these conventional fuels is not a long-term and proper option due to the importance of global warming problem and energy crisis. Several policies are proposed to limit net GHG emissions. A key example is the Kyoto Protocol. Each country's emissions target must be achieved by the period 2008–2012. For example, industrialized countries have committed to cut their combined emissions to 5% below 1990 levels by 2008–2012. The three main gases are carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O).

To overcome the above drawbacks, renewable energies can be integrated into plant for generating steam. Renewable energy offers important potential benefits. Solar energy as the abundant resource has a viable option for consumption

that can free up larger quantities of oil. Moreover, there is growing recognition that alternative use offers environmental benefits in the form of reduced air pollution and emissions of GHG. Because of the concern over global warming, there is considerable worldwide interest in increased utilization of renewable energy sources, including biomass fuels. Biomass not only has considerable potential as a fuel source, it also shows a reasonable cost level in comparison to other renewable energies (Gera et al., 2002). It can be regarded as a local energy source with ecological and regional contributions (Urban et al., 2007). Municipal Solid Waste (MSW) as the proper fuel can be used. Also in the country, the related government organization pays \$12 per ton to the refinery for the bought MSW because of solving the accumulation problem of the garbage. This will decrease the operational costs.

In this chapter, renewable energies are studied for generating steam in the Tehran Oil Refinery by a modern method based on pinch technology. Pinch Technology is a methodology comprising a set of structured techniques for systematic application of the first and some aspects of second laws of thermodynamics. The application of these techniques enables process engineers to gain fundamental insight into the thermal interactions between chemical processes and the utility systems that surround them (Polley and Panjeshahi, 1991). To achieve this aim turbine hardware model, boiler hardware model, and related balances on system components are investigated. The sustainable energies, solar, and biomass are then replaced considering the steam levels properties such as temperatures and pressures. To accomplish the feasible replacement, integration techniques are applied. Simulation and optimization are organized at STAR environment and related coding is done at MATLAB 7.3.

29.2 Steam Network Description

In a steam network system steam levels are specialized through various pressures and temperatures. To investigate the existing steam network, selection of steam levels and determination of the configuration of the operating units between the steam levels are important (Harrell, 2001). To achieve the task, a model is required. This model should allow for the steam generation potential.

29.2.1 Turbine hardware model

Turbine hardware model, THM, is based on shaft work targeting and relies on the principle of the Willans line which provides a linear relation between the steam flow rate (M_t) and the turbine output power (E). The formula of this relation is represented via Eq. (29.1) and the Willans line can be expressed as Eq. (29.2) (Mavromatic and Kokossis, 1998).

$$M_t = mE + C \quad (29.1)$$

$$E = nM_t - E^{loss} \quad (29.2)$$

As shown in Fig. 29.1 point A is the minimum steam flow rate needed to overcome the internal losses, E^{loss} , of the turbine before it starts producing total work. This amount of steam corresponds to constant point C. Point B also represents the maximum steam flow rate that the turbine can take (Mavromatic and Kokossis, 1998).

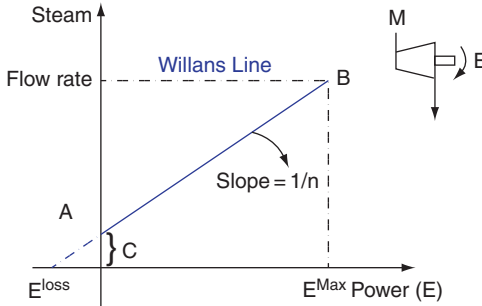


Fig. 29.1 The operation of turbine present by Willans line (Mavromatic, 1998).

29.2.2 Boiler hardware model

Boiler hardware model, BHM, accounted for boiler efficiency to minimize the fuel cost. Moreover, BHM relies on the principle of the calculation of boiler efficiency. Most of boiler models assume boiler efficiency as a constant. For steam networks analysis, model should be capable to account real condition of boilers. BHM is based on efficiency calculation procedure that is expressed by Eq. (29.3). Steam load can be expressed as Eq. (29.4) (Shang and Kokossis, 2004):

$$Q_{\text{fuel}} = Q_{\text{loss}} + Q_{\text{steam}} \quad (29.3)$$

$$Q_{\text{steam}} = (h_2 - h_1) \times M_b \quad (29.4)$$

where h_1 is the boiler inner water enthalpy, h_2 is the enthalpy of steam raised by boiler and M_b is the steam load produced by the boiler. Figure 29.2 shows the variation of boiler temperature versus enthalpy. As per thermodynamic principle the enthalpy difference can be written by Eq. (29.5). The boiler efficiency is expressed via Eq. (29.6) and Eq. (29.7) (Shang and Kokossis, 2004).

$$h_2 - h_1 = (C_p \times \Delta T_{\text{sat}}) + q \quad (29.5)$$

$$\eta = Q_{\text{steam}} / Q_{\text{fuel}} \quad (29.6)$$

$$\eta = ((C_p \Delta T_{\text{sat}} + q) \times M_b) / Q_{\text{fuel}} \quad (29.7)$$

By substituting above equations, the fuel heat is illustrated by Eq. (29.8).

$$Q_{\text{fuel}} = (C_p \Delta T_{\text{sat}} + q) \times M_b + Q_{\text{loss}} \quad (29.8)$$

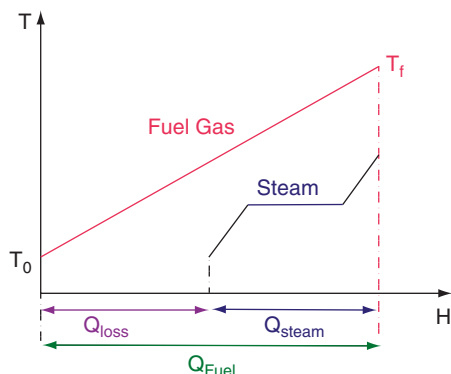


Fig. 29.2 Boiler $T-H$ diagram (Shang and Kokossis, 2004).

29.3 Solar and Biomass Integration to Steam Network

Process integration is a systematic approach that looks at the unity of the holistic system rather than individual units and streams that make up the process. This technique emphasizes on analyzing the overall picture and system insights first and then delving into the details of equipment, simulation, and other details (Mohan, 2005). The integration using pinch analysis technology helps in better understanding of the interactions in the system and results in sound decisions of the performance. The concept of energy integration is aimed at minimizing the energy demands of the process. This is a rigorous and structured approach for identifying the capable opportunities for replacing the alternatives, solar and biomass, considering their temperatures and pressures. This technique helps in minimizing fossil fuel consumption.

Solar thermal energy can be integrated with the supply system or directly at the process level. The integrated solar plant concept was initially proposed by Luz Solar International as a means of integrating parabolic trough solar plant with modern combined cycle power plants. A plant schematic diagram is shown in Fig. 29.3 (Kelly, 2001). The integration of solar thermal energy can be influenced by several factors as shown in Table 29.1 (Schnitzer et al., 2007). Solar thermal stations could also become an interesting way to reduce the environmental impact of energy generation with reasonably economic conditions (El-Sayed, 2005).

Utilizing biomass as a fuel in utility systems supplies heat demand in units of MW. The average majority of biomass energy is produced from wood and wood wastes (64%) followed by solid waste (24%), agricultural waste (5%), and landfill gases (5%) (Demirbas, 2000). Many processes with steam demands can benefit from biomass boilers. In comparison to commonly used boiler types, biomass boilers have a different construction. Compared to gas boilers with the same capacity they are bigger and their dynamic characteristics are not as good. For these reasons, it is advised to operate these boilers in a stable mode without sudden variations. This is possible, when biomass boiler covers only base demand. In

this case, the boiler is operated in a long-term steady state and produces majority of the overall heat. In MSW production plant, the designed biomass boiler capacity is very important (Urban et al., 2007). Figure 29.4 shows elements of a typical energy system by biomass integration (Schnitzer et al., 2007).

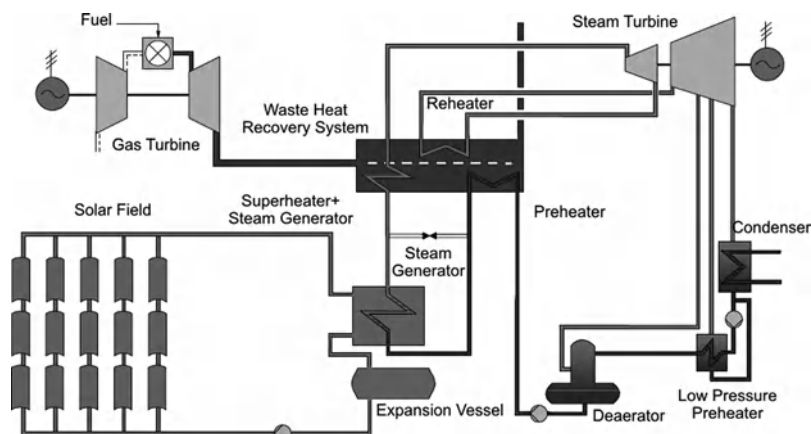
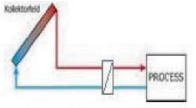
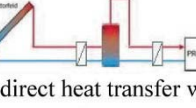


Fig. 29.3 Integrated solar plant schematic diagram.

Table 29.1 System concept of the integration of solar energy.

System	Storage	Heat demand	Heat transfer medium	Type of collector
 Direct heat transfer	No	Always much higher than solar fraction	Air	Air collectors
			Water	Flat plate and vacuum tube collector
			Steam	Parabolic trough collector
 Indirect heat transfer	No	Always much higher than solar fraction	Primary: water, water + glycol, thermo-oil Secondary: air, water, steam	Flat plate and vacuum tube collector
 Indirect heat transfer with storage	Yes	The same or higher than solar fraction	Primary: water, water + glycol, thermo-oil Secondary: air, water, steam	Flat plate and vacuum tube collector

Source: Schnitzer et al. (2007).

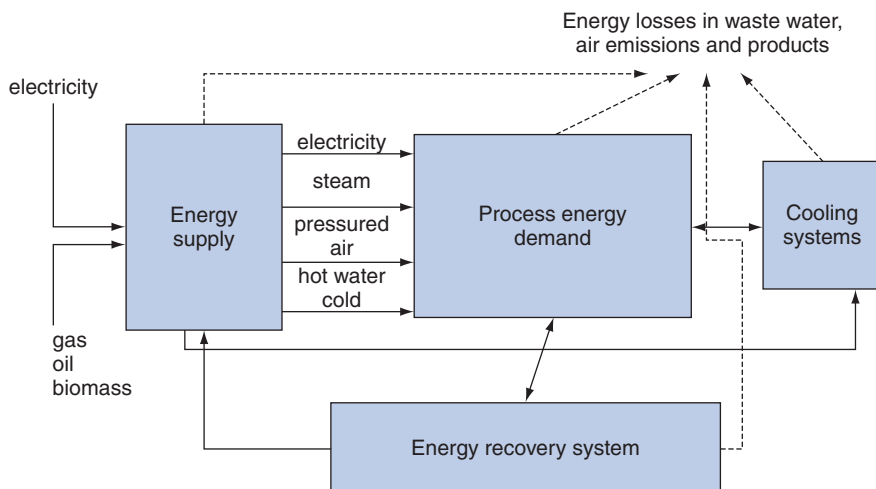


Fig. 29.4 Elements of a typical energy system by biomass integration.

29.4 Optimization Methods

Process optimization is placed to provide an economic, energy, and environmental evaluation of the steam network. The role of process optimization is to strike a proper balance between the holistic approach used in process synthesis and the deterministic approach used for process analysis. The goal of optimization is to identify the best performance of the system which satisfies the overall performance criterion while meeting all the design objectives (Mohan, 2005). This study deals with the optimization of steam-supply systems under variable energy demand. After steam network simulation in STAR software, the steam network must be optimized. This optimization programs can broadly be classified as follows:

1. Linear Programs (LP) at fixed header conditions
2. Nonlinear Programs (NLP) when header condition is allowed to vary

To drastically reduce the complexity of the optimization method developed requires thorough understanding of the unique combinatorial properties of the system in terms of process structures.

29.5 Process Description

Tehran Oil Refinery was established in 1974 by an American company (FLUOR) that involves two similar plants, northern and southern refinery. The steam networks in two oil refineries are similar. A 0.4064 m diameter, 44.8 bar pressure and a 0.2032 m diameter, 4.1 bar pressure steam lines interconnect the north and south refinery steam systems to provide operational flexibility and assist in the start-up of north refinery. In this regard northern refinery steam network is simulated.

There are four boilers which provide 266.4 t/h high pressure steam at 44.8 bar. These headers involve high pressure (44.8 bar), medium pressure (20.68 bar), and 4.1 bar. The high-pressure steam distribution system has let down stations to provide the refinery with 20.68 and 4.1 bar steam. The 44.8 bar steam is used primarily as the energy source to drive three 7500 KW condensing type turbine generators and other back pressure and condensing turbine drives throughout the refinery. The refinery is independent of any outside power supply and facilities are therefore designed to meet all energy requirements for continuous operation of the refinery. Also two condensate headers, hot and cold condensate, are applied at 100°C and 125°C.

Twenty-two steam turbines drivers between HP, MP headers are applied. They do not produce power but they are connected to pumps and compress each other. There are 21 steam consumers and 9 steam producer at different level of steam which connected to different headers. The deaerator must be continuously vented to insure proper deaeration and removal of the non-condensable gases. Also the temperature of the water in the deaerator storage space must be at the saturation temperature corresponding to 0.34 bar. In this plan as it shown in Fig. 29.5, the bigger turbines are steam turbines and the small turbines are steam-only driver turbines. In addition the green color shows deactivate plans. Also the red arrows display steam consuming process and the blue arrows steam producing processes. Table 29.2 indicates the name of process which is connected with steam network in northern refinery (Khodaie and Nasr, 2008).

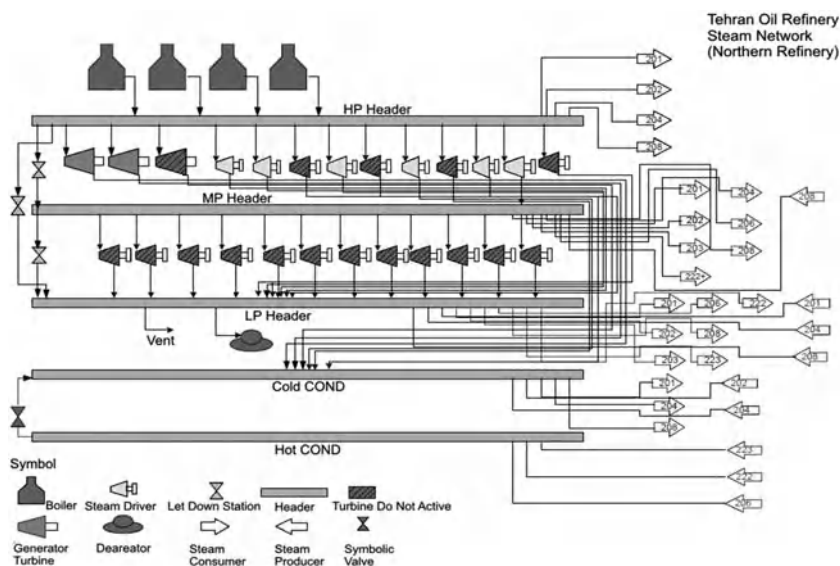


Fig. 29.5 Tehran oil refinery steam network.

Table 29.2 Steam consumer and producer plants in the oil refinery.

NO	Consumer	NO	Producer
201	Crude, vacuum	201	Crude, vacuum
202	Unifier platform	202	Unifier platform
203	Visbreaker	203	0
204	Isomax	204	Isomax
206	LPG unit	206	LPG unit
207	Nitrogen plant	207	0
208	Hydrogen plant	208	Hydrogen plant
216	H ₂ S removal	216	0
223	Tankage	223	Tankage
221	Power station	221	Power station
221	Let-down	221	Let-down
222	Building	222	Building
222	Losses	222	Losses

Source: Khodaie and Nasr (2008).

29.5.1 Scenarios

Four scenarios are suggested in Table 29.3. The first scenario is the base case and the three others are the suggested ones for steam network optimization by replacing renewable energies. The second scenario, Steam Generation by Biomass (SGB), generates MP and LP steam. In the third scenario, Steam Generation at Different levels via Biomass and Solar (SGDBS), the solar generates LP steam and the biomass is replaced for MP steam generation. The fourth scenario, Steam Generation at Same level by Biomass and Solar (SGSBS), is the partial generation of LP steam. It is noted that the processes which can be fed are Unifier plant, Nitrogen plant, Visbreaker, Isomax, LPG, and hydrogen units.

Table 29.3 Suggested scenarios.

Scenario	Description
Base Case	Steam generation through four boilers
SGB	MP and LP steam generation through biomass energy
SGDBS	MP steam generation by biomass and LP steam generation via solar energy
SGSBS	LP steam generation through biomass and solar energies partially

29.6 Results and Discussion

The solar and biomass energies in refineries are utilized as the approximately GHG-free alternatives. The optimization through replacing the solar and biomass is done. The amount of CO₂ and SO₂ reduction through the discussed scenarios is presented in Table 29.4. The results reveal that the SGDBS scenario and SGB scenario achieved the maximum and minimum emission reduction in comparison to the other cases.

Figure 29.6 shows the capital cost comparison of the discussed scenarios. It is shown that the SGB scenario has achieved minimum capital cost and SGDBS scenario has accomplished maximum capital cost.

Table 29.4 Emission reduction.

	CO ₂ reduction (ton/year)	SO ₂ reduction (ton/year)
SGB	2573.15	4.29
SGDBS	3648.30	10.58
SGSBS	3330.07	8.74

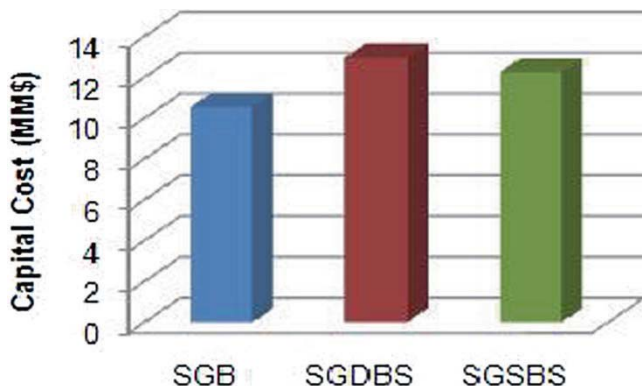
**Fig. 29.6** Capital cost comparison of the discussed scenarios.

Table 29.5 presents the operating cost, energy saving, and payback period of each scenarios. The operating cost of biomass replacement consisted of electricity cost, auxiliary material cost (petrol, chemicals), maintenance cost, water and wastewater disposal cost, and disposal of residual inert material cost. The solar replacement operating cost is included of electricity cost and maintenance cost.

Table 29.5 Total operating cost, energy saving, and payback period of each scenario.

Scenario	Total operating cost (\$/year)	Energy saving (%)	Payback period (year)
Base Case	99,532,524	—	—
SGB	89,857,084	10.25	6.35
SGDBS	89,658,233	10.25	7.81
SGSBS	89,792,267	10.25	8.49

It is noted from the result that the SGDBS scenario has achieved the minimum total operating cost of \$89,658,233/year and the payback period of 7 years and 10 months. However the SGB scenario, which used biomass for replacing, has accomplished the minimum payback period of 6 years and 4 months. As shown in Table 29.5, the total operating cost achieved through SGB is higher than the SGDBS and SGSBS scenarios. It is because of simultaneous replacement of solar and biomass energies in the steam network system. It is shown that the optimum case is the SGB scenario which achieves minimum capital and operating cost. Furthermore, among all suggested scenarios, the SGDBS case achieved maximum emission reduction. It is noted that there is a trade-off between the payback period and emission reduction.

29.7 Conclusions

Steam network optimization is done through replacing biomass and solar energies in Tehran oil refinery. To achieve this aim, a steam network model is introduced. This model allows interactions between the steam sources and consumers to be explored. Having considered solar and biomass energies for generating steam the model is further improved. Three scenarios are investigated to achieve minimum total cost and payback period. In the suggested scenarios, different opportunities for integrating purposes are considered and the optimum case is selected. From this study we can extract the following remarks:

- The results of steam network optimization have indicated 10.25% energy saving and approximately \$10 million operating cost saving per year.
- Application of integrating alternatives in refinery resulted in ecological benefits. High emission reduction of CO₂ and SO₂ is achieved.
- For making decision of the best case, existing trade-off between payback period and emission reduction should be considered.

The investigation of the discussed scenarios reveals that considering the economical aspect, the SGB scenario has achieved minimum payback period. However, on the basis of environmental issue, the SGDBS scenario has accomplished minimum emission.

Nomenclature

A	minimum steam flow rate, kg/s
B	maximum steam flow rate, kg/s
C_p	specific heat, J/kg°C
E	turbine output power, W
h_1	enthalpy of boiler inlet water, kJ/kg
h_2	enthalpy of steam raised by boiler, kJ/kg
H	Enthalpy, kJ/kg
HP	high pressure
LP	low pressure
M	Incremental steam flow rate, s ² /m ²
M	flow rate, kg/s
MP	medium pressure
MSW	Municipal solid waste
N	inverse incremental steam flow rate, m ² /s ²
Q	specific heat load of steam, kJ/kg
Q	heat load, W
SGB	steam generation by biomass
$SGDBS$	Steam Generation at Different levels via Biomass and Solar
$SGSBS$	Steam Generation at Same level by Biomass and Solar
T	temperature, °C

Greek Letters

Δ	difference
H	efficiency, %

Subscripts

B	boiler
T	turbine
F	fuel gas
Sat	saturated

References

- Demirbas, A (2000) Biomass resources for energy and chemical industry. *Energy Edu Sci Technol* 5:21–45.
- El-Sayed, MA H (2005) Solar supported steam production for power generation in Egypt. *Energy Policy* 33:1251–1259.
- Gera, D, Mathur, MP, Freeman, MC, Robinson, A (2002) Effect of large aspect ratio of biomass particles on carbon burnout in a utility boiler. *Energy Fuels* 16:1523–1532.
- Harrell, G (2001) *Steam Survey Guidebook*. U.S. Department of Energy (DOE).
- Kelly, B, Herrmann, U, Hale, MJ. (2001). Optimization studies for integrated solar combined cycle systems. *Solar Energy: The Power to Choose*, ASME Forum. Washington, DC.
- Khodaie, H, Nasr, MRJ (2008) Optimization of Steam Network In Tehran Oil Refinery. International Conference of IETC, Texas Engineering Experiment Station. Texas A&M University.
- MATLAB software, version 7.3.
- Mavromatic, SP, Kokossis, AC (1998) Conceptual optimization of utility networks for operational variations. I. Targets and level optimization. *Chemical Engineering Science* 53:1585–1608.
- Mohan, T (2005) An Integrated Approach for Techno-Economic and Environmental Analysis of Energy from Biomass and Fossil Fuels. MSc. Dissertation. Texas A&M University
- Polley, GT, Panjeshahi, MH (1991) Interfacing heat exchanger network synthesis and detailed heat exchanger design. *Trans I Chem E*. 69:445–457.
- Schnitzer, H, Brunner, C, Gwehenberger, G (2007) Minimizing greenhouse gas emissions through the application of solar thermal energy in industrial processes. *Journal of Cleaner Production* 15:1271–1286.
- Shang, Z, Kokossis, A (2004) A transshipment model for the optimization of steam levels of total site utility system for multi-period operation. *Computers and Chemical Engineering* 28:1673–1688.
- Smith, R (2005) *Chemical Process Design and Integration*. West Sussex: John Wiley & sons Ltd.
- STAR Software, Department of Process Integration, UMIST, Manchester (2005). This product licensed to K.N. Toosi University of Technology, Energy system Laboratory, Department of Mechanical Engineering, Tehran, Iran.
- Urban, L, Masa, V, Pavlas, M, Stehlik, P (2007) Novel type of technology for biomass utilization. *Chemical Engineering Transactions* 12:465–470.

Calculation of Global Solar Radiation Based on Cloud Data for Major Cities of South Korea

Hochun Yoo, Kwanho Lee, Sohee Park and Kyoung Hwan Noh

30.1 Introduction

Energy consumption causes a range of environmental pollution. Furthermore, with the increase in energy demand, the issue of energy shortage becomes increasingly serious. Since there is more and more concern on energy conservation and environmental protection, interest has been increasingly focused on the use of renewable energy. This is considered as a key source for the future, not only for South Korea but also for the world (Ulgen and Hepbasli, 2002). Especially, solar energy as a clean energy source and one kind of renewable energy is abundant in South Korea. Therefore, the precise measurement of the local solar radiation is required.

Also, the solar radiation data are a fundamental input for solar energy applications such as photovoltaics, solar thermal systems, and passive solar design. The data should be contemporary, reliable, and readily available for design, optimization, and performance evaluation of solar technologies for any particular geographical location (Bulut and Buyukalaca, 2007).

Unfortunately, these sites, however, are mainly concentrated in the developed countries and are scarcer within the developing world. Even where measured data are available for a given region, the data become less accurate the further away the location of implementation for use of solar energy is from the measuring station (Younes and Muneer, 2006). So far, a number of formulas and methods have been developed to estimate daily or monthly global radiation at different places in the world. The availability of meteorological parameters, which are used as the input of radiation models, is the important key to choose the proper radiation models at any location. Among all such meteorological parameters, cloud cover and bright sunshine hours are the most widely and commonly used ones to predict daily global solar radiation and its components at any location of interest (Sabziparvar, 2007). The two synoptic parameters (cloud cover and sunshine duration) provide an approximate means for generating those solar

radiation data that are missing from a time series or have clearly been identified as being suspect. There are advantages as well as disadvantages in the use of cloud cover as a means for estimating solar irradiation (Muneer and Fairrooz, 2002).

The aim of this research is the estimation of the solar radiation of four cities (Seoul, Busan, Daejeon, Gwangju) by using cloud cover data. One of the parameters employed, cloud cover, is widely available from multiple regional and national weather stations. In Korea, while the amount of clouds is measured at all of the 42 locations of weather station, solar radiation is measured at just 22 stations. Kasten and Czeplak (1979), and Muneer and Gul (2000) have proposed cloud-based models for the estimation of global horizontal irradiance. For this, solar radiation data are produced from four regions (the regions make meteorological observations about solar radiation and cloud cover) through an equation by the cloud cover. And a correlation between measurement and calculated data is compared. Solar radiation data of the Ulsan area (the regions make meteorological observations about cloud cover) are produced based on the calculated value. This is for evaluation of the effect of distance on solar radiation estimation in non-measured area by substituting four coefficients from different areas for Ulsan's.



Fig. 30.1 The region of South Korea.

30.2 Measured Data

The data of major cities of South Korea used 20 years (1986–2005). All meteorological and solar radiation data that are used in this study have been measured at the Korea Meteorological Administration (KMA).

Seoul and other three regions are among the solar measured areas and Ulsan is not. This study involves four regions of Korea and compares the figures from each region; the solar radiation estimations apply the original coefficient substitution method which Kasten and Czeplak (1979) suggested for the estimation of Hamburg, Germany (1964–1973); solar radiation estimated from the solar altitude and amount of clouds actually measured solar radiation. In addition, through the estimated solar radiation coefficient from this process, coefficients from four different cities – of which distances are all different as you can see in Figure. 30.1–were substituted for Ulsan’s to estimate the City’s solar radiation.

Table 30.1 Five data sets from South Korea.

Regions	Latitude (°N)	Longitude (°N)	Altitude (m)	Data measured at the KMA	
				Solar radiation data	Cloud cover data
Seoul	37.34	126.58	85.5	O	O
Busan	35.06	129.02	69.2	O	O
Daejeon	36.18	127.24	77.1	O	O
Gwangju	35.08	126.55	70.9	O	O
Ulsan	35.33	129.19	31.5	X	O

30.2.1 Cloud cover (CC)

Korea began to measure its cloud amount since 1904 when it established contemporary weather stations. Currently, central meteorological office, 5 regional offices and 36 weather stations, in total 42 stations serve this purpose. Even today observer’s eyes are the tools for this job. Hourly CC data recorded during the 20-year period from 1986 to 2005 within the daytime were gathered for the analysis. Cloud cover data are provided as 3-hour interval, 10 divided method in data provided in KMA. Therefore, in this research, this was converted for the use of the equation used in the preceding research and comparison of data. Data of 3-hour interval produced data through the linear interpolation 1 hour. And 10 divided methods were converted to 8 divided methods (Octas). Skies without any cloud (0 Octas) and heavily covered with cloud (8 Octas) were defined as clear and overcast, respectively. Sky conditions with CC between 1 and 7 Octas were considered partly cloudy.

Hourly CC data from the 20-year measurements were analyzed and the frequency of occurrence is shown in Fig. 30.2. A peak of over 23% is observed at a value of 0 Octas. The second most frequent cloud cover is 8 Octas, accounting

for 22%, 21%, respectively. At round 5%, 3 Octas is the least frequent CC. These suggest that the overcast and clear sky conditions occur almost 21%, 23%, respectively, of the time. For the rest of the time (i.e., 65%), partly cloudy sky conditions prevail (Younes and Muneer, 2006; Danny and Joseph, 2001).

In addition, the average amount of clouds in Seoul and three other regions, and Ulsan, which this study decided to compare, was observed as similar between Ulsan and Busan, and Seoul and Daejeon, respectively. However, Gwangju reported relatively larger average amount. I think it is needed to review whether these similar amounts of clouds in Busan and Ulsan have any influence on solar radiation of the two cities, which are in relatively close range.

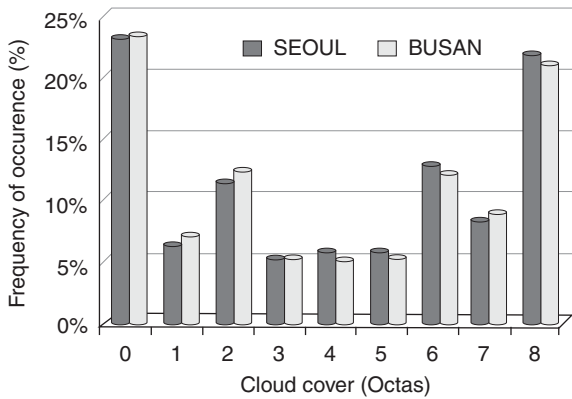


Fig. 30.2 Frequency of occurrence of cloud cover (Seoul and Busan).

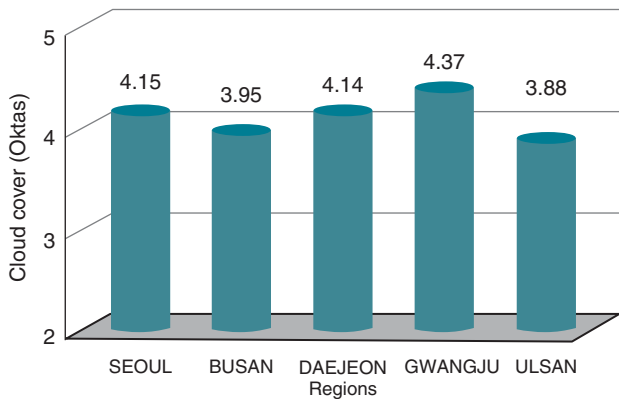


Fig. 30.3 Average of cloud cover.

30.2.2 Solar radiation

Korea introduced silver-disk pyrheliometer into Incheon Observatory with the beginning of Second International Polar Year (IPY) in 1932 to observe atmospheric turbidity, transmissivity, and direct solar radiation. Korean solar radiation observatory network was expanded to 11 direct solar radiation observatories and 3 horizontal solar radiation observatories.

This was interrupted by the Korean War in 1950 and then resumed on January 1, 1957, with the financial support from ICA, into nationwide solar radiation observatory network. Concerning global solar radiation observation, the Meteorological Equipment Modernization Plan has achieved synoptic meteorological observation system completely established in 1999 with horizontal pyrheliometers in a total of 22 stations: central office, 5 regional offices, and 10 weather stations which were designated as climate observatory (Climatic Policy Department, 2004). Like this, solar radiation observation is conducted only in fewer regions compared to the amount clouds of observed.

30.3 The Cloud Cover Radiation Model (CRM)

Kasten and Czeplak formulated equations for the estimation of solar irradiance based on cloud cover information. For their research, Kasten and Czeplak (1979) used 10-year periods from 1964 to 1973 of continuous hourly data from Hamburg, Germany. They also validated their model using German and UK data sets, thus, the coefficients they provide are from German and UK regional climatology. Initially they proceed by calculating the global horizontal irradiance under clear sky conditions I_{GC} , and then the global and diffuse horizontal irradiances are calculated.

$$I_{GC} = 910 \sin \alpha - 30 \quad (30.1)$$

The ratio of global radiation I_G for a given cloud amount N okta, to I_{GC} has been shown to be independent of the solar elevation, r ,

$$I_G = I_{GC}(1 - 0.75(N/8)^{3.4}) \quad (30.2)$$

The diffuse component is calculated as follows:

$$I_D = I_G(0.3 + 0.7(N/8)^2) \quad (30.3)$$

Gul and Muneer (1998) and Muneer and Gul (2000) furthered the work of Kasten and Czeplak to provide equations that can accommodate local coefficients for their data sets, as the original coefficients could not accurately estimate the irradiance in their analysis. The Kasten and Czeplak equations. (30.4–30.5) have

been modified while Eq. (30.6) remains the same in both models. Equations (30.4–30.5) become as follows:

$$I_{GC} = A \sin \alpha - B \quad (30.4)$$

$$I_G = I_{GC}(1 - C(N/8)^D) \quad (30.5)$$

The coefficients of above formula (A , B , C , and D) are applied from estimated coefficient from this study on Seoul, Busan, Gwangju, and Daejeon.

30.4 Results and Discussion

Calculate the global radiation of four cities (Seoul, Busan, Daejeon, Gwangju), where the global radiation is currently measured, by using the cloud amount data. For this, the coefficient of each location needed for global radiation calculation using the altitude of the sun and the cloud amount data in four cities has to be obtained. The global radiation calculated by applying the coefficient of each area will be compared with the global radiation actually measured.

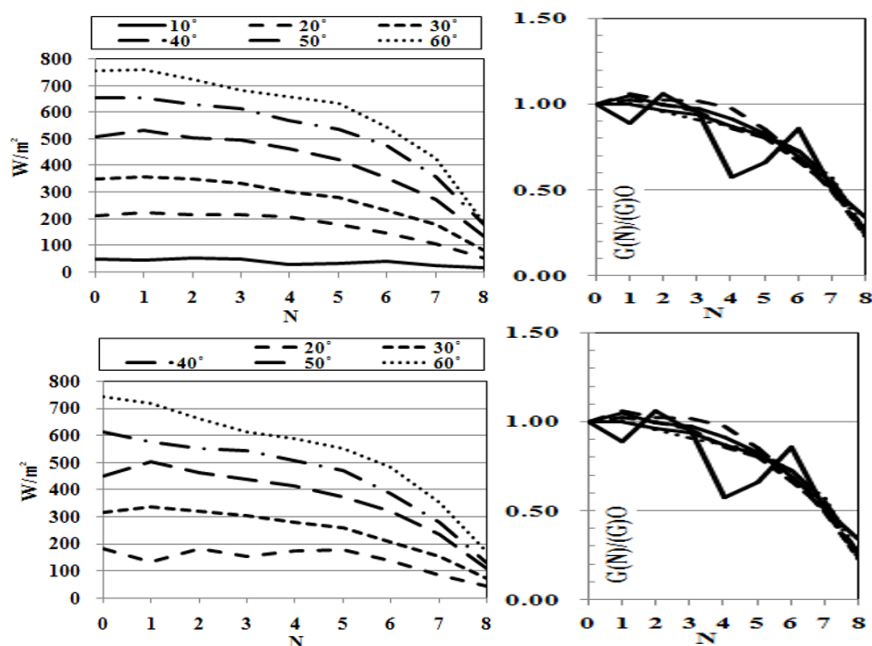
30.4.1 Function of cloud amount and solar altitude for global radiation

Solar radiation coefficient was estimated using clouds amount and solar altitude from the four cities, of which solar radiation is currently measured. The data were first grouped into four seasons: March, April, May (spring), June, July, August (summer), September, October, November (autumn), and December, January, February (winter).

Within each season, the hourly values were assorted into classes of equal mean hourly solar elevation γ by intervals of $\Delta\gamma = 10^\circ$. The radiation data within each of these classes were then assorted according to total cloud amount N . Since the radiation data are hourly sums whereas the cloud are momentaneous observations at the end of the respective hour, only such cases were admitted when the reported cloud amount at the forgoing hour was identical to the hour under consideration (Kasten and Czeplak, 1979).

The clouds amount and solar radiation changes with the solar altitude are shown in Figs. 30.4–30.7. For Seoul, $G(N)/G(0)$, the proportion of clouds amount to change of solar radiation in cloudless day was observed increased from clouds amount $N=1$ octa and then decreased to the point of $N=5$ octa. And at the point of $N=8$ octa it fell to approximately 0.25. In Busan, Gwangju, and Daejeon, $G(N)/G(0)$ increased from the point of $N=1$ octa and then decreased to 0.23, 0.28, and 0.25 respectively, at the point of $N=8$ octa, which was similar to that of Seoul.

The overall changes of solar radiation with the clouds amount and the solar altitude over 20 years (1986–2005) were observed as large in $\gamma=10^\circ$, but in other solar altitude, it showed a gentle decrease. Also, global radiation under cloudless and overcast sky, $G(0)$ and $G(8)$, respectively, is plotted vs. $\sin r$. Multiple reflection between atmosphere and snow covered-ground and less turbidity is supposed to be responsible for the slightly higher winter and spring values. On the yearly average, 20–30% of the incoming global radiation is transmitted through overcast (Kasten and Czeplak, 1979).



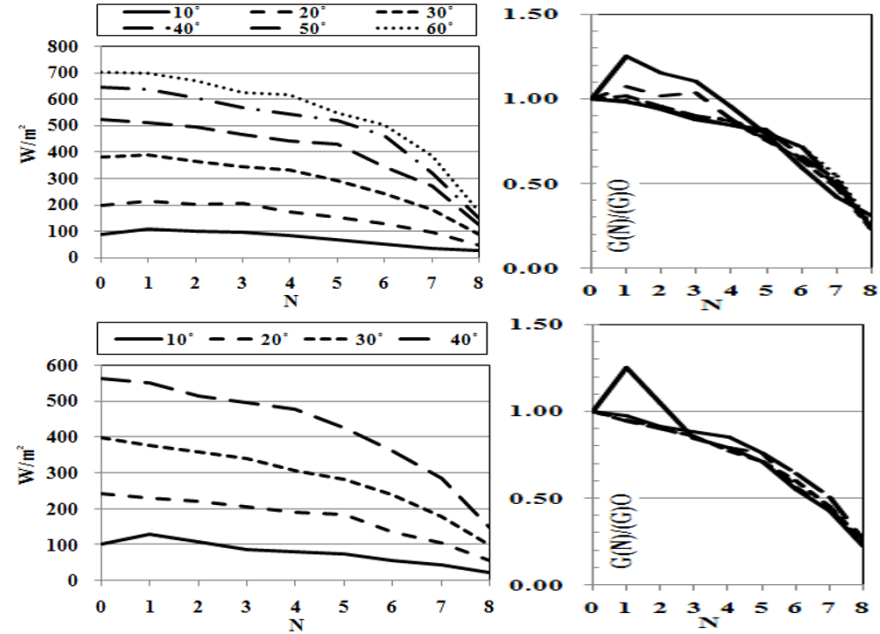
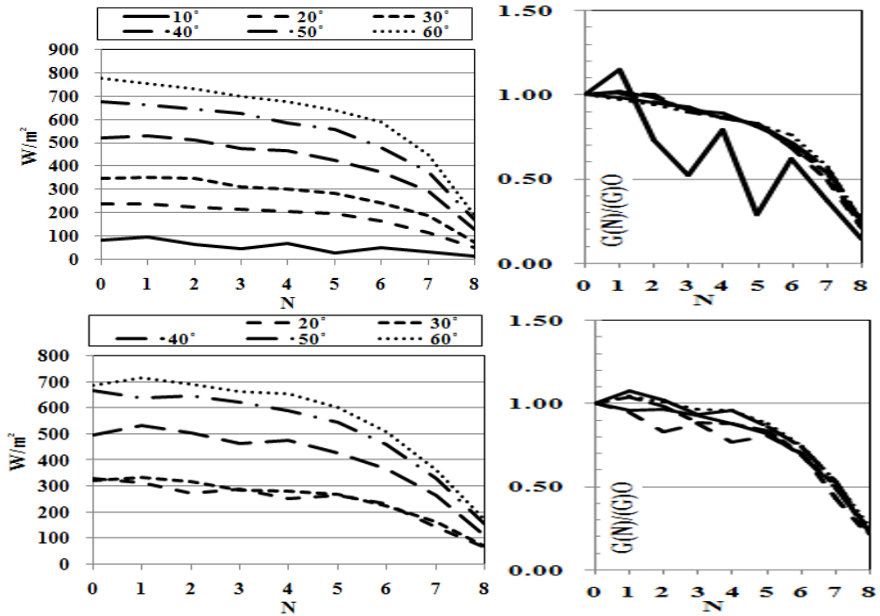


Fig. 30.4 Global radiation G as a function of total cloud amount N for different solar elevations r in the four seasons (from upper: spring, summer, fall, and winter) in Korea.



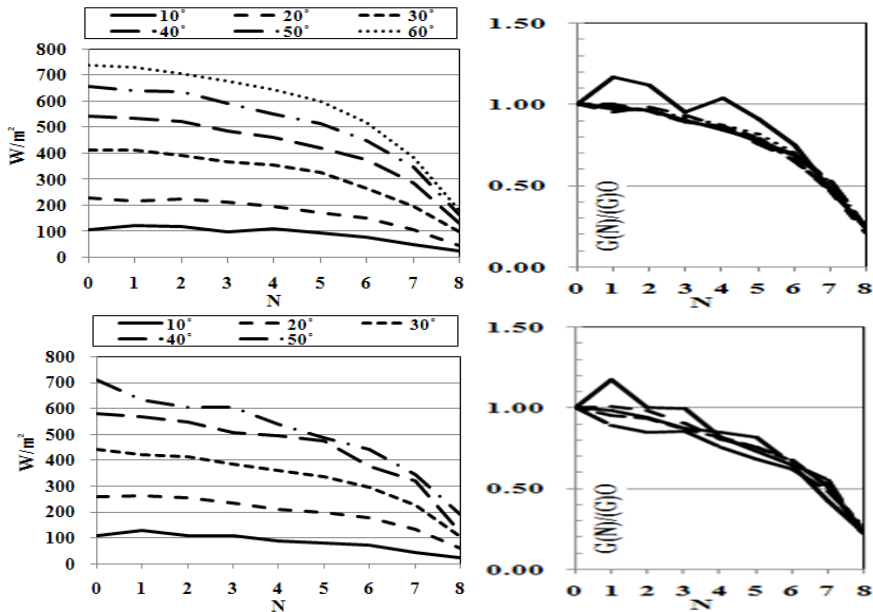
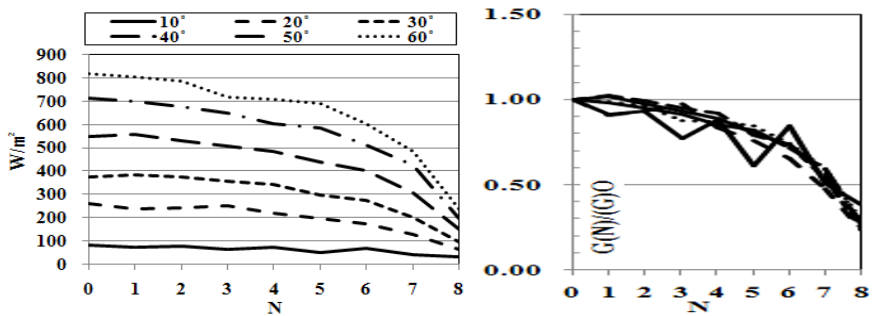


Fig. 30.5 Global radiation G as a function of total cloud amount N for different solar elevations r in the four seasons (from upper: spring, summer, fall, and Winter) in Busan.



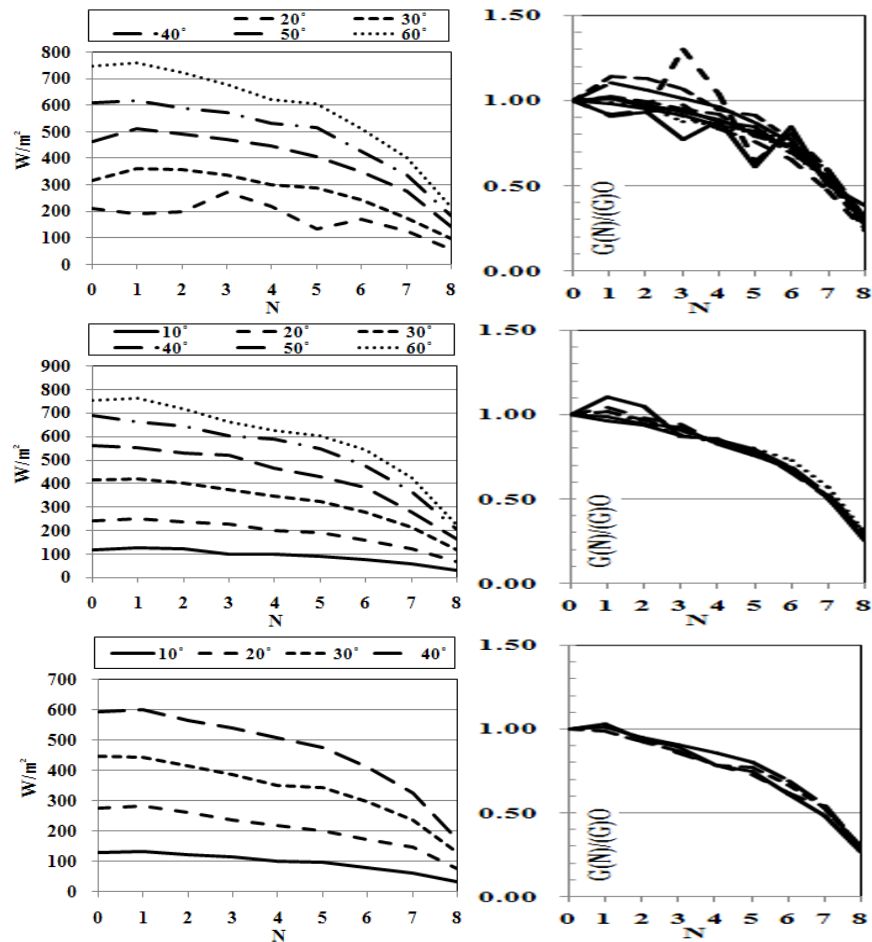


Fig. 30.6 Global radiation G as a function of total cloud amount N for different solar elevations r in the four seasons (from upper: spring, summer, fall, and winter) in Gwangju.

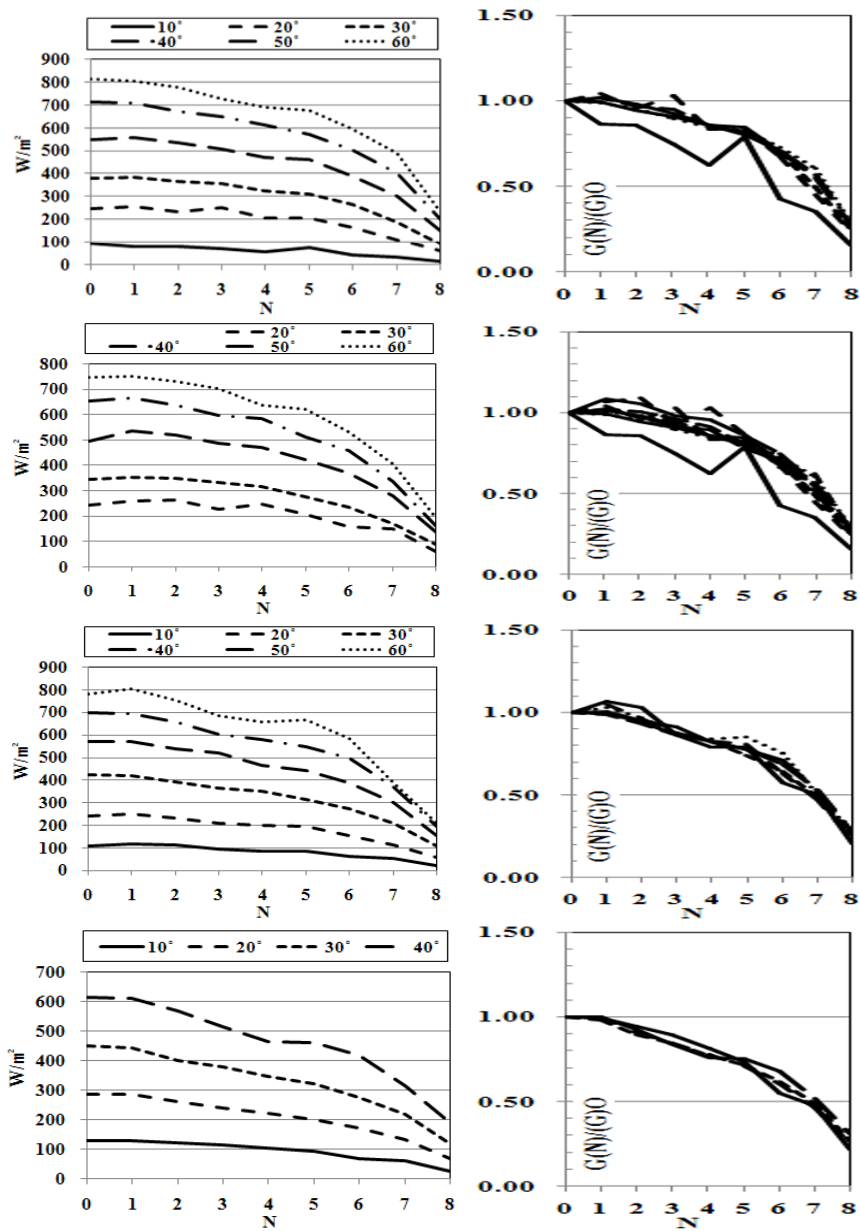


Fig. 30.7 Global radiation G as a function of total cloud amount N for different solar elevations r in the four seasons (from upper: spring, summer, fall, and Winter) in Daejeon.

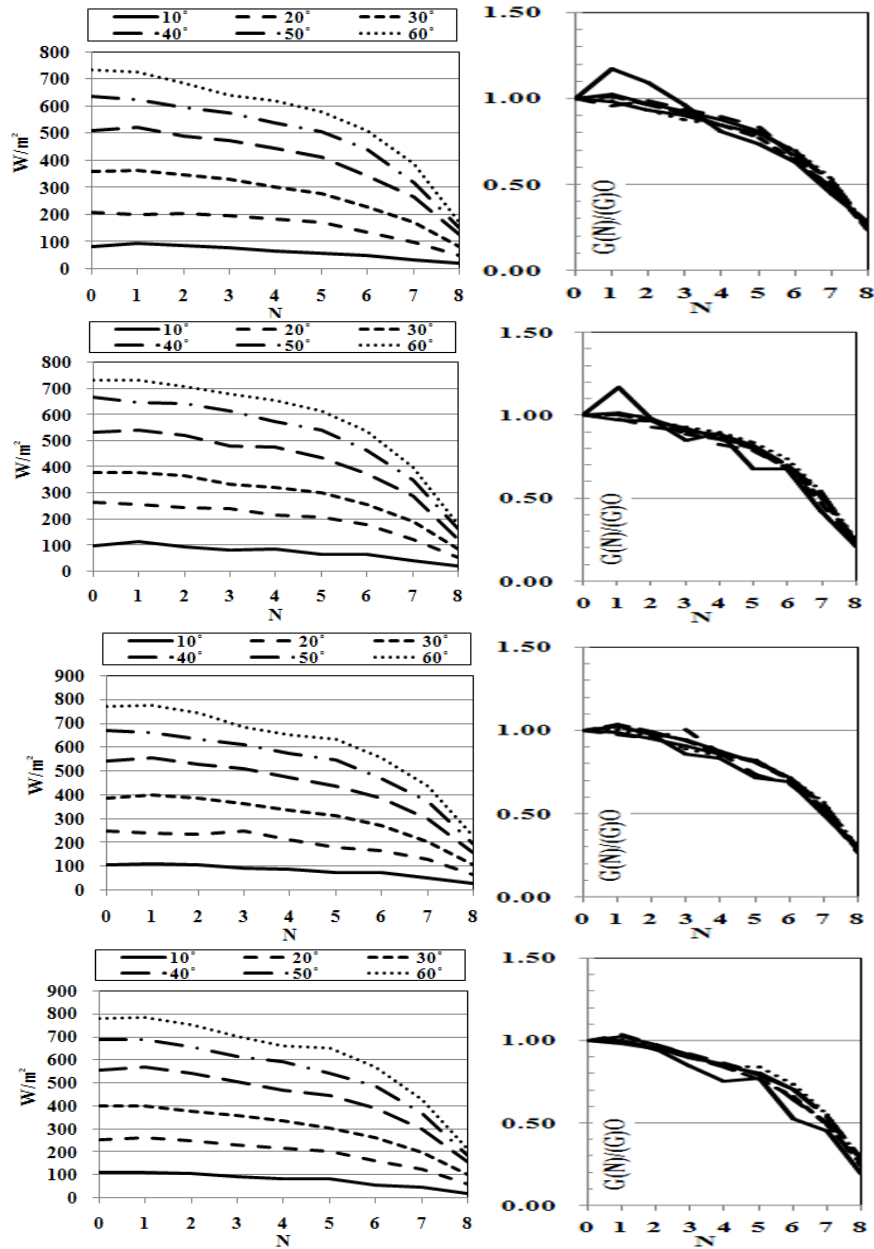


Fig. 30.8 Same as Figs. 30.4–30.7 but for the whole year 1986–2005 (from upper: Seoul, Busan, Gwangju, Daejeon).

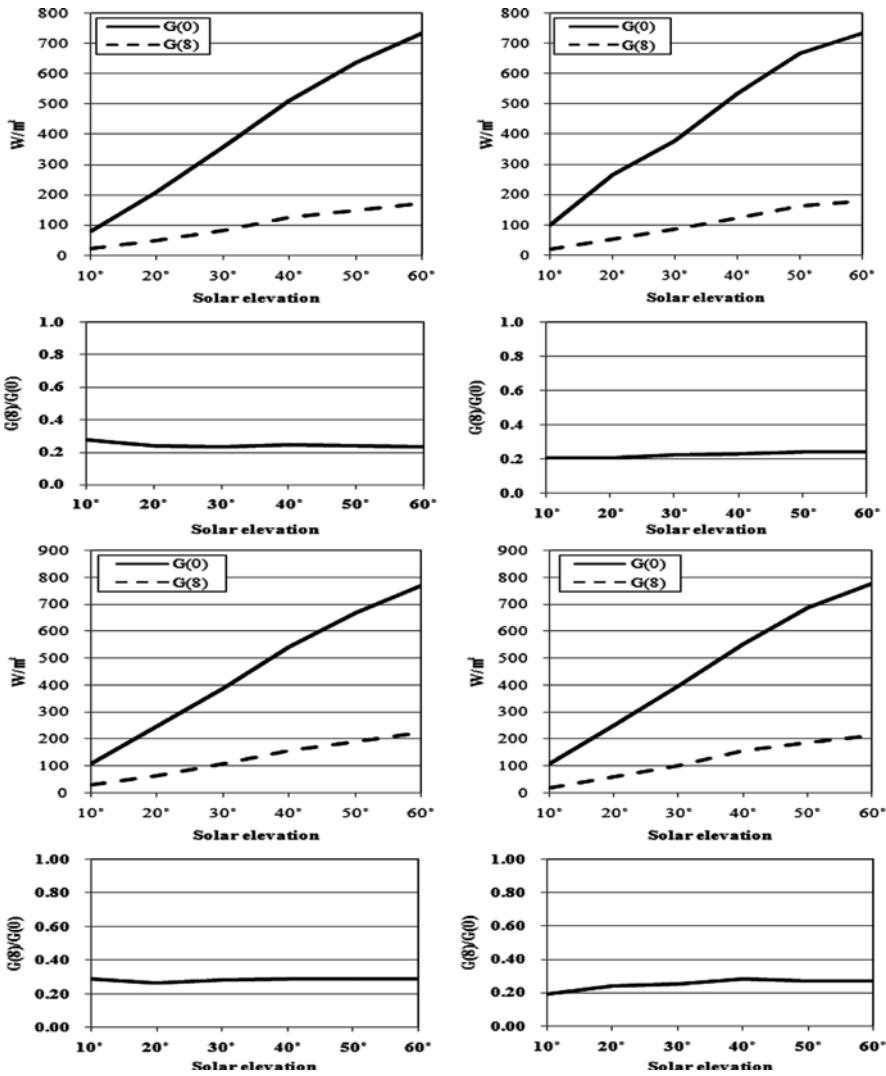


Fig. 30.9 Global radiation as a function of the sine of solar elevation r under cloudless sky: $G(0)$ and under overcast sky: $G(8)$ (from upper left: Seoul, Busan, Gwangju, Daejeon).

30.4.2 Comparison of measured and calculated data

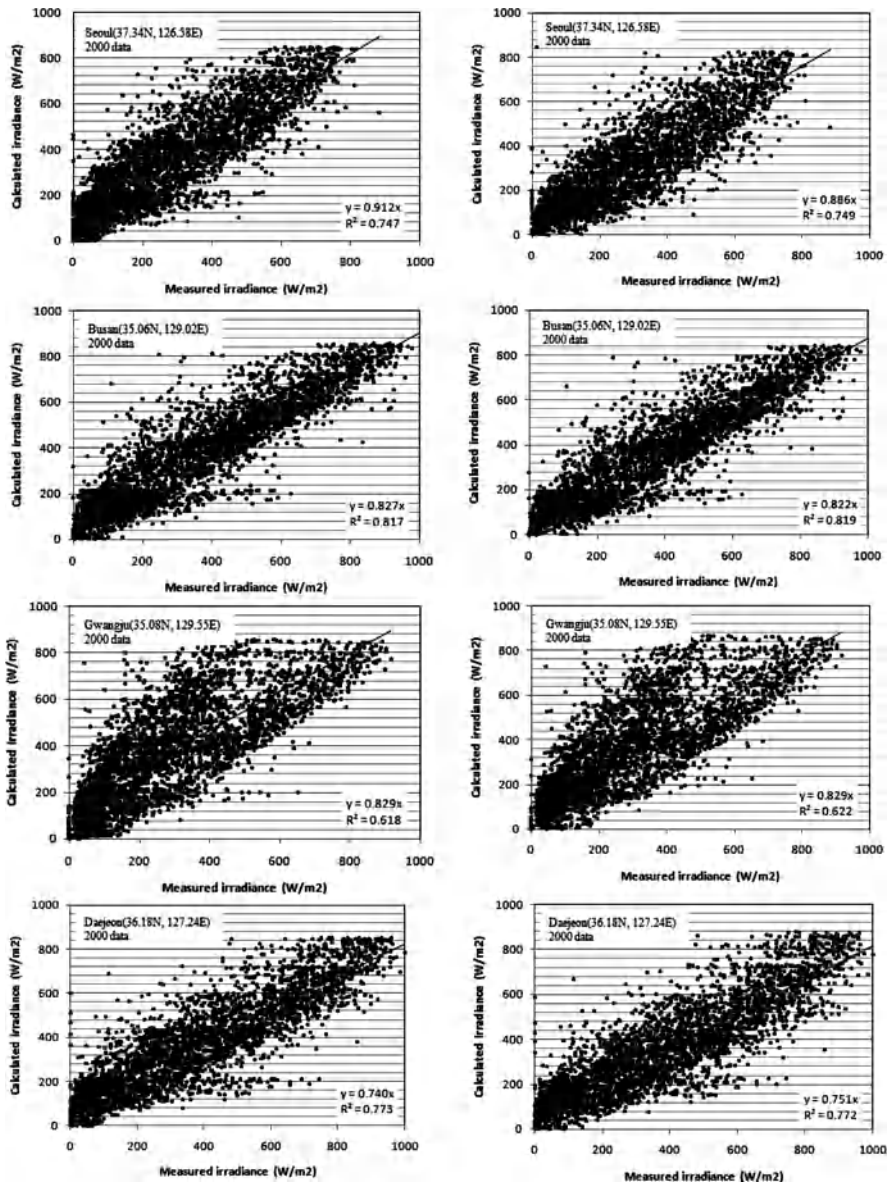


Fig. 30.10 Plot of hourly global solar radiation calculated from CRM model vs. measured data for four cities (left: Original, right: site fitted).

The data calculated applying coefficient of each location as described above will be compared to the data calculated applying the original coefficient. It is to estimate the influence of the coefficient calculated applying geographical climatic factor on the global radiation calculated based on the cloud amount.

A plot of hourly irradiance calculated using CRM (original and site-fitted coefficient) vs. measured values (Karti and Huang, 2006) is shown in Fig. 30.10 for four cities of South Korea. The original coefficients are used as Hamburg coefficients (Muneer and Gul, 2000). The CRM relies heavily on one variable, the cloud amount, and generally underestimates global solar radiation when original or fitted model coefficients are used as clearly indicated by global solar radiation presented in Fig. 30.10.

As a result of the comparison, in the case of Seoul, when the original coefficient and the site-fitted coefficient were applied, the R^2 (coefficient of determination) values were 0.747, and 0.749, respectively, which showed some correlation between the two figures. In case of Busan, the figures were 0.817 and 0.819, respectively, which also showed strong correlation. For Gwangju, like the above two cities, R^2 was reported as 0.618 and 0.622, respectively, showing that site-fitted coefficient produced higher determinant coefficient. Meanwhile, Daejeon's R^2 was reported as 0.772 and 0.773, meaning both of the two cases are correlated, but the original coefficient produced very slightly higher result.

These figures were re-evaluated through 'MAD.' Statistical evaluation of CRM based on original and site-fitted coefficients is presented in Table 30.3. A new performance indicator, the mean of absolute deviations (MAD), is also introduced herein. MAD is defined as

$$\text{MAD} = \sum |C - M| / n \quad (30.6)$$

where C is the calculated and M the measured irradiance; n denotes the number of observations (Gul et al., 1998).

The estimated site-fitted coefficient from this study, as is shown in Table 30.2, was compared with the estimated solar radiation applying original coefficient from Hamburg to reveal the excellence of site-fitted figures, as is indicated in Table 30.3, except that of Daejeon. However, in the other regions, the calculated solar radiation by the Kasten and Czeplak (1979) suggestion was decently satisfactory.

Table 30.2 Coefficients of CRM for South Korean sites (1986–2005).

Region	A	B	C	D
Seoul	963	106	0.75	2.6
Busan	930	64	0.77	2.9
Gwangju	969	77	0.72	2.7
Daejeon	984	76	0.75	2.6

Table 30.3 Statistical evaluation of CRM for South Korean sites (2000).

Region	Hamburg coefficients	Site-fitted coefficients
	MAD(W/m ²)	MAD(W/m ²)
Seoul	81	54
Busan	51	51
Gwangju	117	113
Daejeon	66	72

Figure. 30.11 shows the monthly averaged global radiation calculated from CRM model. In the case of Ulsan, the coefficients were taken from the Seoul, Busan, Gwangju, Daejeon about 380, 55, 330, 360 km away from Ulsan, respectively. Ulsan is a location where the measurement of global radiation is not made. Accordingly, when global radiation is not measured, the coefficients of other locations have to be used checking how big the difference of each location is. As a result of checking above, it was noted that there were some differences between the result of calculation using the different coefficients of the locations near and far. In case of monthly average global radiation for 20 years, when the coefficients of four cities were applied, the difference shown was about 10–380 W/m². Especially the site-fitted coefficient from Busan, of which cloud amount is relatively small, showed the tendency to produce larger solar radiation while the one from Seoul often produced largely reduced figures. However, Gwangju and Daejeon reported similar figures, that is, the regions other than Seoul did not show much difference in solar radiation estimation with the clouds amount. In addition, the tendency observed in Seoul seems to result from the regional characteristics, such as various developed industry and concentration of nearly 1/4 of Korean population. Therefore, for solar radiation estimation for Ulsan, where no solar radiation observation is conducted, site-fitted coefficient from Busan, which is located near Ulsan and also has similar cloud amount to Ulsan’s, seems to be able to give more appropriate estimation than the coefficients from other regions.

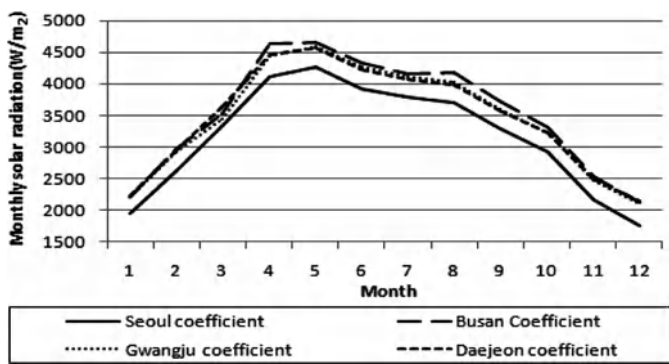


Fig. 30.11 Monthly global solar radiation calculated from CRM model with site-fitted coefficients for Ulsan.

30.5 Conclusions

Estimation of typical solar radiation is very important for the calculations concerning many solar applications. For this, collection and management of sunlight data obtained from actual measurements is important. But solar radiation measurements are not easily available because of the expensive measuring equipment and techniques required. Accordingly, for regions where no solar radiation is measured, solar radiation needs to be estimated using other meteorological data. However, currently in Korea, there is no study on how to do this. In this chapter, the global radiation of the four locations in South Korea where the global radiation is measured using comparatively simple CRM model was calculated, compared, and analyzed. Also, the difference of the result of global radiation calculation caused by change of coefficients was estimated by applying the coefficients calculated for the four locations to Ulsan where global radiation measurement is not made. The result was that the values of the global radiation measured and calculated were similar for major cities. Also, the result of applying the coefficients of the four locations for the calculation of the global radiation of Ulsan, which is located 380, 55, 330, 360 km away from Seoul, Busan, Gwangju and Daejeon, respectively, showed difference of 10–380 W/m². Accordingly, when calculating global radiation of a location where global radiation is not measured, the difference of the coefficient depending on the location should be considered.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R01-2007-000-10231-0)

Nomenclature

A, B, C, D	Coefficients for model
G	Global irradiation
I_D	Diffuse horizontal irradiance
I_G	Total global horizontal irradiation, W/m ²
I_{GC}	Clear sky global horizontal irradiation, W/m ²
N	Cloud cover (Octa)
R^2	Coefficient of determination
A	Solar altitude (radian)

References

- Bulut, H, Buyukalaca, O (2007) Simple model for the generation of daily global solar-radiation data in Turkey. *Applied Energy* 84: 477–491.
Climatic Policy Department, Climatic Bureau (2004) 100 Years of Modern Meteorological History. Seoul: Korea Meteorological Administration.

- Danny, HW, Joseph, CL (2001) An analysis of climatic parameters and sky condition classification. *Building and Environment* 36: 435–445.
- Gul, M, Muneer, T (1998) Models for obtaining solar radiation from other meteorological data. *Solar Energy* 99–108.
- Gul, M, Muneer, T, Kambezidis, HD (1998) Models for obtaining solar radiation from other meteorological data 64: 99–108.
- Kasten, F and Czeplak, G (1979) Solar and terrestrial radiation dependent on the amount and type of cloud. *Solar Energy* 177–189.
- Krarti, M, Huang, J (2006) Development of solar radiation models for tropical locations. ASHRAE.
- Muneer, T, Fairrooz, T (2002) Quality control of solar radiation and sunshine measurements-lessons learnt from processing worldwide databases. *Building Services Engineering*.
- Muneer, T, Gul, M (2000) Evaluation of sunshine and cloud cover based models for generating solar radiation data. *Energy Conversion Management* 461–482.
- Sabziparvar, AA (2007) A simple formula for estimating global solar radiation in central arid deserts of Iran, *Renewable Energy*, 1–9.
- Ulgen, K, Hepbasli, A (2002) Estimation of solar radiation parameters for Izmir, Turkey. *International Journal of Energy Research* 26: 807–823.
- Younes, S, Muneer, T (2006) Improvements in solar radiation models based on cloud data. *Building Services Engineering Research Technology*: 27: 41–54.

Relationship Between Air Pollutants and Some Meteorological Parameters in Erzurum, Turkey

Sevda Ocak and F. Sezer Turalioglu

31.1 Introduction

Air pollution may be defined as an atmospheric problem, which results in the deterioration of the environmental quality. The problem occurs within the atmospheric planetary boundary layer under the combined effects of meteorological parameters, earth surface topographic features and releases air pollutants from various sources. Meteorological parameters affect ambient air pollution in numerous ways. The most important role of the meteorology is in the dispersion, transformation, and removal of air pollutants from the atmosphere.

Ambient concentration of pollutants, such as SO₂ (sulfur dioxide) and TSP (total suspended material), was quite frequently exceeding recognized air quality standards. Particularly, the urban air pollution was much worse in Erzurum city in Turkey where fossil fuels were used to heat homes and buildings for several months of the winter season. Sulfur dioxide is a prominent anthropogenic pollutant resulting from especially residential heating during the winter season (from October to March) in Erzurum city. The pollutant contributes to the formation of sulfuric acid, the formation of sulfate aerosols, and the deposition of sulfate and sulfur dioxide at the ground surface (Aneja, 2001). The environmental effects of SO₂ are associated with acidification of precipitation and have deleterious effects on the human health. Ocak and Ocak (2007a) observed that pH of snowfall varied 4.7–7.3 for the 2002–2003 winter season in Erzurum. SO₂ affects people quickly within a few minutes on exposure. Exposure to SO₂ in the ambient air has been associated with reduced lung function, increased incidence of respiratory symptoms and diseases, irritation of the eyes, nose, and throat, and is linked to an increase in hospitalizations and deaths from respiratory and cardiovascular causes (Mouli et al., 2004). It also harms vegetation, including forest and agricultural crops. Ocak and Ocak (2007b) presented that air pollution levels due to domestic heating in winter season may harm species which are economically important, such as

Picea orientalis L., *A. Nordmanniana* ssp., *Fagus orientalis*, *Pinus sylvestris*, *Quercus* sp., *Alnus* sp., for a long term in Artvin city.

TSPs are complex mixture of small ($<2.5\text{ }\mu\text{m}$) and large ($2.5\text{--}100\text{ }\mu\text{m}$) particles of varying origin and chemical composition. These particles originate from many different stationary and mobile sources. They may be emitted directly by a source or formed in the atmosphere by the transformation of gaseous precursor emissions such as SO_2 and NO_x (Aneja, 2001). Health effects are strongly linked to the particle size. Smaller particles are likely to be most dangerous, because they can be inhaled deeply into the lungs and their constituents tend to be more chemically active and may be acidic. Numerous studies have linked such pollution with acute changes in lung function and respiratory illness, and effects such as asthma and bronchitis, leading to increased mortality (Mouli et al., 2004). In addition, particulates cause adverse impacts on the environment via reduced viability (Elminir, 2005).

The relationship between air pollutants and meteorological parameters such as wind velocity, temperature, and relative humidity can provide important information about air pollution. The wind speeds may transport air pollutants (SO_2 , PM) from distant sources. There are a negative correlation between air pollutants concentration and wind speed data. Analysis of the surface wind speed and direction alone will not adequately explain the variability in the concentrations of air pollutants. Hence, analysis of meteorological parameters affecting ambient concentrations of air pollutants should include an indicator of atmospheric moisture. High humidities may also indicate precipitation events accompanied by in-cloud scavenging, which results in low concentrations of gas and TSP concentrations. For SO_2 and TSP higher concentrations occurred at lower ambient temperature in winter season. Daily polluting concentrations are influenced not only by daily meteorological parameters but also by the values of the previous day. There has been a direct link between air pollutants (SO_2 , PM) concentration and their previous day's concentration (Ocak, 1997).

Given a set of observations from air monitoring and meteorological stations, calculating statistical relationship among the variables is possible by using some statistical techniques such as regression analysis. Some statistical models establish how close relationships are between concentration estimates and values actually measured under similar circumstances. Effects of all factors that determine atmospheric pollutant concentrations are implicitly accounted for in the air quality data used to develop and optimize the models. These models also have low development cost and resource requirements (Turalioglu et al., 2005).

There are numerous research presented with statistical relationship between meteorological parameters and air pollutants. Witz and Moore (1981) showed the relationship between air pollutants (CO , NO , NO_x , hydrocarbons) and meteorological parameters (wind direction, wind speed, early morning temperature, and frequency of inversions) using a stepwise multilinear regression analysis in Los Angeles in 1979. There is a close relationship between air pollutants and meteorological parameters. Ocak et al. (1997) found a moderate correlation using Statgraph program between SO_2 , TSP, and some meteorological parameters (rain-fall, temperature, sunshine hours, wind velocity, relative humidity) in Erzurum for

1989–1996 winter season. According to results, lower temperature and wind velocity increased SO_2 concentration and lower rainfall value increased PM concentration. Cuhadaroglu and Demirci (1997) showed the relation of pollutant concentrations with meteorological factors such as wind speed, relative humidity, and temperature. According to the results obtained from this study, for some months there is a moderate and weak level of relation between the SO_2 level and the meteorological factors in Trabzon city. Ocak and Demircioglu (2002) used multiple linear regression analysis to estimate SO_2 and PM concentrations using meteorological parameters (relative humidity, temperature, wind speed) and previous day's pollutants concentration in Erzurum for 1995–1996 winter seasons. A positive correlation was found between previous day's concentration and the pollutants concentration. Oguz et al. (2003) investigated the relationship of SO_2 and PM in the air to several meteorological parameters such as wind speed, rainfall, temperature, sunshine hours, and relative humidity in Erzurum for 1994–2001 winter seasons. According to the results obtained through multiple linear regression analysis, there are moderate levels of correlation between SO_2 and particle concentrations and meteorological parameters in Erzurum. Turalioglu et al. (2005) predicted SO_2 and PM concentrations using multiple regression equation including previous day's pollutants concentration and meteorological parameters such as wind speed, temperature, relative humidity, pressure, and precipitation for 1995–2002 winter seasons in Erzurum. The results showed good relationship between the meteorological parameters, previous day's SO_2 concentration, and actual SO_2 concentration.

The objective of the present study is to examine the relationship between meteorological parameters and air pollutants such as SO_2 and TSP. For this purpose, SO_2 and TSP concentration is statistically correlated with wind speed, humidity and temperature, and previous day's concentration of the pollutants for 1995–1997 winter seasons.

31.2 Materials and Methods

31.2.1 Description area

Erzurum is one of the cities located in the eastern part of Turkey, situated on plateau surrounded by mountains to east, north, and south. The height of this plateau is 1950 m a.s.l. It lies in a NE–SW direction, on an area about 20 km long and 5 km wide (Fig. 31.1). The altitude difference between the upper and lower limits of the city is approximately 200 m. The annual average temperature of the city is 6°C and the number of days below zero is 161. The city's severe climate and unfavorable geomorphology and topography cause serious air pollution problems. As no important industrial establishment exists in the city, the major source of pollution is domestic heating. For this purpose, various qualities of fuel including coke, local lignite, and fuel oil are consumed.



Fig. 31.1 Map of Erzurum city.

31.2.2 SO₂ and TSP monitoring

Air quality measurements in Erzurum city are conducted by different institutions during every winter season. Ataturk University Environmental Research Center and Erzurum Refik Saydam Sanitation Center used semi-automatic equipment for 24 h to define the concentration of SO₂ and TSP. SO₂ and TSP were measured using acidimetric titration method and reflectometric method. SO₂ measurement range of the acidimetric method varies between 0.01 and 10 ppm. Reliability of the reflectometric method is not high because of dependence on color of particulate matter. SO₂ and TSP together with meteorological parameters (wind speed, relative humidity, and temperature) were monitored in mobile laboratory by Provincial Environmental Directorate. Measurements were carried out for every 15 min. SO₂ concentrations were measured using an instrument that operates on principle of ultraviolet fluorescence (AF 21M). SO₂ measurement range varies between 1ppb and 10 ppm with 1% linearity. TSP measurements were made with beta gauge instrument (KS-301-F). TSP measurement range varies between 0 and 10.000 µg/m³. The laboratory was operative 24 h in a day. The continuous measurements of air quality and meteorological parameters were recorded for only 1995–1997 winter seasons by Provincial Environmental Directorate, and the measurements were not done between 1998 and 2003. The air quality measurements have been conducted after 2003–2004 winter season, but meteorological parameters were not measured again. It was preferred data of Provincial Environmental Directorate in this study because mobile laboratory recorded continuous

measurement every 15 min and its data have more high accuracy than data of semi-automatic equipment. The data used in this study belong to 1995–1997 winter season because continuous measurements of air quality with meteorological parameters were simultaneously conducted by mobile laboratory. The location of the mobile laboratory was selected as the sampling site on the basis of availability of power and security and topography of the area. Care was taken that no high buildings or trees were present for 200 m of the site in any direction. The reason for this condition is to eliminate the effect of downwash due to high structures. The mobile laboratory was fitted with the monitors and meteorological sensors. Twenty-four hour averaged values of SO_2 , TSP, and meteorological data were used in this study. Statistical parameters of SO_2 , TSP, and meteorological data of two winter seasons are given in Table 31.1.

31.3 Data Analysis

Regression analysis can be used to summarize data as well as to study relations between the variables. If the number of independent variables is more than one, multiple linear regression analysis is used and general regression equation with four independent variables can be expressed as

$$Y = A + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + E \quad (31.1)$$

where A is constant of regression and B is coefficient of regression. The values of the constant and coefficients are determined using the least-squares method which minimizes the error, seen as E in the above regression equation (Akkaya, 1998). A commonly used measure of goodness of fit of a linear model is R^2 , sometimes called the coefficient of determination. It is defined as the proportion of the variation in the dependent variable and expressed as

$$R^2 = 1 - \frac{\sum_i (\hat{Y}_i - \bar{Y})^2}{\sum_i (Y_i - \bar{Y})^2} \quad (31.2)$$

where $\hat{Y}_i$ is the value of Y predicted by the regression line, Y_i is the value of Y observed, and $\bar{Y}$ is the mean value of the Y_i s. If all the observations fall on the regression line, R^2 is 1. If there is no linear relationship between the dependent and independent variables, R^2 is 0. The significance level of the constant and coefficients is statistically tested using the T distribution (Koutsoyiannis, 1989; Cuhadaroglu and Demirci, 1997).

A variety of regression models can be constructed from the same set of variables. In the present study, a stepwise regression model was used. Stepwise regression of the independent variables is basically a combination of backward and forward procedures in essence and is probably the most commonly used method. In this method, the first variable is selected in the same manner as in the forward selection. If the variable fails to meet the entry requirements, the procedure terminates with no independent variables entering into the equation. If it passes the criterion, the second variable based on the highest partial correlation is selected. If it passes the entry criterion, it also enters the equation.

After the first variable is entered, stepwise selection differs from forward selection: the first variable is examined to see whether it should be removed according to the removal criterion as in backward elimination. In the next step, variables not in the equation are examined for removal. Variables are removed until none of the remaining variables meet the removal criterion. Variable selection terminates when no more variables meet entry and removal criteria.

In the statistical analysis, the correlations between the air pollutant concentrations and meteorological factors have been analyzed. In spite of establishing the correlations between the air pollutant concentrations and meteorological factors by Eq. (31.1), the equations expressed as

$$Y = f(X_1), Y = f(X_2), \dots, Y = f(X_2, X_3), \dots, Y = f(X_1, X_2, X_3, X_4) \quad (31.3)$$

have also been analyzed separately and the independent variables with small values of R^2 have been eliminated. Using the remaining variables, equations having one, two, three, or four variables are developed (Bowerman and O'Connell, 1987; Cuhadaroglu and Demirci, 1997).

SO₂ and TSP data together with meteorological parameters, such as wind speed, temperature, relative humidity, were analyzed by multiple linear regression using the RATS (Regression Analysis Time Series) program. SO₂ and TSP were considered as dependent variables while previous day's pollutant concentration and meteorological parameters such as temperature, wind velocity, and relative humidity were considered as independent variables.

31.4 Results and Discussion

31.4.1 Evaluation of SO₂ and TSP concentrations and meteorological parameters in 1995–1997 winter season

SO₂ and TSP were monitored between 1995 and 1997 in the city of Erzurum. For SO₂ and TSP, winter season limit values are 250 µg/m³ and 200 µg/m³, respectively, according to the Turkish Air Quality Protection Regulation (MOE, 1986). Daily averages, standard deviations, minimum and maximum concentrations for the city center are summarized in Table 31.1. The daily air pollutants concentration were graphed together with short-term limit (STL) values

as $400 \mu\text{g}/\text{m}^3$ for SO_2 and $300 \mu\text{g}/\text{m}^3$ for TSP in Turkish Air Quality Protection Regulation (MOE, 1986) and are shown in Fig. 31.2.

Table 31.1 The means, maximum, minimum, and standard deviation of meteorological parameters and SO_2 and TSP concentration between years 1995 and 1997.

	Mean	Maximum	Minimum	Standard deviation	Number Of observation
SO_2 concentration ($\mu\text{g}/\text{m}^3$)	252	1915	13	317	185
TSP concentration ($\mu\text{g}/\text{m}^3$)	112	749	0.72	116	185
Temperature ($^{\circ}\text{C}$)	-5.1	9	-26	7.54	185
Relative humidity (%)	60	98	18	21	185
Wind speed (m/s)	0.85	6.83	0	0.95	185

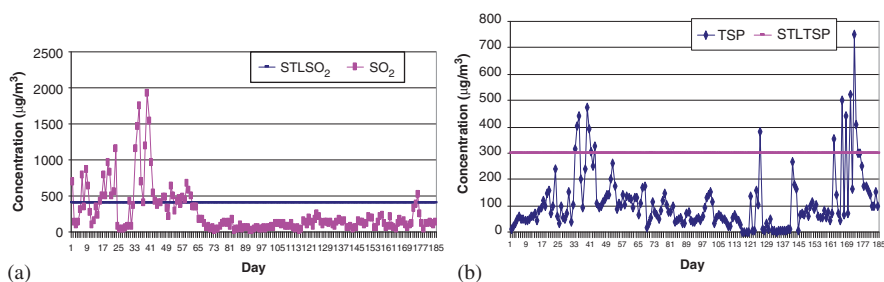


Fig. 31.2 (a) The daily change of SO_2 and (b) TSP concentration in winter periods (STL: short-term limit value).

The monthly averages of SO_2 and TSP values in 1995–1996 are higher than the next winter season due to meteorological parameters. Maximum SO_2 and TSP concentrations occur in January, 645 and $210 \mu\text{g}/\text{m}^3$, respectively. These high SO_2 and TSP values were due to low temperature (-11°C) and low winds (0.6 m/s). The pollutants levels are high also in other colder months as December and February. In winter periods of 1995–1997, the SO_2 and TSP concentration values exceed the short-term limit (STL) of Turkish Air Quality Protection Regulation, and corresponding meteorological parameter values in these days, are listed in Table 31.2.

Table 31.2 The means, maximum, minimum, and standard deviation of SO₂ and TSP concentrations that together exceed STL and corresponding meteorological values.

	Mean	Maximum	Minimum	Standard deviation	Number of observation
SO ₂ concentration ($\mu\text{g}/\text{m}^3$)	1310	1915	417	512	7
TSP concentration ($\mu\text{g}/\text{m}^3$)	380	476	306	65	7
Temperature ($^{\circ}\text{C}$)	-12	1.1	-23.42	9.61	7
Relative Humidity (%)	83	89	77	4	7
Wind speed (m/s)	0.18	0.63	0.10	0.18	7

SO₂ together with TSP values exceeded the STL for 7 days during two winter periods. The values of daily average temperature (-13°C) and wind speed (0.18 m/s) in these days were determined to be below the seasonal average. These episode days may be attributed to the consumption of more fuel due to lower temperatures, resulting in high SO₂ emission and also unfavorable meteorological factors. In addition to the meteorological factors, an inversion event is seen frequently in winter season due to presence of the high mountains surrounding Erzurum which affects air pollutant distribution negatively (Turalioglu et al., 2005).

Air pollution can affect our health either short term or long term. Some effects of air pollutants on human health are shown in Table 31.3. It was considered that 7 days in Table 31.2 were risky days for the chronic bronchitis patients in Erzurum city. Minimum TSP concentrations and SO₂ concentrations for those days were over $300 \mu\text{g}/\text{m}^3$ and $400 \mu\text{g}/\text{m}^3$, respectively.

Table 31.3 Effects of suspended particulate matter in atmosphere.

Concentration ($\mu\text{g}/\text{m}^3$)	Effects	Remarks
100–130	Beginning of respiratory tract disease at children	SO ₂ concentration > $120 \mu\text{g}/\text{m}^3$
300 (daily averaged)	Beginning of serious crisis at chronic bronchitis patients	SO ₂ concentration > $630 \mu\text{g}/\text{m}^3$
750 (daily averaged)	Increasing deaths	SO ₂ concentration > $715 \mu\text{g}/\text{m}^3$

Source: Muezzinoglu (2000).

In addition, average SO₂ and TSP concentrations presented for winter season in Table 31.1 were $252 \mu\text{g}/\text{m}^3$ and $112 \mu\text{g}/\text{m}^3$, respectively. These levels of air pollutants can affect children during the winter season. It has been explained that

the long-term threshold concentration for forest varied between 100 and 150 $\mu\text{g}/\text{m}^3$. In lower value than the threshold concentration, damages for leaves of coniferous trees especially pine, fir, and spruce have been determined (McLaughlin, 1985). It is known that coniferous trees are more sensitive than broad leaf trees during winter season. The most sensitive trees for SO_2 pollution are fir (*Abies sp.*), spruce (*Picea L.*), willow (*Salix L.*). Some of the sensitive trees for SO_2 pollution are lime (*Tilia L.*), beech (*Fagus L.*), pine (*Pinus L.*). Some of the less sensitive trees for SO_2 pollution are oak (*Quercus*), poplar (*Populus L.*), pear (*Pyrus L.*), baxwood (*Carpinus betulus*), juniper (*Juniperus L.*). It was considered that trees affected by air pollution levels during winter season in Erzurum city were willow (*Salix babylonica*), ash tree (*Fraxinus excelsior L.*), ash tree (*F. americana L.*), pine (*Pinus sylvestris*), poplar (*Populus nigra Italica*), poplar (*Populus alba*), elm (*Ulmus glabra*), boxelder (*Acer negundo L.*).

31.4.2 Relationship between SO_2 , TSP, and meteorological factor

The relationship between SO_2 , TSP, and meteorological parameters (temperature, wind speed, relative humidity) and previous day's pollutant concentration in 1995–1997 winter periods was investigated by stepwise multiple linear regression analysis. The correlation (r) between daily average SO_2 , TSP concentrations and daily average meteorological parameters and previous' day pollutants concentration is shown in Table 31.4.

Table 31.4 Correlation (r) between daily average SO_2 , TSP, and daily average meteorological parameters in this study and other studies.

Pollutants	Temperature	Wind speed	Relative humidity	Previous day's Concentration	References
SO_2	-0.45	-0.31	-0.46	0.77	This study
TSP	-0.37	-0.30	0.09	0.42	This study
SO_2	-0.78	-0.49	0.03	0.84	Turalioglu et al. (2005)
TSP	-0.79	-0.64	0.13	0.53	Turalioglu et al. (2005)
SO_2	-0.82	-0.42	-0.19		Gupta et al. (2008)
SO_2	-0.20		0.20		Elminir (2005)
PM_{10}	-0.41		0.25		Elminir (2005)
PM_{10}	0.24–0.48	0.23–0.55	0.08–0.39		Vardoulakis and Kassomenos (2009)

The SO_2 and TSP concentrations as a function of meteorological parameters are shown in Fig. 31.3a–h. As seen from Table 31.4, it was found that the moderate correlation occurs between SO_2 , TSP, and temperature for which $p < 0.01$. It is obvious that the pollutant concentrations decrease effectively with high increasing temperature. There is a negative correlation between

pollutants (SO₂ and TSP) concentrations and wind velocity ($p < 0.01$ for SO₂ and $p < 0.05$ for TSP). SO₂ and TSP concentrations decrease with increasing wind speed, as seen from Fig. 31.3c,g. The relative humidity is a weakly linked parameter to TSP ($p < 0.01$). Also the relative humidity is a moderately linked parameter to SO₂ ($p < 0.05$). The correlation between the previous day's TSP and SO₂ values and actual concentration is investigated and found as 0.77 and 0.42, respectively, and their correlations are shown in Fig. 31.3a and 31.3e ($p < 0.01$). Also, the findings of others related to correlations between SO₂, particulate matter, and meteorological parameters are shown in Table 31.4. It is seen from Table 31.4 that correlations of SO₂ and TSP for temperature, wind speed, and relative humidity obtained at this study are similar to those found in other studies. Also the correlation between SO₂ and previous day's SO₂ (this study) is near that found at Erzurum by Turalioglu et al. (2005). It is obvious that the correlation values are highly site specific (Vardoulakis and Kassomenos, 2009).

31.4.3 The regression analysis

The SO₂ and PM concentrations are considered to be dependent variables, whereas meteorological factors and previous day's air pollutants concentration are considered to be independent variables. Multiple regression analysis was applied for each day, and it was shown that there are relationships between SO₂ concentration and meteorological factors and previous day's SO₂ concentration. In this study, since the relative humidity gave weakest significance in statistical analysis, it was removed from the regression equation for TSP. Consequently, the regression equation for SO₂ is presented as

$$SO_2 = -34 * [\text{wind speed}] - 11.8 * [\text{temperature}] + [\text{relative humidity}] + 0.7 * [\text{previous day's } SO_2] \quad (31.4)$$

$$R^2 = 0.71$$

According to this equation, the concentration of SO₂ decreases with increasing temperature and wind speed, and the concentration of SO₂ increases with increasing relative humidity and previous day's SO₂. The regression equation obtained for the TSP concentration is expressed as

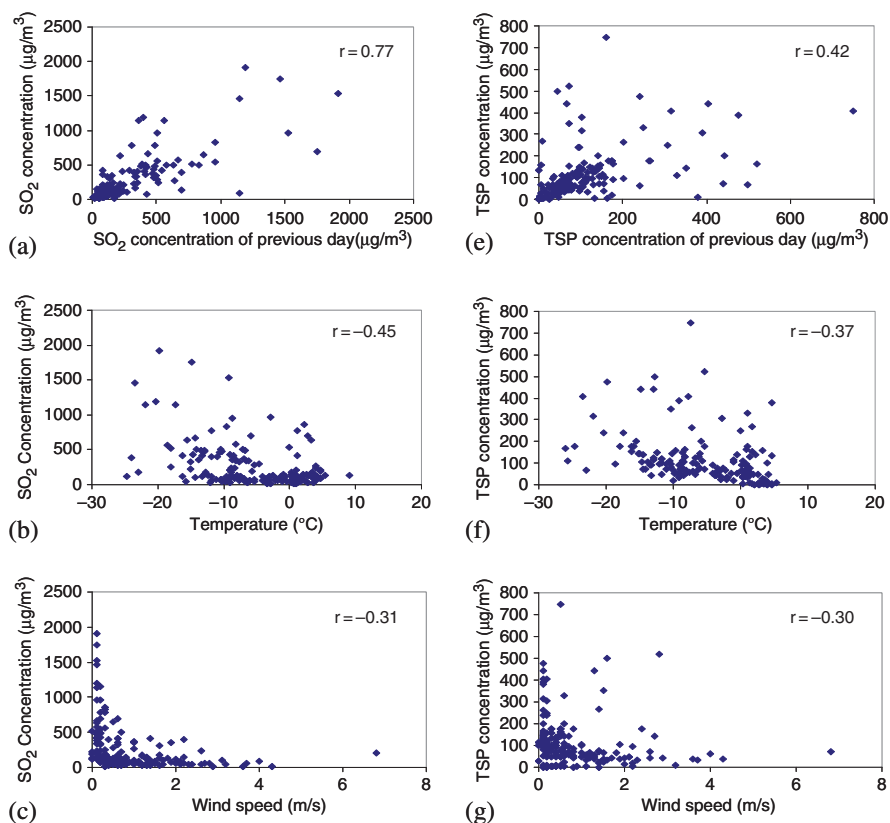
$$TSP = 51.9 - 15 * [\text{wind speed}] - 6.4 * [\text{temperature}] + 0.3 * [\text{previous day's TSP}] \quad (31.5)$$

$$R^2 = 0.43$$

This equation reveals that the TSP concentration decreases with increasing wind speed and temperature but TSP concentration increases with increasing previous day's TSP concentration.

Considering Eqs. (31.4) and (31.5), the measured SO₂ and TSP values were compared with the calculated ones. The data set (all values) of 1995–1997 winter season was used for testing model. As seen in Fig. 31.4a, there is a good agreement between predicted and measured values. The good correlation

coefficients reflect the effectiveness of this equation as well. However, the equation did not enhance the predictions for TSP (Fig. 31.4b). The lower enhancement in Eq. (31.5) may be due to the fact that the lifetime of different-sized TSP in atmosphere is more unstable than gaseous compounds because of prevailing meteorological factors.



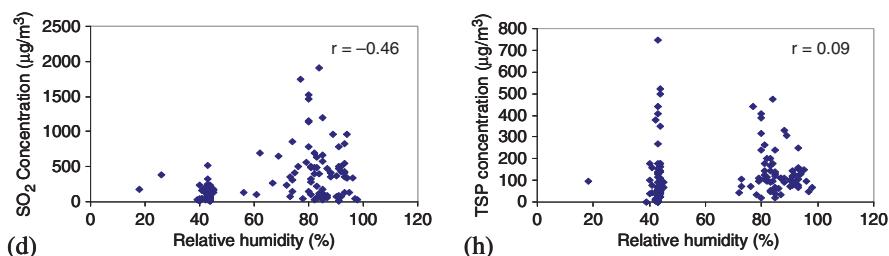


Fig. 31.3 SO₂ concentration versus (a) previous day's SO₂ concentration; (b) temperature; (c) wind speed; (d) relative humidity. TSP concentration: (e) previous day's TSP concentration; (f) temperature; (g) wind speed; (h) relative humidity.

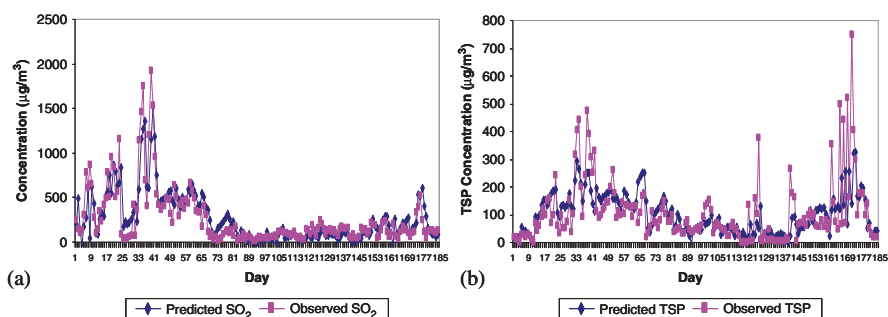


Fig. 31.4 Measured and predicted (a) SO₂ concentration according to Eq. (31.4) and (b) TSP concentration according to Eq. (31.5).

The SO₂ concentration has a good dependence and a 71% coefficient of determination; this means that 71% of SO₂ depends on wind speed, temperature, relative humidity, and previous day's SO₂ concentration, and 29% is indeterminate. As regards the TSP concentration, there is a moderate dependence on wind speed, temperature, relative humidity, and previous day's TSP concentration: 43% of TSP depends on these factors and 57% is indeterminate. Wind speed and temperature are effective meteorological variables in decreasing SO₂ and TSP concentrations. It was found that previous day's pollutants concentrations have slight effect for SO₂ and TSP concentrations.

It is seen from the literature that the number of meteorological parameters included in regression equations are variable. Witz and Moore (1981) found the regression coefficients varied 0.68–0.73 between air pollutants (CO, NO, NO_x, hydrocarbons) and meteorological parameters (wind direction, wind speed, early morning temperature, and frequency of inversions). Ocak et al. (1997) found the regression coefficients between SO₂ and meteorological parameters (rainfall, tem-

perature, sunshine time, wind speed, relative humidity) as 0.43 and the regression coefficients between PM and meteorological parameters (rainfall, temperature, sunshine time, wind speed, relative humidity) as 0.27. In a study performed by Cuhadaroglu and Demirci (1997), the regression coefficient was computed between SO_2 and meteorological factors (wind speed and humidity) as 0.53 and the coefficient between TSP and meteorological parameters (temperature and humidity) was estimated as 0.56. Oguz et al. (2003) found the regression coefficients between SO_2 and meteorological parameters (temperature, sunshine time, wind speed) as 0.66 and the regression coefficients between PM and meteorological parameters (rainfall, sunshine time, wind speed) as 0.53.

There are limited studies in the literature considering the previous day's pollutant concentration in regression equation. Ocak and Demircioglu (2002) calculated that the regression coefficient between SO_2 and meteorological parameters (temperature) was 0.73 and between TSP and meteorological parameters (temperature and wind speed), the coefficient estimated was 0.68. Turalioglu et al. (2005) added previous day's SO_2 concentration in regression equation and R^2 value of 0.92 was found. They added previous day's TSP concentration in the regression equation and R^2 value of 0.89 was found.

The most apparent human impact on climate is the building of cities. The construction of every factory, road, office building, and house destroys existing microclimates and creates new ones of great complexity. Urbanization leads to significant changes in the climate in and around most cities. The cities generally are cloudier, foggier, warmer, and wetter than the countryside. The most known urban climate effect is the urban heat island. There are four major causes of urban heat islands: 1. The rocklike materials from which the city is made have large thermal capacities (ability to store heat). 2. Industry, motor vehicles, and domestic heating release large quantities of heat. 3. Increased atmospheric pollution inhibits the loss of upward-directed radiation from the surface. 4. Tall buildings create a three-dimensional structure that alter the flow of air and create a complex geometry for heat exchange (Lutgens and Tarbuck, 1998; Jonsson et al., 2004). Urban temperature rise is caused by waste heat from heating and air conditioning, power generation, industry, and transportation. Many studies have shown that the magnitude of human-made energy in metropolitan areas can be significant fraction of the energy received from the Sun at surface. The blanket of pollutants over a city, including particulate matter, water vapor, and carbon dioxide, contributes to the heat island by absorbing a portion of the upward-directed long wave radiation emitted at the surface and reemitting some of it back toward the surface. It has been considered that the last freeze of winter season can occur several weeks earlier in the center of Erzurum city than in outlying areas due to the heat-island effect.

31.5 Conclusions

High air pollution level has existed in Erzurum during winter seasons. Maximum SO_2 and TSP concentrations especially occur in the colder months (December, January, and February) in the city. These high SO_2 and TSP values were due to the lower temperature and lower winds. The results from this study show that there are moderate relationships between the meteorological parameters, SO_2 , and TSP in Erzurum within the terms statistically analyzed. The wind speed, temperature, and relative humidity are moderately correlated with SO_2 between 1995 and 1997. The wind speed and temperature are moderately correlated with TSP. The relative humidity is also weakly correlated with TSP. In order to predict the SO_2 and TSP concentrations with regard to meteorological parameters and previous day's pollutant concentration, a statistical model was developed. The correlations between previous day's TSP and SO_2 concentrations and actual TSP and SO_2 concentrations were found as 0.42 and 0.77, respectively. The statistical model of SO_2 and TSP including meteorological parameters and previous day's pollutant concentrations gave R^2 of 0.71 and 0.43, respectively.

Since increasing population, fuel quality change, and requested modifications in urbanization are insufficient in Erzurum city, the statistical model is able to predict well the next several days of SO_2 pollution whenever the days of meteorological parameter values are supplied.

Nomenclature

A	constant
B	coefficient
E	error
R^2	correlation/determination coefficient
SO_2	Sulfur dioxide ($\mu\text{g}/\text{m}^3$)
TSP	Total suspended material ($\mu\text{g}/\text{m}^3$)

References

- Akkaya, S, Pazarlıoglu, MV (1998) Ekonometri II. İzmir: Erkam Yayınevi (in Turkish).
- Aneja, VP, Agarwal, A, Roelle, PA, Philips, SB, Tong, Q, Watkins, N, Yablonsky (2001) Measurements and analysis of criteria pollutants in New Delhi, India. *Environment International* 27: 35–42.
- Bowerman, BL, O'Connell, RT (1987) Time series forecasting unified concepts and computer implementation. Boston: Duxbury Press.
- Cuhadaroglu, B, Demirci, E (1997) Influence of some meteorological factors on air pollution in Trabzon city. *Energy and Buildings* 25: 179–184.
- Elminir, HK (2005) Dependence of urban air pollutants on meteorology. *Science of The Total Environment* 350: 225–237.
- Gupta, AK, Karar, K, Ayoob, S, John, K (2008) Spatio-temporal characteristics of gaseous and particulate pollutants in an urban region of Kolkata, India. *Atmospheric Research* 87: 103–115.
- Jonsson, P, Bennet, C, Eliasson, I, Lindgren, ES (2004) Suspended particulate matter and its relations to the urban climate in Dar es Salam, Tanzania. *Atmospheric Environment* 38:4175–4181.

- Koutsoyiannis, A (1989) Ekonometri Kuramı, Ekonometri Yöntemlerinin Tanıtımına Giriş. Ankara: Verso Yayıncılık (in Turkish).
- Lutgens, FK, Tarbuck, EJ (1998) The Atmosphere. New-Jersey: Prentice-Hall.
- McLaughlin SB (1985) Effects of air pollution on Forests. JAPCA 35: 512–534.
- MOEF (Ministry of Environment and Forest), (1986). Air Quality Protection Regulation (AQPR). Official Gazete numbered 19269, Ankara.
- Mouli, PC, Kumar, MP, Reddy, J (2004) Monitoring of air pollution in Indian metropolitan cities: modelling and air quality indexing. Int. J. Environment and Pollution 21: 365–382.
- Muezzinoglu, A (2000) Hava kirliliğinin ve Kontrolünün Esasları. İzmir: DEÜ Yayınları (in Turkish).
- Ocak, S. (1997) Erzurum’da Hava Kirliliği, Değerlendirmesi ve Atmosferik parametrelerle ilişkilendirilmesi, Yüksek lisans Tezi, Atatürk University, Erzurum.
- Ocak, S, Oguz, E, Erhan, E, Emsen, E, Turahoglu, S, Keskinler, B (1997) Erzurum’da Kış Sezonu Hava Kalitesi Profili. Türkiye’de Çevre Kirlenmesi Öncelikleri Sempozyumu II, Gebze Yüksek Tek. Enst. ve TÜBİTAK MAM, Kocaeli.
- Ocak, S, Demircioglu, N (2002) Erzurum İli Kasım 1995-Nisan 1996 Hava Kalitesi Profili. I. Ulusal Çevre Sorunları Sempozyumu, Atatürk Univ. Çevre Sor. Arş. Mer., Erzurum.
- Ocak, S, Ocak, A (2007a) Erzurum İli Islak Birikim Profili Ve Etkileri. VII. Ulusal Ekoloji ve Çevre Kongresi, İnönü Üniversitesi, Malatya.
- Ocak, S, Ocak, A (2007b) Artvin il Merkezinde Hava Kirliliğinin ve Etkilerinin Belirlenmesi. I. Karadeniz’ de Sanayileşme ve Çevre Sempozyumu. TMMOB Makine Muh. Odası, Trabzon.
- Oguz, E, Kaya, MD, Nuhoglu, Y (2003) Interaction between air pollution and meteorological parameters in Erzurum, Turkey. Int. J. Environment and Pollution 19: 292–300.
- Turahoglu, FS, Nuhoglu, A, Bayraktar, H (2005) Impacts of some meteorological parameters on SO₂ and TSP concentrations in Erzurum, Turkey. Chemosphere 59: 1633–1642.
- Vardoulakis, S, Kassomenos, P (2009) Sources and factors affecting PM₁₀ levels in two European cities: Implications for local air quality management. Atmospheric Environment (Article in Press).
- Witz, S, Moore, AB (1981) Effect of meteorology on the atmospheric concentrations of traffic-related pollutants at a Los Angeles site. JAPCA 31: 1098–1101.

Planning for the Impacts of the Caspian Sea Level Rise and Climate Change in the North of Iran

Yousef Filizadeh, Kamran Zolfinejad and Homan Rajabi Islami

32.1 Introduction

When faced with the issues of climate change and the Caspian Sea level rise (CSLR), decision-makers are unable to wait for scientific uncertainties to be resolved before taking action. The Caspian Sea level rise predictions are complicated by the complex non-linear nature of the climate system and long-term dependence on human choices. This study analyzes the regulatory and institutional structure surrounding coastal zone management in the Anzali Lagoon District in the north of Iran, in order to identify barriers to and opportunities for the Caspian Sea level rise response.

Viewing the problem from a resilience perspective proves valuable as it builds off the social–ecological system concept, embraces change, and attempts to find ways to coexist with uncertainty. The selection of non-catastrophic Caspian Sea level rise scenarios and the creation of a variety of high-resolution, location-specific, inundation maps are used to identify areas of vulnerability. Focusing on local government, four potential sea level rise response options are identified along with associated barriers.

- Increase the update frequency for floodplain maps to more accurately reflect environmental changes.
- Include consideration of a dynamic shoreline when making shoreline armoring, cumulative impacts, and no net loss of ecological function determinations.
- Use shoreline designations in the Shoreline Management Act to tailor responses to the coastal environment.
- Leverage the Guilan Province in the north of Iran, consistency and funding provisions of the Coastal Zone Management Act to enhance response options.

The long-term nature of the Caspian Sea level rise issue provides response opportunities not available in other arenas. By using the tools currently available, local decision-makers can limit the response costs and create a more robust policy

framework capable of incorporating uncertainty and adapting to the Caspian Sea level rise.

Sea levels are rising even faster than scientists predicted, according to a global analysis of data from tide gauges and satellites. The researchers say the study puts to bed claims that climate scientists have exaggerated the consequences of global warming. And because the study shows that sea level is responding even faster than expected, the work suggests governments have even less time to act in order to combat climate change. In the 1990s it was estimated that 21 and 37% of the global population lived within 30 and 100 km, respectively, of the coast (Cohen, 2005). Population densities in coastal areas are three times the global mean, and it is estimated that 50% of the world's population will live within 100 km of the coast by 2030 (Sarewitz et al., 2003). Human settlements, including many large cities, are also concentrated near or on coastlines, and a large proportion of global economic productivity derives from coastal areas (Titus, 1998). Trends toward urbanization are likely to increase population densities in low-lying coastal areas; the population living within 30 km of the coast is estimated to be growing at twice the global average reflecting coastward migration, and GDP growth in coastal areas exceeds the national average in many countries (Adger, 2000). Coastal zones are, therefore, of great importance as zones of settlement and play a vital role in the economic well-being of many nations. Natural disasters become one of the most severe problems at the coastal area. In particular, low-lying areas, which are strongly affected by flooding or by active processes of shoreline erosion and sedimentation, pose the most serious consequences for local communities and tourists (Nicholls and Hoozemans, 2005). Functions and values of the coastal system have been degraded, and public safety and economy have been impacted. These problems could be accentuated due to rapidly increasing population pressures, which often lead to inconsiderate or poorly planned development in natural hazard-prone areas and potential scenarios of climate change/relative sea level rise.

32.2 Global Sea Level Rise Predictions

The physical processes which determine the rates of Greenland ice loss and Antarctic ice sheet melting are not completely understood and have not been adequately modeled (Alley et al., 2005). This means that current model predictions are limited and may not be entirely accurate (Wigley, 2005; Howat et al., 2007; Rahmstorf, 2007). Evidence from paleoclimatic warming events suggests that future rates of melting could be more rapid than current expectations (Overpeck et al., 2006). Acceleration in Greenland ice sheet melt rates comes from increases in glacial velocities (Rignot and Kanagaratnam, 2006; Chen et al., 2006), which also show substantial short-term variability (Howat et al., 2007). In response to model uncertainty, Rahmstorf (2007) proposed the use of a semi-empirical model that, when applied to the IPCC Third Assessment Report emission scenarios, predicts between 0.50 and 1.40 m of sea level rise by 2100 (Fig. 32.1).

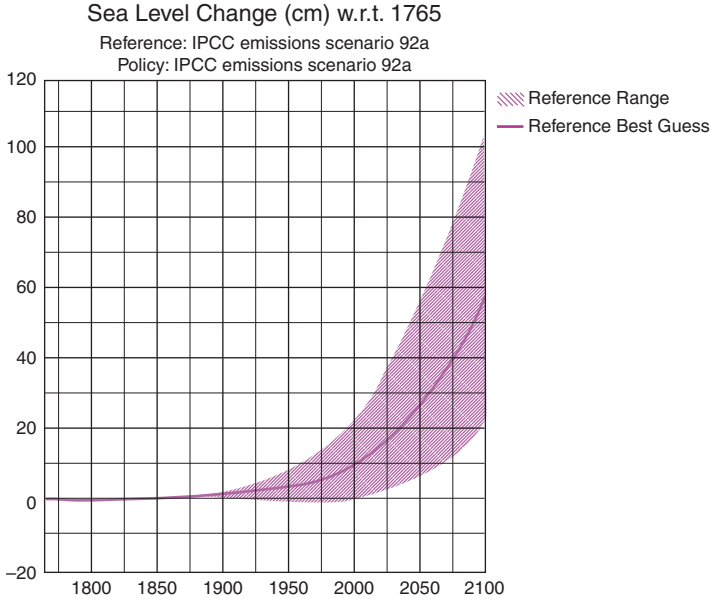


Fig. 32.1 Modeled sea level rise from 1765 to 2100 using the simple models in the MAGICC package.

32.3 Regional and Local Scales Sea Level Rise Predictions

Scaling down global climate predictions to the regional level is a key aspect of current research. Efforts have begun to investigate regional differences in sea level rise (Church et al., 2004). At the regional and local level, relative rates of sea level rise are influenced not only by regional ocean basin differences but also by local vertical land movements. Key processes affecting vertical land movements are glacial isostatic adjustment (Miller and Douglas, 2006) and crustal deformation (Adger; 2000; Verdonck, 2006). In addition to regional differences, the likelihood of future events may not be accurately predicted by probabilities derived from the past. The current techniques developed for dealing with uncertainty and natural variability will not necessarily be effective when faced with future changes. For example, the Anzali Lagoon Project Management Experts (ALPME) use historic analysis to create floodplain maps in the study region and determine base flood elevations representative of the next 10 years floodplain. These maps do not reflect how hydrological regimes will be affected by future climate change. Factors such as increasing the Caspian Sea levels, along with changes in precipitation and snowpack, will affect the flood zones. These factors will need to be considered for ALPME maps to be accurate (Fig. 32.2).



Fig. 32.2 Long-term changes in the Caspian Sea level (a) and Anzali Port in the 20th century and last 20 years (b) UNOP, 2003; The National Research and Study Center of the Caspian Sea, 2007.

32.4 Materials and Methods

The Anzali Lagoon Management Project considers the implications of a rapid rise in the Caspian Sea level due to the collapse of the East North Pole Ice Sheet, high water discharge from the Volga River, which could produce a rise in sea level of 0.20 to 1.5 m. The historical changes are very small compared to the scenario to be considered in Anzali Lagoon Project – a 1.20 m rise in 10 years (or 12 cm/year). As we are dealing with a poorly understood phenomenon, it was felt better to keep the scenario very simple, because the main goal is to understand the response to the scenario. The assumed increases in the Iranian coast at the Caspian

Sea area mean sea level range from 20 cm to 1.20 m, incorporating low (20–40 cm), medium (40–80 cm), and high values (80–120 cm) within the range of possible futures (2016).

This study tests the applicability of using the social–ecological resilience framework to analyze and respond to the Caspian Sea level rise (CSLR). In order to be effective, it focuses on a topical and geographic subset of the Caspian Sea level rise issue. The goal is to provide a detailed evaluation of the impediments and opportunities for the Caspian Sea level rise response in the context of the Caspian Environment Programme (CEP) in Guilan Province. In this study, we show that for many of the possible consequences of global warming and the Caspian Sea level rise on the Anzali Lagoon District in the north of Iran; and develop anticipatory responses that would substantially reduce adverse impacts of global warming with relatively little risk. We suggest a number of criteria for evaluating response strategies and present several example responses in detail particularly focused on a management plan for study district. We hope that this project helps motivate planners throughout the region to begin preparing for the uncertain consequences of a global warming and the Caspian Sea level rise in the next few years.

32.5 Results and Discussion

The CSLR predictions are a complex and multi-faceted issue. Response to this issue requires actions on a variety of fronts and at many levels of government. Only in combination will these semi-independent steps be enough to change the trajectory of climate change, allow societies to adapt to the unavoidable changes, and decrease climate change impacts. The Caspian Sea levels will continue to rise for many centuries and forward-thinking decision-makers will have the ability to design proactive response strategies that will allow for adaptation to those changes. The concepts of resilience provide a framework for analyzing not only potential sea level rise impacts but also policy response options. The effort to determine effective policy response options is aided by the use of current mapping technology. High-resolution data sources provide a powerful and useful tool with which to respond to the CSLR. Computing resources allow for the efficient generation of a variety of relative CSLR scenarios based on the local realities of vertical land movement and topography. The choice of scenarios can build community understanding and highlight areas of vulnerability. The availability of high-resolution data allows for the creation of non-catastrophic scenarios that can be used to inform local decisions and initiate consideration of legal and regulatory opportunities for response.

The greatest effect of CSLR will be the increased risk of inundation around the estuary, the lower rivers, and the Anzali Lagoon in the Guilan Province. The Anzali Lagoon is associated with the greater frequency of extreme tidal water levels. For example, the estimated rise in the Caspian Sea levels by 2016 would lead to changes in water levels, the protection ability provided, and ecological

functions of the Anzali Lagoon. The existing protection provided by minimum ground and floor levels will also be progressively reduced.

An alternative way of assessing the effects of the CSLR is to compare the areas at risk for inundation in similar-sized events with and without CSLR. The indicative inundation areas for a 1% (10-year return period) tidal event associated with 1.20 m SLR estimated that an additional 32,440 km² mostly natural resource and paddy fields of land within the city could be potentially at risk by this magnitude event by 2016. In monetary terms, the costs of the additional assets at risk are significant, being estimated at approximately \$3.2 billion. This represents approximately a 223% increase from the current value of assets at risk in this size event.

The CSLR will not be experienced as the simple changes in inundation elevation depicted in the previous section. It will be experienced through increased flooding as formerly extreme events become relatively less extreme and more frequent. In an attempt to describe those changes, this study creates floodplain maps for the Anzali Lagoon District in the north of Iran. (a) Current sea level and associated floodplain, (b) 0.20 m of Caspian Sea level rise and new floodplain, (c) 0.40 m of Caspian Sea level rise and new floodplain, (d) 0.6 m of Caspian Sea level rise and new floodplain, (e) 0.80 m of Caspian Sea level rise and new floodplain, (f) 1 m of Caspian Sea level rise and new floodplain, and (g) 1.20 m of Caspian Sea level rise and new floodplain (Fig. 32.3).

The maps created in this study are designed to identify areas of potential vulnerability. They should not be used for specific site planning, construction decisions, or high precision planning. The maps are a valuable aid to local decision-makers and planners in the development of non-catastrophic sea level rise response options. The maps colors showed the new shoreline under each of the CSLR scenario. Initially the heavily armored shoreline limits the extent of the floodplain (a). A 0.20 m increase in the Caspian Sea level creates a commensurate 0.20 m increase in the base flood elevation (b). As the Caspian Sea levels increase, the floodplain expands, as does the area potentially vulnerable to large storms and major flood events. With a 0.60 m rise in the Caspian Sea level, the new flood zone is equivalent to the 1 m inundation scenario. In each case, infrastructure within the new flood zone is at risk to impacts from large storm events.

Experts at Anzali Lagoon present maps of likely inundation as a result of SLR of 0.20 m by 2009 and 1.20 m by 2016 which show that the areas between Anzali Lagoon and village and cities could be affected.

In summary, the Caspian Sea levels will continue to rise for many centuries and forward-thinking decision-makers will have the ability to design proactive response strategies that will allow for adaptation to those changes. The concepts of resilience provide a framework for analyzing not only potential sea level rise impacts but also policy response options. The effort to determine effective policy response options is aided by the use of current mapping technology. High-resolution data sources provide a powerful and useful tool with which to respond to the CSLR. Computing resources allow for the efficient generation of a variety of relative CSLR scenarios based on the local realities of vertical land movement and to-

pography. The choice of scenarios can build community understanding and highlight areas of vulnerability. The availability of high-resolution data allows for the creation of non-catastrophic scenarios that can be used to inform local decisions and initiate consideration of legal and regulatory opportunities for response.

32.5.1 Planning responses

The Anzali Lagoon Management Project scenarios on the CSLR (1.20 m in 10 years) will offer some policy plan. 'To avoid higher intensity forms of built development in areas that could be subject to anticipated sea level rise' it is recommended that the Council adopt the following two-tier approach to new land-use developments in areas of potential risk:

- Restrict new land-use developments in areas that within 10 years would be less than 1.20 m Caspian Sea level increase. Restriction below this level is considered appropriate, as extrapolation of existing linear trends in CSRL would result in more inundation areas. These restrictions may take the form of limiting development to open space and reserves and prohibiting the placement of fill. The use of fill to raise ground levels in these areas is not considered appropriate, as with continuing CSLR, the resulting developments would still require protection from inundation at some stage in the future. The implementation of this planning control would allow the water bodies to naturally expand with CSLR into existing undeveloped areas to accommodate ecological migration.
- Control new land-use developments in areas that within 10 years would be below the 0.20–1.20 m tide level with CSLR. Control below this level is considered appropriate as it would allow for low-cost or temporary developments while retaining flexibility of either retreat or more substantial development once some of the uncertainties are clarified. Possible levels of control could involve 'future proofing' building by setting minimum floor levels in the next few years and only consenting relocatable buildings.

32.5.2 Protection responses

There are two types of protection options that need to be considered. The first is the maintenance of existing natural protection systems such as sand dunes, beaches, and vegetation. This form of protection is vital at the Anzali Lagoon. It is recommended that ongoing maintenance programs such as dune restoration, vegetation control, and beach renourishment should be enhanced or implemented now in all of these areas before costly or irreversible losses occur. The second type of protection option is longer term physical engineering works to upgrade existing structures or construct new ones in high-risk areas. Existing structures which will require upgrading at some time after 2009 in order to maintain the current level of protection include the tidal gates, and protection walls around some parts of the Anzali Lagoon. Possible new protection works that will need to be considered in the future include tidal gates on some other parts of the Lagoon (more than four that we did in past). However, before any of the longer term protection

options are considered, it is recommended that the City Council undertake a cost–benefit analysis of implementing these options against the alternative options of do nothing and planned retreat. As well as economics, this analysis should also consider the environmental and social implications of the different options.

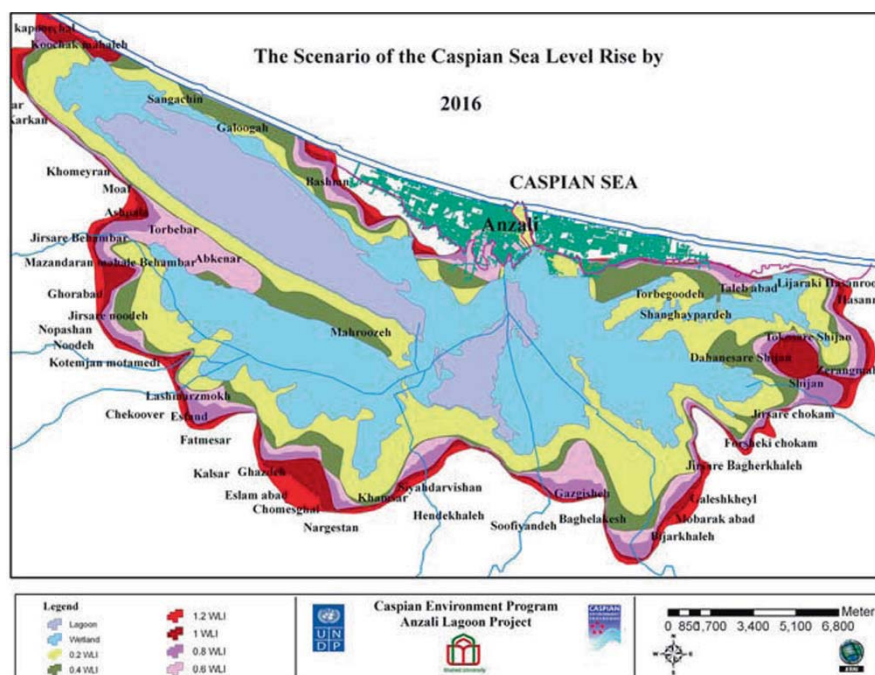


Fig. 32.3 Caspian Sea level rise and the Anzali Lagoon inundation scenarios (0.20 – 1.20 m).

32.6 Conclusions

The greatest effect of CSLR will be the increased risk of inundation around the estuary, the lower rivers, and the Anzali Lagoon. The Anzali Lagoon is associated with the greater frequency of extreme tidal water levels. For example, the estimated rise in the Caspian Sea levels by 2016 would lead to changes in water levels, the protection ability provided, and ecological functions of the Anzali Lagoon. The existing protection provided by minimum ground and floor levels will also be progressively reduced.

The CSLR predictions are a complex and multi-faceted issue. Response to this issue requires actions on a variety of fronts and at many levels of government. Only in combination will these semi-independent steps be enough to change the trajectory of climate change, allow societies to adapt to the unavoidable changes, and decrease climate change impacts.

Acknowledgment

The authors acknowledge the financial support provided by the Caspian Environment Programme (CEP).

References

- Adger, WN (2000) Social and ecological resilience: are they related? *Progress in Human Geography* 23(3): 347–364.
- Alley, R, Clark, P, Huybrechts, P, Joughin, I (2005) Ice-sheet and sea-level change. *Science* 310: 456–460.
- Chen, J, Wilson, C, Tapley, B (2006) Satellite gravity measurements confirm accelerated melting of Greenland ice sheet. *Science* 313: 1958–1960.
- Cohen, S (2005) Climate change will impact the Seattle department of transportation. Submitted to Seattle Mayor and City Council Members. Conducted by the Office of the City Auditor. Constitution of the United States. Amendment V.
- Church, J, White, N, Coleman, R, Lambeck, K, Mitrović, J (2004) Estimates of the regional distribution of sea level rise over the 1950–2000 Period. *American Meteorological Society* 17: 2609–2625.
- Howat, I, Joughin, I, Scambos, T (2007) Rapid changes in ice discharge from Greenland outlet glaciers. *Science* 315: 1559–1561.
- Miller, L, Douglas, B (2006) On the rate and causes of twentieth century sea-level rise. *Phil. Trans. R. Soc. A* 364: 805–820.
- Nicholls, RJ, Hoozemans, FMJ (2005) Global vulnerability analysis. In: Schwartz, M. (ed.) *Encyclopedia of Coastal Science*. Dordrecht, Netherlands, Kluwer Academic Publishers: 486–491.
- Overpeck, J, Otto-Bliesner, B, Miller, G, Muhs, D, Alley, R, Kiehl, J (2006) Paleoclimatic evidence for future ice-sheet instability and rapid sea-level rise. *Science* 311: 1747–1750.
- Rahmstorf, S (2007) A Semi-empirical approach to projecting future sea-level rise. *Science* 315: 368–370.
- Rignot, E, Kanagaratnam, P (2006) Changes in the velocity structure of the Greenland ice sheet. *Science* 311: 986–990.
- Robards, R, Greenberg, J (2007) Global constraints on rural fishing communities: whose resilience is it anyway? *Fish and Fisheries* 8(1): 14–30.
- Sarewitz, D, Pielke, R, Keykhah, M (2003) Vulnerability and risk: some thoughts from a political and policy perspective. *Risk Analysis* 23(4): 805–810.
- Titus, J (1998) Rising seas, coastal erosion, and the takings clause: how to save wetlands and beaches without hurting property owners. *Maryland law Review* 57(4): 1279–1399.
- The National Research & Study Center of the Caspian Sea, (2007), *Water Level Fluctuations of the Caspian Sea in the Hydrological Year 2005–2006*.
- United Nations Office for Project Services, (2003), *Support to the Caspian Centre for Water Level Fluctuations*. Denmark: UNOPS, 2003.
- Verdonck, D (2006) Contemporary vertical crustal deformations in Cascadia. *Tectonophysics* 417: 221–230.
- Wigley, T (2005) The climate change commitment. *Science* 307: 1766–1769.

Impacts of Climate Change on Water Resources in Saudi Arabia

Faisal M. Al Zawad, and Ahmat Aksakal

33.1 Introduction

Climate change issues are discussed widely around the world. Many scientists (Treut et al., 2007) relate global warming and its consequences to human activities and not to natural fluctuations. The reasoning of this approach is the timescale of climate change. Recent warming of the Earth is considered to be abrupt compared to the timescale usually accompanied with natural climate change episodes. Earth's natural climate changes happen gradually in a long period of time (tens of thousands to millions of years), but we are witnessing an abrupt change over the past 200 years. The industrial revolution with fossil fuels as its main source of energy is setting a steady emission increase of carbon dioxide and other greenhouse gases which trap heat causing an increase of temperature in the lower atmosphere. Climate change is recognized as an important issue, and international communities through the United Nations created special groups to focus on climate change effects and initiated protocols to organize a global response to deal with its consequences. Unusually strong tropical storms, heavy precipitations causing devastating floods, more frequent heat waves, frequent droughts, and other similar events are connected to a modern climate change. The government of Saudi Arabia has recognized this by signing the Kyoto Protocol. This calls, among others, for implementation of commitment to stabilize greenhouse emissions and furnish a report about the current status of climate change to the UN Framework Convention on Climate Change (UNFCCC) on the status of greenhouse gases and climate change impacts and mitigation.

Climate is a complex system as it involves air, water, ice, land, and various interactions like water cycle and greenhouse effects. Water is the bond that brings climate and hydrology together. Any changes in solar inputs, the atmosphere, or the hydrological cycle will affect the interactions among the atmosphere, the hydrosphere, the cryosphere, and the biosphere. The impacts of climate change will be devastating to rivers, lakes, sea level, vegetation, ecosystems, and many others.

Latest studies point to a steady increase in temperature during the 20th century and unprecedented increases in the last 50 years (Nakicenovic et al., 2000).

The mean Earth temperature has been on the rise for the past 150 years in an abrupt manner and expected to increase further by the end of the 21st century with the doubling of the current atmospheric carbon dioxide. Climate change interacts with various natural processes in the atmosphere, the hydrosphere, the cryosphere, and the biosphere. There is an increasing evidence that anthropogenic (caused by human's activities) gases are to be blamed in causing the climate change (Treut et al., 2007).

Studying the future state of water resources in a changing climate requires a common ground of approximation. The hydrologist would like to get specific information about future precipitation, temperature, evaporation, runoff, and others on a specific location like an aquifer or a watershed which is mostly on a scale of less than 10^5 km² (Loáiciga, 1997). On the other hand, climatologists run global climate models (GCMs) with a resolution around 300 km to predict the future. From here the need to run a regional climate model (RCM) arises, to include topographical and geographical details to produce high-resolution results.

Climate change is a global issue, but knowing its effect on water resources in a small area requires a great deal of information and analysis. The climate of Saudi Arabia is arid with insignificant contribution to water recharging. Overexploitation of fossil groundwater is apparent everywhere in the Kingdom. No matter what the future brings, being aware of the state of climate change and its impacts on water resources can be of a great benefit to the nation and consist of essential information to aid in protecting and managing the water resources.

33.2 Problem Statement

The importance of water and air in our daily life is clear to everyone, though they represent fragile Earth resources that can change abruptly at times. Understanding the mechanics of climate change provides us with an essential need to prepare for the future. Saudi Arabia has huge ancient groundwater reserves that are continuously under increasing demand. The total number of wells in Saudi Arabia increased by more than 100% from 1982 to 1990, and the total irrigation demand in 1997 was 22,933.4 million cubic meters (Rasheeduddin et al., 2001). This type of research has been applied over Saudi Arabia for the first time and will open many opportunities to investigate the effects of climate change on various sectors and resources in Saudi Arabia. In this study we will shed light on what is expected to face us with regard to precipitation, wind speeds, runoff, temperature, and evaporation. This information can point the sensitive areas that might be affected by climate change and help in designing a proper plan to manage our water resources. This research will provide future climate variables for scenario A2 which calls for high emission of carbon dioxide and explosion of the world population (Treut et al., 2007). Those climate variables can be used by hydrologists to predict the effects of climate change on the recharge of aquifers and consequently the future

status of aquifers in terms of storage and yields by implementing available hydro-logic models.

33.3 Methodology

GCM data covering the region of Saudi Arabia are provided by the UK Met Office. Those data will be used to run a licensed RCM called 'PRECIS' that can be initiated at a resolution of 50 or 25 km. The resolution of 50 km is chosen because a 25 km run will take six times the amount of time needed to run experiments with 50 km resolution.

PRECIS (Providing Regional Climates for Impact Studies) is a regional climate modeling system that can be run on a PC. The UK Met Office's Hadley Center for Climate Prediction and Research is the provider and the developer of this software. The data for the boundary condition are supplied by the Hadley Center Global Climate Model (GCM), UK Met Office. PRECIS comes with a user interface to carry on climate experiments (Jones et al., 2004).

Future projections of climate change are done globally with worldwide support through United Nations Organizations. Very few countries have the capability to designate a dedicated group of highly trained scientists and provide extremely fast computers to run GCMs' models to generate climate change scenarios and perform the necessary analysis to investigate the regional impacts of climate change on their specific regions. The United Nations Development Program (UNDP), the UK Department for Environment, Food and Rural Affairs (DEFRA), and the UK Department of International Development started funding PRECIS to be available to developing countries to generate their own climate change scenarios with using a personal computer only. The UK Met Office's Hadley Center will supply the software, the boundary conditions, and other fields of global quantities required to run PRECIS (Jones et al., 2004). Emission scenarios describing population, energy, and economics are taken from IPCC SRES (A1T, A1FI, A1B, A2, B1, and B2). Concentration estimation of carbon dioxide, methane, sulfates, and other gases is done is carbon cycle and chemistry models. PRECIS will be used to enhance the relatively large-scale output of HadAM3P, a 150 km resolution Hadley Center's global atmospheric model to get fine, detailed information of climatic predictions.

33.3.1 Developing a plan

There are three parts for this research. First is to set up the regional climate model (PRECIS) and run the three experiments. Second is to do basic analysis to the output data to get specific information about climate fields and calculate the predicted state of the future from the simulation and the historical data. Third is to use ArcGIS 9.2 to present the climate variables outputs and do further analysis.

33.3.2 Setting up and running PRECIS

Linux operation system (open SUSE 10.2) and PRECIS (version 1.4.6) were installed on three separate personal computers. Two of them have processors (CPU):

Intel® Pentium® 4 with speed 3.2 GHz. The third one is with an Intel® Centrino® core duo processor with speed of 2.16 GHz.

Three experiments were designed to perform present, future, and reanalysis data (see Section 33.2) in order to get proper statistical information. Present and future experiments were based on Hadley Center's GCM data. The final experiment is dedicated to downscale ECMWF reanalysis data (ERA40) using PRECIS. Each experiment took approximately 3 months of continuous run. The time period for each experiment was 31 years, from which the first year will be discarded as a spin off year. Sulfur cycle is included in the future and present simulations.

33.3.3 Basic Analysis

The outputs of the experiments for the concerned climate fields are organized in three groups: historical, present, and future simulations. A set of equations adopted after Loáiciga (2007) was used to calculate the resultant reading for the future under the IPCC scenario A2. The significant contribution of carbon dioxide is translated in the equations referring to future simulation with the doubling of the present amount of carbon dioxide in the atmosphere. Equation 33.1 gives the average daily temperature at the end of the 21st century (2071–2100) by adding the current average daily temperature (historical value) to the difference between future (2071–2100) and present (1961–1990) simulations for average daily temperature. Equation 33.3 gives the average daily precipitation at the end of the 21st century by multiplying the current average daily precipitation (historical value) by the ratio of future (2071–2100) average daily precipitation over the present (1961–1990) average daily precipitation. The rest of the equations (Eqs. (33.2), (33.4–33.6)) follows similar concepts.

$$T_{\text{Scenario}} = T_{\text{Historical}} + (T_{f2 \times \text{CO}_2} - T_{b1 \times \text{CO}_2}) \quad (33.1)$$

$$W_{\text{Scenario}} = W_{\text{Historical}} + (W_{f2 \times \text{CO}_2} - W_{b1 \times \text{CO}_2}) \quad (33.2)$$

$$P_{\text{Scenario}} = P_{\text{Historical}} \times \left(\frac{P_{f2 \times \text{CO}_2}}{P_{b1 \times \text{CO}_2}} \right) \quad (33.3)$$

$$E_{\text{Scenario}} = E_{\text{Historical}} \times \left(\frac{E_{f2 \times \text{CO}_2}}{E_{b1 \times \text{CO}_2}} \right) \quad (33.4)$$

$$(P - E)_{\text{Scenario}} = (P - E)_{\text{Historical}} \times \left(\frac{(P - E)_{f2 \times \text{CO}_2}}{(P - E)_{b1 \times \text{CO}_2}} \right) \quad (33.5)$$

$$Q_{\text{Scenario}} = Q_{\text{Historical}} * \left(\frac{Q_{f2 \times \text{CO}_2}}{Q_{b1 \times \text{CO}_2}} \right) \quad (33.6)$$

In these equations, T , W , P , E , $(P-E)$, and Q respectively represent temperatures in degrees Celsius, wind speeds in meters per second, total precipitation, surface evaporation in millimeters per day, the resultant of subtraction of surface evaporation from total precipitation in millimeters per day, and the mean runoff in millimeters per day. The subscript (f) represents future simulation, and the subscript (b) represents the baseline simulation.

33.3.4 Using GIS technology

An approach to use GIS in reading meteorological data as features, points, or polygons and carrying basic statistical operations on the resultant layers was performed repeatedly for temperature, precipitation, evaporation, runoff, and wind speeds. Points represent cities and meteorological stations, while the polygons represent defined regions of Saudi Arabia. The defined 6 regions and 37 locations scattered all over Saudi Arabia were studied separately.

GIS data for Saudi Arabia's political boundaries, coastal shores, and identified locations had been utilized. The designated six regions of Saudi Arabia were communicated to GIS by using x and y values for the vortices of each region and then connecting the vortices. Similarly, main cities and meteorological stations were located from their latitudes and longitudes. Enhancement to the map was carried out after testing several ways to get the output data from the climate model to GIS. The climate fields' data were written on Microsoft Office Excel file, then saved as a Microsoft Office access' database which further communicated to GIS by joining features. It was found that a desired column of data from Excel file can be copied and pasted on the desired layer using ArcMap's editors after creating the corresponding field in ArcCatalog. The means of climate fields were created as features in every region and every meteorological station. Historical, predicted, and percentages of climate change results were viewed as multivariable bar charts by implementing 'symbolology' in layer's properties.

33.3.5 Data

Several types of data were used to run the model software (PRECIS):

1. 31 years of boundary data (1960–1990) integration of HadAM3P, a 150 km resolution Hadley Center's global atmospheric model.
2. 31 years of boundary data (2070–2100) integration of HadAM3P consistent with the SRES A2 emissions scenario.
3. 31 years of boundary data (1960–1990) of {ERA40 (1957–2001)} reanalysis data derived from ECMWF (European Center for Medium-Range Weather Forecasting).

4. Local historical data (1961–2005) observed by Presidency of Meteorology and Environment (PME) meteorological stations.

33.3.6 Study area

Saudi Arabia is divided into six regions (Table 33.1), presented in Fig. 33.1. The regions are chosen in relation to geological, meteorological, and hydrological characteristics as given below:

1. **Eastern region:** The area is between 43° and 51° East of longitudes and between 25° and 30° North of latitudes. Dhahran, Dammam, Hafar Al-Batin, Al-Ahsa, Khafji, and Jubail are included in this region.
2. **Central region:** It is bounded by the longitudes of 43° East and 47° East and latitudes of 21° North and 25° North. Riyadh is the major city in this region.
3. **Western region:** This is bounded by longitudes 37° East and 43° East and latitudes 21° North and 25° North. This area includes Makka, Madina, Jeddah, Taif, and Yanbu.
4. **Northern region:** This area is between 35° East and 43° East longitudes and between 25° North and 33° North Latitude. Qasim, Hail, Tabuk, Quriyat, Rafha, Turaif, Ar'ar, AL Jouf, and Al Wejh are among the cities and towns covered by this region.
5. **Southern region:** It is bounded between longitudes 40° East and 47° East and latitudes 15° North and 21° North. This area includes Abha, Khamis Mushait, Najran, and Gizan.
6. **Empty Quarter region:** It is bounded by longitudes 47° East and 56° East and latitudes 17° North and 25° North. Sharoura and Sulayel are included in this region.

Table 33.1 The regions are bounded by rectangular shapes covering the domain of Saudi Arabia.

Number	Name	Western longitude	Southern latitude	Eastern longitude	Northern latitude
1	Eastern	43 E	25 N	51 E	30 N
2	Central	43 E	21 N	47 E	25 N
3	Western	37 E	21 N	43 E	25 N
4	Northern	35 E	25 N	43 E	33 N
5	Southern	40 E	15 N	47 E	21 N
6	Empty Quarter	47 E	17 N	56 E	25 N

33.3.7 Studied locations

Thirty-seven separate locations (Fig. 33.1) were chosen to present the spread effects of climate change and to determine the more sensitive areas to changes in climate. There are 28 stations that are supervised by PME and have continuous records of hourly and daily observations. The need arises to adopt other locations to have a better representation of the area. Reanalysis data (ERA40) are used as a historical data for those stations as well as each of the six regions. PME data are used as historical data for available stations.

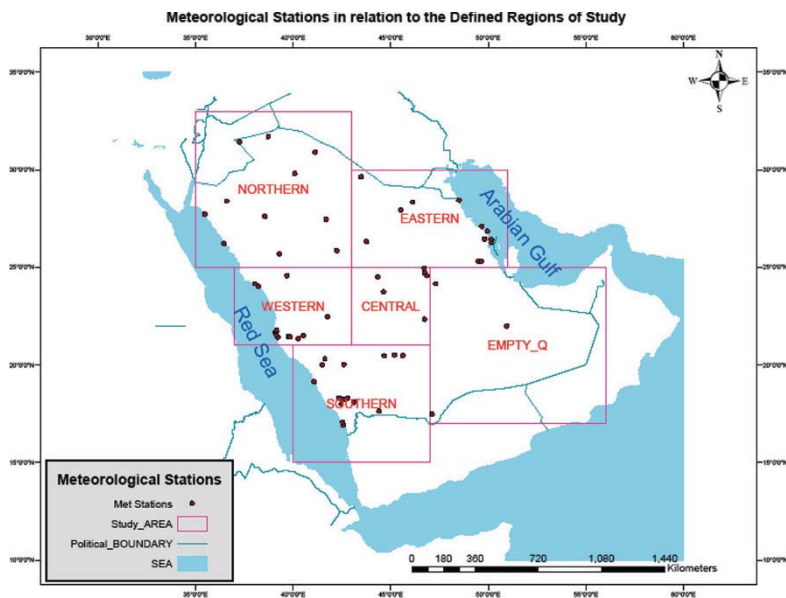


Fig. 33.1 Study area is divided into 6 regions inside which 37 locations are selected represented by black dots.

Table 33.2 PRECIS simulation weighted area daily values for 30 years spanning the years 1961–1990 compared to the ERA40 reanalysis observed values for the same period.

Climate fields	Statistical means		Standrd deviation	
	PRECIS	Observed	PRECIS	Observed
Temperature	21.98	23.97	5.49	4.54
Precipitation	1.16	1.50	1.45	1.73
Evaporation	2.17	2.22	2.29	1.87
Wind speeds	4.56	4.42	1.70	1.44
Runoff	0.0029	0.0028	0.011	0.014

33.4 Validation of the Model

The simulated and observed daily multiannual means are compared for the corresponding climate fields for the period 1961–1990 for the entire used domain (Fig. 33.2) by visual and single values assigned for each climate field. The Visual Climate Data Analysis Tool (VCDAT) is used to extract the statistical mean and standard deviation. We can see that the model has a cold bias and slightly decreases the actual precipitation and evaporation. The model tends to give slightly higher values in wind speeds and runoff (Table 33.2). If the area covering Saudi Arabia is considered instead of the whole domain, the agreements of the model to observation are much better. The statistical standard deviation shows that the mean values for

the model are more spread for temperature, evaporation, and wind speeds than the corresponding observations, while the model's means for precipitation and runoff show less spread values than the corresponding observations.

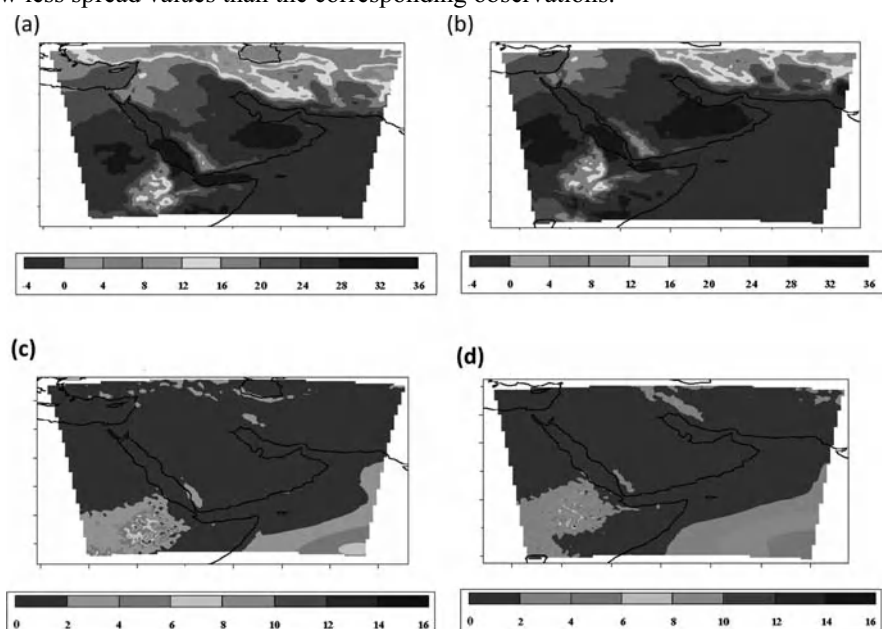


Figure 33.2 Validation of daily mean temperature and precipitation. The model is represented by (a) temperature and (c) the precipitation, while (b) and (d) are for the corresponding observations based on ERA40 reanalysis data.

33.5 Results and Discussion

33.5.1 Eastern province

Table 33.3 shows an increase of 4.47°C , surface wind speeds decreased by 1% precipitation stand tall with substantial increases of 40%, a slight increase of 0.87% in surface evaporation which contributed to an increase of 4% in the soil water balance and an increase of 162% in runoff.

Table 33.3 Eastern region climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature ($^{\circ}\text{C}$)	28.843	24.37	4.473	18.353
Wind speed (m/s)	4.157	4.212	-0.055	-1.307
Precipitation (mm/day)	0.334	0.256	0.078	30.313
Evaporation (mm/day)	0.744	0.737	0.006	0.875
Runoff (mm/day)	0.003	0.001	0.002	162.105
P - E (mm/day)	-0.461	-0.481	0.02	4.199

33.5.2 Central region

An increase in all climate fields is expected in this region (Table 33.4). The average daily temperature is expected to increase by 4.27°C, surface wind speeds will increase by 0.62%, precipitation will increase by 40%, surface evaporation will increase by 3.4%, soil water balance will increase by 3.6%, and runoff will increase by an astonishing 312%.

Table 33.4 Central region climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature(°C)	30.627	26.356	4.271	16.205
Wind speed(m/s)	4.369	4.343	0.027	0.617
Precipitation(mm/day)	0.331	0.235	0.096	40.766
Evaporation(mm/day)	0.861	0.832	0.029	3.44
Runoff(mm/day)	0.006	0.001	0.005	311.971
$P-E$ (mm/day)	-0.575	-0.597	0.022	3.636

33.5.3 Western region

Table 33.5 shows an increase of 4.1°C in temperature, 0.19% in surface wind speeds, 40% in precipitation, 1.9% in evaporation, 3.3% in soil water balance, and 353% in runoff.

Table 33.5 Western region climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature (°C)	30.508	26.379	4.129	15.651
Wind speed (m/s)	4.409	4.401	0.008	0.19
Precipitation (mm/day)	0.249	0.177	0.071	40.292
Evaporation (mm/day)	0.962	0.944	0.018	1.931
Runoff (mm/day)	0.005	0.001	0.004	353.34
$P-E$ (mm/day)	-0.741	-0.766	0.025	3.293

33.5.4 Northern region

Table 33.6 indicates an increase of 4.3°C in temperature, 1.2% in evaporation, and 101% in runoff. A decrease is projected for precipitation and surface wind speeds by 4.1% and 11%, respectively.

33.5.5 Southern region

All climate fields are expected to increase (Table 33.7). Temperature will increase by 3.9°C, surface wind speeds by 1.2%, precipitation by 35.7%, evaporation by 15.4%, soil water balance by 6.1%, and runoff by 233%.

Table 33.6 Northern region climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature(°C)	26.561	22.275	4.286	19.239
Wind speed(m/s)	4.095	4.145	-0.05	-1.194
Precipitation(mm/day)	0.219	0.229	-0.009	-4.081
Evaporation(mm/day)	0.755	0.746	0.009	1.243
Runoff(mm/day)	0.002	0.001	0.001	101.306
P-E(mm/day)	-0.531	-0.518	-0.013	-2.559

Table 33.7 Southern region climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature(°C)	30.921	27.023	3.897	14.422
Wind speed(m/s)	4.134	4.085	0.049	1.197
Precipitation(mm/day)	1.005	0.74	0.264	35.69
Evaporation(mm/day)	1.483	1.286	0.197	15.352
Runoff(mm/day)	0.007	0.002	0.005	233.382
P-E(mm/day)	-0.512	-0.546	0.033	6.124

33.5.6 Empty Quarter

An increase of all climate fields is expected under A2 scenario (Table 33.8). Temperature will increase by 3.2°C, surface wind speeds by 1.8%, precipitation by 38.4%, evaporation by 10.8%, soil water balance by 3.6%, and runoff by 192%.

Table 33.8 Empty Quarter climate fields.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature(°C)	30.921	27.023	3.897	14.422
Wind speed(m/s)	4.134	4.085	0.049	1.197
Precipitation(mm/day)	1.005	0.74	0.264	35.69
Evaporation(mm/day)	1.483	1.286	0.197	15.352
Runoff(mm/day)	0.007	0.002	0.005	233.382
P-E(mm/day)	-0.512	-0.546	0.033	6.124

33.5.7 The 37 locations

Temperatures are expected to increase 2.5 to 5.1°C with a mean increase of 4.4°C for all 37 locations. The biggest increase of 5.1°C is over Hafar Al-Batin and the warmest mean temperature is expected over Obailah in the Empty Quarter with average daily temperature of 35.7°C. There are 15 locations in which the mean increase in temperature equals or greater than 4.8°C. The average precipitation change for the selected locations is an increase of 39%, distributed in the range -0.8% for Ar'ar to 111.1% for Dhahran. From the 37 locations, there are 32 locations with a percentage increase of more than 20%, and 11 locations have a percentage

increase of more than 50%. The average change of surface wind speeds is -4.4% with a maximum change of 25% over Sharoura and a minimum change of -64% at Al-Ahsa. There are 14 locations with a positive change in surface wind speeds, and only 9 locations with a change less than 10% . The average change of surface evaporation is 23.1% with a maximum change of 69.5% over Al-Ahsa and a minimum change of -8.3% over Al Wejh. There are 29 locations with a positive change in surface evaporation, and only 9 locations with a change less than 5% . The average change of soil water balance is 100.9% with a maximum change of 900% over Turaif and a minimum change of -2100% over Al-Ahsa. There are 26 locations with a positive change in the soil water balance, and only 7 locations with a change more than 300% .

The averages of all six regions indicate an increase in temperature, precipitation, evaporation, wind speeds, runoff, and soil water balance (Table 33.9). Daily average temperature is projected to increase by 4.2°C which is 16.5% of the historical value. An increase of 30.2% in precipitation is projected for the future which is an increase of 37.7 millimeters per year (mm/year). The evaporation increase is only 5.6% (20.8 mm/year) which gives an advantageous increase in soil water balance (P–E) by 3.0% or 6.2 mm/year. Runoff is projected to increase by 225.7% (1.1 mm/year). Only a slight increase of 0.01 m/s in wind speeds is projected (0.2%).

Table 33.9 The climate fields averaged over all six regions.

Climate field	A2_Scenario	Historical	A2_Change	A2_Percentage
Temperature($^{\circ}\text{C}$)	29.891	25.676	4.216	16.533
Wind speed(m/s)	156.146	118.408	37.739	30.236
Precipitation(mm/day)	341.32	320.53	20.789	5.615
Evaporation(mm/day)	4.274	4.264	0.01	0.222
Runoff(mm/day)	1.643	0.497	1.147	225.72
P –E(mm/day)	–195.898	–202.122	6.225	3.043

We notice much wider variations of climate changes with respect to the historical values when considering the 37 locations, instead of the selected 6 regions of Saudi Arabia. The reason for this is that a particular region will require a weighted area mean while a particular location represents a single point on an area. The accuracy in an area is better than in a single location which is related to the model resolution. An increase of 4.2°C will increase the energy demand and water irrigations. An increase of more than 30% of precipitation can translate to more flash floods and land erosions in western Saudi Arabia. Sensitivity for soil water balance indicates that future under A2 scenario will be slightly increased in the average (3%) but the northern region will suffer a decrease by 2.6% (Figs. 33.3 and 33.4).

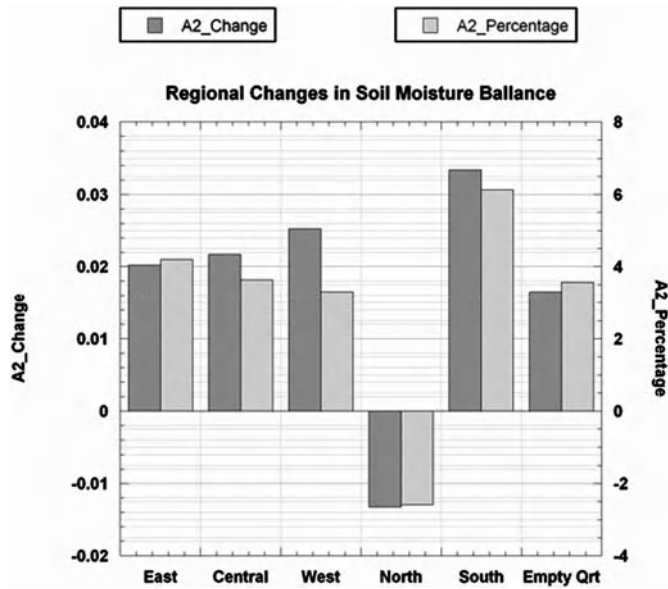


Fig. 33.3 The changes in soil water balance for each region in percentages and in mm/day.

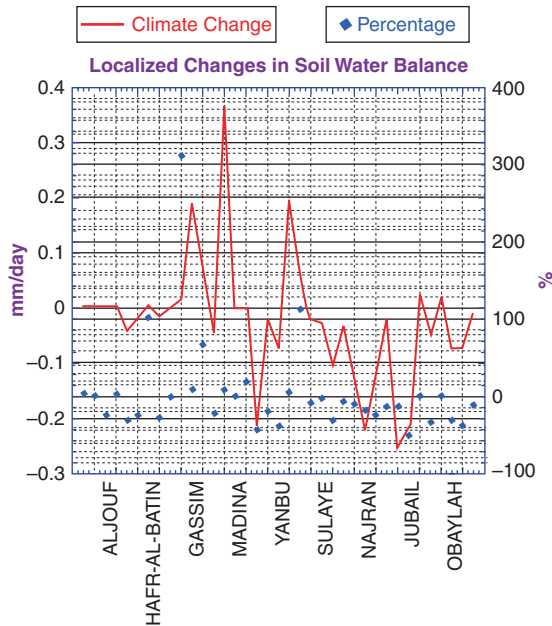


Fig. 33.4 The changes in soil water balance for each location in percentages and in mm/day.

33.6 Conclusions

From this study we can extract the following remarks:

- HadAM3p outputs with PRECIS can produce reasonable high-resolution future climate scenarios.
- Global warming will be felt locally in Saudi Arabia and a change of 3–5°C in mean daily temperature can have big effects on agriculture, energy consumptions, and various aspects of daily life.
- There is a need to expand the research to include hydrologic models for better impact prediction on water resources in Saudi Arabia.
- There is an urgent call for creating a national climate research center to become a focal point to gather information, implement latest technology, and strengthen international cooperation among scientists.

Acknowledgments

The authors acknowledge the cooperation of Presidency of Meteorology and Environment, King Fahd University of Petroleum and Minerals, and the UK Met Office throughout the research period.

References

- Treut, H, Somerville, R, Cubasch, U, Ding Y, Mauritzen, C, Mokssit, A, Peterson, T, Prather, M (2007) Historical Overview of Climate Change. In: *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S et al., (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Loáiciga, HA (2007) Climate Change and Groundwater, available at http://ncsp.vanetwork.org/section/resources/resource_water. (Last accessed 24 January, 2008).
- Loáiciga, HA (1997) Runoff scaling in large rivers of the world. *The Professional Geographer* 49 (3): 356–363.
- Jones, RG, Noguier, M, Hassell, DC, Hudson, D, Wilson, SS, Jenkins, GJ, Mitchell, JFB (2004) Generating high resolution climate change scenarios using PRECIS, Met Office Hadley Center, Exeter, UK, pp. 40.
- Nakicenovic, N, Alcamo, J, Davis, G, de Vries, B, Fenhann, J, Gaffin, S, Gregory, K, Grübler, A, Jung T, Kram T, La Rovere, F, Michaelis, L, Mori, S, Morita T, Pepper, W, Pitcher, H, Price, L, Riahi, K, Roehrl, A, Rogner, H, Sankovski, A, Schlesinger, M, Shukla, P, Smith, S (2000) IPCC Special Report on Emissions Scenarios, available at (<http://www.grida.no/climate/ipcc/emission/501.htm>). Last accessed 24 January 2008.
- Rasheeduddin, M, Abderrahman, WA, Lloyd, J (2001) Management of Groundwater Resources in Eastern Saudi Arabia. *International Journal of Water Resources Development*, 17: 185–210.

Warming Tendency in the Eastern Mediterranean Basin and Its Influence on West Nile Fever Outbreaks

Shlomit Paz

34.1 Introduction

The Eastern Mediterranean (EM) basin, a heavily populated area, is highly sensitive to climatic changes. The region, from the Iskenderun Bay in Turkey to the northeastern shoreline of the Sinai Peninsula, is unique in its climatic aspects, due to its location as the continental junction area between Europe, Africa, and Asia. As a result of this geographical position between different climatic influential areas, the region is highly sensitive to possible climate changes (IPCC, 2007). The millions of people along the EM are vulnerable to this warming trend in many aspects as water supply, crop yields, and human health.

One of the most disturbing impacts of the temperature increase is on human health in various complex ways: increased mortality and morbidity as a result of exposure to extreme heat; increased diseases and injuries due to more frequent and intense extreme weather events (floods, windstorms, droughts); increased diarrheal diseases and other food-and water-related diseases, among other health influences.

During the last decades, the summers in the EM became warmer (Zhang et al., 2005) with an increase in the frequency and the severity of heat waves. In the last 15 years, the region has been affected by the warmest weathers on record (Paz, 2006; Paz et al., 2007). Indeed, recent work by El-Zein et al. (2004) that investigated the linkage between mortality and air temperature variation in Greater Beirut, Lebanon, for the period between 1997 and 1999 showed that a rise of 1°C in temperature yielded a significant increase in mortality. These findings suggest that at regions with moderate to high temperatures such as the EM countries, heat-related mortality can be a significant public health concern.

Temperature increase may have important and far-reaching effects on infectious diseases, especially those transmitted by poikilothermic arthropods as mosquitoes and ticks. Climate change may affect the survival and reproduction of the pathogen or the vector, time of year and level of vector activity, and the rate of

development and reproduction of the pathogen within the vector (Patz et al., 2003). Temperature-related changes in the life cycle dynamics of both the vector species and the pathogenic organisms would increase the potential transmission of vector-borne diseases. There are indications that the warming tendency in the EM is impacting the transmission of infectious diseases. For example, in a recent study Paz et al. (2007) investigated the linkage between local climate change and an ongoing outbreak of *Vibrio vulnificus* disease in Israel since 1996. The survival of this water-borne pathogen is dependent on salinity and temperature. Lag correlation analysis revealed significant correlations between temperature values and hospital admission dates. The authors speculated that an extreme rise in daily temperatures at the beginning of the summer might predict larger *V. vulnificus* populations in fish ponds water.

Another issue is the impact of warming on mosquitoes. Since many mosquitoes and the diseases they carry are sensitive to temperature increase, the potential transmission of many vector-borne diseases carried by mosquitoes, such as malaria, dengue fever, and West Nile virus (WNV), may be increased by the influence of global warming, since the temperatures are related to the life-cycle dynamics of both the vector species and the pathogenic organisms. Warming of the mosquito environment boosts their rates of reproduction and number of blood meals, prolongs their breeding season, and shortens the maturation period for the microbes they disperse (Pats et al., 2003; Epstein, 2005).

Accordingly, this chapter aims to demonstrate the linkage between temperature increase over the EM and West Nile virus outbreaks by focusing on a recent case study from Israel.

34.2 West Nile Virus

West Nile virus (WNV) is a vector-borne zoonotic disease belonging to the Japanese encephalitis serogroup of flaviviruses. These viruses are transferred by carriers, especially mosquitoes, and spread all over the world attacking vertebrates of several types, including birds and mammals. WNV is normally transmitted between birds by the *Culex pipiens*, a mosquito that tends to breed in foul standing water in drains and catch basins (Epstein, 2001; Pats et al., 2003). The disease generally appears at the end of the summer and the beginning of autumn, with incubation period of 3–15 days. West Nile fever (WNF) became recognized as a cause of fatal human meningitis or encephalitis in elderly patients during an outbreak in Israel in 1957. Encephalitis occurs also in horses, as well as causing mortality in certain domestic and wild birds (CDC website, 2004).

WNV is endemic in Africa, south-western Asia, eastern and southern Europe, and parts of the Mediterranean basin (Hubalek and Halouzka, 1999; Dohm et al., 2002). The virus was first detected in the western hemisphere in New York City in 1999 (Nash et al., 2001). The means by which WNV entered the Americas is unknown, but the genetic analysis indicated that the strain responsible for the outbreak was nearly identical to a strain that was circulating in Israel in 1998 (Lancioti et al., 1999). Since 1999, it has moved rapidly westward and was

detected in California in 2004 (Granwehr et al., 2004). Today, WNV exists also in Central and South America and in the Caribbean (Gibbs et al., 2006) and is therefore a vector-borne pathogen of global importance.

34.2.1 WNV and heat conditions

Extreme warm conditions were found to be a crucially important factor that instigated the launching of WNV outbreaks. High temperatures have been shown to speed up the replication of WNV in mosquitoes; this rapid amplification directly affects the likelihood of the mosquito reaching maturity and subsequently infecting other hosts (Epstein, 2001). It has been proven experimentally that high temperatures help increase mosquito abundance, as well as increase vector competency (Turell et al., 2001; Dohm et al., 2002). High temperatures speed up the development of viruses within the mosquito carriers, which only live about 2 weeks (Epstein, 2001 and Pats et al., 2003). Experimental studies on WNV indicate that temperature profoundly influences mosquito-to-vertebrate transmission rates. Summer temperature was found to be one of the most important environmental variables modulating WNV activity in Europe (Savage et al., 1999).

In a study on the linkage between extreme heat and the WNF outbreak in Israel during summer 2000, Paz (2006) found that when the air temperatures do not fall below 25°C for 7 days, the minimum temperatures become the most important climatic factor that encourages the earlier appearance of the disease.

34.2.3 WNF outbreaks

Recent outbreaks of WNV encephalitis in humans have occurred in several places, e.g., in Algeria (1994), in Romania (1996–1997) when the disease course was recognized as more aggressive to humans than in the past, in Russia (1999), in the United States (1999–2004), and in Israel (2000).

Several WNF outbreaks were reported in Israel in the 1950s and one in 1980, but by the end of the 20th century, it was a forgotten disease. After a long absence, WNV was diagnosed in goose flocks in summer 1998. In summer 1999, 3 cases of WNV were reported in humans (2 deaths) and in 2000, a large outbreak occurred with 429 cases (35 deaths) between August and November (ICDC website). This eruption occurred after summers of both medical and climatic warning signs. The three previous summers of 1998, 1999, and 2000 were extremely hot, warmer than ever recorded, with long heat waves (Bin, 2001; Paz, 2006). It is interesting to note that the development of the Israeli outbreak in summer 2000 was comparable to the cases in the Danube Valley in Romania (1996) and in NYC (1999). Despite the climatic dissimilarity between the three regions, all are characterized by warm and humid summers. Each of the three outbreaks appeared after a long period of intense heat (Paz, 2006).

Recent studies observed several impacts of climate change in Israel, as well as in the whole eastern Mediterranean basin: during the second half of the 20th century, an increase in the minimum and maximum summer temperature was detected (Ben-Gai et al., 1999). The frequency of heat waves has risen, with worsening severity (Paz, 2006; Paz et al., 2007). Drought tendency was identified

(Alpert et al., 2002; IPCC, 2007) with an increase in the uncertain behavior of the precipitation patterns (Paz and Kutiel, 2003). As Israel is located along the Syrian-African Rift, it is a major stopover for huge flocks of migrating birds, especially during the transition seasons. Since wild birds are the reservoir of WNV, this geographical location is crucially important for the disease transfer. Indeed, the virus was found in Israel in recent years in a large variety of birds (ICDC website), which frequently interact with mosquitoes in areas of standing water.

34.3 Study Aim

This chapter aims to demonstrate the possible linkages between weather conditions (especially air temperature) and (1) *C. pipiens* mosquito population abundance and (2) WNF frequency in humans, between 2000 and 2005 in Israel. These 6 years follow a long period with a documented tendency for temperature increase in the hot season in the EM.

34.4 Data

1. All reported cases of WNF in Israel (date of admission and patients' address) during the years 2000–2005 (Data source: Israel Ministry of Health, Epidemiology Department, WNV database). Data were collected from all districts from the north to the south.
2. Daily temperature (mean, minimum, and maximum) for the period of 2000–2005 in selected 12 meteorological stations characterized all sub-climatic regions – (Data source: IMS – Israel Meteorological Service).
3. Data of mosquito samplings, generally *C. pipiens* mosquito (the most common species in urban and rural areas of Israel), on chosen dates through the years 2001–2005. This, in selected stations (near the meteorological stations), covers all districts of the country. The samples (collected by the Department for Pest Prevention, Israeli Ministry of Environmental Protection) were classified into three categories that express the increasing severity of the mosquito hazard: 0 = no mosquito hazard, 1 = medium hazard (a few or tens of mosquitoes), 2 = severe hazard (hundreds of mosquitoes or more).

34.5 Methods

WNF cases (date of admission and patients' address) were mapped using Geographic Information System (GIS) for the years 2000–2005. Monthly anomalies of mean monthly temperatures (maximum and minimum) from the perennial monthly averages (maximum and minimum) of the period 1981–2000 for March (end of winter), May (spring), and August (summer) were calculated for selected stations and all characterized as sub-climatic regions. Selected months were mapped using GIS. The relative percentage contribution of seasonal rainfall from the seasonal perennial averages of the period 1971–2000 for winter and spring was calculated. The distribution of mosquito hazard levels was analyzed

using GIS in selected stations along the country. To identify lag correlations between weather conditions and mosquito hazard levels throughout the study period, multinomial logistic regression was calculated between daily temperatures (mean, minimum, and maximum) or daily precipitation amounts and the mosquito hazard samplings. The regression was computed for four main districts from the north to the south. To identify linkages and lag correlations between weather conditions and WNF morbidity, Spearman correlation was calculated between WNF cases (hospital admission dates) and mean daily temperatures/daily precipitation amount, throughout the years 2001–2005. Pearson cross-correlations were calculated between daily minimum, maximum, and mean temperatures (or daily precipitation amounts) and the hospital admission dates in the Tel Aviv metropolis (the region with most of the WNF cases) in 2005 (the year with the highest disease distribution).

34.6 Results and Discussion

Mapping of the geographical distribution of WNF in Israel (2000–2005) indicated that the majority of cases occurred in the densely populated area (Tel Aviv metropolis) along the seashore, and less in the north, which is less populated (Fig. 34.1, see also Paz and Albersheim, 2008). These results reflect the country's population dispersion. The warming tendency that had been detected in the Israeli hot season in past decades (e.g., Paz et al., 2007) was ongoing in the study period. A positive anomaly is apparent in the three examples in Fig. 34.2 (see also Paz and Albersheim, 2008) that illustrates the positive anomalies of the mean monthly temperatures from the perennial averages (maximum and minimum). In four out of the five months of March (2001–2005) an increase in the maximum temperature was found, mostly with an anomaly of more than 3°C (an extreme anomaly of more than 5.5°C was detected in March 2001). In the spring (May) the highest anomaly was detected in 2003, with more than 3°C above the perennial averages for both minimum and maximum temperatures. In four out of five summers, positive anomalies were detected in August with 0.5–1.5°C above the minimum and maximum averages.

Analysis of the distribution of mosquito hazard demonstrated that most mosquito concentrations were found in three main areas (see the locations in Figs. 34.1 and 34.2): (a) along the northern seashore, (b) within the center of Israel, and (c) throughout the southeastern borders between the Dead Sea and the Red Sea. Medium and severe hazards were found near the most densely populated areas (central and northern coastal areas). Medium to severe mosquito hazards appeared in the early spring, weeks before the extreme summer heat. A significant positive linkage with a 2-week lag (result of multinomial logistic regression) was detected between the standardized mean daily temperatures and the mosquito hazard levels (medium and severe hazards) in the North. The same tendency was found during a longer period in the Hadera district, north of Tel Aviv (Paz and Albersheim, 2008).

Precipitation amounts as well as rainfall distribution did not show a spatial coherence along the study period.

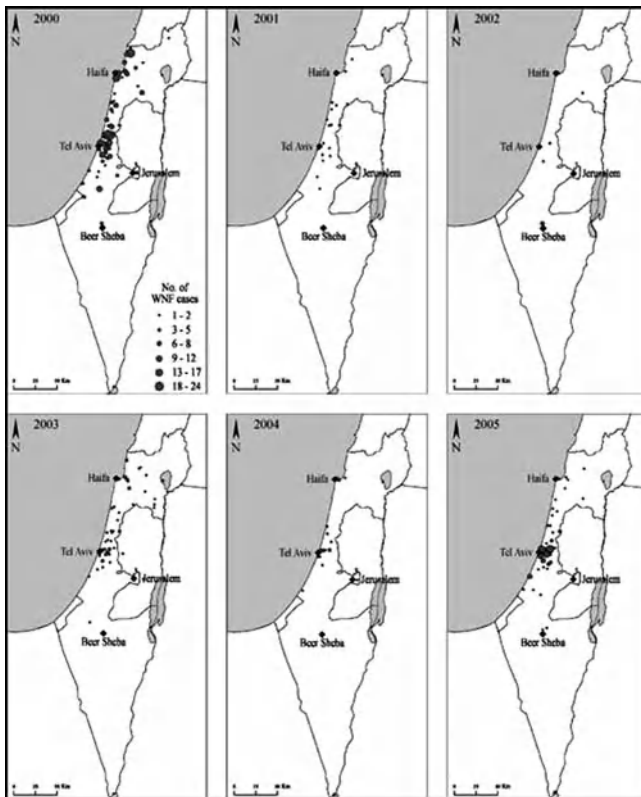


Fig 34.1 WNF cases distribution in Israel, during the years 2000 (initial outbreak with 429 cases in humans), 2001 – 33 cases, 2002 – 7 cases, 2003 – 80 cases, 2004 – 38 cases, and 2005 – 163 cases (Paz and Albersheim, 2008).

Results of Spearman correlation calculation between WNF cases (hospital admission dates) and mean daily temperatures are presented in Table 34.1 (see also Paz and Albersheim, 2008) for three main districts. Values were grouped into 2-week lags (Lag 1 = 2 weeks, Lag 2 = 4 weeks, etc.). High positive significant correlations ($r \leq 0.62$) were found between temperature increase and a rise in WNF cases in the North during a lag of up to 8 weeks and for the Hadera district in a lag of up to 6 weeks. Lower correlation was detected for the Tel Aviv area in a lag of 4 to 6 weeks ($r \leq 0.31$). A similar tendency was found using Pearson cross-correlation calculations between WNF data (admission dates) and minimum/maximum daily temperatures in Tel Aviv area in 2005 (the year with the highest number of WNF cases). Lag correlation analysis using Z-test found significant positive medium linkages ($0.3 \leq r \leq 0.4$). The strongest correlation was found after

~34 days for the daily minimum temperatures and after ~38 days for the daily maximum temperatures.

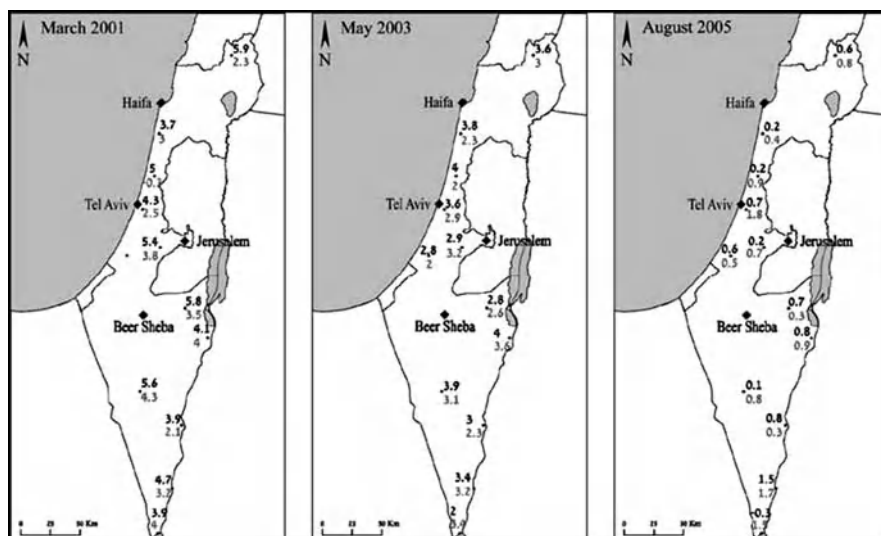


Fig. 34.2 Temperature anomalies in selected months (March 2001, April 2003, and August 2005). The *black* value refers to the monthly maximum temperature, and the *gray* value represents the monthly minimum temperature (Paz and Albersheim, 2008).

Significant lag correlations between daily rainfall amounts and WNF cases were not found. The disease frequency reduce in the years following the WNF outbreak of 2000 was probably a result of appropriate treatment by health and environmental authorities: standing water drying up, pest control systems use, and special programs to increase public awareness of the importance of draining standing water sources and using mosquito repellent. However, the risk was still present.

The warming tendency during the hot season in the EM over recent years (Paz, 2006; Paz et al., 2007) was ongoing during the study period. It was severe at the end of the winter and spring and less severe in mid-summer. The positive lag correlations between air temperature and mosquito hazard level/WNF cases indicate the significance of temperature increase at the beginning of the hot season, weeks before the disease's main appearance at mid-summer (Paz and Albersheim, 2008). This supports Paz (2006) who noted that an early extreme rise in temperature in the hot season could be a good indicator of increased vector populations.

Table 34.1 Results of Spearman correlation calculation between WNF cases in humans (hospital admission dates) and mean daily temperatures, along the period 2001–2005 in three main districts.

		Spearman's Rho	<i>p</i> -value
North	LAG0	0.56	0.00
	LAG1	0.62	0.00
	LAG2	0.62	0.00
	LAG3	0.51	0.01
	LAG4	0.36	0.08
Hadera district	LAG0	0.46	0.01
	LAG1	0.59	0.00
	LAG2	0.62	0.00
	LAG3	0.45	0.01
	LAG4	0.24	0.18
Tel Aviv	LAG0	0.27	0.13
	LAG1	0.24	0.18
	LAG2	0.30	0.09
	LAG3	0.31	0.08
	LAG4	0.28	0.12

Source: Paz and Albersheim (2008).

Along the study period, most of the cases occurred in the Tel Aviv metropolis, a narrow coastal area, where the heat is very intense due to the combination of high temperatures and a high level of air humidity. This region has a high population density and suffers from the urban heat island effect, which tends to worsen the local heat conditions. Gibbs et al. (2006) also found that the risks associated with WNF outbreaks appear to increase in urban and suburban areas as a result of human activity.

The increase in mosquito hazards and in WNF cases in 2003 (Fig. 34.1) could be related to the extreme heat at the beginning of the spring, but also to the unusual increase in rainfall amount in the previous winter and spring. It is reasonable to assume that these precipitations could enlarge the standing water recourses at the beginning of the hot season. This supposition is different from previous studies (Epstein, 2005), which noted that WNF increases after an extreme dry period, since standing water pools become richer in organic materials. The current results claim that these conclusions fit regions with larger amounts of precipitation throughout a longer rainy season. However, in a Mediterranean climate type, when the rainfall regime consists of a long dry summer without any rainfall, the usual conditions are severe drought and dry pools during the summer. Therefore, an increase in rainfall amounts in the spring might be an important parameter that expands the mass of water ponds. This insight is similar to the finding of Hubalek and Halouzka (1999), who noted that heavy rains could increase the incidence of WNF in Europe. Therefore, in a Mediterranean climate type, two indicators may encourage the WNF appearance – rainy spring and/or severe heat.

34.7 Conclusions

The main conclusions are as follows:

1. The disease appearance reflects the population distribution, while the risk tends to escalate around urban areas that are characterized by an urban heat island.
2. Constant positive anomalies of the minimum and maximum temperatures during the study period appear to have facilitated the mosquito abundance and consequently the disease emergence in humans.
3. An important finding is the potential influence of extreme heat in the early spring on the vector population increase and on the disease's appearance weeks later (Paz and Albersheim, 2008). Awareness of such situations at the very beginning of the spring may help authorities to reduce the disease risk before it becomes a real danger.

Climate models project a continuing temperature increase over the next decades in the Mediterranean basin (IPCC, 2007). Despite future uncertainty, the warming tendency has to be considered in predicting further WNV outbreaks in Israel and in the whole eastern Mediterranean basin.

Usually, interactions between climatologists, entomologists, and physicians are limited. They do not exchange information that can be readily employed in vector management. By raising the awareness of the relation between WNV eruptions and extreme heat conditions, the spread of the disease could be halted before it grows into a full-blown outbreak.

Acknowledgment

The author would like to thank the Israel Ministry of Environmental Protection for funding this project.

References

- Alpert, P, Ben-Gai, T, Baharad, A, Benjamini, Y, Yekutieli, D, Colacino, M, et al. (2002) The paradoxical increase of Mediterranean extreme daily rainfall in spite of decrease in total values. *Geophysical Research Letters* 29(11): 1536; DOI:10.1029/2001GL013554.
- Ben-Gai, T, Bitan, A, Manes, A, Alpert, P, Rubin, S (1999) Temporal and spatial trends of temperature patterns in Israel. *Theoretical and Applied Climatology* 64: 163–177.
- Bin, H, Grossman, Z, Pokamunski, S, Malkinson, M, Weiss, L, Duvdevani, P, et al. (2001). WNV in Israel 1999–2000 – from Geese to Humans. *Annals of the New York Academy of Sciences* 951: 127–142.
- CDC website (2004) West Nile virus – background: history and distribution, Available: <http://www.cdc.gov/ncidod/dvbid/westnile/background.htm>.
- Dohm, DJ, O'Guinn, ML, Turell, MJ (2002) Effect of environmental temperature on the ability of *Culex pipiens* (Diptera: Culicidae) to transmit WNV. *Journal of Medical Entomology* 39: 221–225.
- El-Zein, A, Tewfel-Salem, M, Nehme, G (2004) A time-series analysis of mortality and air temperature in Greater Beirut. *Science of the Total Environment* 330:71–80.
- Epstein, PR (2001) WNV and the climate. *Journal of Urban Health* 78: 367–371.
- Epstein, PR (2005) Climate change and human health. *The New England Journal of Medicine* 353(14): 1433–1436.

- Gibbs, SEJ, Wimberly, MC, Madden, M, Masour, J, Yabsley, MJ, Stallknecht, DE (2006) Factors affecting the geographic distribution of WNV in Georgia, USA: 2002–2004. *Vector-Borne and Zoonotic Diseases* 6: 73–82.
- Granwehr, B, Lillibridge, K, Higgs, S, Mason, P, Aronson, J, Campbell, G, Barrett, A (2004) West Nile Virus: where are we now? *Lancet* 4(9): 547–556 B.
- Hubalek, Z, Halouzka, J (1999) WNF – a reemerging mosquito-borne viral disease in Europe. *Emerging Infectious Diseases* 5: 643–650.
- IPCC (2007) IPCC WG1 AR4 final report – Regional climate projections. Available: http://ipcc-wg1.ucar.edu/wg1/Report/AR4WG1_Ch11.pdf.
- Israel CDC (ICDC), WNV. Available: <http://www.health.gov.il/wnf/index.html>.
- Lanciotti, RS, Roehrig, JT, Deubel, V, Smith, J, Parker, M, Steele, K, et al. (1999) Origin of the WNV responsible for an outbreak of encephalitis in the northeastern United States. *Science* 286: 2333–2337.
- Nash, D, Mostashari, F, Fine, A, Miller, J, O’Leary, D, Murray, K, et al. (2001) The outbreak of WNV infection in the New York City area in 1999. *The New England Journal of Medicine* 344: 807–814.
- Patz, JA, Githeko, AK, McCarty, JP, Hussain, S, Confalonieri, U, de Wet, N, (2003) Climate change and infection disease. In: McMichael AJ, Campbell-Lendrum DH, Corvalán CF, et al. eds. *Climate change and human health risks and responses*. WHO, Geneva, 103–132.
- Paz, S, Kutiel, H (2003) Rainfall Regime Uncertainty (RRU) in an eastern Mediterranean region – a methodological approach. *Israel Journal of Earth Science* 52(2): 47–63.
- Paz, S (2006) The WNV outbreak in Israel (2000) from a new perspective: the regional impact of climate change. *International Journal of Environmental Health Research* 15(6): 1–13.
- Paz, S, Bisharat, N, Paz, E, Kidar, O, Cohen, D (2007) Climate change and the emergence of *Vibrio Vulnificus* disease in Israel. *Environmental Research* 103(3): 390–396.
- Paz, S, Albersheim, I (2008) Influence of Warming Tendency on *Culex pipiens* Population Abundance and on the Probability of West Nile Fever Outbreaks (Israeli Case: 2001–2005). *EcoHealth* 5(1): 40–48.
- Patz, JA, Githeko, AK, McCarty, JP, Hussein, S, Confalonieri, U, de Wet, N (2003) Climate change and infectious diseases. In: McMichael AJ, Campbell-Lendrum DH, Corvalán CF, et al., eds. *Climate change and human health risks and responses*, WHO, Geneva, 103–132.
- Savage, HM, Ceianu, C, Nicolescu, G, Karabatsos, N, Lanciotti, R, Vladimirescu, A, et al. (1999) Entomologic and avian investigation of an epidemic of WNV fever in Romania in 1996, with serologic and molecular characterization of a virus isolate from mosquitoes. *American Journal of Tropical Medicine and Hygiene* 61:600–611.
- Turell, MJ, O’Guinn, ML, Dohm, DJ, Jones, JW (2001) Vector competence of North American mosquitoes (Diptera: Culicidae) for WNV. *Journal of Medical Entomology* 38: 130–134.
- Zhang, X, Aguilar, E, Sensoy, S, Melkonyan, H, et al. (2005) Trends in Middle East climate extreme indices from 1950 to 2003, *Journal of Geophysical Research* 110, D22104, doi:10.1029/2005JD006181.

Water Management Works in Târnava River Basin, Romania

Mihai Voda, Victor Sorocovschi and Ramona Ratiu

35.1 Introduction

In order to correctly evaluate the water supply in an area it is necessary to know the natural flow conditions. As a result of human activity the degree of water usage has also risen. Many developing countries are currently faced with several water management challenges and problems that vary according to the physical, socioeconomic, and institutional context of development (Akpabio et al., 2007).

Under the circumstances, in order to find out the potential of natural water resources, it is necessary to make calculations that will eliminate the influence of human factors modifying the flow. The results obtained can be used to indicate a situation where there would not be any flow modifying factors and would allow for a quantitative analysis of water resource trends (Zăvoianu, 1999).

Currently, the immense water course training caused the measured discharge, namely the measured runoff, not to reflect the natural runoff as measured at most hydrometric stations. The reconstruction of natural flow started in 1980, corrections of reconstruction being made every year. The main modifying factors on the hydrologic regime in the river basins are the complex water trainings. The storage reservoirs distribute and regulate the flow during the year. During floods, they minimize the maximum discharges. That is when the reconstruction corrections have positive values ($DQ > 0$). During droughts, storage reservoirs compensate minimum discharges, and the values of the reconstruction corrections are negative ($DQ < 0$).

The river basin size has an important role in the genesis and the evolution of hydrological phenomena. In a small drainage basin, the channel flow evolution follows the rainfall depth, whereas in a significant river basin, the channel flow evolution does not follow exactly the rainfall depth. The river basin surface regulates the runoff. A wider drainage area, as it is in the Blajului and Întresecășe Tablelands, increases the flood routing speed. The river basin average altitude influences the hydrological elements. The higher drainage area elevation receives more precipitation and has more important runoff than the lower one.

The annual runoff in the Târnava river basin is influenced by the rainfall depth, evaporation, morphometrical characteristics of the flood channel, cutoffs coefficient, and hydrogeological conditions of the drainage areas. When calculating the runoff, we should include a series of parameters that will take into account the influence of accumulations and embankments built to prevent floods. Also, other parameters can be mentioned related to the cutoff coefficient, the morphometrical characteristics of the flood channel, and its deposits.

There is emphasis on the practical importance of maximum runoff observation on watercourse management works. The analysis of the maximum runoff genesis as well as the distribution of the values according to genesis was based on a comparative analysis of the climatic and hydrologic variations.

The most serious floods in Târnava river basin occurred in May 1970, July 1975, March 1981, December 1995–January 1996, and June 1998 (Sorocovschi, 2004). The flood analyses between 1970 and 2004 at Sarateni hydrometric post illustrate a great number of important floods in May 1970, July 1975, May 1978, and May 1984, followed by a period of 10 years with modest floods until 1995. The last decade presents floods in April 1999 and 2000 and May and August 2005. Floods vary according to seasons, the most numerous occurring in spring (30%–45%) and less in autumn (6%–10%). The maximum frequency is in April and March, followed by June.

The hydrotechnical works in Târnava basin started as a result of the important damages caused by the floods in 1970 and 1975. They implied the construction of some storage reservoirs, both permanent and non-permanent, to protect different objectives within the territory. By means of redistributing the flow during the year, they created a balance in the hydrologic system, compensating for minimum discharges and decreasing the maximum ones.

35.2 Water Management Works in the Târnava River Basin

35.2.1 The storage reservoirs

The Bezid storage reservoir is situated on Cușmed, the right tributary of Târnava Mică, having the largest surface of tributary basin (157 sq km) and the highest volumes of water in the basin. The storage reservoir is situated upstream from the confluence with the Târnava Mică river, 1.5 km away from Sângeorgiu de Pădure. The aim is to decrease floods and protect against floods all the industrial and residential areas on the Târnava Mică riverside as well as to meet the need for fresh and industrial water supply in Târnăveni. Together with the development of the Târnăveni chemical platform, it was necessary to increase the store discharge from 0.4 m³/s, which would not have been possible given the natural conditions on the Târnava Mică river, only by means of restraining the available discharges in a storage reservoir upstream to supplement the minimum discharges.

The daily average minimum discharge on the Târnava Mare river, with a probability of 95%, is approximately 0.55 m³/s in the entire Odorhei-Mediaș sector, and the monthly average minimum discharge, of the same probability, in-

creases in the same sector downstream from 0.85 m³/s to 1.08 m³/s. These situations have led to the building of the Zetea storage reservoir that not only prevents floods but also ensures and regulates river discharges to meet water requirements. It also ensures the normal quantities of water needed in the next 10–20 years according to the development increase, the water supply scheme, and the improvement of the present urban water supply system.

35.2.2 The detention reservoirs

The non-permanent storage reservoirs mainly aim to decrease floods damage. The most important in the Târnava basin and even in the entire Mureș basin are the storage reservoirs at Vânători (25 Mm³) and Bălăușeri (24.5 Mm³). There is also Nemșa, with a total volume of 7.94 Mm³ on the Moșna creek, left tributary of the Târnava Mică river. The Vânători storage reservoir is situated on the Târnava Mare river in the urban area of Albești, Topa, Vânători, and aims to decrease the floods on the upper stream protecting Sighișoara against floods by reducing the maximum discharge from 1364 m³/s to 1100 m³/s which results from the storage of 25 Mm³ of water, 0.1% insurance. The surface of the storage reservoir at 1% insurance is of 300.5 hectares, and 583 hectares at 0.1% insurance. Bălăușeri storage reservoir is situated on the Târnava Mică riverside having a length of 4500 m, a width of 900 m, and a surface of approximately 325 hectares. It is meant to function only when the discharges exceed the 5% insurance on the Târnava Mică river, otherwise the surface remains dry and is cultivated. The maximum value of the storage reservoir of 0.1% insurance is of 24.5 Mm³.

35.2.3 Water users within the Târnava basin

The water users in the basin are grouped according to the conditions regarding water quality. The stored discharges should be used as fresh water supply for residential areas and then for irrigations. The irrigation canals can carry discharges that will ensure the necessary water for other water users along the way. The water users represent fresh water supplies (34% out of the total volume), industrial water (63.4% out of the stored volume), and irrigation systems (2% out of the stored volume) which are only additional, as irrigation is needed only in drought years. Completing the hydrotechnical works of the hydrologic basins is absolutely necessary at the moment in order to improve the water supply system. It implies an integrating structure based on integration relationships.

35.3 Evaluation Methods and Techniques

In order to correctly evaluate the water supply in an area, it is necessary to know the natural flow conditions. As a result of human activity the degree of water usage has also risen. Under the circumstances, in order to find out the potential of natural water resources, it is necessary to make calculations that will eliminate the

influence of human factors modifying the flow. The results obtained will indicate a situation where there would not be any flow modifying factors, which will allow for a quantitative analysis of water resource trends. Currently, the immense water course training caused the measured discharge, namely the measured runoff, not to reflect the natural runoff as measured at most hydrometric stations.

The natural runoff should be known so as to follow the evolution in time of the natural water resources and evaluate the influence of the human factors on the flow. Reconstruction refers only to the modifications of the natural flow as they appear in riverbeds and does not include the modifications influencing the flow-forming factors. The reconstruction of the natural water flow into riverbeds is defined as the calculations through which, starting from the modified flow hydro-metrically registered, the modifying factors are eliminated or corrected so as the final results reflect the flow irrespective of water trainings (Diaconu et al., 1980).

35.4 Results and Discussion

The main modifying factors on the hydrologic regime in the river basins are the complex water trainings. The storage reservoirs distribute and regulate the flow during the year by minimizing the maximum discharge, when the reconstruction corrections have positive values ($DQ > 0$), namely the compensation of minimum discharge, the values of the reconstruction corrections being negative ($DQ < 0$).

The influence of water users on the hydrologic basin is reduced to diminishing the average monthly discharge with relatively significant values (5%–10%), given by both the water users and the storages of the main storage reservoirs. The approximately constant influence of the water users is generally insignificant when there is a lack of important accumulation in the storage reservoirs, yet it can compensate for important lack of accumulation such as those in January that follow high water periods. The reconstruction of the natural flow started in the 1980s, corrections of reconstruction being made every year even though the average flow was not influenced by any modifying factors for more than 5 years out of the 22 years under analysis.

35.4.1 Changes in the annual mean runoff

The overall evolution of the flow in a waterdrained area of the Târnava hydrographic basin highlights a right connection among K values, DQ correction discharges, and the water volumes consumed by water users. During the years when the K values were most reduced, the percentage of the correction discharges exceeded 5% and the volumes of consumed water were some of the highest; there are years when there was no compensation of minimum discharges because of discharges lower than natural discharges and average multiannual natural discharges.

In Târnava hydrographic basin, the effects of water training and water users were particularly obvious between 1986 and 1990. Significant changes in the annual average flow were registered in 1986 in Târnava Mica basin at Bălăușeri, Târnăveni, and Blaj. The average annual discharges registered at Mihalt hydro-metric station show high values in 1984 and 1985, of 32.2 m³/s and 43.2 m³/s at the beginning of the period analyzed, followed by 10 years of discharges below

the average of $23.6 \text{ m}^3/\text{s}$. Since 1996 there has been an increase in the discharges under observation, reaching the highest values of 50.9 in 1998. The reduced values of the average annual discharges measured in the years 1986, 1987, 1989–1995 and 2001–2004, lower than the reconstructed average annual natural discharges of the same years and inferior to the average multiannual values of natural discharges emphasize the lack of compensation on reduced discharges. The average monthly discharges registered and reconstructed were below the average multiannual values, but water users in the basin consumed 31.6 Mm^3 of water in 1986, almost three times as much as during the previous year, 1985, which registered a high flow capable of compensating the quantities stored and consumed by the water users.

The modifying factors of the natural flow imposed the use of reconstruction modifications in 9 out of the 22 years under analysis. The modifying factors exceeded 5% in 1986–1989, 1990, 1991–1993, 1995, and 2003. The years when the value K coefficients are most reduced coincide with the years when it was necessary to apply the reconstruction correction such as 1986, 1987, 1989, 1990, and 1995. In 1990, the value of the coefficient is 87.46%, which represents the share of the measured discharge out of the reconstructed natural discharge. In the same year 1990 they registered the highest degree of average flow modification from the entire period analyzed.

Although in 1990 registrations did not show the highest annual water storage consumed in the period analyzed, the K values are the lowest because of extremely reduced average annual discharges. In 1995, when they registered the highest net water storage of 34.7 Mm^3 , the K value was 91.79% but the values of the measured and natural average annual discharges almost doubled in comparison with those of the year 1990.

On the Târnava Mica River, at Blaj hydrometric station, the K value is the most reduced in 1986, the year with the most insignificant modifications on the average flow due to the large volumes of water consumed by the water users and also to the low-average discharges measured and reconstructed. At Târnaveni, Târnava Mica hydrometric station, they registered significant influences of different water users on the average flow conditions in 1986, the highest value being $DQ = 6.28\%$. In all these years reconstruction measurements (calculations) were needed. Since 1995, they have registered an increase of the discharges observed in the whole of the Târnava basin, reaching a peak in 1998 with $16.6 \text{ m}^3/\text{s}$. The reduced average annual discharges measured in 1986, 1987, 1989–1994, 2000, 2001, 2003 and 2004, lower than the natural average annual discharges reconstructed in the same years and also lower than the multiannual average values of the natural discharges, emphasize the lack of compensation effects of the minimum discharges.

35.4.2 Effects of water course management on the monthly mean discharges in the Târnava river basin

A high degree of flow modification is noticed in 1986 in the Târnava Mica basin, at Bălăușeri and Târnaveni hydrostations, where the correction discharges

exceeded 5% in 10 months, except for March and April. The natural discharge reconstructed at Bălăușeri in September was $2.14 \text{ m}^3/\text{s}$ as compared to $4.64 \text{ m}^3/\text{s}$ (the multiannual average value of September) and in December $Q_{\text{nat}} = 1.99 \text{ m}^3/\text{s}$ as compared to $5.94 \text{ m}^3/\text{s}$ (the multiannual average value of December). At the hydrometric station of Tarnaveni the natural discharges reconstructed in November were $2.56 \text{ m}^3/\text{s}$ compared to $5.84 \text{ m}^3/\text{s}$ (the multiannual average value of November) and in December $Q_{\text{nat}} = 2.38 \text{ m}^3/\text{s}$ compared to $7.06 \text{ m}^3/\text{s}$ (the multiannual average value of December). In March and April, the K values reflect a reduced value of flow change, but they remain low in the other months of the year, reaching a peak in September and December at the hydrometric station of Bălăușeri, namely in November and December at Tarnaveni.

In 1990, the water management works had a great influence on the discharges in the Târnava river basin. At Mihalt, the volumes stored in this year were 34.7 Mm^3 , a value similar to the one in 1988 in which the discharge was higher, reaching its peak. The highest rates of flow stored were also recorded in August and September, months which presented the lowest monthly rate of flow in 1990 and also the highest correction discharges (Fig. 35.1). The reconstruction correction works were necessary beginning with April (6.88%) till the end of December (15.47%). The highest correction discharges are in August (26.81%) and September (24.16%). In the river basin of Târnava Mica, at the hydrometric station of Tarnaveni, the highest rate of runoff was recorded in August 1990 (Fig. 35.2).

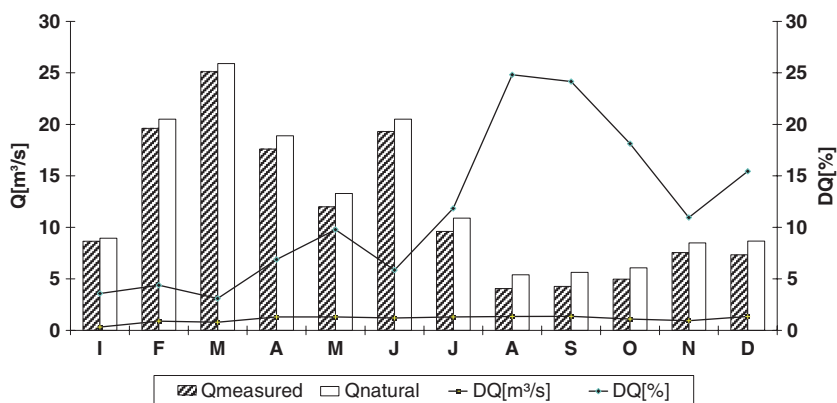


Fig. 35.1 The average natural and reconstructed monthly discharges variation at Mihalt hydrometric station in 1990.

The highest runoff from the whole period analyzed was recorded in 1998. The annual average discharges were $51.6 \text{ m}^3/\text{s}$ at the hydrometric station Mihalt. The discharges of water stored in the basin were $22.1 \text{ m}^3/\text{s}$. Analyzing the variation of the average rate of flow measured and reconstructed as well as the share of correction discharges in 1998 at Mihalt, we observe the positive role of the storage reservoirs in the Târnava basin, put in use after 1990. The mitigation of maximum discharges is illustrated by the $Q_{\text{natural}} > Q_{\text{measured}} > Q_{\text{annual average meas-}}$

ured values of the following months: January, April, June, and July. The accumulations regulated the flow by storing extra volumes, redistributed gradually in time. In some of the months of 1998 important flows were registered (Sorocovschi and Haidu, 2004). A positive influence of water training works is noticed in the basin due to the perennial storage reservoir Zetea and Bezid.

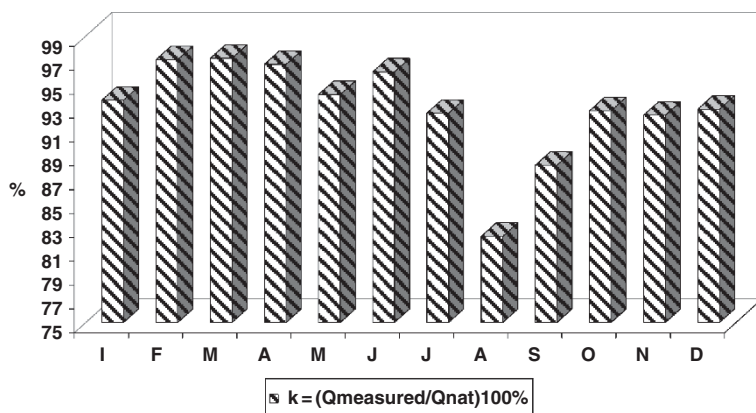


Fig. 35.2 Modification of the monthly average discharges in 1990 at Târnăveni.

35.4.3. Effects of water course management and water users on the minimum runoff

In the Târnava river basin two long intervals of drought were registered, the first one between 1945 and 1951, while the second one was between 1983 and 1994 (Gâștescu and Zăvoianu, 1998). As compared to the previous period, the 1983–1994 droughts present a few particularities, being longer in time, but in the same way less homogeneous than the previous ones. The discontinuities of recorded values were noticed in 1985–1988. A major negative influence of water users on the flow in Târnava basin was noticed in 1986, 1987, and 1990 when the discharges decreased below the multiannual average values, restrictions were not imposed for the storing water and the perennial storage reservoirs to compensate the discharges that did not exist. The drought phenomena must be monitored with great attention, by better control of water users to decrease the risk of pollution, reactivate own sources of water supply so as to reduce discharges consumed from centralized sources. Because of its extensive duration, intensity and effects, the drought in 2000 can be considered one of the most powerful in our country in the 20th century. On the whole territory of the country the rainfall decreased by 33.4% of the usual quantities. In 2000, on small surface creeks in the Târnava basin, the annual flow was lower than the multiannual, some even became dry on the whole river course. For example, The storage reservoirs in the basin played an important part in supplementing the discharges in drought periods thus meeting the water users' needs. In the Târnava hydrologic basin, in 2003, the discharges decreased below the monthly average yet without reaching the warning threshold. On the main

river courses in the basin there were not significant discharge drops to the densely forested areas in the upper basin where the tributaries have an even flow and also to the permanent storage reservoirs, such as Zetea on the Târnava Mare river and Bezid on the Târnava Mica river, which compensate for the little deficit on these water courses.

35.4.4 Effects of water course management on floods in the Târnava river basin

In the Târnava river basin most of the floods are generated by rain. Thus, at Odorhei hydrometric station the highest floods recorded before 1970 were the floods caused by the rainfalls in August 1955, July 1957 and 1959 with peak discharges of 80–90 m³/s. After 1970, the highest discharges of 205 m³/s were recorded on March 13, 1981. At Blaj hydrometric station the most important floods were caused by rainfalls, for example, those in 1953, April–May 1956, and July–August 1960. The peak discharges of 851 m³/s were recorded on July 4, 1975. Because of the significant increase of the basin's storage surface, the mixed floods, with a frequency comparatively inferior to the frequency characteristic to floods caused by rainfalls, could present peak discharges and huge volumes of water.

In 1970, between May 12 and 16 peak discharges of 700 m³/s (May 15, 1970) were recorded at the hydrometrical station from Topa on the Târnava Mare river and 323 m³/s at the hydrometrical station from Sarateni on the Târnava Mica river. The flood was formed because of heavy rainfalls and melting snow in the upper basin. In 1975, they registered the most increased discharges at Simonești, Medias, Blaj, Tarnaveni, and Mihalt stations. Heavy rainfalls on a highly saturated soil caused severe floods on the Târnava Mica and Târnava Mare rivers. Peak discharges of 135 m³/s were registered at Simonești on Feernic on July 2, 1975; 900 m³/s at Medias on Târnava Mare on July 3, 1975; 851 m³/s at Blaj on Târnava Mare, 1 day later and 830 m³/s on July 3, 1975, at Tarnaveni on the Târnava Mica river. At Mihalt hydrometric stations 1350 m³/s were registered. In 1998, two periods of substantial precipitations were recorded in the same month, June. The first between June 11–15, 1998 and the second between June 16–20, 1998. Peak discharges recorded on Târnava Mica were of 335 m³/s at Bălăușeri and of 196 m³/s at Tarnaveni.

The flood analyses from the period of 1972–2004 at the hydrometric post in Tarnaveni show a major flood in July 1975, when, at 5:00 A.M. on July 3, 630 m³/s were registered, a value 60 times higher than the average discharges characteristic of July at this post. Analyzing the flood routing between Sărățeni and Târnăveni, we can observe the increasing speed of the flood wave, from 1.5 to 4 km/h, because of the hydrotechnical works done after 1977. The rainfalls in December 1995 caused peak flows on the Târnava Mică river in the Târnava Mică river basin with high water overrun and serious damages. Serious damages were recorded in the following villages: Suplac: 528 hectares of arable terrain flooded, right river bank eroded in the outskirts; Adămuș: 82 flooded households, 22 houses, and 380 hectares of arable terrain destroyed (Voda, 2007). Consequently, it is absolutely necessary to start flood protection works in the area of Suplac, Adămuș, Cornești, and Crăiești.

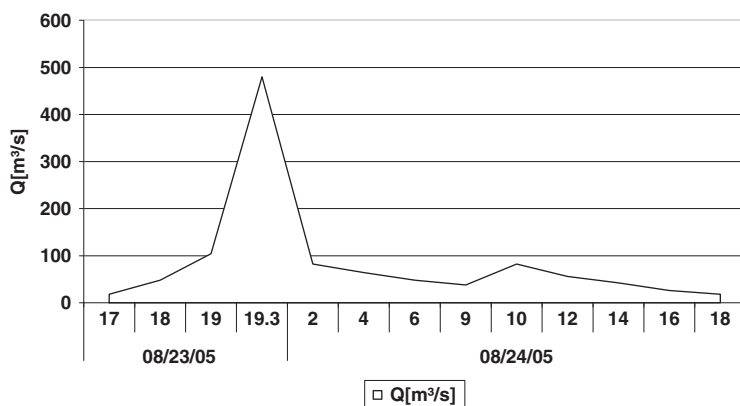


Fig. 35.3 Feernic flood wave hydrograph in 2005 at Simonești.

In August 2005, the flood wave recorded at the Simonești hydrometric station was very strong (Fig. 35.3), the water level grew rapidly, starting at 06:00 A.M. (H – 10, Q – 2.16 m³/s) on August 23 2005, with 70 cm until 17:00 h (H – 80, Q – 18.1 m³/s). This way at 18:00 h (H – 140, Q – 48 m³/s) in one single hour the water level grew by 60 cm, while at 19:00h (H-200, Q – 104 m³/s) by another 60 cm. The highest level of the flood is reached a half an hour later at 19:30 h (H-367, Q-480 m³/s). In an only 30 min spell the water level raised by 1.67m and the water discharge of the Feernic grew by 460%. Practically in 2½ h, between 17:00 and 19:30, the Feernic's water level rose by almost 3m! The danger- quote was exceeded by 217 cm in the evening of August 23, 2005, the water level remained high until 2:00 in the night (H – 180, Q – 82 m³/s), after that it started to lower until the morning of August 24, 2005 at 09:00 A.M. (H – 120, Q – 38 m³/s). It rose again until 10 o'clock (H – 180, Q – 82 m³/s), receding then at 14:00 h below the danger quote (H – 130, Q – 42 m³/s). In 2 h eight localities – Odorheiu Secuiesc, Lupeni, Porumbeni, Simonești, Mugeni, Corund, Feliceni, and Dealu – were covered by the floods started on the surrounding hills and the swollen creeks, which had outran 100 mm in less than an hour. The peak flows killed 13 people in Lupeni, Feliceni, and Simonești, another 3 people were reported missing in these places, probably swallowed by the peak flows that destroyed 55 houses in only a few minutes.

35.5 Conclusions

The floods from August 2005 have lined out the need of the elaboration of a national defense strategy against floods. Adjustments to floods are either structural or non-structural (White, 1945). Structural adjustments are designed to modify flood hazards so that humans are protected and can continue to live in areas that are periodically threatened by floods. Non-structural adjustments are arrangements imposed to restrict the use of floodplains. Despite these, the specialists say that it is impossible to insure a 100% defense. There is a risk if it is thought that the

damages produced by the floods are smaller than the investments made (Tobin and Montz, 1997). The reasons for an increase in flood damages caused by reliance on structural works can be associated with design standards and overconfidence in such adaptations. At present, in Romania there are 10,000 km of embankments and over 1,200 dams and storage reservoir lakes. These numbers make Romania one of the best endowed countries from this point of view, the only problem remains their administration because non-structural works have to be integrated with structural works to reduce the impact of flooding in the Târnava river basin.

Acknowledgment

The authors acknowledge the financial support provided by the Dimitrie Cantemir University of Targu Mures in Romania.

References

- Akpabio, EM, Watson, NM, Ite, UE, Ukpang, IE (2007) Integrated Water Resources Management in the Cross River Basin, Nigeria, *International Journal of Water Resources Development*, 23:4, 691–708. doi: 10.1080/07900620701488612.
- Diaconu, C, Șerban, P, Pașoi, I (1980) Îndrumări metodologice și tehnice pentru reconstituirea scurgerii naturale a râurilor. I.N.M.H. Press, București, Romania.
- Gâțescu, P, Zăvoianu, I (1998) On the genesis and time– space distribution of water resources in Romania. *Geographical aspects*, *Revue roumaine de géographie* 42: 37–45.
- Sorocovschi, V (2004) *Riscuri și catastrofe*. Casa Cărții de Știință Press, Cluj-Napoca, Romania.
- Sorocovschi, V, Haidu, I (2004) Quelques aspects spatiaux des pluies extremes. *Dokumentacja Geograficzna*. Instytutu Geografii i Przestrzennego Zagospodarowania, Warszawa, Poland.
- Tobin, G, Montz, B (1997) *Natural Hazards: Explanation and Integration*. The Guilford Press, New York, USA.
- Voda, M (2007) *Bazinul Tarnave – Amenajari si scurgere lichida*. Casa Cărții de Știință Press, Cluj-Napoca, Romania.
- White, G (1945) *Human Adjustment to Floods*. Department of Geography Research Paper no. 29. The University of Chicago, Chicago, USA.
- Zăvoianu, I (1999) *Hidrologie*. Editura Fundației “România de mâine” Press, Bucuresti, Romania.

North–South Gap in Wastewater Management: A Comparative Study for Germany and Jordan

Matthias Barjenbruch and Kamel K. Alzboon

36.1 Introduction

The Hashemite Kingdom of Jordan covers a land area of 90,000 km². The Jordanian climate is semi-arid where 90% of the country receives an average precipitation of less than 200 mm/year, most of which (about 90%) is lost via evaporation (Hadadin, 2007). The high population growth rate in Jordan together with the country's rapid economic development has been accompanied by an increase in water demand, while the available water resources are limited and decreasing. Jordan's water resources are, on per capita basis, among the lowest in the world. The available water from existing renewable sources is projected to fall from 160 m³/capita/year in 2006 to 91 m³/capita/year by the year 2025, which is very low in comparison with the international water poverty line of 1000 m³/year (Alzboon and Al-Ananzeh 2008; Bataineh et al., 2002). This has enforced Jordan to reuse treated wastewater for agricultural purposes. About 95% of the households are connected to the drinking water network, only 54% are served by public sanitary system (Bataineh et al., 2002). More than 70 million m³/year of reclaimed water, around 10% of the total national water supply, is used either directly or indirectly in Jordan and will increase to a share of more than 15% within the next 30 years (McCornick et al., 2002; Bdour and Hadadin, 2005). Therefore, water reuse is considered an attractive option for increasing the available water resources of Jordan.

On the other hand, Germany is rich in water bodies. The total annual renewable water reserve is about 182 billions and only 20.9% of this amount is actually utilized by all users. About 98% of the population is connected to the wastewater system (ATT et al., 2005; Barjenbruch, 2008). Germany has a good experience regarding wastewater treatment. More than 10,000 wastewater treatment plants are in operation, which provide a good opportunity for researchers to develop and improve wastewater management system.

International cooperation and joint efforts are necessary to set up common goals and strategies and to determine how the environmental work should proceed

to be most efficient. Germany supports – financially and technically – many environmental projects in Jordan, especially in the wastewater treatment sector. In order to optimize the benefits of this cooperation, it is important to evaluate wastewater management systems in both countries and to discuss the weakness and the strength elements. When considering technology transfer between countries, which aim at improving management frameworks, it is important to recognize the differences between host and donor countries.

Characteristics of wastewater vary from location to location depending on land uses, variations in living style, discharges of industrial and commercial wastewater, interference between surface and ground water, and both diurnal and seasonal fluctuations. Of course, a basic variable is the amount of water consumed and the amount of human waste discharged (UNEP, 2006). The effective management of wastewater cannot be achieved without accurate knowledge of its characteristics. Wastewater characteristics are necessary for design, operation, collection, treatment, disposal, and reuse. In addition to wastewater characteristics, the applied standards and regulations regarding the effluent wastewater were also investigated. Jordan plans to reuse all its treated wastewater and therefore has imposed that all new wastewater treatment projects must include feasibility and design aspects for wastewater reuse (Bataineh et al., 2002). To ensure that this reuse has no adverse effect on health and environment, the government of Jordan has responded by enacting a series of regulations. Germany also has imposed strict standards to protect its water resources, which has improved the water quality of the receiving streams remarkably (Pfister et al., 1998).

This chapter focuses on management elements in both countries (Germany and Jordan) as an example of the cooperation between north and south countries. This chapter also compares the applied treatment technologies in both countries to determine the effect of these technologies on the efficiency of treatment. This comparison could be helpful in transferring experiences, technologies, and management from the developed countries to the developing ones.

36.2 Methodology

The characteristics of wastewater for four wastewater treatment plants in Jordan, which are Al-Samra (ASTP), Irbid (ITP), Ramtha (RTP), and Wadi Hassan (WTP), were determined. The selected plants treat about 90% of the domestic wastewater in Jordan and serve more than 2 million inhabitants (WAJ, 2006). Because ASTP is the largest plant in Jordan and treat more than 76% of municipal wastewater, most of the environmental studies concentrate on the performance of this plant and the possible actions to enhance its efficiency. The plant consists of three parallel trains with total areas of 181 hectare (WAJ, 2006). There are two aerobic ponds, four facultative ponds, and four maturation ponds in each train. The other treatment plants, which are ITP, RTP, and WTP, are operated as activated sludge with different modes. In order to determine the characteristics of wastewater for the selected plants, representative weekly samples were taken from the inlet and outlet of these plants during June 2005 to March 2006. Samples were

properly labeled with the plant reference number, date, and sampling location (inlet and outlet).

BOD and COD are the most important parameters used to define the characteristics of municipal wastewater. Also, TSS, NH_4 , and P were used for comparison purposes. Representative samples were collected very carefully to avoid agitation or any contact with air. Plastic containers were used to collect the samples. During collection and transportation the samples were ice-bounded. When the collection was completed, the samples were directly carried to the laboratory at AL-Huson College and stored in the refrigerator at 4°C. All analyses were conducted within 24 h of collection. Samples were collected, preserved, transported, incubated, prepared, and analyzed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998). After dilution, the BOD samples were incubated at 20°C for 5 days. The change in DO concentration during the incubation period was measured to determine the BOD concentration. The amount that was used (mg/l) is an indication of wastewater strength. Closed reflux method was used to determine COD concentration, while colorimetric method was used for phosphorus measurement. In order to determine TSS and TDS concentrations for each sample, a well-mixed sample was filtered through a weighed standard glass fiber filter, and the residue retained on the filter (2 μ diameter) was dried to a constant weight at 103°C to 105°C. The increase in weight of the filter represents the total suspended solids. The filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids (APHA, 1998).

In Jordan, wastewater treatment plants are operated by the water authority. Wastewater treatment plants are requested to measure the wastewater flow as well as the concentrations of COD, BOD₅, $\text{NH}_4\text{-N}$, TSS, and phosphorus of the raw and treated wastewater. Usually, at these plants, BOD of the influent is measured daily; COD, TSS, and NH_4 are measured weekly, while P measurement is unavailable in most of the plants.

Data regarding the other plants (17 plants) were obtained from water authority of Jordan (WAJ) where daily samples were collected by the laboratory staff and based on regular measurement campaigns performed during 2006 for all wastewater treatment plants (WAJ, 2006). Similar data for 6086 treatment plants in Germany also were obtained. Detailed data concerning wastewater characteristics, treatment, operations, and method of treatment for 398 treatment plants in the northern eastern districts of Germany were used for statistical purposes (DWA, 2006). The mean value of typical composition is being analyzed in this study based on 1 year (2006) sampling data of raw and treated sewage taken from the inlet and outlet of the treatment plants. The average monthly concentration for each plant was used to calculate and analyze the overall efficiency indicators.

36.3 Results and Discussions

36.3.1 Comparisons according to wastewater characteristics

The average concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP), ammonium (NH_4), and total suspended solid (TSS) of wastewater generated in Germany were 305, 547, 8.2, 72, and 336 mg/l, respectively. In case of Jordan's wastewater, the concentrations for the same parameters were 741, 1660, 30, 85, and 695 mg/l, so it was classified as a strong wastewater as shown in Table 36.1. The high strength of Jordan's wastewater was related to the illegal connections of industries and slaughterhouses, and to the low water consumption. The average supplied water in Jordan is about 120 l/c.d. Due to the high water losses (52%), the actual water consumption is far below this value and it is estimated to be about 60 l/c.d. The average water consumption in Germany is about 127 l/c/d (DWA, 2006).

Table 36.1 Wastewater characteristics in Germany and Jordan.

Indicator	Influent (mg/l)		Effluent (mg/l)	
	Germany	Jordan	Germany	Jordan
Number of (plants)	6086	20	6086	20
BOD	305	741	4.7	49
COD	547	1660	29	191
TN	50.7	*	8.3	*
TP	8.2	30	0.78	23
NH_4	72**	85	1.65	27.8
TSS	336	770	5.1	62

* Not measured, ** For 389 plants in the northern districts.

36.3.2 Comparisons according to the treatment efficiency

Similar to the case of influent, the effluent from treatment plants in Jordan contains higher concentrations of pollutants (organic and nutrients) compared with that treated in Germany's plants as shown in Table 36.1. High effluent of organic material can reduce or deplete oxygen in water bodies, resulting in fish kills, odors, and overall degradation of water quality. Nutrients (N, P) can cause eutrophication phenomenon in water bodies, which results in undesirable offensive conditions.

The average removal efficiencies of BOD, COD, NH_4 , TP for Germany's plants were 98.6%, 95%, 94%, and 91%, respectively, in comparison with 92.8%, 87.9%, 55.8%, and 23% for Jordan's plants as shown in Fig. 36.1. The treatment

plants in Germany also have high removal efficiency of TN (88%), while this parameter is not considered in the case of Jordan's treatment plants. The higher removal efficiency of treatment plants in Germany was attributed to many factors: applying of modern treatment technologies, high-qualified operators, strict regulations and the moderate strength of influent wastewater. On the other hand, Jordan still depends on natural stabilization ponds, which treats around 80% of its wastewater. The lack of expertise and limited financial support also contribute to the low treatment efficiency. Regarding BOD, COD, and TSS, 70% of the present plants have good removal efficiencies and comply with Jordanian standards for water discharged to the streams. Based on flow parameters, only 25% of the influent flow was treated with efficiency level >80% as shown in Figs. 36.2 and 36.3. Results also indicated that the organic load generated by 79% of the population equivalent was not reduced to the allowable standards. In Germany, 99%, 98%, 99%, 98%, and 99% of the treatment plants achieved the standard effluent limits in terms of BOD, COD, NH_4 , TN, and TP, respectively, as illustrated in Table 36.2.

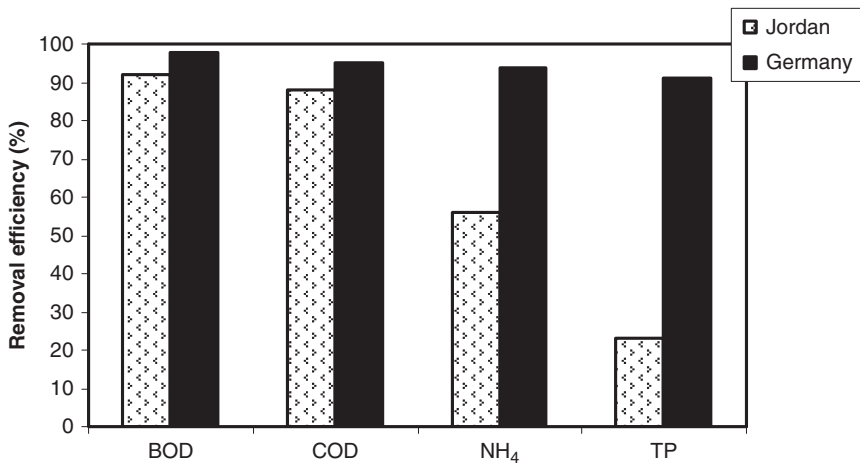


Fig. 36.1 Removal efficiencies based on the average (by numbers) of all plants.

36.3.3 Comparisons according to the used technologies

There are 23 plants for municipal wastewater treatment in Jordan, 5 of which are stabilization ponds, 16 are mechanical mode, and 2 are used to treat the septic waste. Table 36.3 illustrates the applied technologies used to treat wastewater in Jordan. It is clear that about 80% of wastewater is treated naturally by stabilization ponds, which depends on the activity of bacteria, algae, and other plants found in ponds. The activities of these consumers increase as temperature and sunshine period increase, so the treatment is climate dependent, which explains the low efficiency obtained by these plants especially during winter season. All stabilization ponds in Jordan are overloaded based on both hydraulic and organic load, which is

considered as an additional reason for low efficiency (Ammary, 2007). Most of the treatment plants do not have any technique to eliminate nitrogen, the reason of high concentration of ammonium in the effluent of these plants. Mechanical treatment plants (activated sludge and trickling filter) have higher removal efficiencies in comparison with waste stabilization ponds. It is important to mention that all of the waste stabilization ponds in Jordan will be converted to mechanical mode (Ammary, 2007). The recent trend of using modern mechanical treatment plants needs cooperation with well-qualified partners.

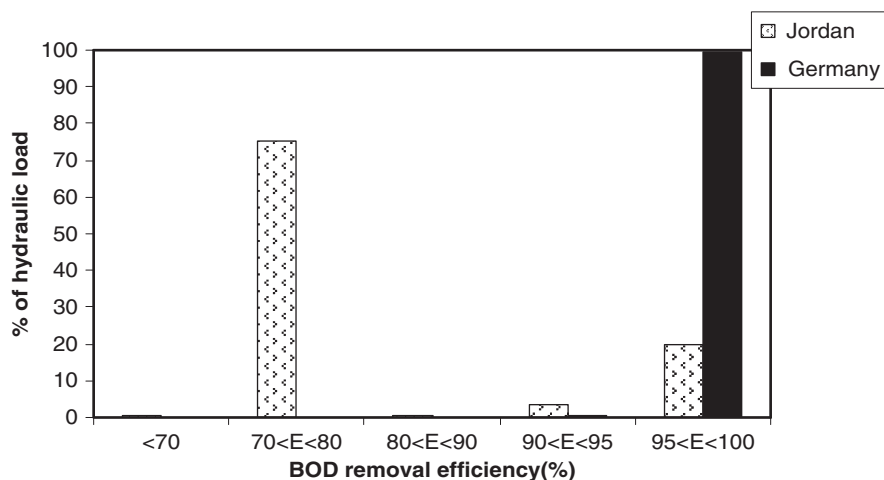


Fig. 36.2 BOD removal efficiency based on the applied hydraulic load.

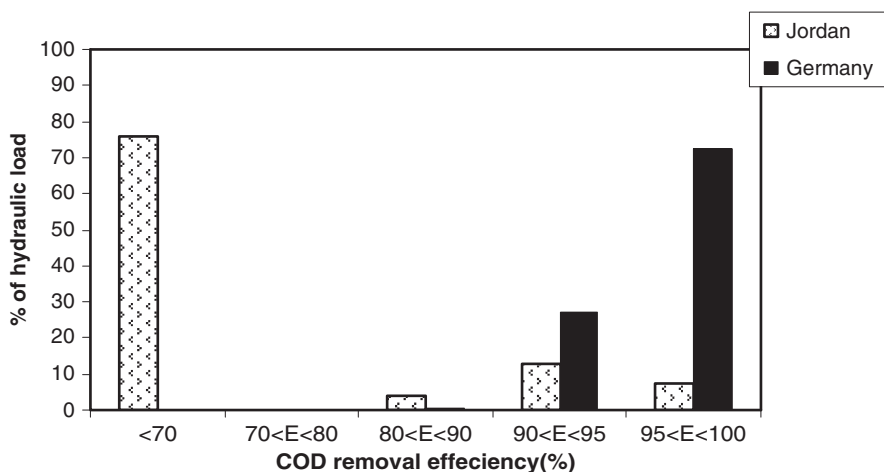


Fig. 36.3 COD removal efficiency based on the applied hydraulic load.

Table 36.2 Efficiency of treatment plants in Germany.

Plant category (Population equivalent)	Number of plants	Number of plants violating BOD standards	Number of plants violating COD standards	Number of plants violating NH ₄ standards	Number of plants violating TN standards	Number of plants violating P standards	Violation %
≤ 1000	89	1	2	—	—	—	3.3
>1,000 and ≤5,000	79	0	0	—	—	—	0
>5,000 and ≤10,000	53	0	0	2	—	—	3.7
>10,000 and ≤100,000	146	1	2	1	4	4	8.2
>100,000	22	0	1	0	4	0	22.7
Sum	389	2	5	3	8	4	
Violation %		0.5	1.3	0.8	2.1	1.0	
Compliance %		99.5	98.7	99.2	97.9	99	

Table 36.4 shows that 56% of the treatment plants in Germany are activated sludge mode, 13% are stabilization ponds, 4% use sequencing batch reactor methods (SBR), 2% are trickling filter, and 25% are operated either by multiple methods or by other techniques such as wetland and membranes. When Germany's authorities decide to construct a new treatment plant, the preferred technology is selected based on the desirable efficiency. In case high quality is required, or in case of sensitive water bodies, modern technologies are used such as membrane or multi-treatment stages.

Table 36.3 Methods of wastewater treatment in Jordan.

Type of treatment*	Number of plants	Hydraulic load %	Organic loads %	Removal efficiency (%)	
				BOD	COD
WSP	5	79.7	78.8	83	76.6
AS	9	11.7	11	97.1	93
AS+TF	3	6.6	7.8	95.2	91.8
TF	2	1.1	1.7	95	90.2
AP	1	0.9	0.6	94	88.6
Sum	20	100	100		

* WSP: waste stabilization ponds, AS: activated sludge, TF: trickling filter, AP: aerated ponds, ASS: activated sludge simultaneous with sludge stabilization.

Table 36.4 Methods of wastewater treatment in Germany.

Type of treatment	Number of plants	Hydraulic load %	Organic loads %	Removal efficiency (%)	
				BOD	COD
WSP	53	0.7	0.8	96	91
AS	218	77.5	77	99	95
ASS	79	16.7	15.9	97	96
TF	7	0.10	0.1	94	87
SBR	15	0.8	0.8	99	96
AS+TF	2	2.9	3.2	98	96
Others	15	1.3	1.4	98	94
Sum	389	100	100		

36.3.4 Comparisons according to the discharge regulations

Most of the treated wastewater in Jordan is reused to irrigate many types of plants (vegetable, fruits, fodder crops), fishponds, or discharged to the wadis (a dry streambed). Therefore, allowable discharge concentrations are stated based on reuse categories. Because the present treatment plants – with the applied technologies – are incapable of achieving effective treatment, the Jordanian standards are not as stringent as the German standards as shown in Table 36.5. Jordan standards limit effluent concentration only and do not take into account the environmental load in the receiving bodies. For this reason, many locations such as King Talal Dam were pressured by high-polluted discharges (Ammary, 2007). The stated regulations should be based on the sensitivity of the rivers or valleys and on the water quality level for the predominant downstream water reuse.

Unlike Jordan, the German standard for treated wastewater is variable and stated based on two limitations: the first is the concentration and the second is the discharged load. While the standard permits higher effluent concentration for the small plant, it is stricter in case of larger ones. Wastewater treatment facilities are designed and operated to meet effluent standards that are compatible with the maintenance of a desired water quality in the receiving waters. Germany's standards prohibit reusing of wastewater for irrigation, so the main criteria of the effluent discharge is how much it affects the receiving watercourses (rivers, lakes, sea) and the sensitivity of the receiver. As a result of strict regulations a noticeable improvement in the environment quality is observed, for example, the concentration of oxygen in the river Rhine has increased from an annual average value of around 5 mg/L in the 1970s to current values around 10 mg/l (UNEP, 2006).

Table 36.5 Jordanian and German standards for treated wastewater discharged to the streams.

Parameter	Jordan	Germany	Remarks for Germany plants
BOD	50	15–40	Depends on the plant size
COD	200	75–150	Depends on the plant size
NH ₄	15	10	Unlimited for plants <5,000 population equivalent
TN	50	13–18	Unlimited for plants <10,000 population equivalent
P	15	1–2	Unlimited for plants <10,000 population equivalent

36.4 Conclusions

From this study we can extract the following remarks:

- Wastewater in Jordan contains high concentrations of pollutants, which affect the efficiency of treatment.
- Strength of waste, overloads, lack of expertise, and limited budget are the main obstacles facing wastewater management in Jordan, while modern treatment technologies, high-qualified operators, and strict regulations are the main strength points of wastewater management in Germany.
- Wastewater reuse should be considered as a non-conventional water resource in Jordan.
- To achieve better treatment efficiency, the capacity of the present plants should be enlarged to deal with the overloads and new modern technologies are required.
- Reuse of treated wastewater should be controlled by strict standards that comply with WHO and FAO guidelines, as a minimum objective of treatment. These standards must prevent pollution of the receiving watercourse, protect human health and the environment, and must be suitable for end reuse objectives and the method of application.
- In Germany, most of the wastewater volume is treated with the highest Europe standards (biological treatment with nutrient elimination).
- The cooperation between Germany and Jordan should be employed beneficially in enhancing wastewater sector in Jordan, especially by experience interchange, technology transfer, and increased financial support.

References

- Al-Zboon, K, Al-Ananzeh, N (2008) Performance of wastewater treatment plants in Jordan and suitability for reuse. *African Journal. of Biotechnology* 7(15): 2621–2629
- APHA, American Public Health Association (1998) *Standard Methods for the Examination of Water and Waste water*. 20th ed. Washington, D.C: American Public Health Ass., WPCF, and AWWA.

Ammary, B (2007), Wastewater reuse in Jordan: Present status and future plans. *Desalination Journal* 211(1-3)10: 164–176.

ATT, Association of Drinking Water from Reservoirs (ATT), Federal Association of the German Gas and Water Industries (BGW), German Alliance of Water Management Associations (DBVW), The German Technical and Scientific Association for Gas and Water (DVGW), German Association for Water, Wastewater and Waste (DWA), Association of Local Utilities (VKU) (2005), Profile of the Germany Water Industry.

Barjenbruch, M, Al-Zboon, K (2008) North –south gap in wastewater management, a comparison study for Germany and Jordan. GCGW conference, Istanbul, July, 2008.

Bataineh, F, Najar, M, Malkawi, S (2002) Wastewater Reuse, in water demand management forum, Amman, Jordan.

Bdour, A, Hadadin, N (2005) Potentials and Limitations of Wastewater Reuse in Rural Areas in Jordan: The Reuse Options in the Jordan Valley. *Journal of Agronomy* 1.4: N.4.

DWA (2006) German Association for Water. Wastewater and Waste (DWA), Annual report.

Hadadin, A (2007) Environmental Issues in Jordan, Solutions and Recommendations. *American Journal of Environmental Sciences* 3(1): 30–36.

McCornick, P, Hijazi, A, Sheikh, B (2007) From Wastewater Reuse to Water Reclamation: Progression of Water Reuse Standards in Jordan. http://www.idrc.ca/en/ev-68342-201-DO_TOPIC.html, accessed on November 2007.

Pfister, A, Stein, A, Schlegel, S, Teichgraber, B (1998) An integrated approach for improving the wastewater discharge and treatment systems. *Water Science and Technology Journal* 37 (1): 341–346.

UNEP, United Nations Environment Program (UNEP) (2006), Wastewater characteristics, online: <http://www.unep.org>, accessed on December 2007.

WAJ, Water Authority of Jordan (WAJ), annual report (2006).

A Pervaporation Application for Treating Methyl *tert*-Butyl Ether (MTBE)-Contaminated Water/Wastewater

Nilufer Durmaz Hilmioglu, Ahmet E. Yildirim and Sema Tulbentci

37.1 Introduction

Contamination of groundwater and soils with volatile organic compounds (VOCs) is a problem at many industrial sites. Soil contamination by VOCs is a source for continuous air pollution and is also a source for groundwater pollution. The level of volatile organic compounds allowed in discharged wastewater or drinking water is lowered every few years. Examples of contaminants are petroleum hydrocarbons, methyl *tert*-butyl ether, chlorinated hydrocarbons such as trichloroethylene and carbon tetrachloride. Many of the VOCs are potential carcinogens.

MTBE, widely used as an octane enhancer, has relatively high water solubility and vapor pressure. MTBE is very toxic and is also suspected for its carcinogenic properties. Recently, MTBE has been detected in lakes, reservoirs, and groundwater used as potable water supplies in concentrations exceeding, in some cases, allowed levels for taste, odor, and human health.

There is a need to develop separation systems that can remove organics from already contaminated sites and systems to prevent future contamination. There are several alternative methods which can be applied to the VOCs removal, including air stripping, carbon adsorption, biological treatment, steam stripping, and incineration. Some of them can generate secondary wastes. This, coupled with a growing interest in recycling both for economical and environmental reasons, opens new opportunities for membrane technologies like pervaporation. Pervaporation can be used for effectively removing VOCs from water, concentrating them for economical disposal or recycle/reuse using specially designed hydrophobic membranes.

The separation achieved is determined by the individual rates of permeation through the membrane and the relative volatility of the components of the feed mixture. Usually the VOCs permeate through hydrophobic membrane orders of magnitude faster than water, as a result of which the VOCs are highly concentrated.

MTBEs are examples of VOCs which can be found in the effluents from many chemical, pharmaceutical, or petrochemical, factories (Kujawski, 2000; Keller et al., 2007).

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It is considered as an attractive alternative to other separation methods for a variety of processes. For example, with the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes. Pervaporation is also used for the dehydration of organic solvents and the removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for separation of heat-sensitive products.

Pervaporation involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. A concentrate and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeated vapors. Pervaporation is typically suited to separating a minor component of a liquid mixture, thus high selectivity through the membrane is essential. Figure 37.1 shows an overview of the pervaporation process.

Pervaporation can be used for breaking azeotropes, dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol removal, and wastewater purification.

Characteristics of the pervaporation process include

1. Low energy consumption
2. No entrainer required, no contamination
3. Permeate must be volatile at operating conditions
4. Functions independent of vapor/liquid equilibrium

Liquid transport in pervaporation is described by various solution–diffusion models. The steps included are the sorption of the permeate at the interface of the solution feed and the membrane, diffusion across the membrane due to concentration gradients (rate determining steps), and finally desorption into a vapor phase at the permeate side of the membrane. The first two steps are primarily responsible for the permselectivity. As material passes through the membrane a ‘swelling’ effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated.

The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation, respectively (Kumar M.S., 2007).

Literature searches for MTBE/water mixtures were given in Table 37.1. Separation factors are not available in the literature. It is concluded that from the literature survey that PEBA membrane is suitable for the MTBE removal from water.

Table 37.1 Separation of MTBE/water mixtures by pervaporation.

Membrane material	Feed concentration (MTBE)	Separation factor	Reference
PVAC-modified silica	0.01 vol%	68	(Yoshida and Cohen, 2004)
PEBA, PDMS	1 wt %	Not given	(Kujawski and Ostrowska-Gumkowska, 2003a)
H polysiloxane co styrene isoprene	1 wt %	3200	(Kujawski et al., 2003b)
FAS grafted ceramic	0 – 3.5 wt%	Not given	(Kujawski, 2007)
Commercial organophilic	0.1 vol %	Not given	(Urkiaga et al., 2002)
PEBA 4033	1 wt %	33	(Kujawski and Roszak, 2002)

In this study PEBA membrane was developed for the pervaporation separation of MTBE/water mixtures. The effects of feed concentration on the separation performance were investigated experimentally and the flux and the selectivity of the membrane were evaluated. Pervaporation that uses PEBA membrane could be an alternative separation technology for the original environmental problems like this study.

37.2 Materials and Methods

37.2.1 Materials

MTBE was purchased from Merck. The hydrophobic PEBA 2533 granulates were provided by Atochem. PEBA is the general name of a class of block copolymers in which the polyether soft segments are alternatively linked with harder polyamide segments. The physical properties of these materials can be varied in a large range by changing the nature and/or the length of the soft and hard segments. Two types of PEBA materials are manufactured by Elf-Atochem: hydrophobic PEBA materials with poly(tetramethylene) glycol soft segments and hydrophilic PEBA materials with polyethylene glycol soft segments. In this work, a hydrophobic type of PEBA 2533 was used. The number 25, 35, and 40 represents the Shore D hardness of the polymer (Sampranpiboon et al., 2000).

The PEBA polymer consists of linear chains of polyamide and polyether segment (block) in an orderly pattern. The combination of the hard polyamide segment and the soft polyether segments yields a block copolymer that exhibits a two-phase structure on a microscopic scale: a crystalline phase due to the polyamide and an amorphous phase due to the polyether. The crystalline phase allows the copolymer to behave as a thermoplastic and the amorphous phase imparts elastomeric characteristics (Sampranpiboon et al., 2000).

In this study PEBA 2533 was used, because it was concluded that the most suitable polymer for the separation of MTBE/water mixtures is PEBA 2533 (Durmaz Hilmioglu et al., 2005).

37.2.2 Membrane preparation

The membranes were prepared by using solution casting method. The membranes were prepared by casting a solution of polymer in the mixture of 1-butanol and 1-propanol (4:1). The membrane was prepared by dissolving 10 wt% of the polymer in solvent mixture at elevated temperature. Solutions were casted on a heated glass plate at a thickness of 1000 μm . Films were dried in nitrogen atmosphere for 3 days. The membrane was completely dried under reduced pressure for a few days. The final thickness of the membranes was about 100 μm (Yildirim et al., 2008).

37.2.3 Sorption experiments

Initially, a piece of the dry membrane was weighed and immersed and left for swelling. The swollen membrane was taken out of the solution, wiped out quickly with a filter paper to remove adherent solvent, and weighed. After the equilibrium was attained the degree of swelling (DS) was calculated (Yuzhong, 1993):

$$\text{DS} = (W_s - W_d) / W_d \quad (\text{g/g}) \quad (37.1)$$

where W_d is the weight of the dry membrane and W_s is the weight of the membrane swollen in the solution. Sorption measurements were derived for single components and for the mixtures containing different concentrations of MTBE in water.

37.2.4 Pervaporation experiments

A schematic presentation of the pervaporation apparatus is presented in Fig. 37.1. The pervaporation cell was constructed by stainless steel. The feed tank and pervaporation cell were placed in an incubator to adjust the operation temperature. The effective surface area of the membrane is 28.26 cm^2 . The membrane was left for swelling in the feed mixture before pervaporation experiments. The membrane was placed on a porous material as a support material. The pressure on the permeate side was measured 0.3 mbar with a vacuum gauge. Permeated vapors were completely condensed in a trap placed in a dewar flask cooled by liquid nitrogen. Two serial traps were established for continuous work. The feed mixture was re-circulated by a circulation pump. The permeate and feed compositions were analyzed by refractometer.

Performance of a membrane in pervaporation is characterized by flux (J) and selectivity (α_{ij}). The separation factor (selectivity) is calculated by using Eq. (37.2) (Huang, 1991):

$$\alpha_{ij} = (y_i/y_j)/(x_i/x_j) \quad (37.2)$$

where i and j represent the components of MTBE and water, respectively, and y and x represent the weight fractions of MTBE in permeate and feed mixture, respectively. The flux was obtained taking the ratio of the weight of the permeate collected to effective area of membrane and time collection of the sample in $\text{kg/m}^2\text{h}$. The pervaporation experiments were driven for the different concentrations of feed mixtures.

Fixed Temperature Oven

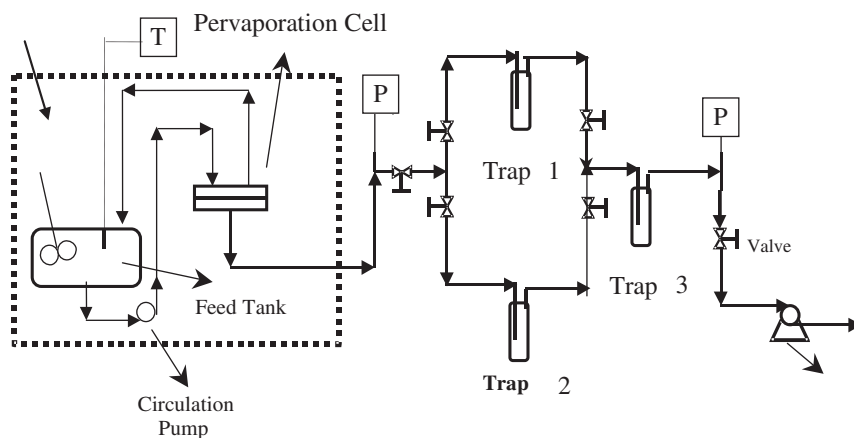


Fig. 37.1 Experimental pervaporation setup.

37.3 Results and Discussion

37.3.1 Sorption results

Sorption experiments were carried out for the mixtures of MTBE/water with the concentration 4 – 8 MTBE vol% at room temperature. Figure 37.2 is a plot of degree of sorption versus MTBE concentration in the mixtures (x : volume fraction), representing the concentration dependence of the sorption characteristics of membranes.

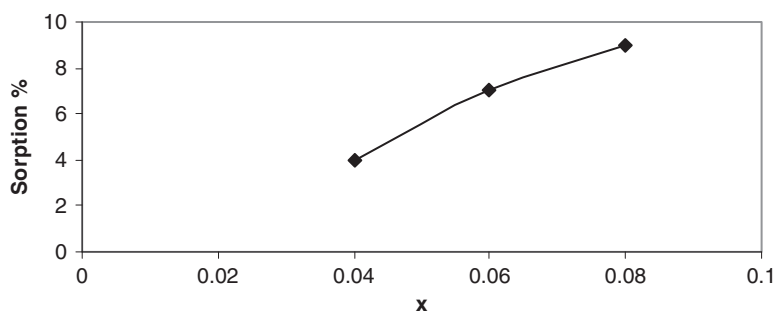


Fig. 37.2 Concentration effect on sorption in the mixtures of MTBE/water for PEBA 2533 at room temperature.

According to sorption results, MTBE sorption was much higher than water. This is due to the hydrophobic structure of the membrane material. For all concen-

tration ranges, sorption values increase as the MTBE content in the mixture increases. From these results, it can be concluded that the polymers have higher affinity for MTBE than water. Decreasing sorption ability results in a decreasing penetration concentration in the membranes and consequently will result in a decreasing permeation rate of sorption values at low levels. This means pervaporation flux will be at low levels also. The relationships between the composition of feed mixture (x) and the composition of sorbed liquid in the membrane (z) and the composition of pervaporate in permeate (y) as MTBE vol% fraction for the membrane are given in Fig. 37.3.

From these figures it is observed that sorption values are very near to pervaporation values and they have the same tendency. Both (y and z) values are at high levels. This means pervaporation selectivity (separation factors) will be at high levels also.

Sorption results show that MTBE/water mixture can be separated by pervaporation using PEBA 2533 membranes prepared.

37.3.2 Pervaporation results

Pervaporation experiments were carried out for the mixtures of MTBE/water with the concentration 4–8 MTBE vol% at room temperature. Figures 37.4 and 37.5 present pervaporation performance of the membranes (flux and separation factor).

According to the pervaporation results, membrane was permselective for MTBE over the entire range of the feed concentrations. It is found that flux increases with increasing MTBE concentrations in the feed mixture, while selectivity decreases. This can be explained by the sorption behavior of the membranes, which means the higher the swelling, the higher the flux.

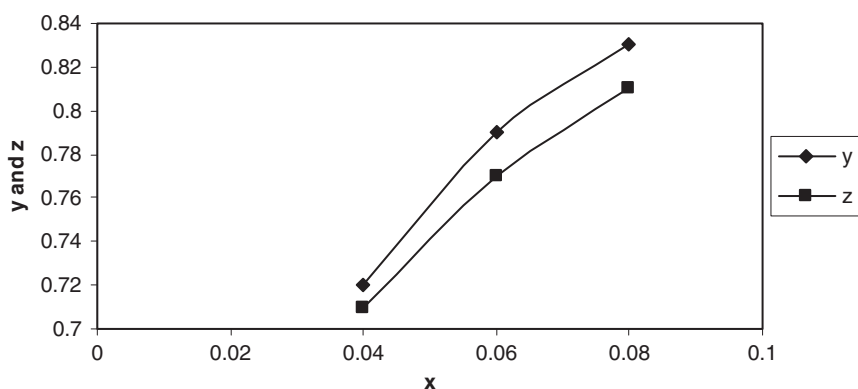


Fig. 37.3 The relationship between the compositions (x : feed mixture, y : pervaporate, z : membrane) for MTBE/water mixtures through PEBA 2533 at room temperature.

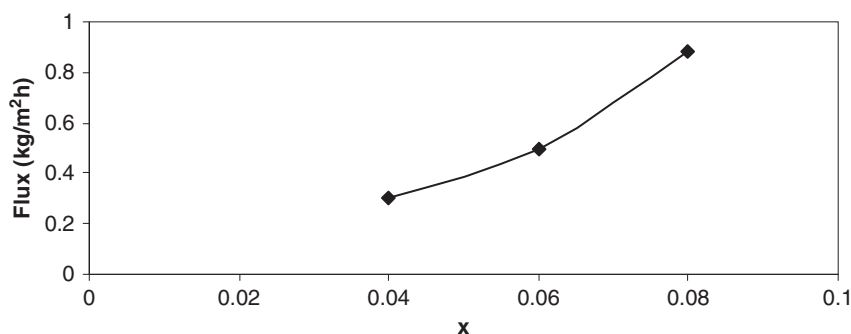


Fig. 37.4 Concentration effect on the flux in the mixtures of MTBE/water for PEBA 2533 at room temperature.

MTBE and polyether segment of PEBA consist of similar ether group. According to solution–diffusion model similar groups interact with similar ones and so the permselective transport occurs. Since PEBA 2533 has the highest polyether segment between the other PEBA membranes such as PEBA 3533 and PEBA 4033, it shows both the high flux values and the high selectivity values than the others (Hilmioglu et al., 2005). It has a strong influence on the separation characteristics such as flux and selectivity.

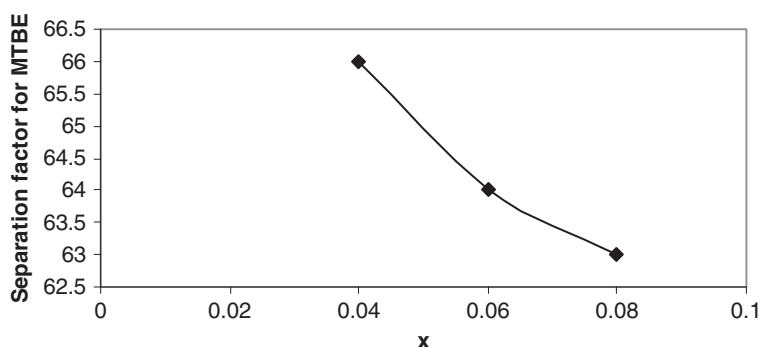


Fig. 37.5 Concentration effect on the separation factor in the mixtures of MTBE/water for PEBA 2533 at room temperature.

Pervaporation results show that PEBA 2533 membranes prepared can be used for separation of MTBE/water mixture at room temperature. Separation factors obtained are high enough for pervaporation applications.

37.4 Conclusions

- After more than 25 years of worldwide intensive research, pervaporation has evolved from a novel research topic to a commercially viable process for certain applications. However, pervaporation must be regarded as a young membrane process compared to other membrane processes like reverse osmosis, ultrafiltration, dialysis, and even electrodialysis.
- There are several practical advantages of pervaporation when compared with other conventional technologies: simple operation and control, reliable performance, high flexibility, unproblematic part-load operation, high product purity (no contamination by entrainer), no environmental pollution, high product yield, low-energy consumption, compact design (low space requirements), short erection time, and uncomplicated capacity enlargement. Nowadays there are also several areas of the technoeconomical success of pervaporation. In general, pervaporation and vapor permeation will, especially, be used in those cases where a small quantity has to be removed from a large quantity. In all the above applications, the most successful processes require integration with existing conventional separation, unit operations. Nevertheless, pervaporation has been identified as areas of vast potential for future research and commercial development.
- In this study, the separation of MTBE from water/wastewater by pervaporation using PEBA membrane was investigated. The sorption and pervaporation experiments were carried out for the different concentrations of feed mixtures at room temperature. PEBA 2533 membrane was prepared and exhibited high separation performances for separating MTBE from wastewater.
- The selectivity values are close to commercial scale; the flux values can be increased easily by membrane module applications. Thus, application of PEBA membranes in industrial-scale pervaporation units may be feasible for separation of MTBE in wastewater.

Nomenclature

α_{ij}	Selectivity
DS	Degree of swelling
W	Weight of the membrane
X	Weight fraction in feed
Y	Weight fraction in permeate
Subscripts	
D	Dry
I	MTBE
S	Swollen
J	Water

References

- Durmaz, Hilmioglu N, Yildirim, AE, Tulbentci, S (2005) Pervaporative separation of methyl tert butyl ether from wastewater. Application of Nanotechnologies for Separation and Recovery of volatile Organic compounds from Waste Air Streams (ANVOC), 30–31 May, Istanbul, Turkey.
- Huang, RYM (1991) Pervaporation membrane separation processes. The Netherlands, Elsevier.
- Keller, AA, Sandall, OC, Rinker, RG, Mitani, MM, Bierwagen, B, Snodgrass, MJ (2007) Cost and performance evaluation of treatment technologies for MTBE-contaminated water. http://www.tsrtpt.ucdavis.edu/mtberpt/vol5_3.pdf. Accessed on May 30.
- Kujawski, W (2000) Application of pervaporation and vapor permeation in environmental protection. Polish Journal of Environmental Studies 9: 13–26.
- Kujawski, W, Roszak, R (2002) Pervaporative removal of volatile organic compounds from multicomponent aqueous mixtures. Separation Science and Technology 37 (15): 3559–3575.
- Kujawski, W, Ostrowska-Gumkowska, B (2003a) Preparation and properties of organophilic membranes for pervaporation of water-organics mixtures. Separation Science and Technology 38 (15): 3669–3687.
- Kujawski, W, Keres, J, Roszak, R (2003b) Application of AB-crosslinked polymers composed of styrene/isoprene–siloxane copolymers to pervaporative removal of volatile organic compounds from water. Journal of Membrane Science 218: 211–218.
- Kujawski, W (2007) Pervaporation properties of fluoroalkylsilane (FAS) grafted ceramic membranes. Desalination 205: 75–86.
- Kumar MS (2007) Pervaporation: an overview. <http://www.cheresources.com/pervaporation.shtml>. Accessed on May 31.
- Sampranpiboon, P, Jiratananon, R, Uttapap, D, Feng, X, Huang, RYM (2000) Pervaporation separation of ethyl butyrate and isopropanol with polyether block amide (PEBA) membranes. Journal of Membrane Science 173: 53–59.
- Urkiaga, A, Bolano N, Fuentes, L (2002) Removal of micropollutants in aqueous streams by organophilic pervaporation. Desalination 149: 55–60.
- Yildirim, AE, Durmaz, HN, Tulbentci, S (2008) Separation of benzene/ cyclohexane mixtures by pervaporation using PEBA membranes. Desalination 219 (1–3): 14–25.
- Yoshida, W, Cohen, Y (2004) Removal of methyl *tert*-butyl ether from water by pervaporation using ceramic-supported polymer membranes. Journal of Membrane Science 229: 27–32.
- Yuzhong, Z, Keda, Z, Jiping, X (1993) Preferential sorption of modified PVA membrane in pervaporation. Journal of Membrane Science 80: 297–308.

Temperature Variations and Their Effects on Rainfall in Nigeria

Osita Ibe and E.F. Nymphas

38.1 Introduction

Nigeria is located between Latitude 4° and 14°N and Longitude 2°45' and 14°30'E. To the north, the country is bounded by the Republics of Niger and Chad, in the west by the Republic of Benin, in the east by the Republic of Cameroon, and to the south by the Atlantic Ocean. Approximately 13,000 km² of the land is covered by water (1.4%) and the remaining 98.6% of the land cover ranges from thick mangrove forests and dense rain forests in the south to a near-desert condition in the northeastern corner of the country. The country takes its name from its most prominent river, the Niger. Nigeria has a land area of about 910,770 km² (Adeyinka et al., 2005); a north–south length of about 1,450 km and a west–east breadth of about 800 km. Its total land boundary is 4,047 km while the coastline is 853 km.

Nigeria is located primarily within the lowland humid tropics just north of the equator and is generally characterized by a high–temperature regime almost through the year. In the far south, mean maximum temperature is about 32°C while in the north it is 41°C. However, the mean minimum temperature is 21°C in the south and under 13°C in the north which has a much higher annual range. The mean temperature for the country is 27°C, in the absence of altitudinal modifications. Over the last few decades, there has been a general increase in temperature throughout Nigeria (UNFCC, 2003).

Nigeria, by virtue of its location, experiences a warm tropical climate with two seasons – the rainy or wet season that lasts from mid-March to November in the south and from May to October in the north; and the dry season occupies the rest of the year (Oyenuga, 1967).

The Nigerian climate varies from tropical in the coastal area to sub-tropical up north. There are two regimes of climate: a dry season and a wet season. The seasonal pattern of climatic conditions over Nigeria gives rise to four seasons in

the south and two in the north. This is the result of annual total rainfall occurrence and distribution, which is more predominant in the south than in the north. The mean annual rainfall along the coast in the southeast is 4000 mm while it is only 500 mm in the northeast.

Southern Nigeria: The four observed seasons are

- The long rainy season: This starts in February/March and lasts to the end of July, with a peak period in June over most parts of southern Nigeria. It is a period of thick clouds and is excessively wet particularly in the Niger Delta region and the coastal lowlands.
- The short dry season: This is experienced in August for 2–3 weeks known as ‘August break.’
- The short rainy season: This brief wet period follows immediately after the ‘August break’ from early September to mid-October, with a peak period at the end of September. The rains are not usually as heavy as those in the long rainy season, although the spatial coverage over southern Nigeria is similar. The two periods of rainfall intensity give the double maxima phenomenon of the rainy season characteristic of southern Nigeria.
- The long dry season: This period starts from late October and lasts till early March with peak dry conditions between early December and late February. The period witnesses the prevailing influences of the dry and dusty northeast winds, as well as the ‘harmattan’ conditions.

Nigeria can, thus, be broadly divided into the following climatic regions:

- (a) the humid sub-equatorial, in the southern lowlands
- (b) the hot tropical continental, in the far north
- (c) the moderated sub-temperate in the high plateaus and mountains
- (d) the hot, wet tropical, in the hinterland (the middle belt) (Online Nigeria, 2002).

In general there are fewer dry season in the extreme southern tip of the country, the wet season often does not exceed 5 months in the northeastern part. Similarly annual rainfall totals range from 2,500 mm in the south to less than 400 mm in parts of the extreme north (FMEN, 2001).

38.2 Methodology

38.2.1 Data used

The data used for the study cover an average of 30 years and it was collected from the Nigerian Institute of Meteorological Agency (NimetAg). It includes daily maximum and minimum temperatures, rainfall, and relative humidity of the affected localities. The study area covers the six geo-political zones of the country viz, southwest (SW), northwest (NW), southeast (SE), northeast (NE), south–south (SS), and north central (NC).

A total of 16 states of the Nigerian federation were covered in the study. The duration of study was 30 years on the average. Table 38.1 gives the summary of the analogy. The discrepancy in the duration of the data as against the period of coverage specified is informed by the missing data of some years. Figure 38.1

is the current map of Nigeria, showing some of the locations covered by the study in thick circles.

Table 38.1 Study area locations, population, and duration.

S/ N	Study areas	Geographical location	Latitude (°N)	Longitude (°E)	Population	Duration of study (Years)	Missing data (%)
1	Benin	South-south	6.33	5.63	3,218,332	1971–2002 (32)	0.0
2	Ibadan	Southwest	7.38	3.90	5,591,589	1971–2003 (33)	0.0
3	Lokoja	North central	7.80	6.73	3,278,487	1971–2002 (31)	3.1
4	Oshogbo	Southwest	7.83	4.58	3,423,535	1971–2003 (33)	0.0
5	Bauchi	Northeast	10.31	9.84	4,676,465	1971–2002 (24)	25.0
6	Maiduguri	Northeast	11.85	13.16	4,151,193	1971– 2000(30)	0.0
7	Nguru (Yobe)	Northeast	12.88	10.45	2,321,591	1971–2002 (28)	12.5
8	Warri	South-south	5.52	5.75	4,098,391	1971–2003 (33)	0.0
9	Ikeja	Southwest	6.45	3.47	9,013,534	1971–2002 (30)	6.3
10	Port Harcourt	South-south	4.78	7.00	5,185,400	1971–2002 (28)	12.5
11	Sokoto	Northwest	13.07	5.24	3,696,999	1971–2003 (33)	0.0
12	Owerri	Southeast	5.50	7.02	3,934,899	1974–2003 (28)	6.7
13	Calabar	South-south	4.96	8.3 1	2,888,966	1971–2002 (31)	3.1
14	Kano	northwest	12.00	8.52	9,383,682	1971–2000 (27)	10.0
15	Jos	North Central	9.93	8.89	3,178,712	1971–2000 (30)	0.0
16	Yola	northeast	10.6	7.22	3,168,101	1971–2000 (29)	3.3
Average		-	-	-	-	1971–2003(30)	

38.2.2 Data analysis

Since the data represented a daily minimum and maximum temperature as well as daily rainfall in the localities of interest, it was reduced into the monthly and yearly average. The monthly average for the temperature situation was calculated with the relation below:

$$T_{\text{avg}} = (\sum \text{Daily Temperatures}) / \text{Number of days of the month} \quad (38.1)$$

Since rainfall is not a daily event, the relation below was employed in the calculation of monthly rainfall situation:

$$R_{\text{total}} = \sum \text{Daily precipitation} \quad (38.2)$$

The average for all the years studied at the different localities and the cumulative average for all the localities altogether were computed.



Fig. 38.1 Map of Nigeria showing some of the stations covered by the study.

Since the maximum and minimum daily temperature situation was taken at each location, formula below was employed in computing the annual temperature average

$$T_{\text{avg}} = \frac{T_{\text{max}} + T_{\text{min}}}{2} \quad (38.3)$$

Equation (38.4) is used for the computation of the annual rainfall average

$$R_{\text{avg}} = (\text{Total rainfall}) / \text{Duration} \quad (38.4)$$

Also, the monthly averages of temperature and rainfall were equally deduced for all the years. In a bid to establish the relationship between the variables, the average temperature and rainfall against the months of the years of study were plotted for all the stations.

38.2.3 Trend analysis

Various trend-detection studies have been carried out in different parts of the world, mostly for the identification of climatic change, if any. Some of these cases have shown significant trend components, especially during the last 40 years (Karl et al., 1993). Different techniques, such as parametric and non-parametric tests, are used for testing whether there have been statistically significant trends. However, the physical interpretation has related, at times, to the greenhouse effect, global warming, urban heat islands, and to aerosols that exert cooling effects on our climate (Balling, 1992). The data are analyzed in order to identify meaningful long-term trends by making use of the sequential version of the Mann–Kendall rank statistics, the effective application of which includes the following steps in sequence:

- (i) The values of x_i of the original series are replaced by their ranks y_i , arranged in ascending order.
- (ii) The magnitudes of y_i ($i = 1, \dots, N$) are compared with y_j ($j = 1, \dots, i-1$). At each comparison, the number of cases $y_i > y_j$ is counted and denoted by n_i .
- (iii) A statistic t_i is, therefore, defined as follows:

$$T_i = \sum_{j=1}^i n_j \quad (38.5)$$

- (iv) The distribution of the test statistic t_i has a mean and a variance as

$$E(t_i) = \frac{i(i-1)}{4} \quad (38.6)$$

and

$$\text{Var } t_i = \frac{i(i-1)(2i+5)}{72} \quad (38.7)$$

- (v) The sequential statistic $U(t_i)$ is then computed as follows:

$$U(t_i) = \frac{[t_i - E(t_i)]}{\sqrt{\text{var } t_i}} \quad (38.8)$$

Herein, $U(t_i)$ is a standardized variable that has zero mean and unit standard deviation. Therefore, its sequential behavior fluctuates around zero level. Furthermore, $U(t_i)$ is a Gaussian normal variate.

(vi) Similarly, the values of $U'(t_i)$ are computed backward starting from the end of the series.

Although, the Mann–Kendall test can successfully locate the trends, it is not able to provide a measure of the amount of change involved during a defined period. However, the linear changes are estimated by the least squares regression analysis (Kadioglu, 1997).

38.2.4 Least squares regression analysis

The name ‘least square’ comes from the process of defining a trendline

The least squares line method uses a *straight line*

$$y = a + bx \quad (38.9)$$

to approximate the given set of data, $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$, where $n \geq 2$. Where ‘ a ’ stands for the intercept and ‘ b ’ stands for the slope. The slope is equivalent to variation in temperature (or rainfall) per year (Kadioglu, 1997).

38.2.5 Correlation analysis

In probability theory and statistics, correlation also called correlation coefficient indicates the strength and direction of a linear relationship between two random variables.

Correlation is a measure of association between two variables. The variables are not designated as dependent or independent.

The value of a correlation coefficient can vary from minus one to plus one. A minus one indicates a perfect negative correlation, while a plus one indicates a perfect positive correlation. A correlation of zero means there is no relationship between the two variables. When there is a negative correlation between two variables, as the value of one variable increases, the value of the other variable decreases, and vice versa. In other words, for a negative correlation, the variables work opposite each other. When there is a positive correlation between two variables, as the value of one variable increases, the value of the other variable also increases. The variables move together.

38.3 Results and Discussion

Extensive work has been carried out on the rainfall and temperature situations in Nigeria but research work on the possible fallout of the interplay between rainfall and temperature in Nigeria appears scanty.

Seasonal variations of rainy days of different categories in Nigeria, changing pattern or rainy days in Nigeria (Olaniran, 1990), regional variations in fluctuations of seasonal rainfall over Nigeria, variation of surface temperature with solar activity are few of the many researches that have been carried out on temperature and rainfall. Adedoyin (1989) carried out a research on the global scale sea-surface temperature anomalies and rainfall characteristics but with emphasis on northern Nigeria. The present work covers the entire country and the results are presented according to the geographical regions of the country. The least squares regression plots for all the zones are as shown in Figures 38.2a,b,c,d,e,f.

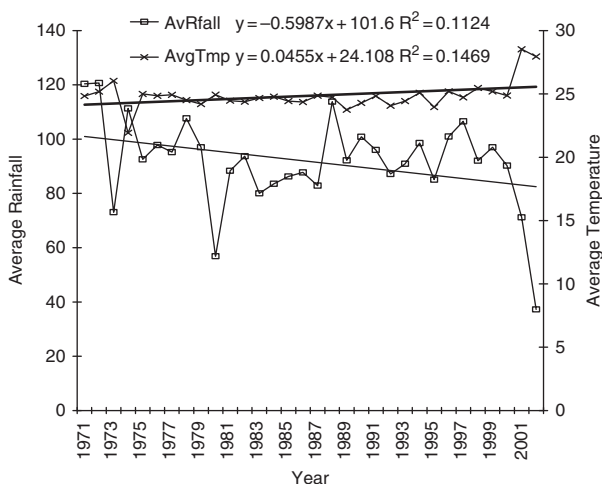


Fig. 38.2.a Least squares regression plots for the north central zone.

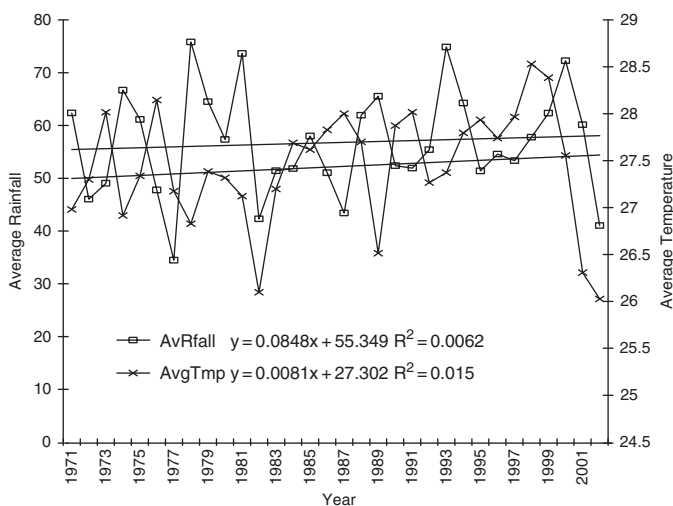


Fig. 38.2.b Least squares regression plots for the northeast zone.

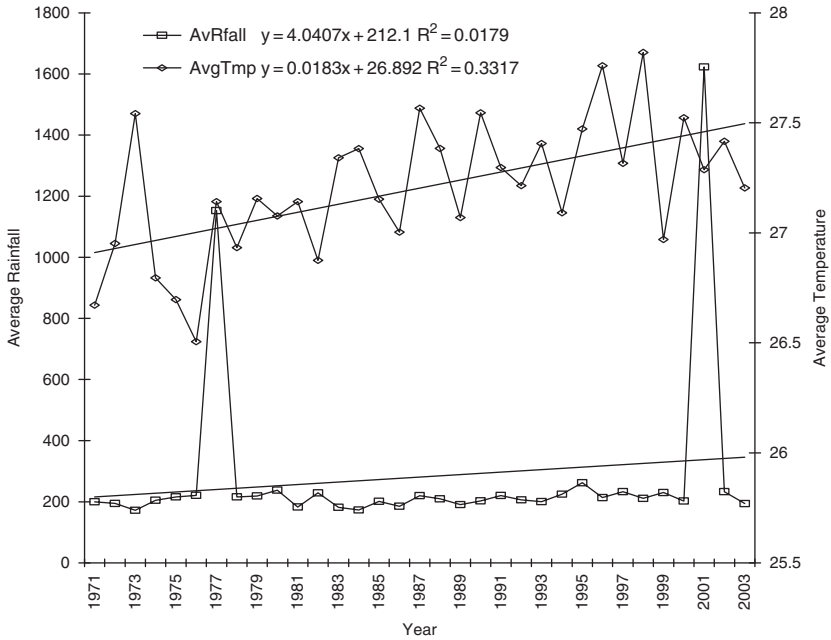


Fig. 38.2.c Least squares regression plots for the south-south zone.

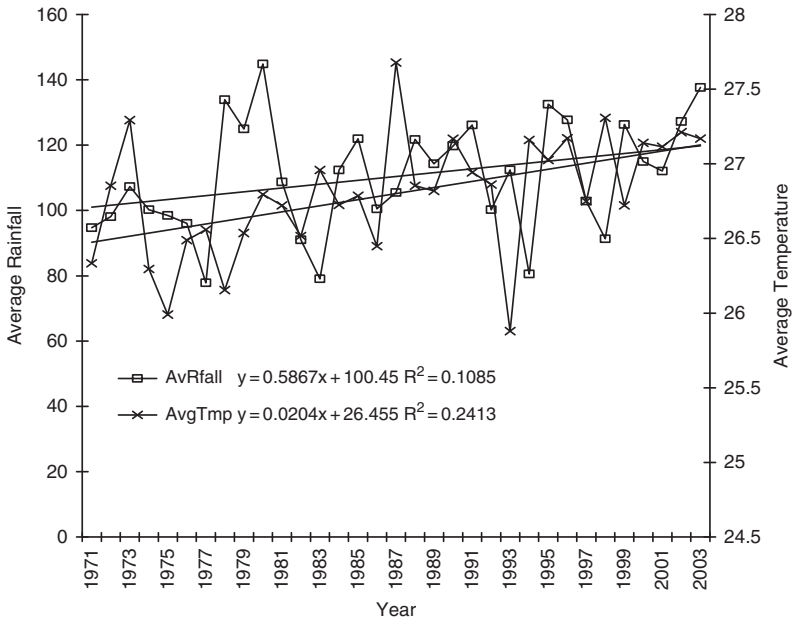


Fig. 38.2.d Least squares regression plots for the southwest zone.

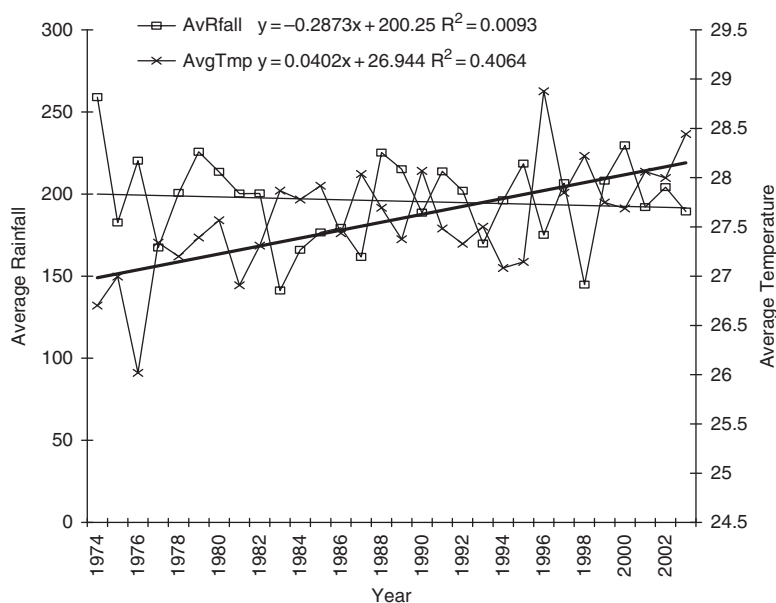


Fig. 38.2.e Least squares regression plots for the southeast zone.

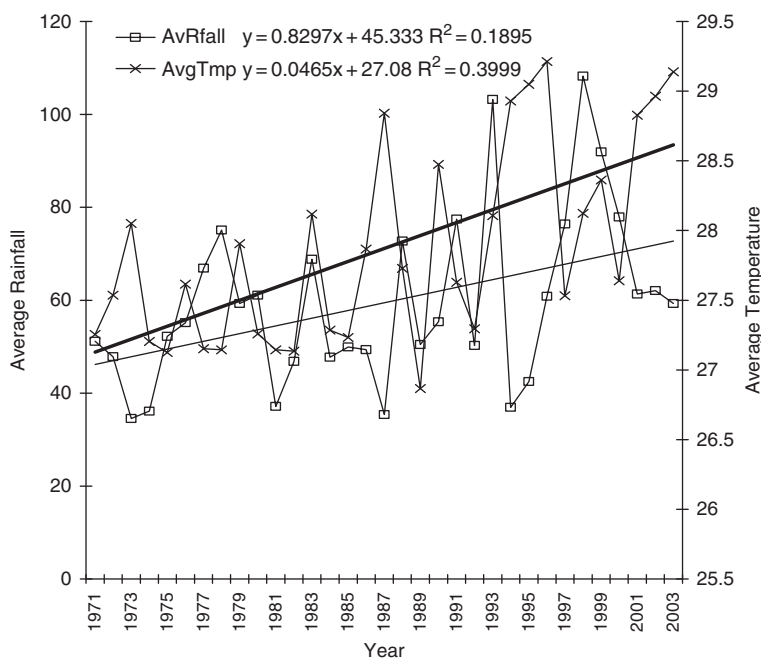


Fig. 38.2.f Least squares regression plots for the northwest zone.

Table 38.2 below is the tabular representation of the least square regression analysis of the rainfall/temperature variations at six geopolitical zones of the country.

Table 38.2 Regression analysis results of the rainfall/temperature variations.

S/N	Zone	Rainfall variation/ annum(mm)	Temperature variation/ annum (°C)
1	North central	-0.5987	0.0455
2	Northeast	0.0848	0.0081
3	Northwest	0.8297	0.0465
4	Southeast	-0.2873	0.0402
5	South-South	4.0407	0.0183
6	Southwest	0.5867	0.0204

From Table 38.2 above, the North Central and South East geopolitical zones witnessed negative regression in the rainfall trend while all other zones witnessed a positive trend; The temperature variations in all the zones regressed positively. In effect, only the North Central and South East geopolitical zones witnessed a decrease in the rainfall pattern; all other geopolitical zones experienced some increase. The temperature situation in all the geopolitical zones was of increasing trend.

38.3.1 Analysis of rainfall and temperature trends

By the use of the Mann-Kendall non-parametric tests, the trends represented by Figs. 38.3.a and 38.3.b were generated.

38.3.2 Correlation analysis of temperature and rainfall

When the rainfall was correlated against the temperature on the basis of the six geo-political zones (refer to Table 38.3), the results of the correlation coefficients are as presented in Table 38.4.

Table 38.3 Summary of average rainfall and temperature variations in Nigeria (1971–2003).

Year	AVRfall	AvMxTp	AvMnTp	AvTP
1971	105.6816	32.24316	20.58701	26.41508
1972	101.4489	32.58167	20.94658	26.76413
1973	87.23662	33.33338	21.4432	27.38829
1974	129.6859	31.54399	20.40155	25.97277
1975	117.2148	32.08727	20.96188	26.52458
1976	123.0084	31.82155	21.38619	26.60387
1977	265.827	32.17625	21.25547	26.71586
1978	134.8733	31.80759	21.11623	26.46191
1979	131.7137	32.08383	21.43744	26.76063
1980	128.6203	32.13945	21.5118	26.82562
1981	115.1485	31.96624	21.20101	26.58363
1982	117.2709	31.63429	21.13824	26.38626
1983	100.4001	32.30803	21.74502	27.02653
1984	105.8013	32.37619	21.50636	26.94128
1985	115.6764	32.08798	21.62686	26.85742
1986	108.9178	32.07368	21.57288	26.82328
1987	108.117	32.99266	22.00327	27.49797
1988	134.1874	32.16349	21.86823	27.01586
1989	121.391	31.87779	20.9181	26.39795

1990	120.0189	32.53531	21.93756	27.23644
1991	130.9435	32.08429	21.98338	27.03384
1992	116.8451	31.96757	21.37686	26.67221
1993	125.2546	31.9999	21.56633	26.78312
1994	116.9129	32.59916	21.78698	27.19307
1995	132.0527	32.56329	21.6333	27.09829
1996	122.0929	33.10353	22.21658	27.66006
1997	129.8261	32.46584	21.57914	27.02249
1998	117.5948	33.04568	22.11288	27.57928
1999	135.9347	32.5367	21.92083	27.22876
2000	131.2478	32.45771	21.68301	27.07036
2001	353.2994	32.97443	22.40049	27.68746
2002	117.5228	32.9501	22.2391	27.5946
2003	145.0544	32.83385	23.14399	27.98892
Average	131.7219	32.34594	21.58205	26.96399

Table 38.4 Correlation results of the average rainfall against temperature for the geo-political zones.

Geo-political zones	Correlation coefficient
North central	-0.408
Northeast	-0.039
Northwest	0.055
Southeast	-0.481
South-South	0.018
Southwest	0.116

The correlation analysis across the six geo-political zones, which represent the whole of the Nigerian federation (please refer to Table 38.3), yielded a value of 0.199.

38.4 Conclusion

From the foregoing research work, the following can be deduced:

- Throughout the period of study, the country witnessed an average of 131.72 mm rainfall and the average temperature was 26.96°C.
- The trend analysis of the country-wide variation indicates that there is a general increase in rainfall and temperature over the years. The 0.756°C increase over the years appears to fall within 0.6±0.2 range predicted by the Inter-Governmental Panel on Climate Change (IPCC, 2001).
- The correlated value of 0.199 throughout the country and the maximum value of 4.0407 mm rainfall variation per annum in the coastal areas suggest that the country is at the brink of global warming and the coastal areas are the worst hit.
- The gradual drying up of Lake Chad and the creeping down of the Sahara Desert are danger signals of the possible negative impacts of the temperature increase. An evidence of regional climate change in Nigeria is the current southward drift of the Sahara Desert which has been estimated to be about 5 km/year (Madueme, 1994). This incidence of increased drought is bound to impact negatively on agriculture and food supply.

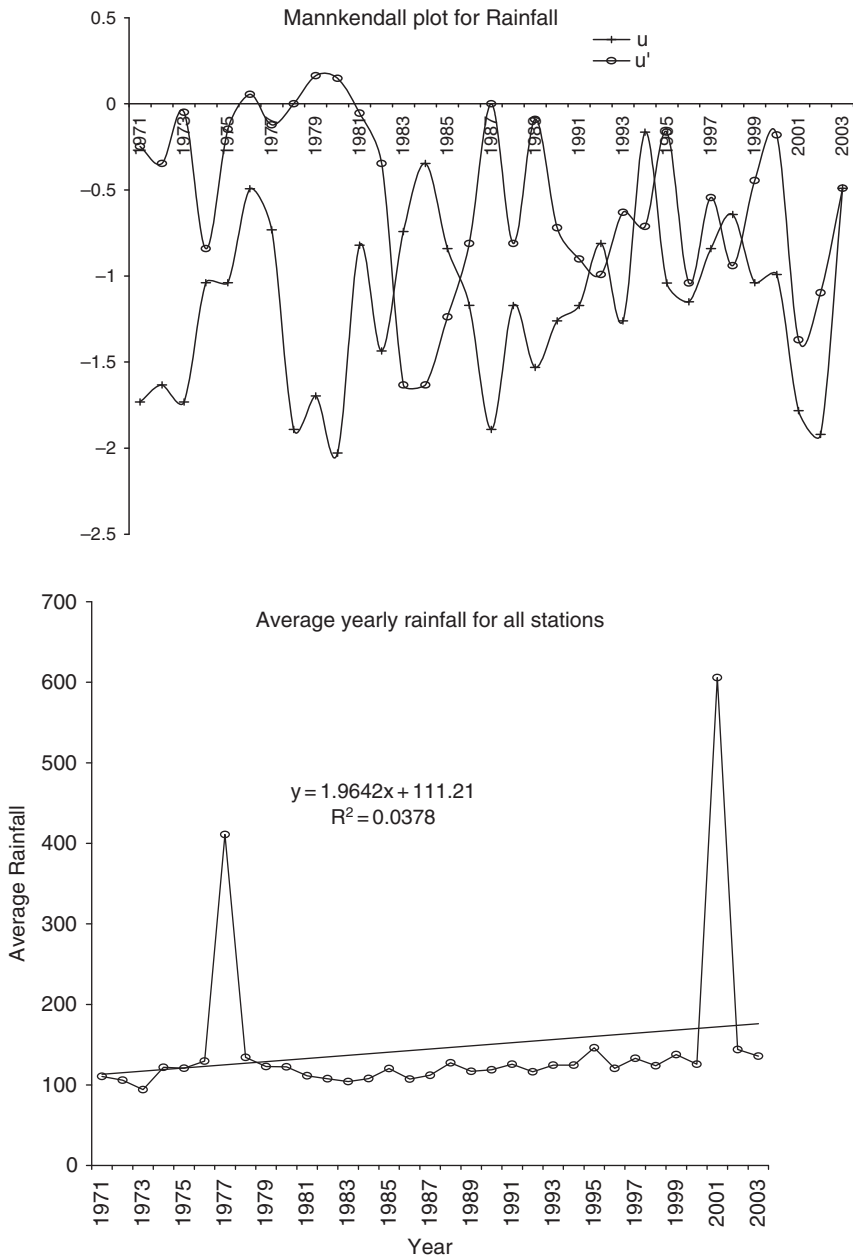


Fig. 38.3.a Time series of average rainfall and the sequential version of the Mann–Kendall tests for the period 1971–2003.

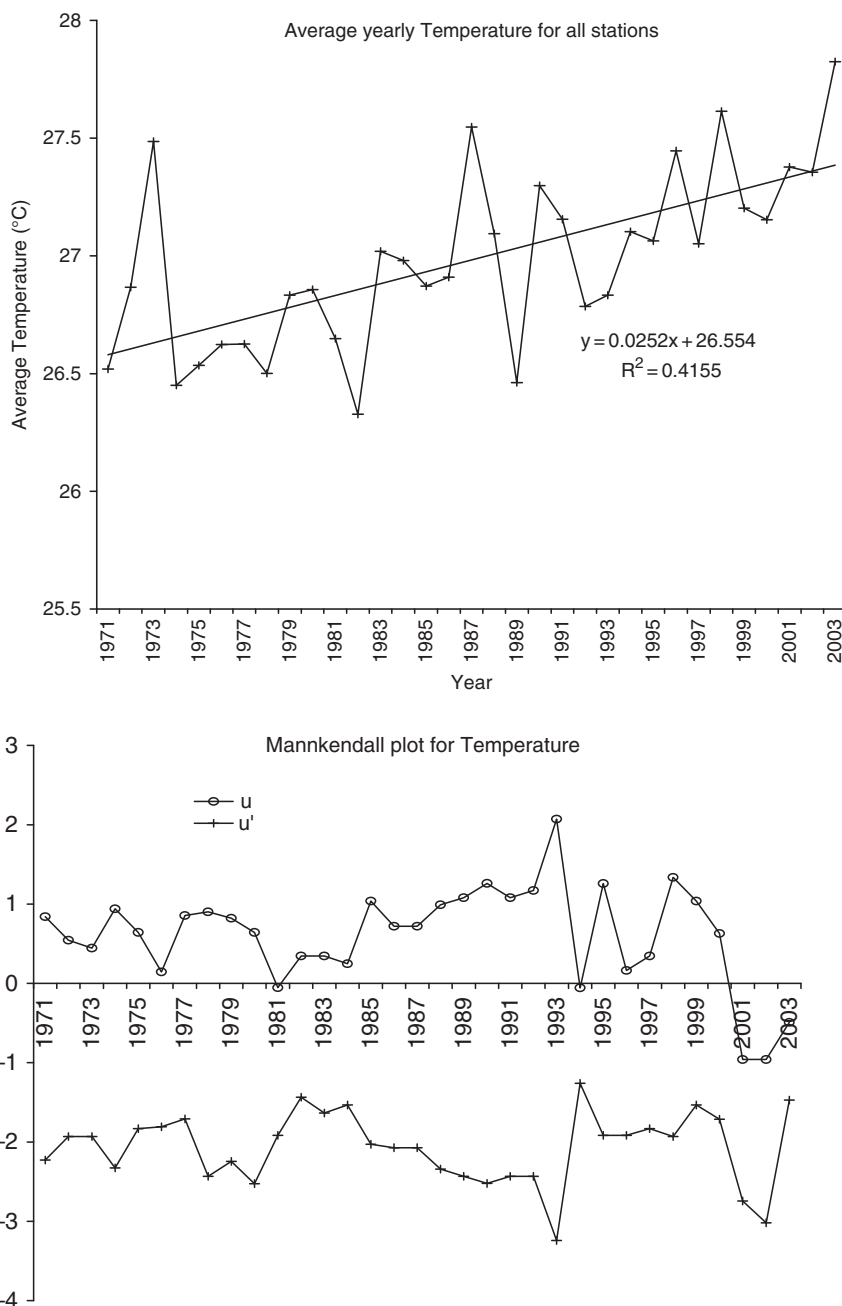


Fig. 38.3.b Time series of average temperature and the sequential version of the Mann-Kendall tests for the period 1971–2003 for all stations.

References

- Adedoyin, JA (1989) Global-scale sea surface temperature anomalies and rainfall characteristics in northern Nigeria. *International Journal of Climatology* 9: 133–144.
- Adeyinka, MA, Bankole, PO, Olaye, S (2005) Environmental statistics: situation in Federal Republic of Nigeria. Federal Ministry of Environment and Federal Office of Statistics, Nigeria. pp. 2.
- Balling, RC Jr (1992) The Heated Debate: greenhouse predictions versus climate reality. Pacific Research Institute for Public Policy, San Francisco, pp. 1955.
- FMEN (Federal Ministry of Environment of Nigeria) (2001). National Action Programme to combat desertification. <http://www.unccd.int/action-programmes/Africa/national/2001/Nigeria-eng.pdf>.
- IPCC (2001) Climate Change 2001: Impacts, adaptation, and vulnerability, contribution of working Group II to the third assessment report of the intergovernmental panel on climate change. [McCarthy JJ, Canziani OF, Leary NA, Dokken DJ, and White KS (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, USA, p. 1032.
- Kadioglu, M (1997) Trend in surface air temperature over Turkey. *International Journal of Climatology* 17: 511–520.
- Madueme, TC (1994) Some aspects of global and regional climate change on power Generation in Nigeria. Available: http://dwb.unl.edu/Teacher/NSF/C09/C09,Links/www.ccnnet.com/~mcumolu/globclim.html#SECTION_4 [Accessed 21 September 2007].
- Olaniran, OJ and Summer, GN (1990) Long-term variations of annual and growing season rainfalls in Nigeria. *Theoretical Applied Climatology*, 41: 41–53.
- Online Nigeria (2002) Climate–Nigeria. Available: <http://www.onlinenigeria.com/links/adv.asp?blurb=69> [Accessed 24 September 2007].
- Oyenuga, VA (1967). *Agriculture in Nigeria*. Food and Agriculture Organization of the United Nations. FAO, Rome, Italy, pp. 308.
- UNFCCC (2003) Nigeria's First National Communication Available: unfccc.int/resource/docs/natc/niganc1.pdf [Accessed 8 December 2007].

Multimedia Pollutant Sources and Their Effects on the Environment and Waste Management Practice in Turkish Shipyards

Ugur Bugra Celebi, Fuat Tolga Akanlar and Nurten Vardar

39.1 Introduction

Shipbuilding industry is one of the oldest and the heaviest production industries all over the world. There are several production processes which result in hazardous waste and pollutants to the environmental safety and health. Shipyards are often categorized into two basic subdivisions: new shipbuilding division and ship repairing division. The area of the shipyard describes their proficiency; some shipyards build only large ships and also have repair and dry dock facilities while other shipyards have facilities for building small- and medium-sized vessels such as patrol boats, fire and rescue boats, water taxis, ferries, tug boats, fishing boats, and shallow-drafted barges.

The production and repair process used in shipbuilding and repair industry requires numerous pre-treatments such as surface preparation, painting and coating, metal plating and surface finishing, solvent cleaning and degreasing, machining and metal working, welding, vessel cleaning, and fiberglass operations. The consumption of various products results with production of different forms of pollutants (solid, liquid, and gaseous). The amount of outcome such as wastes and pollutants is a major risk from an environmental and ecological point of view. These wastes can be grouped as particulates, VOCs (styrene, acetone, methylene chloride, etc.), metal mists and fumes for pollutants, paint chips, cleaning and paint stripping solvents, oil residues from bilge and cargo tanks, emulsified lubricating and cutting oils and coolants for wastewater and paint chips (containing metals, tributyltin), spent abrasives, surface contaminations and cargo tank residues, spent plating solutions and cyanide solutions, waste cutting oil and lube oils for the residual wastes.

The definition and characterization of these waste waters may help us to manage these wastes and pollutants in the shipyard industry. The best solution to prevent these waste products will be to prevent them at the beginning of the process before existence. Alternatives to reduce the pollution may be to decrease the material inputs, to improve the engineering processes, to reuse the materials, to improve the management practices, and to use alternatives to toxic chemicals. Most of the processes such as welding, painting, blasting, fiberglass production that have a direct effect on workers health, i.e., exposure to VOCs, fumes resulting from burning through base metal, and from burning the interior and exterior coatings that are often left in place, can cause acute and chronic health problems. In Turkish shipyards, the importance of environmental and human health awareness is not well known. When blasting, welding, and painting processes are investigated, the result shows the significance of the situation. Occupational safety risks of workers are well known. But the main threat can be named as the potential environmental and human health hazardous wastes from production processes such as blasting, welding, and painting (Celebi, 2008).

This study focuses on the production processes, their pollutant emissions, effects of these pollutants to the shipyard workers, and alternative ways to reduce these wastes and pollutants resulting from shipbuilding and ship repair activities. There are several wastes and pollutants being released during shipbuilding and ship repairing processes. Minimizing or avoiding these wastes and pollutants is the most important point to protect environment and ecology. Especially the climate change, mostly being discussed and studied for recent years, will be affected by improving these shipyard production processes.

In recent years, there are several studies on production processes, contaminants, their effects on human health and environment, and management of wastes in shipyards. Kura and Lacoste (1996) studied wastes from shipyard production processes. Kura and Tadimalla (1998) worked on prevention technologies of contamination for shipyards. Kura (2002) studied computer-aided decision systems for shipyard environment management. Iborra et al. (2001) designed an environmental-sensitive blasting robot prototype for the ship production process with grid as blasting material. Austin et al. (2002) studied the comparison of the advantages and disadvantages for abrasive blasting technologies. Hewett (1995) studied a mathematical model to calculate the effects of submerged metal arc welding and gas metal arc welding on workers health. Lin and Leung (1996) studied the VOC control in industrial facilities and their effects on health. Kura and Kura (2006) studied the volatile organic compounds (VOC) and hazardous air pollutants (HAP) of painting processes. Malherbe and Mandin (2005) focused on volatile organic compounds released from processes with paint and solvents in uncovered shipyard areas. Champ (1999) studied the globally forbidden tributyltin (TBT) containing anti fouling paints, commentary of the decisions, and their effects on marine transport, ship production, and paint producers.

39.1.1 Shipyard processes and pollutant sources

The shipbuilding and repair industry processes include surface preparation, painting and coating, metal plating and surface finishing, solvent cleaning and degreas-

ing, machining and metal working, welding, vessel cleaning, and fiberglass operations. They consume various types of products and produce solid, liquid, and gaseous pollutants. Many different production processes employed in shipbuilding and repair require a vast amount of material inputs and generate huge amounts of waste and considerable emissions. Raw material inputs to the shipbuilding and repair industry are primarily steel and other metals, paints and solvents, blasting abrasives, and machine and cutting oils. In addition, a variety of chemicals are used for surface preparation and finishing such as solvent degreasers, acid and alkaline cleaners, and plating solutions containing heavy metal and cyanide ions. Pollutants and wastes generated include volatile organic compounds (VOCs), particulates matter (PM), waste solvents, oils and resins, metal-bearing sludges and wastewater, waste paint, waste paint chips, and sent abrasives. Figure 39.1 shows basic shipyard processes (Celebi and Vardar, 2006). There are 42 shipyards for new shipbuilding and repair in Istanbul of Turkey. Figure 39.2 is a map of Istanbul including Tuzla region where shipyards are located.

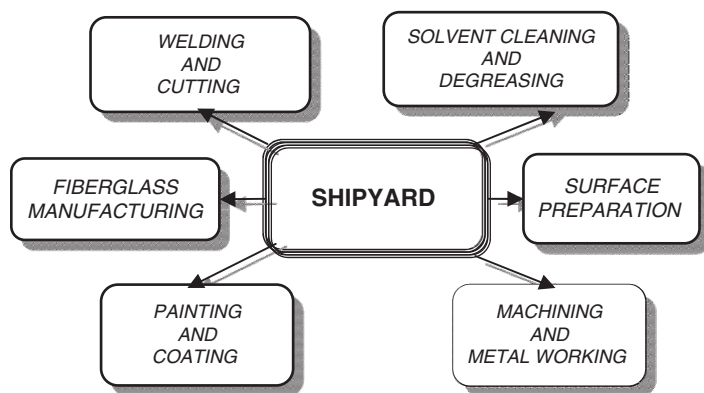


Fig. 39.1 Basic shipyard processes.

Some of the important shipyard processes and waste emissions from these operations are discussed briefly in the following sections.

39.1.2 Surface preparation process and wastes

Surface preparation is an important step in the shipbuilding industry. Common surface preparation methods adopted by shipyards are dry and wet abrasive blasting, hydroblasting, thermal, chemical, and mechanical stripping. Material inputs used for preparing surfaces include abrasive materials such as steel shot or grit, glass, garnet, copper, or coal slag; cleaning water; detergents; and chemical paint strippers. In the case of hydroblasting only water and occasionally rust inhibitors are required.

Various methods are available to prepare metal surfaces for painting. The choice of the method to be used is based on several factors such as –whether the surfaces are painted or covered with a rust scale, which surface characteristics are

required by the paint that is to be applied, the size and shape of the surface to be prepared, and the type of metal. Common surface preparation methods adopted by the shipyards are dry abrasive blasting, wet abrasive blasting, hydroblasting, thermal stripping, chemical stripping and mechanical stripping. Material inputs used for preparing surfaces include, abrasive materials such as steel shot or grit, glass, garnet, copper, or coal slag; cleaning water, detergents, and chemical paint strippers (e.g., methylene chloride-based solutions, caustic solutions, and solvents). In the case of hydroblasting only water and occasionally rust inhibitors are required. Air emissions from surface preparation operations include particulate emissions of blasting abrasives and paint chips. Particulates emissions can also contain toxic metals which is a concern both in the immediate area surrounding the work and if they are blown off-site or into surrounding surface waters. Other air emissions that could potentially arise during surface preparation operations are VOCs and hazardous air pollutants arising from the use of solvent cleaners, paint strippers, and degreasers. The primary residual waste generated is a mixture of paint chips and used abrasives. Blasting abrasives and paint chips that collect in tank vessels, ship decks, or drydocks should be thoroughly cleaned up and collected after work is completed or before the drydock is flooded or submerged. Particular attention should be paid to the cleanup of paint chips containing the antifouling tributyltin compounds which have been shown to be highly toxic to oysters and other marine life. A significant quantity of wastewater can be generated when cleaning ship cargo tanks, ballast tanks, and bilges prior to surface preparation and painting. Such wastewater is often contaminated with cleaning solvents, and oil and fuel from bilges and cargo tanks, paint chips, and surface contaminants (Celebi and Vardar, 2006).

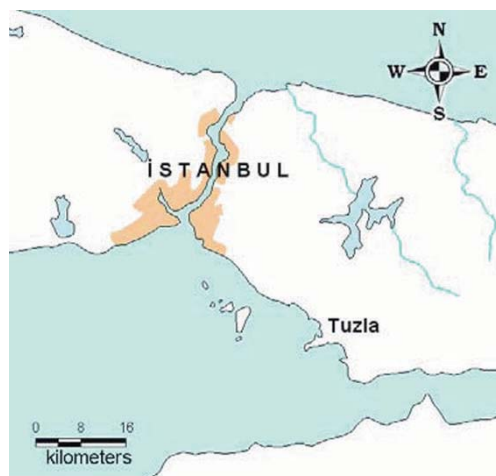


Fig. 39.2 Map of Istanbul and Tuzla shipyards area (scale 1/600,000).

Abrasive blasting materials as aluminum, arsenic, chromium (III), chromium (VI), cobalt, copper, iron, manganese, lead, tin, zinc can be grouped as hazardous air pollutants. The long- and short-term exposure of these HAP's may cause respiratory irritation, manganism, chronic lung inflammation, pulmonary fibrosis headaches, subclinical neurological disturbances, allergic dermatitis with skin contact, lung and nasal cancers, and asthma.

39.1.3 Painting and coating process and wastes

Material inputs for painting are primarily paints and solvents. Solvents are used in the paints to carry the pigment and binder to the surface and for cleaning the paint equipment. Paints contain toxic pigments such as chromium, titanium dioxide, lead, copper, and tributyltin compounds. The organic solvents contained in marine paints and used for thinning and cleaning are also likely to contain toluene, ethyl benzene, xylene, methyl ethyl ketone, ethylene glycol, *n*-hexane, and acetone.

Painting wastes are believed to be the largest category of hazardous wastes produced in a shipyard. In a typical shipyard it may account for more than half of the hazardous wastes produced. This may include leftover paint, overspray, paint that is no longer usable, rags, and other materials contaminated with paint. In many cases the amount of paint can be reduced through the use of improved equipment, alternative coatings, and good operating practices. Equipment cleaning also generates hazardous waste in the form of solvents, thinners, and acids. Painting activity involves significant air emissions. Volatile organic compounds and hazardous pollutants result from painting operations that are of concern (Vardar, 2004).

The nature of shipbuilding and repair requires several types of paints to be used for a variety of applications. Paint types range from water-based coatings to high-performance epoxy coatings. Antifouling paints are used to prevent the growth of marine organisms. Copper-based and tributyltin (TBT)-based paints are widely used as antifouling paints, though TBT may only be used on vessels longer than 25 m and with regulatory authority approval. Most of these toxic agents are heavy metals or organometallic compounds, such as cuprous oxide, lead oxide, and tributyltin compounds (Celebi and Vardar, 2006).

VOCs belong to a special category of air pollutants that can adversely affect human health. Industrial operations are important sources of VOCs and there are various technologies that can reduce VOC emissions from these industrial processes (Celebi and Vardar, 2008). Organic solvents are useful to dissolve and disperse lubricants, oils, waxes, paints, varnishes, rubber and so on and are widely used in many industrial processes. Most of them are also recognized as extremely hazardous chemicals and some of them might cause Alzheimer's disease, leukoencephalopathy, multiple sclerosis, neurobehavioral disorders, and so on. Solvent vapors comprised of VOCs and HAPs are a significant pollutant output of cleaning and degreasing operations. Both halogenated and nonhalogenated solvents are used and mixtures of different solvents are common. Typical cleaning and degreasing solvents include mineral spirits, aromatic hydrocarbons (e.g., xylenes,

toluene), aliphatic hydrocarbons, ketones, esters, alcohols, glycol ethers, phenols, turpentine, and various halogenated solvents (Celebi and Vardar, 2006).

Another contaminant type can be named as volatile organic compounds (VOCs) that belong to a special category of air pollutants with hazardous effects to human health. The common usage of organic solvents in production industry is to clean lubricants, oils, waxes, paints, etc. These extremely hazardous pollutants might cause several important diseases such as Alzheimer's disease, leukoencephalopathy, multiple sclerosis (MS), and neurobehavioral disorders.

39.1.4 Machining and metalworking process and wastes

The common types of metal cutting processes are broaching, cutting, drilling, forging, grinding, milling, planing, polishing, reaming, sawing, shaping, stamping, threading, and turning. In most cases, the cutting tool travels along the surface of the work piece and shaves off the metal in front of it. The high friction at the cutting edge of the blades creates heat. If allowed to become excessive, this heat can permanently deform the part that is being formed, or the cutting tool. To prevent this undesirable effect, some form of coolant is needed. Usually, a liquid is supplied to the leading edge of the blade to create a medium with which the heat can be moved to a coolant sump. The major hazardous wastes from metal machining are waste cutting oils and degreasing solvents. Metal shavings are usually recycled as scrap metal. Metal chips are separated from coolants and recycled as scrap metal (Vardar, 2004).

39.1.5 Solvent cleaning and degreasing process and wastes

Shipyards use solvents in a variety of cleaning and degreasing operations including parts cleaning, process equipment cleaning, and surface preparation for coating applications. Some of the major solvents used are petroleum distillates, oxygenated solvents, and halogenated solvents. Most common cleaning and degreasing operations include cold cleaning and vapor degreasing (Kura et al., 1998).

Major wastes and materials that become contaminated with the solvents in cleaning and degreasing are various types of solvents that are employed in the process. Waste rags, empty containers, process spills are a few examples. Air emissions include VOCs and HAPs. Liquid wastes include the aqueous cleaners used, liquids contaminated with solvents. Solvent vapors comprised of VOCs and HAPs are a significant pollutant output of cleaning and degreasing operations.

39.1.6 Welding and cutting process and wastes

The primary raw material for ship construction is steel plates. All types of metal arriving at the shipyard are in standard size and length plates, shapes, and sections that may need customized sizing based on different requirements. Therefore, before welding, fabrication, and ship construction or repair, the material must be cut

to required sizes, shapes, and lengths. Metal cutting in the shipyard is performed by either mechanical or thermal hot metal cutting operations (Kura et al., 1998).

Various types of welding processes are used to join the different types of metals used in the construction of ships. Fusion welding, in particular, is performed at almost all locations in the shipyard. An important factor in welding processes is shielding. In most welding processes, this shielding is accomplished by addition of a flux, a gas, or a combination of the two.

The waste generally depends on the methods and magnitude of welding employed. The waste generated by welding of thin metals by any method is the used diluted acids. The wastewater is sent for on-site/off-site treatment and other wastes such as slag are disposed as solid wastes. Welding rod stubs, wire stubs contaminated with flux and welding wire spools are the solid wastes that come from these activities. Welding fumes and particulate emissions are the potential air emissions from these operations.

39.2 Results and Discussion

39.2.1 The effect of shipyards on global warming

Fossil fuel combustion, industrial production processes, solvent usage, etc., are potential sources of non-methane (NM) VOCs. Chemical reactions of NMVOCs have effect on human health and ozone layer.

In the atmosphere many VOCs react with nitrogen oxides (NO_x) and oxygen (O_2) in a complex network of photochemical process. The result of these processes is photochemical formation of ozone (O_3) and other oxidants which share the term 'photochemical smog.' Most VOCs do not contribute directly to global warming, but since VOCs cause formation of CO_2 and CO_2 absorbs infrared light from the sun, all the VOCs indirectly contribute to global warming.

Halogenated volatile organic compounds such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and chlorinated compounds (e.g. trichloroethane) contribute significantly to global warming, hundreds or thousands of times more than CO_2 . Methane (CH_4) has a small contribution to photochemical smog formation (about 100 times less than most other VOCs). However, the substance contributes directly and significantly to global warming.

39.2.2 Chlorinated solvents

Not all of the chlorinated solvents cause depletion on ozone. There are several chlorinated solvents such as perchloroethylene, trichloroethylene, and methylene chloride and can be used safely for human health, safety, and environment. They are not listed as a source to damage ozone layer or to cause global warming or acid rain. When used with care, there is no risk for environment, human health, or safety. They are mostly used in dry cleaning, metal cleaning, and adhesive industry. But there is a specific solvent named trichloroethane and is regulated by the international protocols since 1990. Methylene chloride is generally used in pharmaceuticals, chemical processing, aerosols, and surface treatment.

39.2.3 Waste management in shipyards

The management of the wastes mentioned above is extremely important for environmental safety and human health. Waste management is the prevention, minimization, reuse, recycling, energy recovery, or disposal of waste materials (Fig. 39.3). The term is usually related to materials produced by human activity and is generally undertaken to reduce their effect on health, aesthetics, or amenity. Waste management is also carried out to reduce the effects of waste materials on the environment and to recover resources from them.

Waste management practices differ for developed and developing nations, for urban and rural areas, and for residential and industrial producers. Management for non-hazardous residential and institutional waste in metropolitan areas is usually the responsibility of local government authorities, while management for non-hazardous commercial and industrial waste is usually the responsibility of the generator. The methods for shipyard waste management are described below.

39.2.3.1 Source reduction

Source reduction aims to reduce the hazardous materials, pollutants, or contaminants to release to environment, prior to recycling, treatment, or disposal and minimize the hazards to human health and the environment. Source reduction can be achieved with the improvement and substitution on technological methods, production processes, raw materials with better housekeeping, maintenance, training, and stock control.

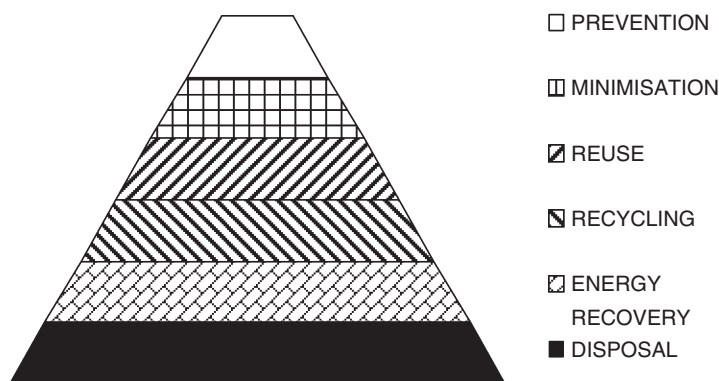


Fig. 39.3 Waste management hierarchy.

39.2.3.2 Reformulation or redesign of products

Some of the most common practices include eliminating metals from paints, reformulating paints and adhesives to eliminate tributyltin (TBT)-based paints and solvents, and replacing chemical-based cleaning solvents with water-based or citrus-based products.

Switching from solvent-based to water-based cleaners will reduce solvent volume and disposal cost, but is likely to dramatically increase wastewater volume. In-process recycling involves the reuse of materials, such as cutting scraps and blasting material, as inputs to the same process from which they came or use them in other processes or for other uses in the facility.

39.2.3.3 Recycling

The main aim of recycling is to collect the wastes and clean through a process to reuse. This process can be described in brief during following discussion.

The biological treatment of wastes can be categorized into two main divisions as aerobic and anaerobic treatment. Aerobic and anaerobic treatments are the ways of the biological treatment of wastes. Oxygen-requiring microorganisms are used during an aerobic biological treatment in order to decompose organic and non-metallic constituents into carbon dioxide, water, nitrates, sulfates, simpler organic products, and cellular biomass. Microorganisms are used during an anaerobic biological treatment, in the absence of oxygen, to transform organic constituents and nitrogen-containing compounds into oxygen and methane gas.

39.2.4 Best Management practice (BMP) study in a Turkish shipyard

There are several management improvement practices achieved in time that are named as Best Management Practices (BMPs). Their main target should be the minimization or prevention of pollution with material management, housekeeping, and maintenance. With these BMP applications the advantages from the reduction of operational and workplace costs are observed. The practice can focus on source control for waste reduction at the source or treatment of the residual wastes, contaminants, and pollutants released or received after the process.

Best Management Practices are needed to reduce and prevent contamination of the aquatic environment and to improve air quality. Some BMP examples in shipbuilding industry are the treatment of paint washing water containing toxic metallic components; cleaning of drydock and vessel before floated; usage of alternative raw material such as tin-free, TBT-free, or low-VOC paint; and filtration of volatile organic pollutants of main processes such as blasting, welding, and painting.

A Best Management Practice (BMP) on a selected shipyard in Tuzla region was carried out as part of a postgraduate thesis (Celebi, 2008). Several meetings with the shipyard management were held. First the current situation in European shipyards was presented to the management in order to convince them of the benefits of BMP. After persuading, the management's first step was to examine the general situation of the shipyard. The project was completed successfully with the support of the management.

39.2.7.1 Previous situation

Training of the managers and employers about waste management is unarguably the first and the most important stage of the waste management. For this reason our practice study started by informing the managers and workers about the wastes and their hazards, threats of wastes on human health and environment,

and management of wastes. A visit was paid to the shipyard in order to see the general situation of the shipyard before the application of BMP. Safety issues, threats to workers' health and environmental risks were obtained. Scrap metal sheets and used paint boxes were lying around the production area (see Fig. 39.4); the used grid blasting abrasives were not removed from the area. Also welding workers were not using necessary protective equipment during their work. When production processes such as painting and blasting, which are main cause of waste and pollutants, were observed, it was seen that there was no waste management policy of the shipyard. As a first step for waste management, a waste material bill-board (see Fig. 39.5) was located in the shipyard where workers could easily see.

All different wastes and residual materials were planned to be collected in a segregated area/container. The separation of process wastes from blasting, welding, and painting is observed as a main problem in waste flow. For instance, flammable, combustive, and hot waste materials should be kept separate due to the risk of fire.



Fig. 39.4 Randomly collected wastes from the production area.



Figure 39.5 Waste material description according to the color codes.

39.2.7.2 Current situation

There are containers with different colors situated in suitably chosen places in the docking area. The meaning of all colors is explained in Fig. 39.5. Although all workers are trained to get familiar with BMP, due to the busy traffic of different

production processes going on mutually, it is a difficult task to make workers change their habits as to waste management. However, it is good to see in the shipyard that the workers know what to do with wastes. They are also aware of cleaning methods for the production area and of delivering the wastes to the related containers. Figure 39.6 shows waste container management system for production wastes in docking area. The difference between Fig. 39.4 and Fig. 39.6 and Fig. 39.7 is the success of BMP project, which is achieved by correctly explaining the problems to the related people.



Fig. 39.6 The production area is organized with waste container management.



Fig. 39.7 Waste container management system for production wastes in docking area.

39.3 Conclusions

New shipbuilding and ship repair industry is one of the heaviest industrial zones. Production processes which are used in shipbuilding industry are variable and complicated. This study demonstrates the shipyard industry production processes and the possible wastes outcome after these operations and the prevention, minimization, and reuse of these waste products. These wastes and residual materials are a risk for workers health and a main environmental hazard. The most common problem about Tuzla Bay Shipyards is the inadequate layout planning during the construction phase. The depth of the area is limited and does not allow enlarging the shipyard areas. With recent plans, different locations in Turkey are being defined as the shipyard construction areas and new shipyards are being built nowadays. The most important point is to plan environmental risks, waste reduction, and management during the build phases.

The most important issues being followed by the legal authorities on environmental point of view are paint and the abrasive blasting materials. These two processes have to be investigated for recycling and reuse for further steps. The paint shops have to be the covered areas with filter ventilation systems and the workers have to be fully equipped with suitable type of material depending on the paint type. In addition to these items, welding fumes and their effects to workers are not negligent. Priority should be the to train the workers for environmental protection knowledge.

Building human and environmental friendly shipyards is the most important point of reducing the global effect of wastes. To limit this hazardous waste material and to keep the workers health issues on a minimized level, alternative pro-

duction materials to replace these traditional production processes should be considered during all phases. These alternative ways must be defined and necessary training should be imported to high- and medium-level management of the shipyards in Turkey.

References

- Austin, D, Benze, R, Kura, B (2002) Recent advances in closed loop abrasive blasting ship production symposium, Boston, MA, September, 2002.
- Champ, MA (1999) An overview of the science and regulation of TBT and the potential for future liability for contaminated harbor sediments. Treatment of Regulated Discharges from Shipyards and Drydocks Proceedings of the Special Sessions Oceans '99, Washington, (4), 137–152 ISBN No. 0-933957-24-6.
- Celebi, UB, (2008), Wastes from Shipbuilding Processes and Paint Emission Estimation, PhD thesis, Yildiz Technical University, Institute of Science And Technology.
- Celebi, UB, Vardar, N (2006) Wastes and pollutant sources resulted from shipbuilding industry in Turkey. Ovidius University Annual Scientific Journal, Mechanical Engineering Series 8, 1, 24–30.
- Celebi, UB and Vardar N., (2008). Investigation of VOC Emissions from Indoor and Outdoor Painting Processes in Shipyards', *Atmospheric Environment*, 42(22):5685–5695.
- Hewett P (1995) Estimation of regional pulmonary deposition and exposure for fumes from SMAW and GMAW mild and stainless steel consumables. *Am Ind Hyg Assoc J.* 56(2): 136–142.
- Iborra, A, Alvarez, B, Ortiz, F, Marín, F, Fernández, C, Fernández-Meroño, JM (2001) Service robot for hull-blasting. IECON'01 the 27th Annual Conference of the IEEE Industrial Electronic Society 3: 2178–2183.
- Kura, B, Lacoste. S, Patibanda, P (1998) Multimedia Pollutant Emissions from Shipbuilding Facilities. United States and Japan Natural Resources (UJNR) Conference, Washington, D.C., 1998.
- Kura, B, Lacoste, S (1996) Typical waste streams in a shipbuilding facility. Proceedings of Air & Waste Management Association's 89th Annual Meeting & Exhibition, Nashville, TN, June 24–28, 1996.
- Kura, B, Tadimalla, R (1998) Pollution prevention technologies for shipyards. United States Japan Natural Resources (UJNR) Conference, Washington, D.C., 1998.
- Kura, B, (2002) A decision support system for shipyard environmental management. International Conference on Computer Applications in Shipbuilding (ICCAS-2002), Malmo, Sweden, September, 2002.
- Kura, B and Kura K (2006). VOC-HAP Compliance Management System for Shipyard Painting Operations. 5th International Conference on Computer Applications and Information Technology in the Maritime Industries, 116–126.
- Malherbe L, Mandin, C (2005) VOC emissions during outdoor ship painting and health risk assessment. In: First International Conference on Harbors and Air, Italy.
- Vardar, N (2004), "Pollutant sources in the shipbuilding and repair industry, Ship Building Industry", Turkish Shipbuilding Association, Turkey.

Nitrous Oxide Emission from Agricultural Practices in Japan

Shin-Ichiro Mishima, Hiroko Akiyama and Kazuyuki Yagi

40.1 Introduction

Nitrous oxide (N_2O) is a greenhouse gas emitted from the natural ecosystem (10 Tg year^{-1} globally) and anthropogenic sources (5.7 Tg year^{-1}). Agriculture, which comprises about 68% of total anthropogenic N_2O emissions (Schlesinger, 1997), is the most important source of global N_2O emissions. The Greenhouse Gas Inventory Office (GIO) estimated that total Japanese N_2O emissions were 87 Gg in 2005, 46% of which originated from agriculture (GIO, 2007), illustrating the importance of agriculture in N_2O emissions. GIO (2007) summarized and indicated agricultural N_2O emissions into three sources: manure handling, agricultural land, and crop residue burning. However, in terms of agro-environmental science, this division is too crude to enable the responsibility of each agricultural sector to be analyzed.

In this study, we estimated N_2O emissions from nine agricultural sectors in Japan (see Framework section) in 1985, 1990, 1995, 2000, and 2005. We then evaluated the direct and indirect emissions from crop production and livestock husbandry and the problems of each agricultural sector. We also discussed the uncertainties around methods of estimation and the mitigation of N_2O emissions for future sustainable agriculture.

40.2 Method

40.2.1 Framework

The framework of the study is set out in Fig. 40.1. The livestock sector includes cattle, pigs, and poultry. Because numbers of other livestock, such as horses and

goats, are few, they were ignored. The crop sector includes paddy rice, upland fields, vegetables, tea, orchards, and forage.

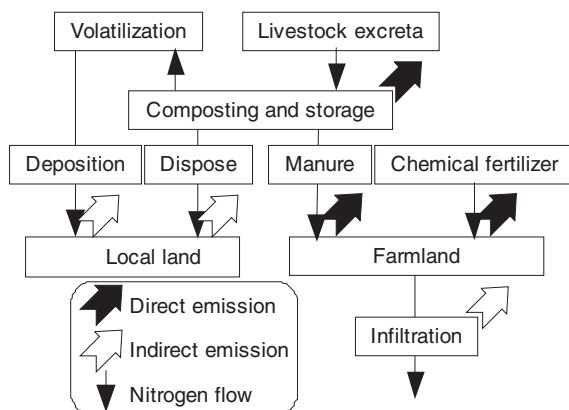


Fig. 40.1 Framework of N_2O emission associated with agricultural N flow.

40.2.2 Data sources

Basic statistical data, such as livestock numbers and areas of planted crops, were obtained from the Statistical Yearbook of the Ministry of Agriculture, Forestry, and Fisheries (MAFF 1986b, 1991b, 1997, 2002b, 2006b, 2007).

Chemical fertilizer nitrogen (N) applications for each crop type in 1985 and 1990 were derived from the results of MAFF questionnaires from 1981 to 1989. MAFF Production Environmental Statistics for 1997, 2002, and 2003 (MAFF 1998, 2002a, 2003) were used to derive chemical fertilizer applications in 1995 and 2005. The average values were applied to 2000.

Basic units of livestock N excrement were derived from Tsuike and Harada (1997), and N volatilization rate during composting and storage was derived from Mishima et al. (2008). Rate of excreta use and disposal was calculated from MAFF Cost of Livestock Products (MAFF 1986a, 1991a, 1996, 2001, 2006a) and Association of Livestock Production (1999). The amount applied to each kind of crop was calculated from the total amount of excreta used, and the amount applied to each kind of crop as a percentage of the total was calculated from results of MAFF questionnaires and Production Environment Statistics on chemical fertilizer use for each year.

The N_2O emission factor during composting and storage was derived from the IPCC default value (GIO, 2007). Factors for direct emission from farmland were calculated according to Akiyama et al. (2006), while those for indirect emissions were found according to IPCC default values (GIO, 2007).

40.2.3 Calculation

We followed IPCC Tire 2 method for N_2O estimation. The specific calculation is as follows:

Livestock husbandry part

Amount of livestock excreta N (N_{excreta}), volatilization ($N_{\text{volatilization}}$), utilized part (N_{use}), and disposed part (N_{disposed}) were calculated as follows:

$$N_{\text{excreta}}^i = N_{\text{numhead}}^i \times BU^i \quad (40.1)$$

$$N_{\text{volatilization}}^i = N_{\text{excreta}}^i \times V^i - N_2O_{\text{excreta}} \quad (40.2)$$

$$N_{\text{use}}^i = (N_{\text{excreta}}^i - N_{\text{volatilization}}^i) \times U^i \quad (40.3)$$

$$N_{\text{disposed}}^i = (N_{\text{excreta}}^i - N_{\text{volatilization}}^i) \times (1 - U^i) \quad (40.4)$$

where BU is the basic unit of N excrement per head of each kind of livestock, V is N volatilization rate (%), and U is utilization rate (%) of each kind of livestock in each year. N_2O_{excreta} is described below.

Crop production part

Chemical N fertilizer (N_{chemical}) and manure (N_{manure}) application for each kind of crop were calculated as follows:

$$N_{\text{chemical}}^i = A^i \times CF^i \quad (40.5)$$

$$N_{\text{manure}}^i = A^i \times N_{\text{manure}}^i \times AR^i \quad (40.6)$$

where A is planted area, CF is chemical N fertilizer application per planted area, and AR is rate of application for each crop type.

40.2.4 N_2O emission

Direct N_2O emission from livestock excreta (N_2O_{excreta}) and indirect N_2O emission were calculated as follows:

$$N_2O_{\text{excreta\_direct}}^i = N_{\text{excreta}}^i \times EF_{\text{excreta}}^i \times \frac{22}{14} \quad (40.7)$$

$$N_2O_{\text{excreta\_indirect}}^i = \quad (40.8)$$

$$((N_{\text{volatilization}}^i - N_2O_{\text{excreta\_direct}}^i) \times 0.01 + N_{\text{disposed}}^i \times 0.0124) \times \frac{22}{14}$$

where EF_{excreta} is emission factor for excreta manipulation.

Direct and indirect N_2O emission by fertilization was calculated as follows:

$$N_2O_{\text{fertilizer\_direct}}^i = (N_{\text{chemical}}^i + N_{\text{manure}}^i + N_{\text{residual}}^i) \times EF_{\text{farm}}^i \times \frac{22}{14} \quad (40.9)$$

$$N_2O_{\text{fertilizer\_indirect}}^i = (N_{\text{chemical}}^i + N_{\text{manure}}^i) \times 0.3 \times 0.0124 \times \frac{22}{14} \quad (40.10)$$

where N_{residual} is N in crop residue estimated by Mishima (2006) and EF_{farm} is emission factor.

The basic data for activities and emission factors are listed in Tables 40.1 and 40.2.

Table 40.1 Activity data and emission factors for crop production.

	Area (1000 ha)					Fertilization (kg ha ⁻¹)					EF	Residue (kg ha ⁻¹)				
	1985	1990	1995	2000	2005	1985	1990	1995	2000	2005		1985	1990	1995	2000	2005
Paddy rice	2318	2055	2106	1763	1702	114.4	101.8	79.9	77.2	71.8	0.31	41.1	41.8	41.8	44.1	43.7
Upland crop	1030	1090	736	812	775	122.0	130.0	111.3	94.6	91.8	0.62	33.4	29.3	33.2	31.7	35.4
Vegetables	639	625	669	620	563	248.8	288.7	264.2	268.7	283.0	0.62	33.7	33.7	31.1	33.7	29.4
Orchard	484	684	341	292	265	219.1	182.0	207.4	173.6	146.5	0.62	27.3	15.6	30.6	31.4	31.7
Tea	61	59	54	50	49	670.7	739.9	768.1	611.5	482.1	2.82	54.8	54.8	54.8	54.8	54.8
Forages	1049	1096	1013	1026	1030	143.4	106.1	150.4	127.5	121.5	0.62	50.0	51.3	51.4	48.7	44.4

Table 40.2 Activities and emission factors data for livestock husbandry.

	Head (1000 head)					N _{excreta} (g head ⁻¹ d ⁻¹)	EF _{excreta} (%)	N _{volatilize} (%)	AR	
	1985	1990	1995	2000	2005				Max	Min
Dairy cattle	2,103	2,068	1,927	1,725	2,254.9	158.6–305.5	0.1–5	72.2	0.87	0.67
Beef cattle	2,639	3,435	2,901	2,806	2746.6	129.8–146	0.1–5	72.2	0.90	0.40
Pig	11,060	11,837	9,900	9,788	9723.4	9.5–51	0.1–5	49.8	0.74	0.16
Poultry	194,014	201,548	201,562	196,458	189,690	1.54–3.28	0.1–5	80.4	0.98	0.97

40.3 Results and Discussion

40.3.1 Data validation

The difference between total chemical N fertilizer application estimated in this study and demand (MAFF 1986b, 1991b, 1997, 2002b, 2007) ranged from –10% to +5%. This difference would be due to the different recording periods (January to December for application and June to May for demand), stock on the market or farm, etc. Estimated N₂O emissions in each year are shown in Fig. 40.2, together with CO₂ equivalents (upper line graph). The estimations are lower than reported by GIO (2007), although the difference was less than 10%. The similarity of these independently estimated results demonstrates the validity of our estimations; however, the uncertainties and differences in the basic concept of the N framework which caused the differences are discussed later.

40.3.2 Direct and indirect emissions from agriculture

Direct and indirect N₂O emissions from livestock husbandry and crop production are shown in Fig. 40.2 (bar graph). Total N₂O emissions peaked in 1990 (46,672 Mg) as a result of an increase in livestock husbandry, then declined until 2005 (37,620 Mg). The decline in N₂O emissions resulted mainly from a decline in crop production from 17,644 Mg in 1985 to 12,088 Mg in 2005. Livestock husbandry also declined between 29,381 Mg in 1990 and 25,532 Mg in 2005, however less than crop production. Mishima (2006) indicated that crop production and non-utilized N by agricultural production peaked in 1985, then declined until 2002. The main cause of this decline was a reduction in the use of chemical N fertilizer in crop production. Livestock excreta N production, which reflects livestock production, peaked in 1990 then declined more slowly than the rate of reduction in chemical N fertilizer application. Livestock husbandry comprised a higher proportion of total agricultural N₂O emissions than crop production. Direct N₂O emissions exceeded indirect, and originated mainly from livestock excreta handling. We used the N volatilization rates of Mishima et al. (2008) (72% for cattle, 50% for pig, and 80% for poultry), which are higher than those of GIO (10% for cattle, 20% for pig, and 30% for poultry). Therefore, our estimates of indirect emissions by N deposition would be greater than those of GIO (2007), although, because

GIO did not report indirect emissions, we could not compare the amounts. Crop production was responsible for less N_2O emissions than livestock husbandry. Crop production direct emission was larger than indirect emission. The emission factor indicated by Akiyama et al. (2006), which has been proposed as a Japanese emission factor, is smaller than the IPCC default value. Therefore, the proportion of direct emissions might be still smaller in Japan than in other countries. Because there are insufficient data for estimation of the indirect emission factor, we used the IPCC default value in our estimation. Indirect emissions have been little discussed (e.g., van der Gon and Bleeker, 2005), and more studies on indirect emissions are needed for precise estimation of N_2O indirect emissions.

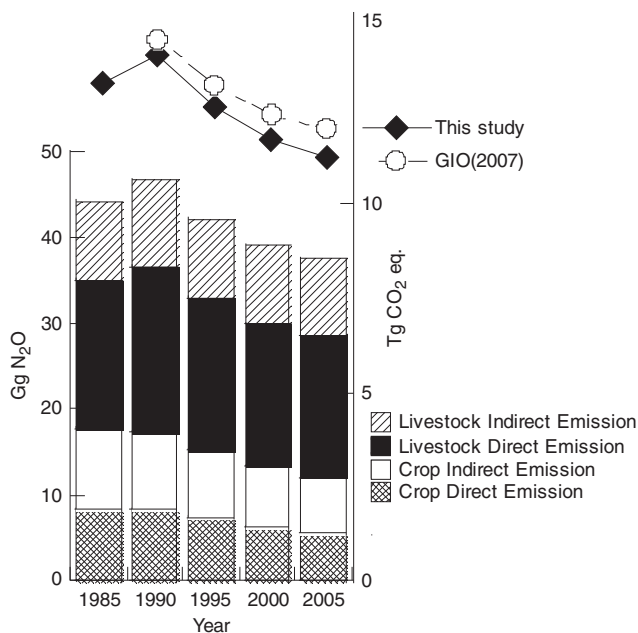


Fig. 40.2 Direct and indirect N_2O emission from crop production and livestock husbandry.

N_2O emissions per unit of cultivated area peaked in 1990 (8.489 kg ha^{-1}) then declined in 2005 (8.015 kg ha^{-1}) as a result of a fall in crop production from 3.275 kg ha^{-1} in 1985 to 2.575 kg ha^{-1} in 2005 (Fig. 40.3). N_2O from livestock husbandry peaked in 1990, then slightly decreased. N_2O from crop production declined as a result of a reduction in chemical N fertilizer and manure input per cultivated area (Mishima et al., 2009). Crop production in Japan, as measured by cultivated area and quantity of N fertilizer applied, has been declining (Mishima et al., 2009). This trend is reflected in N_2O emissions. However, livestock husbandry has declined more slowly than crop production and its relative importance to agriculture has therefore increased. This trend may have significant environmental implications.

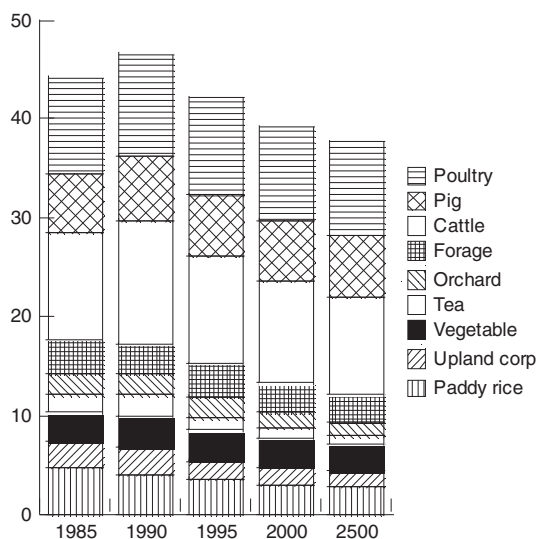


Fig. 40.3 N₂O emissions from each kind of agricultural sector.

40.3.3 N₂O emissions from each sector and their trends

Livestock husbandry

Cattle (12,401 Mg in 1990) were the largest source of N₂O emissions, pigs (6,608 Mg in 1990) the smallest, and the rest was poultry (10,372 Mg in 1990) (Fig. 40.4), a result related to the different amounts of livestock excreta produced by these classes of livestock. N₂O emissions by cattle, pigs, and poultry during the period were relatively constant at 40%, 25%, and 35% of total, respectively.

Crop production

In 1985, when crop N₂O emissions were highest, paddy rice (4,714 Mg) was the largest source of N₂O and forage crops (3,376 Mg) the second highest, because these crops occupied about 60% of farmland (Fig. 40.4). In 2005, when N₂O emissions were lowest, 70% of N₂O came from paddy rice (2,770 Mg), vegetables (2,810 Mg), and forage fields (2,850 Mg). Over the study period, the area of paddy rice declined from 27% to 23% and that of vegetables increased from 17% to 23%. N fertilizer input to paddy rice declined from 114 to 72 kg N ha⁻¹ and N fertilizer input to vegetables increased from 180 to 201 kg N ha⁻¹. Tea comprised 10% to 13% of total crop production of N₂O emissions during the period. Although the area planted in vegetables and tea was small (12% and 1% of total planted area in 2005, respectively), vegetables and tea were significant sources of N₂O. This result shows that vegetables and tea are hotspots of N₂O emissions in the crop production sector, because of the higher chemical N fertilizer and manure input to vegetables than other crops and a high emission factor for tea. Tea received the highest

rate of chemical N fertilizer among the crops during the period, but application levels declined from 613 kg N ha⁻¹ in 1985 to 459 kg N ha⁻¹ in 2005.

40.3.4 Differences and uncertainties

There are several reasons for the difference between our estimations and those of the GIO (2007). Our framework includes disposal of livestock excreta but not burning of excreta and crop by-products. N volatilization rate during excreta handling also differed greatly (50% to 85% in this study and 10% to 30% on GIO). These factors would have made our estimation of indirect emissions by N deposition that account as indirect emission from livestock production larger than that of GIO, although GIO did not indicate indirect emissions. Because the emission factor for indirect emissions is larger than that for direct emissions from farmland (except tea), estimated N₂O emissions would be larger than GIO. Because our estimation of the basic unit of livestock N excretion was larger than that of the GIO (2007), our estimation of N excreta-related N₂O emissions was greater than that of the GIO's. Because N volatilization was much higher than GIO, residual N as manure was less than half of GIO. Chemical N fertilizer application was sometimes estimated to be lower than chemical N fertilizer demand (e.g., about -10% in 2005). Lower N input to farmland caused lower direct emission than GIO and N infiltration, and lower indirect emissions than the GIO's estimation on crop production. These differences in estimations resulted from differences in the basic concept and framework established to reflect real Japanese agricultural practices.

Our estimation contains many uncertainties, such as the emission factor itself. Akiyama et al. (2006) reviewed the Japanese native emission factor, therefore these values might relatively be reasonable than IPCC default value. Because little research has been done on indirect emissions, we used the IPCC default emission factor. The other factors, such as N leaching rate (30% of chemical N fertilizer and manure N input), were also uncertain. Because paddy rice fields have an infiltration soil layer and are waterlogged during summer, N leaching by water would be low. Because tea is generally grown on sandy soil, N leaching would be high. Methods of livestock excreta handling related to direct N₂O emissions might have changed during the period, but we used data from the 2001 surveys by Japan Livestock Technology Association, because no other appropriate data were available. These uncertainties should be resolved by future research.

40.3.5 Future themes of sustainable agriculture in relation to N₂O emissions

In Japan, the focus of sustainable agriculture is on crop production practices, such as low input of chemical fertilizer for carrot to conserve groundwater quality (Kagamihara City Groundwater Study, 1989). Japanese laws on the agro-environment and sustainability refer to livestock husbandry only in terms of manure application for soil fertility and soil health and livestock excreta management. The primary aim of these regulations is to preserve water quality in the environment and to reduce the direct effects on people (e.g., preventing excreta odors). However, the contribution of agricultural practices to global warming is a

significant aspect in the evaluation of sustainable farming. Livestock husbandry had a greater influence on N_2O emissions than crop production over the study period. Direct and indirect N_2O emissions from livestock husbandry during livestock excreta management, which are the main sources of N_2O emissions, are not addressed by any existing laws. Deodorization during composting by trapping NH_3 or excreta handling to prevent NH_3 effluence and changing the conventional method of composting to reduce the high levels of N_2O emissions would be possible mitigation options. Over the study period, a reduction in crop production reduced total N_2O emissions and emissions per unit area cultivated. Therefore, efforts to reduce N_2O emissions from livestock husbandry should be the primary aim in future.

The decline in N_2O emissions resulted mainly from a reduction of N input from 126 kg N ha^{-1} in 1985 to 92 kg N ha^{-1} in 2005. Although the decline in the area planted in crops caused other problems, such as a reduction in crop production and rate of self-sufficiency of Japanese food production, reducing N input might have environmental benefits. However, trends in N input per area differ among crop types (e.g., Mishima et al., 2006). The successful reduction in N inputs to vegetables and tea is a recent need.

40.4 Conclusions

Trends and future themes in reducing N_2O emissions in Japan include the following:

- N_2O emissions peaked in 1990 then declined until 2005. Emissions from livestock production caused the peak, and reduced emissions from crop production caused this decline.
- Livestock production emissions were greater than crop production emissions. Proportions of the total emissions derived from cattle, pigs, and poultry were relatively constant. Reductions after 1990 were small in total and constant per unit area of farmland. The proportion of the total emissions derived from rice declined and that from vegetables increased. Because their planted areas were small, vegetables and tea were hot spots of N_2O emissions.
- Lowering N_2O emissions from livestock production is important in sustainable agriculture, although this aspect has received little attention to date. Changing composting methods and deodorization by trapping NH_3 would be possible mitigation options. Reducing N input to vegetables is important for reducing N_2O emissions from crop production.
- Our estimation of N_2O emissions contains many uncertainties, and because there were not enough data available relating to indirect emissions, we had to use the IPCC default value. Increasing the data on indirect N_2O emissions is one of the themes of future basic research.

References

- Akiyama, H, Yan, X, Yagi, K (2006) Estimation of emission factors for fertilizer-induced direct N_2O emissions from agricultural soils in Japan: Summary of available data. *Soil Science and Plant Nutrition*. 52: 774–787.
- van der Gon, HD, Bleeker, A. (2005) Indirect N_2O emission due to atmospheric N deposition. *Atmospheric Environment* 39: 5827–5838.
- The greenhouse gas inventory office (2007) National Greenhouse Gas Inventory Report of Japan. <http://www-gio.nies.go.jp/aboutghg/nir/2007/nir2007ver5.0e.pdf>.
- Japan Livestock Industry Production (1999) Japanese feed standard. Tokyo (in Japanese).
- Japan Livestock Technology Association (2001) Emission control of global warming gas on livestock production. Tokyo (in Japanese).
- Kagamihara City Groundwater Study (1989) Analyze and future prediction of groundwater contamination under Kagamihara table land. *Quarterly Journal of Environmental Study* 75: 21–32.
- MAFF (1986a) Cost of livestock products. Tokyo MAFF (in Japanese).
- MAFF (1986b) The 61th Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo, MAFF.
- MAFF (1991a) Cost of livestock products. Tokyo MAFF (in Japanese).
- MAFF (1991b) The 66th Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo, MAFF.
- MAFF (1996) Cost of livestock products. Tokyo MAFF (in Japanese).
- MAFF (1997) The 71th Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo, MAFF.
- MAFF (1998) Agricultural Production Environment Report. Tokyo, MAFF (in Japanese).
- MAFF (2001) Cost of livestock products. Tokyo, MAFF (in Japanese).
- MAFF (2002a) Agricultural Production Environment Report. Tokyo, MAFF (in Japanese).
- MAFF (2002b) The 76th Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo, MAFF.
- MAFF (2003) Agricultural Production Environment Report. Tokyo, MAFF (in Japanese).
- MAFF (2006a) Cost of livestock products. Tokyo, MAFF (in Japanese).
- MAFF (2006b) The 80th Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo, MAFF.
- MAFF (2007) The 81st Statistical Yearbook of Ministry of Agriculture, Forestry and Fisheries. Tokyo MAFF.
- Mishima, S, Taniguchi, S, Kodama, M (2006) Recent trends in nitrogen and phosphate use and balance on Japanese farmland. *Soil Science Plant Nutrition* 52: 556–563.
- Mishima, S, Akiyama, H, Yagi, K, Kohyama, K (2008) Recent trend of livestock manure qualities and estimation of nitrogen loss rate by composting. *Japanese Journal of Soil Science and Plant Nutrition* 79: 370–375 (in Japanese).

Mishima, S, Endo, A, Kohyama, K (2009) Recent trend of residual nitrogen on the national and regional scale in Japan and its relation with ground water quality Nutrient Cycling in Agroecosystems 83: 1–11.

Schlesinger WH (1997) Biogeochemistry. London, Academic Press.

Tsuiki, M, Harada, Y (1997) Present state of livestock excreta production and future work in Japan. Environmental preservation and new livestock production.

Phenological Adaptation of Cereal Weeds to Climate Variations

Mohamed Fenni and Mustapha Bounechada

41.1 Introduction

Phenology is the study of the relationships between various climatic factors and occurrence of successive stages in the life cycle of plants or animals (McCarty, 1986). Early attempts to describe phenological events date back to seventeenth century, Carl Von Linné in 1751 noted phenological stages of the species collected (Bergmeier, 1998). The scientific approach to phenological investigation is a fairly recent development. Since 1947, several authors have intensively studied agronomic crops (Kirby et al., 1999; Baker and Reddy 2001) and weeds phenology. Swanton et al. (1999 and 2000) reported the life cycle for *Setaria viridis* L. and *Echinochloa crus-galli* (L.) Beauv. Huang et al. (2001) studied pattern of *Sinapis arvensis* L. growth stages. Among weed species whose phenology was described recently and whose one or several stages phenologic were quantified using ecological factors such as the temperature, we quote: *Galium aparine* L (Vander Weide, 1992), *Solanum nigrum* L. (McGiffen and Masiunas, 1992), *Cynodon dactylon* (Satorre et al., 1996), *Ranunculus repens* L. (Harris et al., 1998), and *Alopecurus myosuroides* Huds. (Chauvel, 2000).

The knowledge of phenological aspects is an essential element for any plan of integrated weed management. Timing of phenological events is one of the most important factors determining the success of plants in capturing resources. Therefore, understanding the factors that control phenological variability is crucial for the design of durable weed management practices. In Algeria, the low grain yield (700 kg ha^{-1}) is partly due to the erratic and low rainfall and also due to the use of unimproved production practices, which do not give attention to the control of weeds. The wheat yield losses caused by weed flora in the Setifian region vary from 30% to 60% depending on weed density and environmental conditions. The objectives of this research were to determine phenological characteristics of 14 cereal weeds and their relations with the climatic variations.

41.2 Materials and Methods

Growth stages of major weeds in cereals of the Setif high plains (North-East, Algeria) were recorded for 5 years: 1994/1995, 1996/1997, 1998/1999, 2000/2001, and 2004/2005. The field experiment is located 2 km south of Setif city, at an altitude of 1100 m. The soil is clay loam, the pH (1:5 H₂O) is 7.9, and the percentage of the organic matter is 0.45. Setif region climate is characterized by a cold and wet winter, a hot summer, generally very dry. The climatic area is semi-arid.

Climatic characteristics of 5 years of observations, compared with the average period of 1981/2005, are reported in Table 41.1. We noted that 1999 and 2001 are relatively warm and dry. Their average temperatures exceed that of the 1981/2005 period, successively, by 1 and 1.1°C. The total of monthly average temperatures of these 2 years exceeds that of the 1981/2005 period of 11.7 and 13.2°C, respectively.

Table 41.1 Climatic characteristics of 5 years of observations.

Years characteristics	1995	1997	1999	2001	2005	1981/2005
Annual average temperatures (°C)	14.4	15.1	15.5	15.6	14.5	14.5
Sum of monthly average temperatures (°C)	172.2	181.6	186.0	187.5	173.8	174.3
Rainfall (mm)	422.4	402.4	384.0	251.7	373.8	403

Observations were made since the sowing of durum wheat (*Triticum durum* Desf.) until its stage of maturation, at 5–8 day intervals, in four plots of 25 m². Sowing took place during the 5 years of experimentation between November 1 and 20. Weed species were identified following the “Nouvelle flore d’Algérie” of Quezel and Santa (1962–63). Phenological stages of these species were recorded according to the BBCH scale (Lancashire et al., 1991) as first leaf, vegetative development (development of harvestable vegetative plant parts), flowering maturity of seed (ripening of fruit and seed), and senescence (leaves change color and fall).

The models developed on the basis of heat units expressed as degree-days have been widely used for predicting growth and development weeds (Forcella, 1998, Baker and Reddy, 2001). In order to determine relations between phenological cereal weeds and climatic variations, degree-days were computed using the following equation:

$$ADd = \sum_{i=1}^n Dd = \sum_{i=1}^n \frac{T_{\max} - T_{\min}}{2} - T_b \quad (41.1)$$

where *ADd* is the accumulated degree-days, *i* is the day of year, *T*_{max} is the daily maximum temperature, *T*_{min} is the daily minimum temperature, and *T*_b is the base temperature.

The base temperature is a function of the plant species and varies between 0 and 10°C (Vander Weide, 1992; Satorre, 1996). The *T*_b used in this method was 5°C. Temperature data were used from the weather station of Setif, 2 km east of the field experiment. During the 5 years of observations the first rains were noted

at the end of November. December 1 was taken as initial date to count number of days and the number of degree-days. The obtained data were subjected to an analysis of variance.

41.3 Results and Discussion

The 5-year study involved 14 species belonging to 12 plant families. Prevalent families were Brassicaceae and Apiaceae. Some families give few species of weeds, but very noxious (Convolvulaceae and Polygonaceae). The most abundant species were *Veronica hederifolia*, *Papaver rhoeas*, *Vaccaria pyramidata*, *Fumaria parviflora*, and *Polygonum aviculare*.

Species are classified in Tables 41.2 and 41.3 according to the date of flowering. The earliest flowering recorded was for *Ranunculus arvensis* and *V. hederifolia*, with degree-days accumulation of 316 and 426, respectively, and the latest was for *Scolymus hispanicus* and *P. aviculare* with degree-days accumulation of 2021 and 1297, respectively.

Just after the first rains of autumn, weed seeds inflate and germinate; these two processes take place during December. The first leaf appears for the majority of species at the end of December and beginning of January. It is only from the stage vegetative development that we can notice differences between species phenology. Those which have weak thermal requirements achieve their stages of vegetative development quickly and arrive in first at stage of flowering (March–beginning of April); it was the case with *V. hederifolia* and *R. arvensis*, and they are winter–spring species. Most of their cycles of development take place in winter. They reach the maturity of seed with less than 600 degree-days. Species which require higher temperatures require more time in their development and reach their stages of flowering from May to June; it was the case of *Diploaxis virgata*, *V. pyramidata*, and *P. aviculare*. These are spring–summer species whose stage of vegetative development is spread out until spring. They require between 1900 and 2300 degree-days to mature their seeds (Table 41.2). Between the two preceding groups of species, we have an intermediate group composed of *F. parviflora*, *Rapistrum rugosum*, *Galium tricornue*, *Bifora testiculata*, *Turgenia latifolia*, *Vicia monantha*, *Papaver rhoeas*, and *Bromus rubens*; these are characteristic species of the cereals weed flora in North Africa and they require temperature between 800 and 1200°C to mature their seeds.

The analysis of the variance showed that the year of observation had no significant effect on the sum of degree-days required by every species to carry out its life cycle or to carry out its phenological stages. The sum of degree-days required by every species was almost constant during the 5 years of observation; it was the same during relatively warm years (such as on 1999 and 2001) or during the three other normal years. According to McCarty (1986), each plant operates under a specific set of thermal requirements that determine time of germination, emergence, and subsequent developmental stages. Thus, the apparent variation in

times of occurrence from year to year of various phenological stages may be based on some specific sets of weather conditions like temperature.

Until senescence the species which had the shortest cycle and which lasted less than 160 days were *R. arvensis* and *V. hederifolia*, these species emerged early and started quick growth during relatively cool temperatures, utilizing the normally abundant winter rainfall and available soil water. Species which have the longest cycle and which lasted more than 240 days were *S. hispanicus* and *P. aviculare* (Table 41.3). These species spend the winter as rosettes and show active growth in the spring.

Table 41.2 Degree-days accumulation by phenological stages of each species (average of 5 years).

Weed species	Phenological stages				
	First leaf	Vegetative development	Flowering	Maturity of seed	Senescence
<i>Ranunculus arvensis</i> L.	120 ⁽¹⁾	87 207 ⁽²⁾	109 316	149 465	311 776
<i>Veronica hederifolia</i> L.	108	100 208	218 426	137 563	155 718
<i>Fumaria parviflora</i> Lamk.	120	245 365	120 485	375 860	366 1226
<i>Rapistrum rugosum</i> (L.)All.	133	211 344	166 510	458 968	497 1465
<i>Galium tricornue</i> Witth.	120	245 365	212 577	284 861	366 1227
<i>Bifora testiculata</i> Hoffm.Roth.	147	368 515	91 606	431 1037	519 1556
<i>Turgenia latifolia</i> Hoffm.	120	396 516	201 717	321 1038	519 1557
<i>Vicia monantha</i> Retz.	120	396 516	330 846	192 1038	519 1557
<i>Papaver rhoeas</i> L.	120	441 561	348 909	302 1211	620 1831
<i>Bromus rubens</i> L.	120	441 561	348 909	215 1124	656 1780
<i>Diploaxis virgata</i> DC.	120	597 717	494 1211	346 1557	447 2004
<i>Vaccaria pyramidata</i> Medik.	133	712 845	366 1211	173 1384	509 1893
<i>Polygonum aviculare</i> L.	133	712 845	452 1297	595 1892	410 2302
<i>Scolymus hispanicus</i> L.	160	1396 1556	465 2021	223 2244	200 2444

⁽¹⁾ Counted from December 1

⁽²⁾ Cumulate

Table 41.3 Dates and durations (days) of phenological stages of major cereal weeds in Setif region (average over 5 years).

Weed species	First leaf	Vegetative develop- ment	Flowering	Maturity of seed	Senescence
<i>Ranunculus arvensis</i> L.	12-25 / 1-5 ⁽¹⁾ 36 ⁽²⁾ 11.81 ⁽⁴⁾	1-5 / 3-1 54 (90) ⁽³⁾ 13.09	3-1 / 3-20 19 (109) 8.04	3-20 / 4-10 20 (129) 27.61	4-10 / 5-10 30 (159) 18.40
<i>Veronica hederifolia</i> L.	12-20 / 1-1 32 10.95	1-1 / 3-1 59 (91) 6.88	3-1 / 4-5 35 (126) 5.38	4-5 / 4-20 15 (141) 17.54	4-20 / 5-5 15 (156) 20.05
<i>Fumaria parviflora</i> Lamk.	12-20 / 1-5 36 11.30	1-5 / 3-25 78 (114) 15.28	3-25 / 4-10 15 (129) 8.10	4-10 / 5-15 35 (164) 14.61	5-15 / 6-10 25 (189) 15.34
<i>Rapistrum rugosum</i> (L.)All.	1-1 / 1-10 41 9.87	1-10 / 3-25 73 (114) 11.41	3-25 / 4-15 20 (134) 7.74	4-15 / 5-25 40 (174) 12.60	5-25 / 6-25 30 (204) 25.53
<i>Galium tricornne</i> Witth.	12-25 / 1-5 36 16.50	1-5 / 3-25 78 (114) 8.14	3-25 / 4-20 25 (139) 5.58	4-20 / 5-15 25 (164) 19.78	5-15 / 6-10 25 (189) 22.54
<i>Bifora testiculata</i> Hoffm.Roth.	1-5 / 1-15 46 12.46	1-15 / 4-15 89 (135) 7.97	4-15 / 4-25 10 (145) 7.05	4-25 / 5-30 35 (180) 13.64	6-1 / 6-30 30 (210) 17.48
<i>Turgenia latifolia</i> Hoffm.	1-1 / 1-5 36 19.41	1-5 / 4-15 99 (135) 12.14	4-15 / 5-5 20 (155) 7.90	5-5 / 5-30 25 (180) 16.49	5-30 / 6-30 30 (210) 20.27
<i>Vicia monantha</i> Retz.	1-1 / 1-5 36 10.25	1-5 / 4-15 99 (135) 15.35	4-15 / 5-15 30 (165) 6.60	5-15 / 5-30 15 (180) 17.51	5-30 / 6-30 31 (211) 17.57
<i>Papaver rhoeas</i> L.	1-1 / 1-5 36 9.84	1-5 / 4-20 104 (140) 14.48	4-20 / 5-20 30 (170) 8.03	5-20 / 6-10 20 (190) 14.72	6-10 / 7-20 30 (220) 16.05
<i>Bromus rubens</i> L.	1-1 / 1-5 36 11.10	1-5 / 4-20 104 (140) 10.05	4-20 / 5-20 30 (170) 5.64	5-20 / 6-5 15 (185) 9.12	6-5 / 7-10 35 (220) 8.61
<i>Diploaxis virgata</i> DC.	1-1 / 1-5 36 11.82	1-5 / 5-5 119 (155) 11.21	5-5 / 6-10 35 (190) 7.87	6-10 / 6-30 20 (210) 22.54	6-30 / 7-20 20 (230) 15.72
<i>Vaccaria pyramidata</i> Medik.	1-5 / 1-10 41 14.11	1-10 / 5-15 124 (165) 13.65	5-15 / 6-10 25 (190) 6.49	6-10 / 6-20 10 (200) 12.05	6-20 / 7-15 25 (225) 21.57
<i>Polygonum aviculare</i> L.	1-5 / 1-10 41 15.36	1-10 / 5-15 124 (165) 15.70	5-15 / 6-15 30 (195) 5.27	6-15 / 7-15 30 (225) 11.78	7-15 / 7-30 18 (243) 19.63
<i>Scolymus hispanicus</i> L.	1-5 / 1-20 51 10.82	1-20 / 6-30 160 (211) 12.14	6-30 / 7-20 21 (232) 4.90	7-20 / 7-30 10 (242) 25.49	7-30 / 8-7 8 (250) 17.25

⁽¹⁾ Dates, ⁽²⁾ Duration in days, ⁽³⁾ Cumulate in days, ⁽⁴⁾ CV % : coefficient of variation (ratio of the standard deviation to mean, reported as a percentage).

Phenological similarities may be considered as an expression of physiological and genetic similarities of species and may be used as a measure of relationship. On the basis of duration of the vegetative cycle, the season during which most of this cycle takes place and period of flowering, species reported in Table 41.3 were grouped as winter–spring species (*R. arvensis*, *V. hederifolia*, *F. parviflora*, *R. rugosum*, *G. tricornis*, *B. testiculata*, *T. latifolia*, *V. monantha*, *P. rhoeas*, and *B. rubens*), and spring–summer species (*D. virgata*, *V. pyramidalis*, and *P. aviculare*). The variability which exists in each group depends on the temperature. Maturity of seeds was ranged from early April to the beginning of June for the first group, and from beginning of June to July for the second group.

S. hispanicus can be counted like summer species; its stage of development was spread out until the end of June and it flowered and matured in July. When it is present in large quantities in the fallow, it dominates the summer floristic aspects.

The results of analysis of durations (in days) of the phenological stages of all species showed that the coefficients of variation were relatively high for the stages of first leaf, vegetative development, maturity of seed, and senescence (Table 41.3). It means that the duration of these stages varied from 1 year to the next; indeed, during relatively warm years the duration of these phenological stages was short compared with normal years. So, the cereal weeds show an adaptation to the global warming by modulating the duration of their phenological phases. The lowest coefficients of variation were noted for flowering stage of all species; this phenological event was affected by the temperature and day length.

Increases in temperature due to global climate changes could significantly impact weed competitiveness and crop–weed interactions (Tungate et al., 2006). During warm years, weeds accelerate their development and become more concurrent toward cereals. It is necessary to note that they are less demanding for water than the cultivated plants and their seeds are in the ground well before the arrival of the cereals seeds; therefore they use the soil humidity to inflate and start their germination, before even the ploughing. Under these conditions, competition is really strong and early. In this order Fuhrer et al. (2006) noted that warming accelerates plant development and reduces grain-fill, reduces nutrient-use efficiency, increases crop water consumption, and favors C_4 weeds over C_3 crops. Overall, intensive agriculture may have the potential to adapt to changing conditions, in contrast to extensive agricultural systems or low-input systems which may be affected more seriously.

41.4 Conclusions

Understanding the factors that control phenological variability is crucial for the design of durable weed management practices. Studies of this nature will be useful to predict weeds growth, and determine the appropriate timing for the application of herbicides in order to optimize their use and avoid secondary effects of herbicides treatment such as soil and water pollution. Phenological characteristics of 14 cereal weeds and their relationships with the climatic variations were studied for

5 years. Two groups were identified. Winter–spring species, most of their development cycles take place in winter, they reach the maturity of their seeds with less than 1200 degree-days, and spring–summer species, of which vegetative development stage is spread out until spring, this species require between 1900 and 2300 degree-days to mature their seeds. Variability in phenology of these weeds was dependent on temperature patterns of the year. Cereal weeds adapt with the climatic variations by modulating the duration of their phenological phases. The results showed that phenological events of these species have been increasing in earliness during the warm years.

Acknowledgment

We would like to thank the anonymous reviewers for their comments and recommendations.

Nomenclature

ADd	Accumulated degree-days
CV%	Coefficient of variation (reported as a percentage).
T_b	Base temperature (°C)
T_{max}	Daily maximum temperature (°C)
T_{min}	Daily minimum temperature (°C)

References

- Baker, JT, Reddy, VR (2001) Temperature effects on phenological development and yield of muskmelon. *Annals of Botany* 87: 605–613.
- Bergmeier, E (1998) The phenological approach in mediterranean landscape analysis. *Phytocoenologia* 28: 145–156.
- Chauvel, B, Munier-Jolain, N, Letouzé, A, Grandgirard, D (2000) Developmental patterns of leaves and tillers in a black-grass population (*Alopecurus myosuroides* Huds.). *Agronomie* 20: 247–257.
- Forcella, F (1998) Real time assessment of seed dormancy and weed management. *Seed Science Research* 8: 201–209.
- Fuhrer, J, Beniston, M, Fischlin, A, Frei, CH, Goyette, S, Jasper, K, Pfister, C (2006) Climate risks and their impact on agricultural land and forests in Switzerland. *Climate Change* 79: 79–102.
- Harris, SM, Doohan, DJ, Gordon, RJ, Jensen, KIN (1998) The effect of thermal time and soil water emergence of *Ranunculus repens*. *Weed Research* 38: 405–412.
- Huang, JZ, Shrestha, A, Tollenaar, M, Deen, W, Rajcan, I, Rahimian, H, Swanton, CJ (2001) Effect of temperature and photoperiod on the phenological development of wild mustard (*Sinapis arvensis* L.). *Field Crops Research* 70: 75–86.
- Kirby, EJM, Spink, JH, Frost, DL, Sylvester-Bradley, R, Scott, RK, Foulkes, MJ, Clare, RW, Evans, EJ (1999) A study of wheat development in the field : Analysis by phases. *European Journal of Agronomy* 11: 63–82.
- Lancashire, PD, Bleiholder, H, Van Den Boom, T, Langelüddeke, P, Stauss, R, Weber, E, Witzemberger, A (1991) A uniform decimal code for growth stages of crops and weeds. *Annals Applied Biology* 119: 561–601.
- McCarty, MK (1986) A fifteen year phenological record of pasture plants near Lincoln, Nebraska. *Weed Science* 34: 218–224.

- McGiffen, ME, Masiunas, JB (1992) Prediction of black and eastern black nightshade (*Solanum nigrum* and *S. ptycanthum*) growth using degree-days. *Weed Science* 40: 86–89.
- Quezel, P, Santa, S (1962–63) Nouvelle Flore de l'Algérie et des Régions Désertiques Méridionales. Centre National de la Recherche Scientifique, France.
- Satorre, EH, Rizzo, FA, Arias, SP (1996) The effect of temperature on sprouting and early establishment of *Cynodon dactylon*. *Weed Research* 36: 431–440.
- Swanton, CJ, Huang, JZ, Deen, W, Tollenaar, M, Shrestha, A, Rahimian, H (1999) Effects of temperature and photoperiod on *Setaria viridis*. *Weed Science* 47: 446–453.
- Swanton, CJ, Huang, JZ, Shrestha, A, Tollenaar, M, Deen, W, Rahimian, H (2000) Effects of temperature and photoperiod on the phenological development of barnyardgrass. *Agronomy Journal* 92: 1125–1134.
- Tungate, KD, Israel, DW, Watson, DM, Rufty, TW (2006) Potential changes in weed competitiveness in an agroecological system with elevated temperatures. *Environmental and Experimental Botany* 60: 42–49.
- Vander Weide, RY (1992) Phenology of arable and hedgerow populations of *Galium aparine* L. in relation to climate and soil conditions. *Weed Research* 32: 249–258.

Chemical Characteristics and Source Reconciliation of Organic Aerosols in Algiers City Area

Noureddine Yassaa, Riad Ladji, Angelo Cecinato and Brahim Y. Meklati

42.1 Introduction

Aerosols affect environment at the local, regional, and global levels. At the local level, aerosols are now becoming recognized as a significant health problem, especially in regard to respiratory illnesses, including asthma (Dockery et al., 1993). At global scale, atmospheric aerosols influence climate in two main ways, referred to as direct forcing and indirect forcing (Charlson et al., 1992). In the direct forcing mechanism, aerosols reflect sunlight back to space, thus cooling the planet. The indirect effect involves aerosol particles acting as (additional) cloud condensation nuclei, spreading the cloud's liquid water over smaller droplets. This makes clouds more reflective and longer lasting.

Atmospheric particles are a complex mixture of many species derived from various sources including direct emissions and secondary carbon produced by oxidation. Thus, a deep understanding of their chemical composition is necessary if the source identification is attempted with the purpose of pollution control or abatement. Organic compounds of direct biogenic and anthropogenic origin often represent cumulatively an important fraction, up to 40%, of total particulate matter mass, while individual concentrations range from few picograms up to hundreds of nanograms per cubic meter. Anthropogenic emissions include fossil fuel (diesel and gasoline) combustion from mobile and stationary sources, biomass burning (forest fires, landfills, agricultural activities, and incinerators), and natural gas, wood, and coal combustion. Wind erosion of leaf epicuticular waxes, vegetation debris, microbial degradation, and volcanoes eruption are considered the most important natural sources. The organic compounds associated with particles have been chemically characterized in several studies and comprise: *n*-alkenes, carboxylic and dicarboxylic acids, carbonyls, steroids, aromatic compounds, etc. (Yassaa et al., 2005 and references therein). Among minor components found in ambient aerosols, polycyclic aromatic hydrocarbons (PAHs) are recognized to play a key role with respect to air quality, because they include potent carcinogenic and/or

mutagenic compounds. Most PAHs are released by combustion processes applied by man to industrial technologies like energy or steel generation, vehicle and machine engine operation, mineral/crude oil extraction and petroleum refining processes, domestic heating and food cooking, waste/refuse incineration, and smocking.

Algiers (latitude 36° 42' N, longitude 3° 13' E), the capital of Algeria, is one of the largest cities in the North Africa. The city is located in the North of the country, facing the Bay of the Mediterranean Sea. It is the largest city of Algeria, developing over an area of 273 km². It is the political, economic, and cultural center of the country and is one of the leading ports of North Africa. Nowadays, Algiers is experiencing a rapid urbanization so that its population is approaching six million inhabitants (Statistics, 2006), that is around 20% of the total Algerian population. Starting from the end of last century, the huge migration of peoples to Algiers, combined with the opening of economy to foreign market adopted by the Government, induced the fast increase in traffic circulation which adversely impacted the air quality in many urban areas of Algiers. As a result, large amounts of both volatile and particulate organic compounds could be found and determined in Algiers city.

This chapter presents an overview of the aerial concentration behaviors and seasonal and annual variations of organic compounds comprising *n*-alkenes, polynuclear aromatic hydrocarbons (PAH) and their nitrated derivatives (N-PAH), and their major contributing sources in Algiers. The data set obtained through the investigations conducted from 1998 to 2006 in different locations in Algiers city characterized by different features, urban, industrial, and waste landfill provides useful information for establishing effective control measures to reduce organic pollution in Algiers.

42.2 Experimental

42.2.1 Sampling protocol and rationale

Contents of particulate organic matter (POM) in the air were measured during the period 1998–1999 and 2005–2006 in the heart of Algiers, where several cases of annoyances were reported during hot and sunny days, possibly related to the presence of organic compounds in air. During 1998–1999 and 2002–2003, POM was also measured at the biggest waste landfill of Algeria located in Oued Smar, Algiers, where the emissions are not yet subjected to any control from Public Authorities. There, the global emission budget results from the contributions of open-air accumulation, waste degradation, and different combustion processes (from private houses, industries, and hospitals). It determines the formation of *dirty fogs*, which often envelops the region; that occurs mainly at night time or at sunrise, when meteorological stability is well developed (i.e., when the low wind rate and the thermal inversion are observed). Through the knowledge of composition of aerosol, information could be obtained concerning the ambient impact subsequent from the different sources of organic pollution, and Public Authorities could be helped to assume strategies aimed to get better air quality of that region. The results obtained should give big information about nature and

concentrations of pollutants experienced by the region investigated and on sources of pollution. Therefore, it acts as an useful “database” for more extensive campaigns, which will be performed in the future.

Figure 42.1 provides the general view of Algiers Bay as well as a detailed position of the sites investigated. Urban POM was investigated by collecting samples at downtown Algiers. Because of the big number of cars and trucks running in the urban area of Algiers, high levels of NO_x , volatile organic compounds (Yassaa et al., 2005), and black carbon were expected.

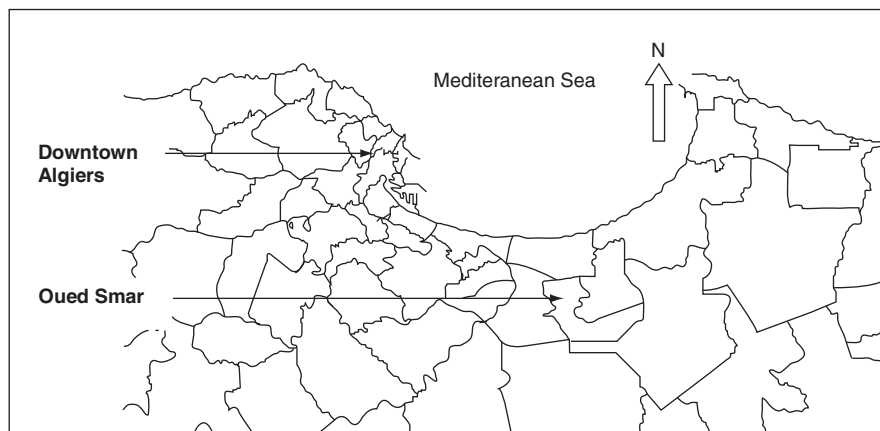


Fig. 42.1 General view of Algiers bay.

The second sampling station was located 50 m from the Oued Smar waste landfill, which is the largest one existing in Algeria. Oued Smar is located at about 13 km from downtown Algiers, southeast side to the city, and represents an important emission source for a number of atmospheric pollutants. The landfill lies in the west side of the industrial zone of Oued Smar and covers about 37.5 hectares. Emission from landfill comprises gaseous species (volatile organic compounds, SO_2 , NO_x , CO , NH_3) as well as solids (dusts, ashes, soot). According to a recent estimation, 4000 tons day^{-1} of wastes are stored there. Municipal wastes account for 1600 tons day^{-1} and the industrial ones, including toxic or dangerous substances, contribute for 2400 tons day^{-1} . All these products are usually burned at open air, without any control of combustion parameters and release.

42.2.2 Sampling procedure

PM_{10} aerosols were collected by means of a medium-volume sampler operating at the flow rate of 39 L min^{-1} , equipped with an electronic volume counter. Each sampling was carried out over 24 hours and the particles were collected onto 47 mm diameter quartz filter membranes. The particle-loaded filters were directly kept in dichloromethane solution to prevent any degradation and stored at low temperature (4°C) until chemical characterization.

42.2.3 Sample extraction and clean-up

Chemical determination of organic aerosols was performed by applying a procedure described extensively elsewhere (Yassaa et al., 2005). Briefly, samples were spiked with a solution of perdeuterated species adopted as internal reference compounds. Then, the organic content was extracted by refluxing aerosol-enriched filters in soxhlet, using a dichloromethane–acetone (4:1) mixture for 16 hours. The extract was evaporated and the residue was divided into two aliquots. Most of the extract (4/5 of the total) was fractionated through a column chromatography on neutral alumina (2 g, partly deactivated with 2.5% ww of water). Non-polar aliphatic compounds were first eluted with *iso-octane* (6 mL), while the bulk of medium-polar organics were collected by passing dichloromethane-*iso-octane* (3:2, 6 mL) through the column; this fraction comprised PAH, N-PAH; polar species were eluted with a third solvent, i.e., acetone (6 mL). All sample fractions were stored in the dark at low temperature (4°C) until the analysis.

42.2.4 Analysis

PAH and N-PAH were determined by using a *Trace GC* gas chromatograph coupled with a *Trace Q* mass spectrometer. For PAH and N-PAH, the detector was operated in the selected ion monitoring (*sim*) modality. The instrument was purchased from *Thermo*, Rodano MI, Italy. Separations of analyses were obtained through a 25-m-long, RT5MS-type (methylphenyl silicone stationary phase; i.d. = 250 µm, film = 0.33 µm) capillary column provided by *Superchrom*, Milan, Italy. The mass spectrometer system was operated in electron impact mode (ion source energy = 70 eV) and GC/MS data were acquired by a dedicated software (*Excalibur*) purchased from *Thermo*. *n*-Alkanes were processed through a second *Trace GC* system equipped with a similar GC column combined to a flame ionization detector.

Compounds identification was based upon comparison of eluted peaks with authentic analyze standards, GC retention times, mass spectra derived from reference (NIST) as well as home-made libraries and interpretation of mass spectrometric fragmentation patterns. Quantification of the compounds was conducted by comparing GC peak areas with those of known co-injected standards (internal standard method), after checking for the concentrations lied within the detector operative ranges (usually 3–1000 times the respective detection limits). Filter blanks, occurring only for some semivolatile *n*-alkanes (up to C₁₈), phenanthrene and pyrene among PAH, were subtracted to obtain neat aerial concentrations of compounds. Analytical uncertainty in any case did not exceed 15%.

42.3 Results and Discussion

42.3.1 *n*-Alkenes

The season averaged concentrations of individual *n*-alkanes found at both in downtown Algiers (1998–1999 and 2005–2006) and waste landfill of Oued Smar (1998–1999 and 2002–2003) are listed in Table 42.1. The *n*-alkanes concentrations in the cold time were always higher than in the warm one at both sites. This seems to be in good agreement with the general evolution of meteorology dominating the Algiers region, although the nature of incinerated waste could influence to some extent the seasonal variability in Oued Smar. Indeed, the inversion of temperature at the low troposphere is very frequent in winter over the Algiers region and prevents the dispersion of the pollutants, so they accumulate over the earth surface layer, while the low ambient temperature shifts the partition of semi-volatile species toward condensed phase.

The *n*-alkanes concentrations measured in downtown Algiers in 2005–2006 were much higher than those recorded in 1998–1999. This is mostly due to the fast increase in traffic circulation experienced recently in Algiers city in addition to other factors described earlier in the first section. The concentrations of *n*-alkanes measured recently in Algiers (2005–2006) were similar to those reported for the industrialized area of Prato (Italy) (37–205 ng m⁻³) (Cincinelli et al., 2003), but lower than those measured in New Delhi (India) (138–598 ng.m⁻³) (Sharma et al., 2003) and Qingdao (China) (53–371 ng m⁻³) (Guo et al., 2003).

Table 42.1 Seasonal average *n*-alkanes concentrations (ng m⁻³ of air) in downtown Algiers and waste landfill (sum. means summer and wint. means winter).

Site	Downtown Algiers				Waste landfill			
Year	1998–1999		2005–2006		1998–1999		2005–2006	
Compound	Sum.	Wint.	Sum.	Wint.	Sum.	Wint.	Sum.	Wint.
<i>n</i> -C ₁₆	0.1	5	0.1	5	0.1	5	0.1	5
<i>n</i> -C ₁₇	0.5	14.9	0.5	14.9	0.5	14.9	0.5	14.9
<i>n</i> -C ₁₈	2.5	12.2	2.5	12.2	2.5	12.2	2.5	12.2
<i>n</i> -C ₁₉	1.6	9.8	1.6	9.8	1.6	9.8	1.6	9.8
<i>n</i> -C ₂₀	2.9	10.9	2.9	10.9	2.9	10.9	2.9	10.9
<i>n</i> -C ₂₁	5.7	7.5	5.7	7.5	5.7	7.5	5.7	7.5
<i>n</i> -C ₂₂	8.6	8.9	8.6	8.9	8.6	8.9	8.6	8.9
<i>n</i> -C ₂₃	9.5	5.2	9.5	5.2	9.5	5.2	9.5	5.2
<i>n</i> -C ₂₄	7.3	5.8	7.3	5.8	7.3	5.8	7.3	5.8
<i>n</i> -C ₂₅	4.4	3.9	4.4	3.9	4.4	3.9	4.4	3.9
<i>n</i> -C ₂₆	2.8	2.7	2.8	2.7	2.8	2.7	2.8	2.7
<i>n</i> -C ₂₇	3.1	2.7	3.1	2.7	3.1	2.7	3.1	2.7
<i>n</i> -C ₂₈	1.2	1.9	1.2	1.9	1.2	1.9	1.2	1.9
<i>n</i> -C ₂₉	3.4	1.4	3.4	1.4	3.4	1.4	3.4	1.4
<i>n</i> -C ₃₀	0.5	0.8	0.5	0.8	0.5	0.8	0.5	0.8
<i>n</i> -C ₃₁	0.8	0.6	0.8	0.6	0.8	0.6	0.8	0.6
Total	55	94	55	94	55	94	55	94
<i>CPI</i> ₂₅	2	1.2	2	1.2	2	1.2	2	1.2

The whole *n*-alkanes contents ($\Sigma n\text{-C}_{16}$ to $n\text{-C}_{31}$: 1192 and 5787 ng m⁻³ in warm and cold seasons, respectively) measured in waste landfill of Oued Smar in 2002–2003 were compared with those recorded at the same site during the summer 1998 and winter 1999 ($\Sigma n\text{-C}_{16}$ to $n\text{-C}_{31}$: 82 and 401 ng m⁻³, respectively) (see Table 42.1). The new recordings were 14 times higher than those previously reported. This unexpected increase in the concentrations would be explained by three assumptions: (1) the waste composting procedures undertaken by the Authorities to improve the air quality are not respected or badly concretized in the field; (2) these procedures are applied only in small part of the landfill; and (3) severe multiplication of the quantities of waste amounts deposited and burnt in the Oued Smar landfill passed over any composting procedure operated. It is worth to remark, at this respect, that population and human activities in the Algiers region are both rapidly increasing that leads to the concurrent generation of garbage and refuses. In conclusion, at least two main sources are promoting the occurrence of *n*-alkanes in the atmosphere of Oued Smar, the former quite unchanging in composition and possibly modulated in amount with year time, and the latter changing in composition, and certainly modulated in amount with year time.

To distinguish the role played by natural sources for the presence of *n*-alkanes in airborne particles we applied the *Carbon Preference Index* (CPI) computation. The CPI rate was calculated through the following formula:

$$CPI_{25} = \frac{1}{2} \times \left[\frac{(C_{24} + C_{26} + C_{28} + C_{30})}{(C_{25} + C_{27} + C_{29} + C_{31})} + \frac{(C_{26} + C_{28} + C_{30} + C_{32})}{(C_{27} + C_{29} + C_{31} + C_{33})} \right]$$

where the subscript “25” indicates the *n*-pentacosane homologue is chosen as odd-carbon-numbered lower end point (this assumption allows to reduce the uncertainty related to partial volatility of compounds). According to technical literature (Rogge et al., 1993), the CPI₂₅ rate allows to assess the plant wax contribution versus petroleum-derived fuels to aliphatic contents in aerosols: in fact, CPI₂₅ values close to 1 are characteristic of mineral oil burning, whereas high figures (up to 10) are associated with plant wax release. Since the CPI₂₅ rate remained ≤ 1 over the most of the time at both investigated sites, the predominance of anthropogenic source was confirmed in Algiers city area.

In conclusion, the *n*-alkanes pattern observed in downtown Algiers was similar to that of motor vehicular exhaust emissions, allowing us to identify the main source of carbon particles there. Stocking and burning of several kinds of materials including biomass and refuses, i.e., plants, foodstuffs, animals, and plastics, caused the huge presence of *n*-alkanes in the aerosols at the Oued Smar site. The air contamination consequent from anthropic activities appeared more severe at Oued Smar than in downtown Algiers.

42.3.2 Polycyclic aromatic hydrocarbons (PAH)

Table 42.2 reports the aerial content of individual PAH in downtown Algiers and Oued Smar. Two “diagnostics ratios” referring to PAH are also reported, i.e.:

- $[FA]/([FA]+[PY]): [Fluoranthene]/([Fluoranthene]+[Pyrene])$ and
- $[IPY]/([IPY]+[BPE]): [Indenopyrene]/([Indenopyrene]+[benzoperylene])$

The total PAH concentrations recorded recently in downtown Algiers varied from 13 to 29 ng m⁻³, and maximum levels were recorded in winter. PAH reached concentration levels similar to those recorded in the atmosphere of Prato, Italy (Cincinelli et al., 2007), but lower than those found in Thessaloniki, Greece (Manoli et al., 2004). The concentrations of benzo(a)pyrene, often used as *PAH indicator* and regarded by the WHO as index for PAH-associated carcinogenicity (Yassaa et al., 2005), were in the range of 0.31–0.71 ng m⁻³ in downtown Algiers during 2005–2006, respectively, meeting the air quality guidelines of 1 ng m⁻³ (WHO, 2000). The rates reached by *benzo(a) pyrene-equivalent carcinogenic power* associated with airborne particulates (BaPE) were also calculated. This index, similar to TCDD-equivalence index defined for dioxin-like compounds, has been proposed to parameterize aerosol carcinogenicity better than having recourse to the benzo(a)pyrene alone. This approach seems suitable as far as sources do not emit BaPY at extents comparable to other “carcinogenic” PAH, or the same compound is decomposed much more extensively than congeners.

Table 42.2 Seasonal average PAH concentrations (ng m⁻³ of air) and some characteristic ratios in downtown Algiers and waste landfill. For compound identification, see the text.

Site	Downtown Algiers				Waste landfill			
Year	1998–1999		2005–2006		1998–1999		2005–2006	
Compound	Sum.	Wint.	Sum.	Wint.	Sum.	Wint.	Sum.	Wint.
FL	n.ev.	n.ev.	2.47	1.31	n.ev.	n.ev.	5.07	0.27
Phe	n.ev.	n.ev.	1.14	1.99	n.ev.	n.ev.	42.38	4.41
Ant	n.ev.	n.ev.	0.23	0.50	n.ev.	n.ev.	18.23	0.27
Me-PHE/AN (S)	*	*	2.04	3.18	*	*	26.96	5.66
FA	1.0	5.9	1.22	1.54	1.6	17.5	12.69	4.45
PY	0.9	7.9	1.39	1.76	1.7	14.7	18.68	3.11
Me-FA/PY (Σ)	*	*	1.37	4.52	*	*	3.77	1.79
CPPY	0.2	5.6	0.08	0.25	0	4.8	0.24	0.63
BaA	0.5	2.9	0.60	1.32	1.0	7.8	1.28	1.31
Chr	1.1	4.0	0.38	1.18	3.1	13.8	1.90	1.26
BFA	1.4	4.9	1.35	1.57	1.8	11.7	2.45	2.94
BePY	0.7	2.4	0.57	1.14	1.1	3.9	1.04	0.95
BaPY	0.4	2.3	0.36	0.71	0.3	3.9	0.65	1.17
Pery	1.1	3.6	0.06	0.28	0.3	2.7	0.09	0.14
3-Me-CH	*	*	n.d	n.d	*	*	0.64	1.03
IcdPY	0.7	1.4	0.50	1.12	0.1	2.0	0.93	1.29
DahA	0	0.1	0.02	n.d	0	0.3	0.47	0.65
BghiP	n.ev.	n.ev.	0.91	1.78	n.ev.	n.ev.	1.55	1.68
CO	n.ev.	n.ev.	0.53	1.13	n.ev.	n.ev.	1.09	1.16
DBPY (Σ)	n.ev.	n.ev.	0.00	0.97	n.ev.	n.ev.	1.48	1.50
Total met-alkyl-PAH	5.4	19.0	3.4	7.7	13.8	53.5	31.37	8.48
TOTAL	13.4	60	15.2	26.2	24.8	136.6	141.6	35.7
[FA]/([FA]+[PY])	0.54	0.43	0.47	0.47	0.48	0.54	0.37	0.59
[IPY]/([IPY]+[BPY])	0.35	0.49	0.35	0.39	0.21	0.50	0.33	0.55

n.d: not detected, n.ev.: not evaluated, total met-alkyl-PAH: total methyl-alkylated PAH, FL: Fluorene, Phe: Phenanthrene, Ant: Anthracene, Me-PHhe/AN (S): Methyl-phenanthrene/anthracene (Sum), FA: Fluoranthene, PY: Pyrene, Me-FA/PY (S): Methyl-fluoranthene/pyrene, CPPY: Cyclopentapyrene, BaA: Benzo(a)anthracene, Chr: Chrysene, BFA: Benzo(a)fluoranthene = sum of Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)fluoranthene, BePY: Benzo(e)pyrene, BaPY: Benzo(a)pyrene, Pery: Perylene, 3-Me-CH: 3-methylcholanthrene, IcdPY: Indeno(1,2,3-cd)pyrene, ΔhA: Dibenzo(a,h)anthracene, BghiP: Benzo(ghi)perylene, CO: Coronene, DBPY (Σ): Dibenzopyrene = ΣDibenzo(a,l)pyrene + Dibenzo(a,e)pyrene + Dibenzo(a,i)pyrene + Dibenzo(a,h)pyrene).

BaPE was calculated by using the following formula, drawn from the National Toxicological Committee for Italy in 1991 on the basis of carcinogenic potency studies:

$$[\text{BaPE}] = [\text{BaPY}] + 0.06 * [\text{BaAN}] + 0.07 * [\text{BF}] + 0.08 * [\text{IPY}] + 0.6 * [\text{DahA}].$$

The BaPE values in downtown Algiers in 2005–2006 ranged from 0.41 to 0.99, with the highest ones corresponding to winter samples. These values were similar to those observed previously in 1998–1999 (Yassaa et al., 2005), but lower than those recorded in Oued Smar in 1998–1999 and 2002–2003 (Ladji et al., 2007) and in urban atmosphere of Guangzhou, China (Bi et al., 2003).

The approach of “diagnostic ratios” between selected PAH congeners (DR_{PAH}) was attempted in the aim of drawing information about the nature of airborne particulates sources in Algiers. This approach relies on the peculiarity of ratio rates with respect to the kind of emission and the concurrent influence of atmospheric reactivity versus target pollutants. Unfortunately no DR_{PAH} exists, so peculiar and even so independent of ambient conditions, to certainly identify the PAH source; this is the reason why recently some criticism has been moved to that methodology. Nevertheless, the use of more DR_{PAH} involving congeners of similar volatility and ambient inertness allows drawing enough insights to distinguish petrogenic from wood and coal-associated fuels, and concerning the aging of air parcels holding particulates. For instance, $[\text{FA}]/([\text{FA}]+[\text{PY}])$ rates close to 0.40, 0.48, 0.55, 0.67, and 0.9 were calculated for electric power plant, motor vehicle, biomass burning, coke plant, and urban refuse incinerator exhausts, respectively. In Oued Smar samples of 2002–2003, the ratio $[\text{FA}]/([\text{FA}]+[\text{PY}])$ was around 0.37 and 0.55 in summer and in winter, respectively.

Thus, it was similar to that of the tailpipe emission, especially from old motor vehicles and very close to that of biomass burning. This seems to indicate that while self-combustion of mixed wastes remains the main source of PAH, the influence of the automobile source (trucks and machines used in the landfill) onto the Oued Smar ambient air cannot be neglected. Several studies reported that the ratio of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) ($[\text{IPY}]/([\text{IPY}]+[\text{BPE}])$) depends upon the kind of combustion source. Documented values of this ratio are 0.18 for gasoline exhausts, 0.37 for diesel particulates, 0.56 for coal soot, and 0.62 for wood-burning emissions (Gogou et al., 1996). In downtown Algiers the recent value (2005–2006) of the $[\text{IcdP}]/([\text{IcdP}]+[\text{BghiP}])$ ratio was all-the-time equal to 0.36 ± 0.3 , emphasizing the importance of diesel emissions in Algiers atmosphere. This finding was further confirmed by the rates calculated for the fluoranthene/(fluoranthene+pyrene) $[\text{FLT}]/([\text{FLT}] + [\text{PY}])$ ratio (Cincinelli et al., 2007), equal to 0.46 ± 0.02 in downtown Algiers in 2005–2006 investigations.

42.3.3 Nitro-polycyclic aromatic hydrocarbons (NPAH)

The oxidative capacity of the atmosphere of Algiers is mirrored somewhat by the presence of 2-nitrofluoranthene (2-NFA) and 2-nitropyrene (2-NPY) reported in Table 42.3. This finding confirms also the ubiquitous occurrence of these two 2-NPAH in the troposphere, while the absence or rather low levels of 1-nitropyrene

which is directly emitted by diesel-powered vehicles and other combustion processes (Ciccioli et al., 1996) supports the idea that photochemistry is the sink way of the reactive PAH, rather than the scarce release from their emission sources.

Table 42.3 Mean 2-nitrofluoranthene (2-NFA) and 2-nitropyrene (2-NPY) concentrations (ng m^{-3} of air) in Algiers compared with those reported in other sites.

Site	2-NFA	2-NPY
Algiers urban area, Algeria		
1998–1999		
Summer	0.06	0.02
Winter	0.45	0.02
2002–2003		
Summer	0.059	n.d.
Winter	0.002	0.007
Oued Smar, Algiers, Algeria		
1998–1999		
Summer	0.02	0.01
Winter	0.31	0.01
2002–2003		
Summer	0.004	n.d.
Winter	0.046	n.d.
Bab-Ezzouar, Algiers, Algeria	1.50	n.d.
Milan, Italy (Cecinato et al., 1998)	0.55	0.12
Rome, Italy (Cecinato et al., 1998)	0.28	0.13
Naples, Italy (Ciccioli et al., 1996)	0.10	0.06
Montelibretti, Italy (Ciccioli et al., 1996)	0.09	0.02
C.Porziano, Italy (Ciccioli et al., 1996)	0.06	0.01
Barcelona, Spain (Bayona et al., 1994)	0.12	0.02
Madrid, Spain (Ciccioli et al., 1996)	0.07	0.02
Athens, Greece (Marino et al., 2000)	0.09	0.06
Birmingham, UK (Dimashki et al., 2000)	0.22	n.ev.
Paris, France (Wortham et al., 1990)	0.22	n.ev.
Vienna, Austria (Schneider et al., 1990)	0.30	n.ev.
Zabre, Poland (Warzecha, 1993)	0.35	n.ev.
Claremont, CA, USA (Zielinska et al., 1989)	0.41	0.05
Torrance, CA, USA (Arey et al., 1989)		
Night-time	0.32	0.03
Daytime	0.28	0.04
Deer Park, TX, USA (Wilson et al., 1995)		
Autumn	0.07	n.ev.
Winter	0.02	n.ev.

As displayed in Table 42.3, the levels of these 2-nitroarenes are somehow comparable to those measured in different sites around the world having different typologies. This suggests that gas-phase reactions were so pronounced that their formation starting from their parent PAH was promoted. In fact, so far it has consistently reported by literature that 2-NFA and 2-NPY are lacking in the direct emissions and their occurrence in the atmosphere can be solely explained by in situ generation through a two-step gas-phase reaction comprising (i) the addition of an OH or NO_3 radical at position 1 of the parent PAH, followed by (ii) a further NO_2 fixation onto position 2, and (iii) loss of water or nitric acid, giving rise to NPAH derivative. Finally the products formed are rapidly adsorbed onto

suspended particles (Ciccioli et al., 1996). The ratio of 2-NFA versus 2-NPY has been used to assess the importance of daytime against nighttime formation mechanisms of nitrated PAH. In this respect, laboratory studies reported (Ciccioli et al., 1996) that ratios close to 10 are representative of OH radical-initiated reactions developing at the light, while figures approaching 100 are related to the formation at the dark, promoted by NO₃ radicals. Values of this ratio always below 10 found in Algiers highlight the prevalence of daytime nitration of PAH initiated by OH radicals.

42.4 Conclusions

Long-term study of organic compounds in the particles suspended in the atmosphere was conducted in Algiers city area from 1998 to 2006. Wide year-time modulations were observed which is mostly attributed to rapid growth of population in Algiers and hence fast increase in traffic road in one hand and the emission from industrial installations, on the other hand. The year-time variability of organic aerosol composition in the biggest waste landfill of Algiers located in Oued Smar, Algiers, was influenced by the meteorological conditions in addition to rate and nature of waste deposited and burnt day-by-day into the landfill.

Combining the results of diagnostic ratios of PAH, the distribution profiles of linear-chain alkenes and carbon preference index (CPI) for the whole period, it was concluded that

- the automobile exhaust emissions are the main source of particulate organic matter in downtown Algiers;
- the year-time dependence of organic fraction content of aerosol in Algiers appeared to be related to average meteorological conditions which led *n*-alkanes and PAH to be present at pronounced levels during the cold season;
- the distribution profiles of linear-chain alkenes in the waste landfill indicated that they were of petrogenic origin, although some contribution derived from other anthropogenic sources including tire burning-dust; and
- the incomplete combustion of mixed organic material (whose nature could be fully determined) was recognized as a source of PAH.

The results obtained in this work indicate that the traffic road and municipal waste landfill of Oued Smar are the most important sources of organic aerosols affecting the Algiers city air.

References

- Arey, J, Atkinson, R, Zielinska, B, McElroy, PA (1989) Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical smog pollution episode in Glendora, California. *Environmental Science and Technology* 23: 321.
- Bi, XH., Sheng, GY, Peng, PA, Chen, YJ, Zhang, ZQ, Fu, JM (2003) Distribution of particulate and vapor phase *n*-alkenes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmospheric Environment* 37: 289.
- Cecinato, A, Ciccioli, P, Brancaleoni, E, Zagari, M (1998) PAH and NPAH in urban atmosphere of Rome and Milan. *Annali di Chimica* 88: 369.
- Charlson, RJ, Schwartz, SE, Hales, JM, Cess, RD, Coakley, JA, Hansen, JE, Hoffman, DJ (1992) Climate forcing by anthropogenic aerosols. *Science* 255: 423.

- Ciccioli, P, Cecinato, A, Brancaleoni, E, Frattoni, M, Zacchei, P, Miguel, AH, Vasconcellas, PC (1996) Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. *Journal of Geophysical Research* 101(19): 567.
- Cincinelli, A, Del Bubba, M, Martellini, T, Gambaro, A, Lepri, L (2007) Gas-particle concentration and distribution of n-alkenes and polycyclic aromatic hydrocarbons in the atmosphere of Prato, Italy. *Chemosphere* 68: 472.
- Cincinelli, A, Mandorlo, S, Dickhut, RM, Lepri, L (2003) Particulate organic compounds in the atmosphere surrounding an industrialised area of Prato, Italy. *Atmospheric Environment* 37: 3125.
- Dimashki, M, Harrad, S, Harrison, RM (2000) Measurements of nitro-PAH in the atmospheres of two cities. *Atmospheric Environment* 34: 2459.
- Dockery, DW, Pope, CA, Xu, X, Spengler, JD, Ware, JH, Fay, ME, Ferris, BG, Speizer, FE (1993) An association between air pollution and mortality in six US cities. *New England Journal of Medicine* 329: 1753.
- Guo, ZG, Sheng, LF, Feng, JL, Fang, M (2003) Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China. *Atmospheric Environment* 37: 1825.
- Manoli, E, Kouras, A, Samara, C (2004) Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* 56: 867.
- Marino, F, Cecinato, A, Siskos, PA (2000) Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere* 40: 533.
- Rogge, WF, Mazurek, MA, Hildemann, LM, Cass, GR (1993) Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmospheric Environment* 27: 1309.
- Scneider, E, Krenmayr, P, Varmuza, K (1990) *Monatshefte fur Chemie* 121: 393.
- Sharma, DN, Sawant, AA, Uma, R, Cocker, DR (2003) Preliminary chemical characterization of particle-phase organic compounds in New Delhi, India. *Atmospheric Environment* 37: 4317.
- Yassaa, N, Meklati, BY, Cecinato, A (2005) Organic pollutants in airborne particulates of Algiers city area. In *Environmental Chemistry, Green Chemistry and Pollutants in Ecosystems*, edited by E. Lichtfouse, J. Schwarzbauer and D. Robert Editors. Springer-Verlag, Berlin, Germany, pp. 371.
- Zielinska, B, Arey, J, Atkinson, R, Winer, AM (1989) *Atmospheric Environment* 23: 223.
- Warzecha L (1993) *Chemica Analytica* 38: 303.
- WHO (1987) Polynuclear aromatic hydrocarbons (PAH). In *Air Quality Guidelines for Europe*. WHO Regional Publications, European Series N°23. World Health Organization, Geneva, pp. 105–117.
- Wilson, NK, McCurdy, TR, Chuang, JC (1995) Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmospheric Environment* 29: 2575.
- Wortham, HM, Masclet, PA, Mouvier, G (1990) Nitro PAH formulation in atmosphere: gaseous and particulate phases. *Analytical method, Analysis* 18: 536.

Removal of Cu^{2+} and Ni^{2+} from Aqueous Solution by Algerian Clay Materials

Soraya Dib, Ali Khouider and Makhlouf Boufatit

43.1 Introduction

Numerous studies illustrate the important role of material clays as adsorbents for removal of hazardous organic pollutants and of heavy metal ions from wastewater, (Boufatit et al., 2007; Jaynes et al., 1991; Khazali et al., 2007; Kocaoba et al., 2007; Kwon et al., 2001; Sheng et al., 2001; Uribe et al., 2002). Adsorption of heavy metals onto clay minerals is one of the interests in the adsorption of metal ions for recovery purposes, because of its simplicity and efficiency (Kocaoba et al., 2007). The removal of heavy metals from industrial wastewater, which are hazardous and potentially toxic to the environment, remains a challenge and constitutes a difficult problem.

In this study, the Algerian bentonite clay type was chosen and used as adsorbent for removal of pollutants from wastewater and equilibrium studies of Cu^{2+} and Ni^{2+} adsorption onto clay have been investigated. The experimental results obtained in this study show that the adsorption efficiency was dependent on a number of factors: solution pH, amount clay, shaking time, concentration of Cu^{2+} , and Ni^{2+} . The aim of this work was to study the adsorption of heavy metals from aqueous solutions onto clay by means of low-cost materials and basic methods. The use of local material clay for removing heavy metal ions such as Cu^{2+} and Ni^{2+} from industrial wastewater is the topic of the present study.

43.2 Materials and Experimental Methods

43.2.1 Instrumentation

A Varian type SAA-110, flame atomic absorption spectrometer, instrument with deuterium background corrector was used. All measurements were carried out in air/acetylene flame. The operating parameters for working elements were set as recommended by the manufacturer.

- A pH meter, of type Cyber Scan pH 500, was employed for measuring pH values in aqueous phase.
- A mechanical shaker of type Janke, Hunkel Ika. Werk (KS 500).

43.2.2 Reagent and solutions

All chemicals used in this work were of analytical reagent grade and were used as delivered (without further purification). These are obtained from: NaOH, $M = 40$ g/mol (Carlo Erba 98%); KOH, $M = 56.11$ g/mol (Fluka 99.5%); HCl, $M = 36.5$ g/mol (Merck, 37% pa, $d=1.18$); CuCl₂, $M = 134.45$ g/mol (Fluka, 97%); Ni SO₄ 6H₂O, $M = 262.86$ g/mol (Merck, pa, 99%). The elements standard solutions used were prepared with distilled water.

43.2.3 Characterization of Algerian clay

The natural clay used in this study was an Algerian montmorillonite, a bentonite type from Mostaganem (NW Algeria). It was kindly supplied by ENOF (a Ltd Algerian Betonies Company). The specific surface analysis was found to be 52 m²/g by using analyzer (Micromeritics ASAP 2020 equipment, using N₂ as an adsorptive). The procedures for treatment and purification of this material clay were prepared according to literature methods (Olphen, 1963). The chemical and mineral compositions were determined. It was composed of 55–65 % SiO₂ ; 12–19 % Al₂O₃; 0.5–1.8 % K₂O ; 2–3 % MgO; 0–2 % Fe₂O₃; 1.5–5.5 % CaO ; 1–3 % Na₂O (Internal study – ENOF, 2007).

The ignition loss of the clay at 1000 °C was found to be 7.5% (w/w). The other characteristics were found to be: the humidity, 15%; the swell, 0.8%; and viscosity, 15 cp min.

43.3 Results and Discussion

43.3.1 Characterization of clay

In this study, we have examined an Algerian clay mineral montmorillonite, a bentonite type, from Mostaganem (NW Algeria).

43.3.1.1 XRD Study

X-ray diffraction patterns were obtained using a Philips PW 1730 diffractometer equipped with Cu-K α radiation (40 kV, 30 mA). The X-ray diffraction patterns of the sample clays in the purified fraction confirm the characteristics of montmorillonite type. It shows quartz impurities, (Fig. 43.1).

43.3.1.2 Infrared Spectroscopy Study

The FT-IR spectra of natural and treated bentonite clays with HCl acid (different concentrations) were obtained in the region 4000–500 cm⁻¹ by using FT-IR Spectrometer, type Perkin Elmer Spectrum one model, at room temperature dispersed in KBr discs, (Fig. 43.2).

IR data are reported in Table 43.1. The characteristic peaks of the bentonite clays used in this study and the detailed vibrational frequencies with possible as-

signments being given are obtained from studies by Ledoux et al. (1964), Van der Marcel et al. (1979), and Slosiarikova et al. (1992).

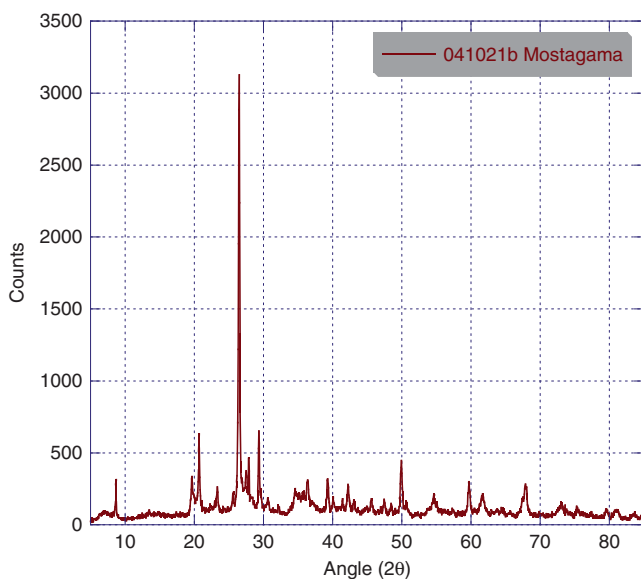


Fig. 43.1 X-ray diffraction patterns of the bentonite clay without any specific treatment.

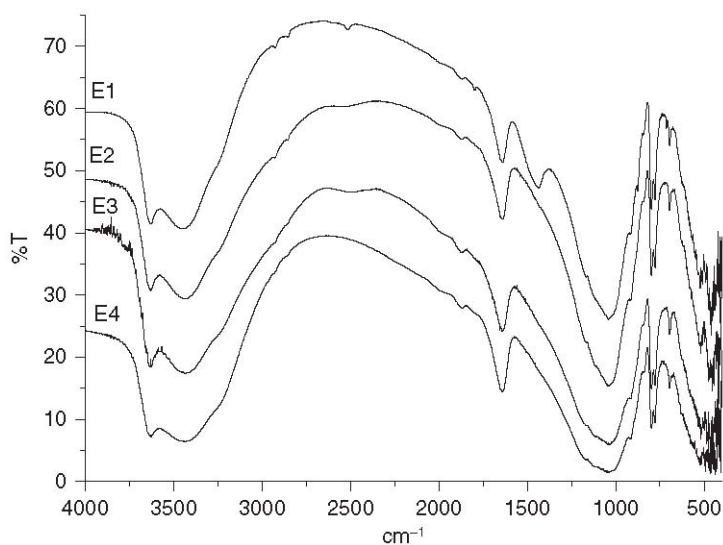


Fig. 43.2 Compared infrared spectra of clay material untreated and treated with HCl (*E1*: untreated; *E2*: HCl, 0.01 M; *E3*: HCl, 0.05 M; *E4*: HCl, 0.1 M).

As we can see, all products exhibit two moderately intense bands between 3624.64 and 3450.33 cm^{-1} , which might be ascribed to the stretching frequencies of the OH functional groups of co-ordination water and of the hydration OH stretching. The absorption peaks between 1642.52 and 1635.53 cm^{-1} can be taken as both due to OH stretching vibration and $\delta(\text{H}_2\text{O})$ deformation. The rest of the bands between 1064.98 and 522 cm^{-1} in all samples are due to stretching vibration of Si–O, Si–O–Si, OH attached to (Al^{3+} , Fe^{3+} , and Mg^{2+}) groups, and the silica quartz impurities. The main changes found after acidic treatment, reported in Table 43.2, are the shift of absorption of some peaks.

Table 43.1 Compared infrared spectra of natural and treated with HCl bentonite clays.

E.1	E.0.01	E.0.05	E.2	E.3	Assignments
3624.64	3630.25	3630.25	3624.64	3630.25	OH functional group of coordination water
3450.33	3438.53	3433.93	3446.54	3435.59	Hydration OH stretching
2515	2504.20	–	–	2492.99	Impurities
1642.52	1640.53	1640.21	1637.12	1640.52	(H_2O) deformation
1041.86	1042.05	1038.74	1040.62	1033.28	Stretching vibration of Si–O, Si–O–Si, and Al–O
914.68	914.68	914.68	914.68		OH deformation attached to Fe^{3+} , Al^{3+} , and Mg^{2+}
7798.47	798.60	797.33	798.25	798.66	Vibration of Si–O, Si–O–Si and Al–O
777.62	777.62	777.62	777.62	777.62	Vibration of Si–O, Si–O–Si and Al–O
693.00	693.00	693.00	693.00	693.00	Silica quartz impurity
523.26	522.78	506.99	517.48	514.68	Silica quartz impurity

Table 43.2 Compared infrared spectra of natural and treated with HCl bentonite clays.

E.1	E. 0.01	$\Delta\nu$	E.0.05	$\Delta\nu$	E.2	$\Delta\nu$	E.3	$\Delta\nu$
3450.33	3438.53	11.80	3433.93	16.40	3446.54	3.79	3435.59	14.74
1642.52	1640.53	1.99	1640..21	2.30	1637.12	5.40	1640.52	2.00
1041.86	1042.05	–0.19	1038.74	3.12	1040.62	1.24	1640.52	8.58
798.47	798.60	–0.13	797.33	1.44	798.25	0.22	798.66	–0.19
523.26	522.78	0.48	–	–	–	–	–	–

E.1: natural clay; E. 0.01: clay treated with HCl, 0.01M; E.0.05: clay treated with HCl 0.05M (E.2; E.3): clay treated with HCl, 0.1M

43.3.1 Effect of shaking time

An adsorption kinetic study was carried out for both natural and treated clays by adding 1 g of the clay material to 50 mL of solution with fixed concentration of

Cu^{2+} and Ni^{2+} . Each experiment was repeated two times. The suspension in different conical flasks was then shaken at room temperature and the concentration of the supernatant of metal ions was determined using SAA method with an accuracy of 0.5 and 0.3–0.4% Cu^{2+} and Ni^{2+} , respectively. The removal percentage increases with the increasing shaking time (Fig. 43.3). The optimum metals adsorption percentages were constant at 80.59% and 93.25% at 30 min for Cu^{2+} and Ni^{2+} , respectively. Thus 30 min of shaking time was chosen as the optimum time for studying both nickel and copper. The adsorption percentage (Removal %) was calculated as:

$$\text{Removal (\%)} = \left(\frac{C_o - C_e}{C_o} \right) \cdot 100 \quad (43.1)$$

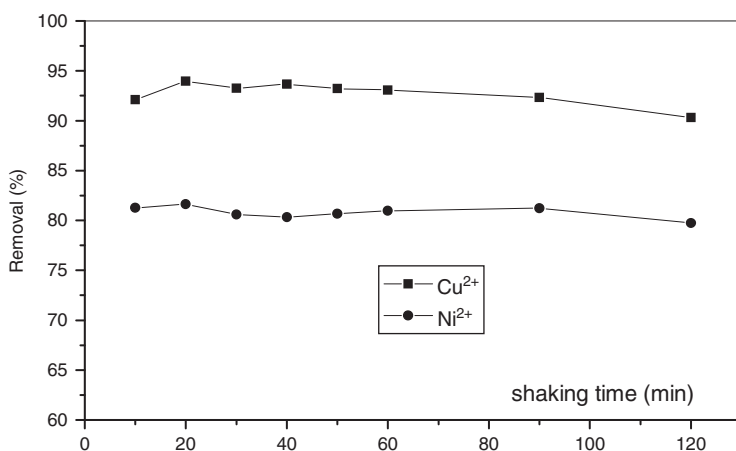


Fig. 43.3 Effect of shaking time on removal of Cu^{2+} and Ni^{2+} (metal concentration: 10 mg/L; pH: 3; V : 50 mL; T : 25°C).

43.3.2 Effect of pH

Figure 43.4 illustrates the effect of pH on removal of heavy ions by natural clay. The effect of pH on the adsorption of Cu^{2+} and Ni^{2+} was investigated at pH values 1–6. The adsorption of these metal ions from aqueous solution is remarkably influenced by the pH values in the range from 1 to 6 (obtained with a pH - meter of Cyber Scan type pH 500, prepared and adjusted by using either HCl acid or NaOH solutions).

The adsorption percentage was increased in the range of pH: 1–4 to reach 96.26% at pH 4 for copper. This maximum is 91.21% at pH 5 for nickel. The pH values 4–6 were chosen as the optimum for studying of all metals in avoidarder to precipitation of metals which limits the process greatly and the adsorption of metal

ions on clay is difficult to be quantified at pH greater than 6. Therefore, the pH 4.5 and 5 were selected for all further studies of copper and nickel, respectively.

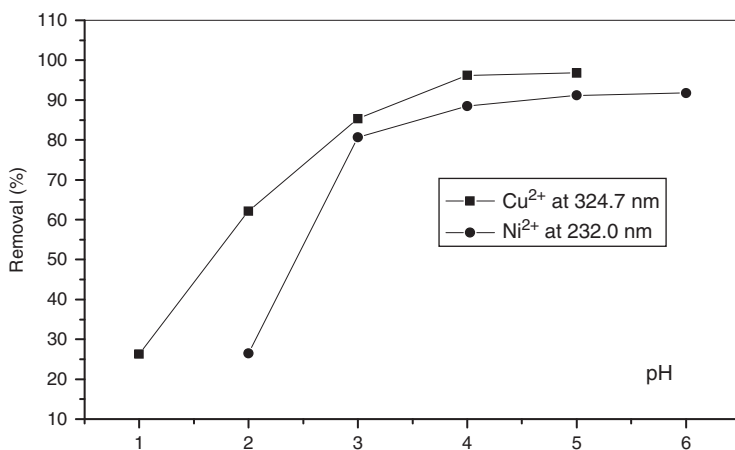


Fig. 43.4 Effect of pH on the removal of Cu²⁺ and Ni²⁺ (metal concentration: 10 mg/L; shaking time: 2 h; *V*: 50 mL; *T*: 25°C).

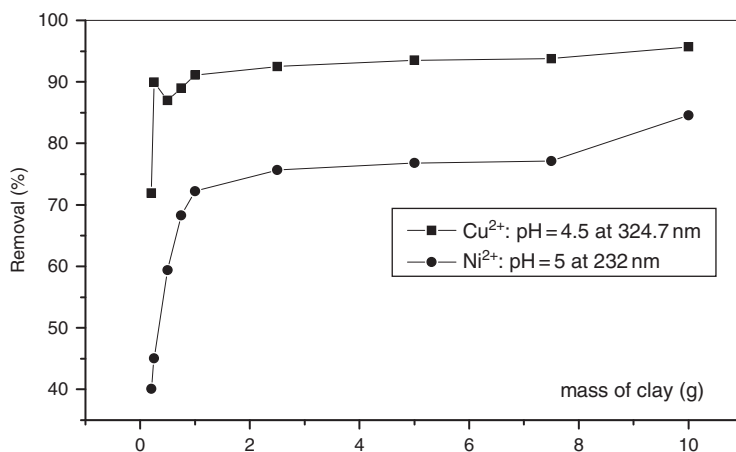


Fig. 43.5 Effect of dosage of Algerian clay on the removal of Cu²⁺ and Ni²⁺ (metal concentration: 10 mgL⁻¹; shaking time: 2 h; *V*: 50 mL; *T*: 25°C).

43.3.3 Effect of mass of clay

The adsorption of metal ions on the natural bentonite clay amount was studied on variable mass of clay from 0.25 to 10 g in constant solution volume of 50 mL with 2 h stirring time.

The effect of clay amount on metal ions removal is shown in Fig. 43.5. The result indicates that the adsorption percentage increased with the increasing amount of the bentonite clay in the two cases of clay–metal interactions. This adsorption percentage was constant at higher amounts than 2 g. The optimum metals adsorption percentages were 92.5% and 75% for Cu^{2+} and Ni^{2+} , respectively.

43.4 Conclusions

In this study, the experimental results suggest that Algerian bentonite clay can be used for the adsorption of Cu^{2+} and Ni^{2+} from aqueous solutions. The availability and the low cost of this material clay make it a good candidate in adsorption processes for use in water treatment and purification. These results have shown that different experimental parameters such as solution pH, shaking time, and amount of clay must be optimally selected to obtain the highest percentage of adsorbent of Cu^{2+} and Ni^{2+} from aqueous solutions using Algerian bentonite clay.

References

- Anonymous (2007) Internal study – ENOF Subsidiary, Algerian Bentonite Co. (Bental).
- Boufatit, M, Ait Amar, H, McWhinnie, WR (2007) Development of an Algerian material montmorillonite clay. Adsorption of phenol, 2-dichlorophenol and 2, 4, 6-trichlorophenol from aqueous solutions onto montmorillonite exchanged with transition metal complexes. *Desalination* 206: 394–406.
- Boufatit, M, Ait-Amar, H (2007) Removal of N, N-dimethylaniline from dilute aqueous solution by Na^+/K^+ saturated montmorillonite. *Desalination* 206: 300–310.
- Jaynes, WF, Boyd, SA (1991) Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals* 39 (4): 428–436.
- Khazali, O, Abu-El-Halawa, R, Al-Sou'od, K (2007) Removal of copper (II) from aqueous solution by Jordanian pottery materials. *Journal of Hazardous Materials* 139 (1): 67–71.
- Kocaoba, S, Orhan, Y, Akyuz, T (2007) Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. *Desalination* 214: 1–10.
- Kwon, OY, Park, KW, Jeong, SY, (2001) Preparation of porous silica-pillared montmorillonite: simultaneous intercalation of amine-tetraethylorthosilicate into H-Montmorillonite and intra-gallery amine-catalyzed hydrolysis of tetraethylorthosilicate, *Bulletin Korean of Chemical Society* 22 (7): 678–684.
- Ledoux, RL, White, JL (1964) Infrared study of selective deuteration of kaolinite and halloysite at room temperature. *Science* 145: 47–49.
- Marcel, Van der HW, Spacher, HB (1979) Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier, Amsterdam, 275–276.
- Olphen, HV (1963) An introduction to clay colloid chemistry. App. I: Preparation of clay suspensions, Interscience Publishers, John Wiley and Sons, N.Y, London, pp 239–243.
- Sheng, G, Johnston, CT, Teppen, BJ, Boyd, SA (2001) Potential contributions of smectite clays and organic matter to pesticides retention in soils. *Journal of Agricultural and Food Chemistry* 49(6): 2899–2907.

Slosiarikova, H, Bujdak, J, Hlauaty, V, (1992) IR spectra of octadecylammonium-montmorillonite in the range of Si-O vibrations. *The Journal of inclusion phenomena and molecular recognition in chemistry* 13(3): 267–272.

Uribe, A, Bishop, PL, Neville, GP (2002) The influence of pH and temperature changes on the adsorption behaviour of organophilic clays used in the stabilisation/solidification of hazardous wastes. *Journal of Environmental and Engineering Science* 1: 123–133.

Health Impacts of Heat Waves of 2007 in Hungary – Background and Experiences

Anna Paldy and Janos Bobvos

44.1 Introduction

In the second half of July 2007 a record breaking heat wave arrived in Central–Eastern Europe. For Hungary it was the ever recorded longest and hottest heat wave concerning both daily maximum, minimum, and mean temperature. During the summer 2007 there was a milder heat wave between June 19 and 23, between July 16 and 24 an extremely intensive heat wave affected the country, and the last heat wave affecting only some parts of the country arrived to Hungary between August 23 and 26.

Hungary took part in the PHEWE (Phewe, 2002–2005) project funded by the EC FP6 framework program. The aim of PHEWE project was to study the association of temperature and mortality – in the frames of this project Hungary’s task was to develop a heat health watch warning system under the guidance of the Chair of Climatology of the University of Birmingham. Since 2005 Hungary participated in the EuroHeat (Euroheat, 2005–2007) project funded by the Public Health Program of the EC. This project offered possibilities to further develop the heat alert system and to elaborate the recommendations for adaptation measures to help decrease the health impact of heat.

Heat wave was defined by evaluation of a time series of daily weather and mortality data of Budapest for 31 years (1970–2000). The three-level heat alert system is based on these estimates (Paldy et al., 2006). International literature data and the EuroHeat working group recommended collecting real time mortality data to monitor the impact of heat during heat waves. Based on the heat plan of Hungary (Bujdosó et al., 2006), the chief medical officer ordered for the Central Hungarian Institution of the National Public Health and Medical Officers’ Service to collect real time mortality data from general practitioners and from hospitals in the Central Hungarian Region (CHR). Based on these data the impact of heat waves could be estimated for the summer period in 2007. The comparison of the mortality prediction based on the risk estimates of the time series analysis of 1970–2000

data with the mortality–temperature relationship of 2007 could help answer whether the excess mortality of the 2007 heat waves fell in the range projected by using the risk estimate of the temperature mortality association of the 31 years’ time series.

44.2 Data and Method

Daily maximum, minimum, and mean temperature data were supplied by the National Meteorological Service. The data of an outskirt and a downtown sampling site were used in the analysis. Population data were gained from the Central Statistical Office, the number of population in the CHR is 1 697 724 in Budapest and 1 150 926 in County Pest.

Mortality data were collected by the Central Hungarian Institution of the National Public Health and Medical Officers’ Service and were forwarded to the National Institute of Environmental Health in Budapest. During the July heat wave mortality data were collected every day, out of this period they were collected from general practitioners weekly between June 1 and August 31, 2007. Thirty-five capital institutions and 11 hospitals of County Pest provided daily crude mortality data. These data contain some uncertainty due to administrative reasons, the exact analysis can only be carried out in the second half of 2008 when the Central Statistical Office provides the exact number of daily mortality stratified by age, gender, and cause of death.

Temperature and mortality data were first analyzed by descriptive statistical methods. Excess mortality was compared to “a baseline” mortality – to the mean mortality of cool days of the summer period defined above. Excess mortality is the difference between the observed mortality of a given day and the mean mortality of cool days. It was separately counted for death cases in hospitals and out of hospitals. The time series of mortality of the summer period allowed assessing “the harvesting” effect (short term mortality displacement after the heat wave). Using the collected mortality data of the Central Hungarian Region and relying on the association established we attempted to assess the rate of excess mortality for the whole country. The association between daily mortality and daily mean temperature was assessed using the data of 92 days of the summer period of 2007 by generalized additive regression model (GAM). The estimates related to Budapest were compared to that of the previous results of 1970–2000.

44.3 Results and Discussion

44.3.1 Characterization of temperature

The temperature data of the previous years are summarized in Table 44.1. By using the temperature data of the outskirt measuring site of Budapest (Pestszent-lorinc): summer mean temperature was the highest in the year of 2003 concerning the last 5 years, from 2005 the mean temperature showed a slight increase and in

2007 its value was close to that of 2003. Maximum temperature (41°C) was the highest in 2007 (highest ever recorded in Budapest). Days with daily mean temperature over 30°C were recorded for the first time in Hungary also in the year of 2007. The number of heat waves (when daily mean temperature exceeded 25°C at least on three consecutive days) and the number of days during the heat wave were the most in the last 2 years (5 and 3, respectively, 30 and 19 days).

Table 44.1 Summer temperature and related data in Budapest 2003–2007.

	2003	2004	2005	2006	2007
Summer mean temperature (°C)	23.6	20.8	20.5	21.5	23.3
Summer maximum temperature (°C)	39	34	35	37	41
Number of days with mean temperature. <25 °C	44	82	78	51	46
Number of days with mean temperature. >25 °C	35	8	9	30	29
Number of days with mean temperature. >27 °C	13	2	5	11	12
Number of days with mean temperature. >30 °C	0	0	0	0	5
Number of heat waves	2	1	1	5	3
Number of days of heat waves	11	4	5	30	19

Concerning time series of temperature, long lasting heat periods occurred in the second half of July, there was a heat wave in nearly each year in this period. There were more heat waves in warmer years; however, the number of heat waves is defined by the distribution of hot days. In the warmest year in 2003, there were less extreme hot days than in the years with lower summer mean temperature of 2006 and 2007.

Comparing the temperature data of the outskirt (Pestszentlőrinc) and the downtown in 2007, no difference could be observed in the daytime maximum temperatures, for the whole summer period the difference was only 0.2°C for the outskirt station. However, the difference was higher in the minimum temperatures, the downtown minimum temperature was by 1.2°C higher on average than in the outskirt. The biggest difference was recorded during the hottest days of the heat wave. Due to the different variation in daily temperature, the summer mean temperature was by 0.5°C higher, it was 23.8°C measured in the downtown. During the 5 days of the first heat wave the daily maximum temperature was 35°C; the mean was 25.9°C. During the 10 days period of the July heat wave the daily maximum temperature was over 40°C, the mean was 29.9°C. Within the 10 days period, daily mean temperature was over 30°C for 5 days. The highest minimum temperature was measured on July 20 (24°C), the highest mean (32°C) and daily maximum temperature (41°C) were recorded on the following day, on July 21. During the 4-day-long heat wave in August the daily maximum temperature was 35°C and the mean of the 4 days' temperature was 27°C.

44.3.2 Mortality rates and excess mortality due to extreme high temperature

Mortality shows a seasonal variation, highest during wintertime and lowest during summer. Mortality is higher in January by 9–10% than the yearly mean, while lowest mortality is recorded in July and August; the mean difference is around 10%. Mortality data of the period studied are summarized in Fig. 44.1. The mean daily mortality of the region – based on the reported data was 84.5 death cases, out of which 64.9 deaths occurred in Budapest and 199.6 cases in County Pest, which meant 2.96 cases per 100 000 inhabitants in the region, 3.82 cases in Budapest and 1.17 cases per 100 000 in County Pest. A difference was observed also concerning the place of death: 75% of deaths occurred in hospitals in Budapest; this rate was only 57% in County Pest.

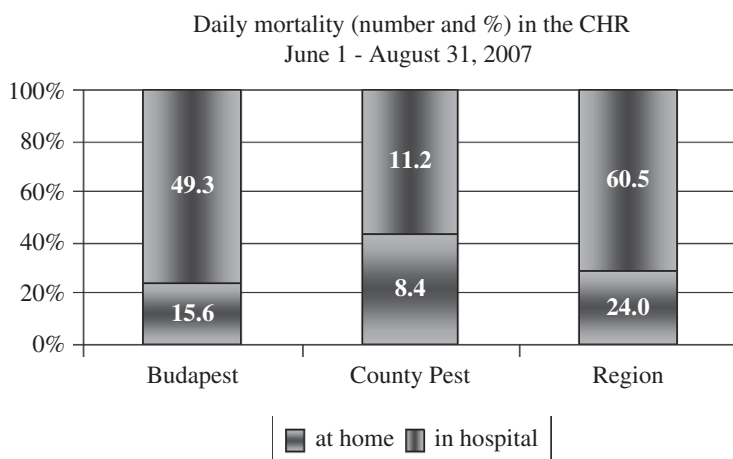


Fig. 44.1 Daily mortality in the CHR between June 1 and August 31, 2007.

Previous assessment of time series of mortality and temperature showed that summer heat is an important risk factor of mortality (Paldy, 2004). Mortality rate increases in relation to the increase of daily mean temperature (Fig. 44.2).

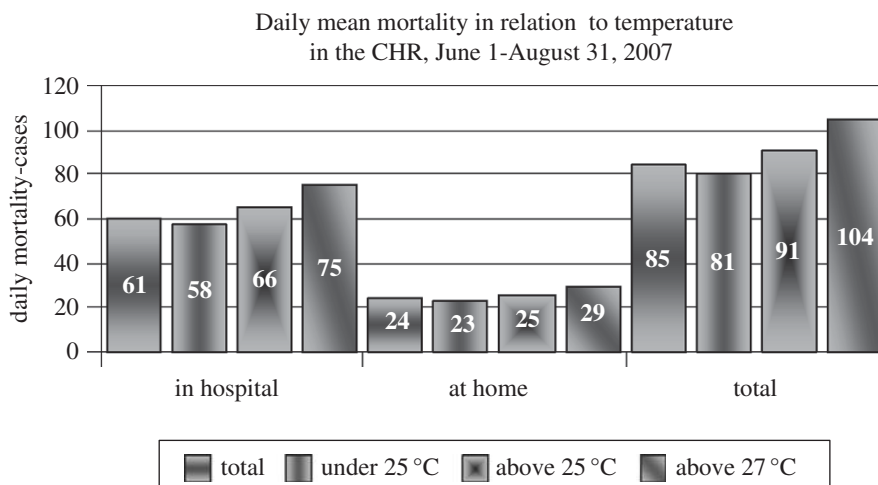


Fig. 44.2 Association of daily temperature and mortality between June 1 and August 31, 2007 in the CHR.

The slope becomes steeper with the increase of temperature. In average, mortality was by 14% higher on days when daily mean temperature was above 25°C compared to the mortality of days with mean temperature lower than 25°C, this difference was 8% concerning mortality at home. Mean mortality on days with daily mean temperature above 27°C was by 29% higher in hospitals and by 26% higher at home than on days with mean temperature lower than 25°C. The observed similar increase of mortality supports the fact that the impact of heat affects not only seriously ill patients who need hospital treatment but also other groups of population, however, to somewhat less extent.

The computation of excess mortality was based on the temperature threshold values of the first and second level of heat alert and the temperature values measured in the downtown were used. The baseline mortality was the mean mortality of days with daily mean temperature lower than 25°C. In the year 2007 the number of such “cool” days was 46, which equals to the half of the summer season. Figures. 44.3 and 44.4 show the number and percentage of excess deaths on days when the mean temperature was above 25 and 27°C (the threshold of second and third level of heat alert) as well as above 30°C – never been recorded before.

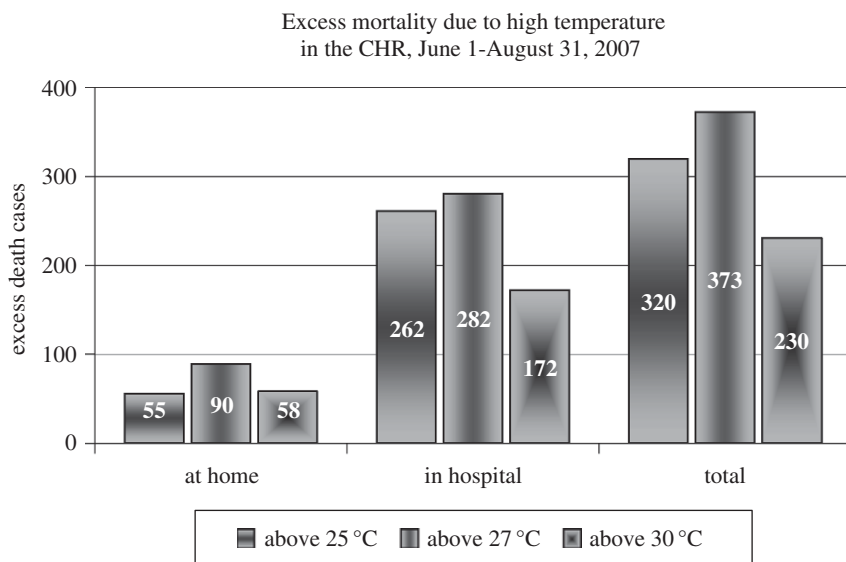


Fig. 44.3 Excess mortality due to high temperature between June 1 and August 31, 2007 in the CHR.

On days when mean temperature was above 25°C the excess mortality was 320 cases related to mean mortality on cool days. On days when the mean temperature was above 27°C excess mortality was 373 cases, and on days with mean temperature above 30°C, the excess was 230 cases. The rate of mortality was around three times higher in hospitals than out of them, this increased in relation to the increase of temperature.

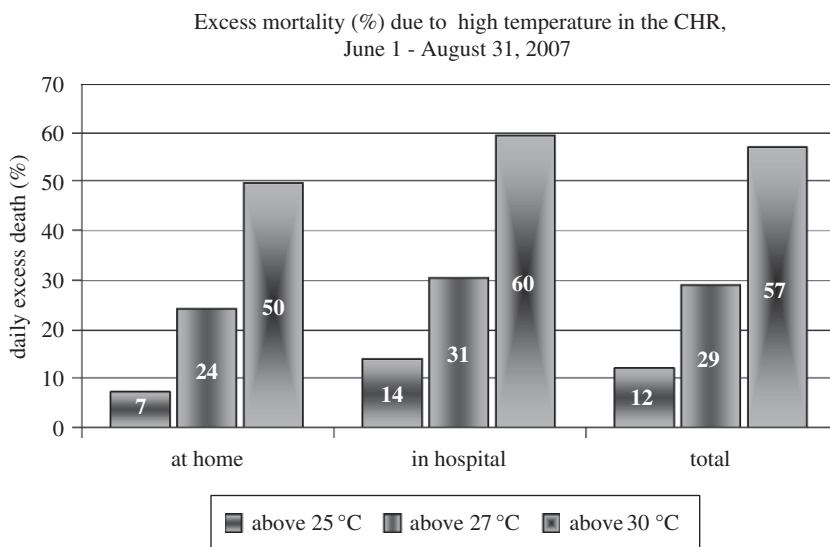


Fig. 44.4 Excess mortality (%) due to high temperature between June 1 and August 31, 2007 in the CHR.

The description of daily data can help assess the relationship between temperature and mortality. Daily death cases showed a great variation with considerable deviation (Fig. 44.5). The minimum and maximum values of mortality at home were 10 and 43 cases respectively; these values in hospital were 36 and 115 cases respectively. The mean deviance from the summer mean was 6.8 cases of mortality at home and 12.8 cases in hospital representing 28 and 21% of mean mortality, respectively. Daily death counts were above the mean mortality with the exception of 1–2 days, variation was much higher in 2 months.

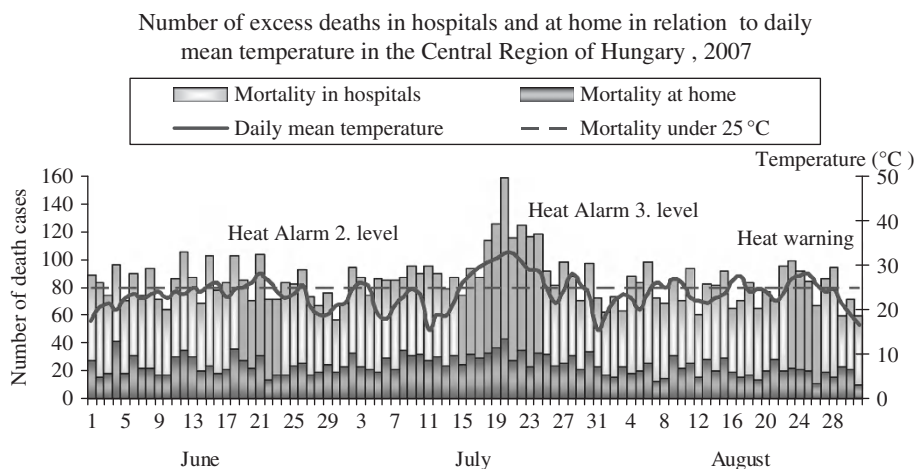


Fig. 44.5 Daily in/out of hospital death counts and daily mean temperature in CHR in 2007.

Based on the analysis of daily mortality during and after the July heat wave the following can be stated concerning mortality displacement (harvesting). A temporal decrease of daily mortality can be expected after an event (a heat wave) causing a rapid increase in mortality. The event affects the vulnerable population, and another similar event might not display an effect on the remaining resistant group of population. This could result in a temporal decrease of daily mortality; however, such an effect cannot be detected in the mortality data after the July heat wave. After the heat wave, the number of death cases remained in the range of daily variation. The minimum of daily mortality was recorded in a different period of the summer. The June and August heat waves did not cause an excess mortality; displacement could not be detected after these events. No harvesting effect could be seen during the summer 2007, which supported the assumption that excess mortality could be attributed to the impact of heat.

The number of excess death cases is shown in Table 44.2. The baseline value was the mean mortality of days with mean temperature under 25°C. Daily mortality slightly differed from the mean mortality of cool days during the first heat wave; it was even smaller than the mean. During the July heat wave with heat records, daily mortality significantly increased and stayed high, 278 excess cases were recorded during the 10-day period, which mean a 33% increase in daily mortality. Maximum mortality was recorded on July 20 with 43 cases at home and 115 cases in hospitals which were almost twice as much as the average counts on the cool days. During the August heat wave, affecting Central and Eastern Hungary mortality increased to a small extent, by around 1%.

Table 44.2 Excess mortality in CHR in relation to mean mortality of days with mean temperature < 25°C during 2007 heat waves.

	June 19–23 alert second level 5 days	July 15–24 alert third level 10 days	August 23–26 heat warning 4 days
Number of death cases	400	1123	341
Number of excess death cases	–22.5	278	3
Mean daily excess death cases	–4.5	27.8	0.75
Daily excess mortality (%)	–5.3	32.9	0.9

An attempt was made to estimate the rate of excess mortality for the country by considering the rates of mortality in the capital and in County Pest, the settlement structure of the country and the rate of population in different types of settlements. Assuming that association between mortality and temperature values did not differ significantly in bigger towns and in their agglomeration form that of the Central Hungarian Region, the findings valid for the Central Hungarian Region can be extrapolated for the country. During the 10 days of the heat wave, 218 excess death cases occurred in Budapest and 60 in the County of Pest (out of the 278 cases), which mean 13 and 5.2 cases, respectively, per 100 000 population.

The total number of population of the cities with more than 100 000 inhabitants is 1.6 million. Excess mortality in these ten cities is 210 cases assuming mortality rates similar to Budapest. The population of the remaining part of Hungary is 5.55 million, where the excess mortality can be 290 cases assuming situation similar to County Pest. On this basis the total excess mortality due to the July heat wave can be 780 cases during the 10 days, corresponding to 7.8 cases per 100 000. An additional factor can also be considered based on the data of the Central Statistical Office. The rate of hospital beds is higher in the Central Hungarian Region than the national average; it is by 16% higher for 2.85 million inhabitants than elsewhere. As around 60% of excess mortality occurred in hospitals, this is by 10% higher in the Central Hungarian Region than in other parts of the country, meaning an excess of 28 death cases. If the number of excess cases is corrected by this number on national level, then the total number of excess might be 730 cases.

44.3.3 Comparison of the previous and present associations of daily mortality and temperature

Based on international literature data and national assessment, a nonlinear association can be stated between temperature and mortality in different temperature ranges in the countries with moderate climate. The association is U shaped in Budapest (Paldy, 2005a), mortality increases in both the low- and high- temperature ranges. The optimal or threshold temperature differs in different populations in relation to the adaptation capacity to local weather conditions. The slope of mortality steeply increases in relation to temperature increase. We wanted to investigate whether the association changed in 2007, when a heat health-warning system was in operation; the extreme weather had a different impact as it was observed in the time series of 31 years.

In the previous studies the permanent population of Budapest was studied, the data of 2007 related to the Central Hungarian Region. In order to compare the effect, the analyzed data were restricted to the death cases that occurred in Budapest (in and out of hospital) and the daily death counts were adjusted to the number of the population of the capital which allowed the assessment of differences expressed in percentage. Plotting the curves of nonlinear association in the same graph, the major characteristics can be examined (Fig. 44.6).

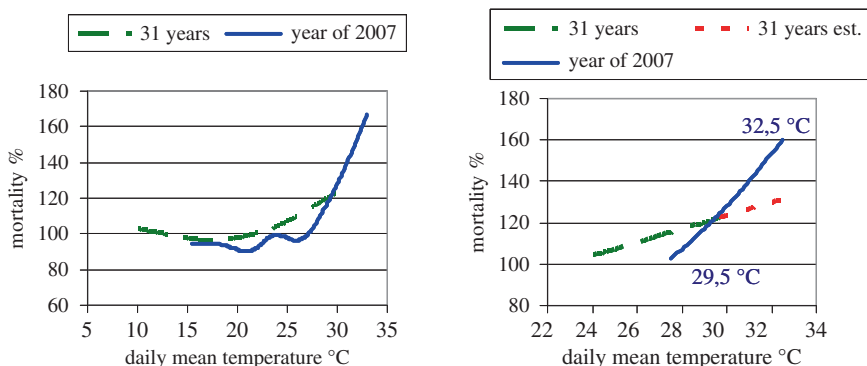


Fig. 44.6 Association of daily mean temperature and mortality in Budapest between 1970–2000 and in 2007.

By linearization of the part of the curve belonging to the high-temperature ranges the differences can be studied. The minimum of the curve of the time series of 31 years was around 18°C; it reached its maximum value at 29.5°C of daily mean temperature. The minimum of the curve of 2007 was above 21°C, it showed a fluctuation till 26°C then it increased steeply. In the range over 30°C, never recorded before, the association displayed an increase of mortality around 3.7 times higher (10.2 cases/1°C) than could be expected by extrapolating the results of the 31 years' analysis (2.7 cases/1°C). The 2007 observation was the first one for this temperature range, which allowed stating that excess mortality was significantly higher than it was forecast, in spite of heat alert.

The relationship of daily mortality was assessed by using the data of Central Statistical Office and permanent population of Budapest. These validated mortality data are however accessible with a considerable delay. Based on the EuroHeat project real time mortality data were collected in the Central Hungarian Region in 2007. The benefit of real time data collection is that the impact of heat wave can be promptly assessed by using mortality data submitted within 48 hours. On the other hand these are crude mortality data, do not provide information of the causes of death, and the data provision may not be complete. The results gained by the evaluation of real time data need reinforcement by analyzing the validated data of the Central Statistical Office.

The impact of heat waves on mortality is not only heat stroke but heat can affect many other disease outcomes. Excess mortality attributable to heat can be assessed by comparing mortality of hot days to a baseline mortality, e.g., to that of the cool days. There are different methods described in the literature, the baseline mortality can be a moving average of mortality of the year previous to heat wave, or the mean mortality of the same days of the previous year by applying a statistical smoothing function. The results depend on the methods applied (Whitman, 1997). The data of mortality due to heat waves and applied methods published so far in literature are summarized in Table 44.3. There are great differences of excess mortality of different heat waves, even relating to the same event. The events should be compared with caution, while not only the statistical methods are different, but the heat waves as well. The heat wave of the year 2003, for example, affected the countries in Europe to a different extent, temperature and duration were different. Similar temperature situations may cause different effect depending on the duration of the event and the adaptive capacity of the population. Heat waves of the early summer period may have a stronger effect than that of the late summer. The findings of the 2007 heat wave in Hungary are in line with this statement.

Table 44.3 Heat-wave events and attributed mortality in Europe.

<i>Heat-wave event</i>	<i>Attributable mortality (all cause)</i>	<i>Baseline measure</i>	<i>References</i>
1976–London, United Kingdom	9.7% increase England and Wales and 15.4% Greater London	31-day moving average of daily mortality in same year	McMichel A.J. and Kovats R.S. 1998
1981–Portugal (month of July)	1906 excess deaths in Portugal, 406 in Lisbon	Predicted values	Garcia A. et al. 1981
1983–Rome, Italy	35% increase in deaths in July 1983 in 65+ age group	Compared to deaths in same month in previous year	Todisco G. 1987
1987–Athens, Greece 21/7–31/7	Estimated excess mor- tality >2000	Time trend regression ad- justed	Katsouyanni K. et al. 1988
1991–Portugal 12/7–21/7	997 excess deaths	Predicted values	Nogueira P.J. and Dias C.M. 1999
1995–London, United Kingdom 30/7–3/8	11.2% (768) in England and Wales, 23% (184) Greater London	31-day moving average of daily mortality in pre- vious 2 days	Rooney C. et al. 1998
1994–The Nether- lands 19/7–31/7	24.4% increase, 1057 (95% CI 913, 1201)	31-day moving average of daily mortality in pre- vious 2 years	Huynen M. et al. 2001
2003–Italy 1/8–31/8	9704 (23.7%) through- out the country	Deaths in same period in 2002	Instituto Nazionale di Statistica (ISTAT) 2004
2003–Italy 1/6–15/8	3134 (15%) in all Italian capitals	Deaths in same period in 2002	Conti S. et al. 2005
2003–France 1/8–20/8	14 802 (60%)	Average of deaths for same period in years 2000–2002	Hemon D. and Jouglas E. 2003
2003–Portugal 1/8–31/8	1854 (40%)	Deaths in same period in 1997–2001	Bothello J. et al. 2005
2003–Spain 1/8–31/8	3166 (8%)	Deaths in same period 1990–2002	Martinez-Navarro F. et al. 2004
2003–Switzerland 1/6–31/8	975 deaths (6.9%)	Predicted values from Poisson regression model	Grize L. et al. 2005
2003–The Nether- lands 1/6 – 23/8	1400 deaths	Number of degrees above 22.3. C multiplied with the estimated num- ber (25–35) of excess deaths per degree	CBS. 2003
2003–Baden- Württemberg, Ger- many 1/8 – 24/8	1410 deaths	Calculations based on mortality of past 5 years	SBW. 2004
2003–Belgium 15/5–15/9	1297 deaths for age group over 65	Average of deaths for same period in years 1985–2002	Sartor F. 2004
2003–England and Wales 4/8–13/8	2091 (17%). Mortality in London region: 616 deaths (42% excess)	Average of deaths for same period in years 1998–2002	Johnson H. et al. 2005
2006–England and Wales, first and second heat waves	680 (6%) excess mor- tality on the second heat wave	No data available	Health Statistics Quarterly. 2006

The frequency of heat waves has been increasing since the early 1990s. Between 1992 and 2000 six heat waves arrived to Hungary, two heat waves affected the country in 1994, 1998, and 2000. Excess mortality was detected in each event, the rate was between 12% (August 1994) and 52% (June 2000). Between 2001 and 2007, 14 heat waves affected the country; excess mortality was between 17 and 32% for the years 2001–2003.

In the year of 2007, Hungary suffered the hottest heat wave ever recorded, affecting the whole country. Daily mean temperature was above 30°C for 5 days. The impact of the heat wave could not be forecast properly, while the mean temperature was always below 30°C during the previous 17 heat waves. The excess mortality was 38% during the 10 days of the July heat wave; a significant increase could be seen from the third day of the heat wave reaching a maximum on the sixth day (95%) when the night minimum temperature was the highest. In the previous, milder and shorter heat waves excess mortality increased already in the first day itself. During the July 2007 heat wave mortality did not increase in the first 3 days, but a delayed effect of heat could be observed like in Paris in 2003 (Pirard, 2005). This delayed effect was not detected in the previous milder and shorter heat waves in Hungary (Paldy, 2005b). During the first heat wave of 2007 no excess mortality could be detected, and the August event caused only a slight increase in mortality (0.9% excess). The third heat wave did not affect the whole country, as it was forecast by the National Meteorological Service, consequently there was no heat alert announced; only a warning was issued. Daily mortality did not decrease after the July heat wave and, no short time mortality displacement was observed. Further research is necessary to study years of life lost due to the impact of heat.

Real time data collected from general practitioners and hospitals allow a rapid timely evaluation of the impact. These data can, however, be compared to that of previous years with caution. However, new knowledge was gained by the evaluation of real-time data. Mortality was much higher in Budapest than in County Pest and significantly increased in those 5 days when the mean temperature was over 30°C. Mortality of urban population was higher in hospitals than at home during the heat waves. The analysis did not allow answering the question whether the patients delivered earlier to hospital died or patients hospitalized during the heat waves lost their lives. Further, the real-time data collection did not allow analyzing the data stratified by sex, age, and cause of death. Some differences may be explained by the assumption that population living in the agglomeration of the capital prefers hospitals in the capital; furthermore, specialized national institutions (oncology, cardiology, pulmonology) are accessible in Budapest. Probably higher rate of rural population needs home care than of big cities.

Several aspects were considered in the extrapolation of excess mortality due to the July heat wave. If the 33% excess mortality of the population of the Central Hungarian Region were compared to the population of the country, excess mortality for the country would be 970 cases. If the national excess mortality were defined from national daily mortality statistics – taking into account the yearly distribution – excess mortality would be 1050 cases. This value can be regarded as a maximum estimated value for the country. The minimum values could be the sum

of 278 cases of the region and the value of the extrapolation of the mortality rate of Pest County to the country which equals to 570 cases ignoring the estimated effect of bigger cities. We consider that the rates of big cities and countryside and the accessibility of hospitals can better model the national impact of heat waves. On this basis the national excess mortality could be between 600 and 800 cases. If the temperature–mortality association significantly differs in some parts of the country from that of the Central Hungarian Region, national excess mortality may differ to a greater extent. The estimation should be controlled by analyzing the validated mortality data in the future.

The summer temperature and mortality relationship was quasi-linear in the higher temperature ranges in the time series analysis of the Budapest data of 1970–2000. Mortality was the lowest at daily mean temperature at 18°C, above 22°C of daily mean temperature the association is steeper. The optimal daily mean temperature was 22°C in the 2007 analysis. The difference between the two results can be explained by the adaptation of the population to increasing summer temperature. In 2007 mortality was lower in the temperature range of 22–29°C than in the period of 1970–2000, the decrease can be explained by the heat health-warning system introduced in 2004 by raising the awareness of the general population and information of the health-care system. However, lower rate of excess mortality should have occurred (instead of 57% increase registered in 2007, only 15% increased) based on the extrapolation of the estimates of 31 years' time series in the range over 30°C.

Based on the results it is necessary to consider what kind of short-, middle-and-long term measures can effectively and efficiently decrease excess mortality, regarding that several climate models forecast the probability of similar or even hotter heat waves taking place more frequently (Bartholy, 2007; Revesz, 2007). Real-time data collection can be recommended for monitoring effect of heat waves. Continuous evaluation of the heathealth watch warning system even allows modifying the measures during a heat wave.

44.4 Conclusions

The summer of 2007 was the most extreme season ever recorded; three heat waves affected the country. During the first and third heat wave excess mortality was less than 5%. During the second event between July 16 and 24 the daily mean temperature was above 30°C for 5 days. The impact of high temperature on daily mortality could be stated; heat-related excess mortality was higher in hospitals than elsewhere. However, the rate of excess mortality was less than the impact of the heat wave of 2003 in France, although during the five hottest days the average excess death rate was 57%. Based on the association stated for the Central Hungarian Region, excess mortality cases could be assumed between 600 and 800 for the whole country.

- Using the estimates of the time series analysis of the data of 1970–2000, a lower excess mortality could be predicted over 30°C daily mean temperature,

while under this temperature higher excess mortality was forecast compared to the rates detected in 2007.

- In order to compare the excess mortality of the previous years with that of the year 2007, some assumptions were set up; therefore the results must be handled with care. Similarly there is a lot of uncertainty concerning the extrapolation of the results for the whole country. Further evaluation of the validated mortality data is necessary to qualify the association.
- We could state that the measures applied so far during the heat alert can reduce the impact of heat wave with a mean temperature of 25–29°C, on the other hand, excess mortality significantly increased on extreme hot days. It is necessary to consider what measures can reduce excess mortality effectively and efficiently during extreme hot days.
- Real-time mortality data collection proved to be a good tool to monitor the impact of heat waves. In the future the legal basis and technical options of electronic collection of real-time mortality and other types of health data (like emergency ambulance calls) should be considered and elaborated.

Acknowledgment

The analysis was carried out with the help of the project “Preparation to Climate Change,” Hungarian Academy of Science - BCE 2006TKI246 (Harnos, 2007).

References

- Bartholy, J, Pongracz, R, Gelybo, GY, Szabo, P (2007) Changes in temperature extremes expected in the Carpathian Basin by the end of the 21st century. “KLIMA-21” Brochures 51: 3–17.
- Botelho, J, Caterino, J, Calado, R, Nogueira, PJ, Paixao, E, Falcao, JM (2005) Onda de calor de Agosto de 2003. Os seus efeitos sobre a mortalidade da populacao portuguesa. Instituto Nacional de Saude Dr. Ricardo Jorge, Lisboa.
- Bujdosó, L, Paldy, A (2006) State Epidemiologic and Health Officer Services tasks for the prevention of health effects due to climate change. “KLIMA-21” Brochures 48: 60–67.
- CBS (2003) Ruim duizend doden extra door warme zomer Central Bureau of Statistics, The Netherlands.
- Conti, S, Meli, P, Minelli, G, Solimini, R, Toccaceli, V, Vichi, M, Beltrano, C, Perini, L (2005) Epidemiologic study of mortality during the summer 2003 heat wave in Italy. *Environmental Research* 98: 390–399.
- EuroHeat project: Improving public health responses to extreme weather/heat-waves <http://euroheat-project.org/dwd/>. Accessed on April 28, 2008.
- Garcia, AC, Nogueira, PJ, Falcao, JM (1981) Onda de calor de Junho de 1981 em Portugal: efeitos na mortalidade. *Revista Portuguesa da Saude Publica* 1: 67–77.
- Grize, L, Hussa, A, Thommena, O, Schindler, C, Braun-Fahrlander C (2005) Heat wave 2003 and mortality in Switzerland. *Swiss Medicine Weekly* 135: 200–205.
- Harnos, ZS (2007) Domestic research in relation to climate change: VAHAVA continued. “KLIMA-21” Brochures 49: 3–15.
- Health Statistics Quarterly (2006) <http://www.statistics.gov.uk>. Accessed on April 28, 2008.
- Hemon, D, Jougl, E (2003) Estimation de la surmortalite et principes characteristics epidemiologiques. Rapport d’etape 1/3. INSERM (Institut National de la santé et de la recherche medicale), Paris.

- Huynen, M, Martens, P, Schram, D, Weijenberg, M, Kunst, AE (2001) The impact of heat waves and cold spells on mortality rates in the Dutch population. *Environmental Health Perspectives* 109: 463–470.
- Instituto Nazionale di Statistica (ISTAT) 2004 <http://www.istat.it/english/>. Accessed on April 28, 2008.
- Johnson, H, Kovats, RS, McGregor, GR, Stedman, JR, Gibbs, M, Walton, H, Cook, L, Black, E (2005) The Impact of the 2003 heat wave on mortality and hospital admissions in England. *Health Statistics Quarterly* 25: 6–11.
- Katsouyanni, K, Trichopoulos, D, Zavitsanos, X, Touloumi, G (1988) The 1987 Athens heat wave [letter]. *Lancet* ii: 573.
- Martinez-Navarro, F, Simon-Soria, F, Lopez-Abente, G (2004) Valoracion del impacto de la ola de calor del verano de 2003 sobre la mortalidad. [Evaluation of the impact of the heat-wave in the summer of 2003 on mortality] *Gac-Sanit* 18: 250–258.
- McMichael, AJ, Kovats, RS (1998) Assessment of the impact on mortality in England and Wales of the heat wave and associated air pollution episode of 1976. Report to Dept. of Health London, Dept of Epidemiology and Population Health, LSHTM, London.
- Nogueira, PJ, Dias, CM (1999) Associacao entre morbilidade e clime em Portugal Continental. *Observacoes ONSA* 6.
- Paldy, A et al. (2006) Lessons learned from heat alerts. *Budapesti Népegészségügy* 2: 99–105.
- Paldy A et al. (2005a) The effects of temperature and heat waves on daily mortality in Budapest, Hungary, 1970–2000. In: *Extreme weather events and public health responses*, edited by W. Kirch, B. Menne, R. Bertollini, Mass: Springer-Verlag, Berlin Heidelberg. 99–108.
- Paldy, A, Bobvos, J, Vamos, A, Kishonti, K (2005b) Excess mortality during heat waves in Budapest 2001–2003. *Egészségtudomány* 49: 249–332.
- Paldy, A, Erdei, E, Bobvos, J (2004) Health impacts of climate change. *Egészségtudomány* 48: 220–236.
- PHEWE project: Prevention of acute Health Effect of Weather conditions in Europe <http://www.epiroma.it/phewe/>. Accessed on April 28, 2008.
- Pirard, P, Vandentorren, S, Pascal, M, Laaidi, K, Le Tertre, A, Cassadou, S, Ledrans M (2005) Summary of the mortality impact assessment of the 2003 heat wave in France. *Euro Surveill.* 10(7): 153–156.
- Revesz, A, Szenteleki, K (2007) Investigation of the stochastic behaviour of heat waves and temperature. "KLIMA-21" Brochures 51: 18–33.
- Rooney, C, McMichael, AJ, Kovats, RS, Coleman, M (1998) Excess mortality in England and Wales, and in Greater London, during the 1995 heatwave. *Journal of Epidemiology and Community Health* 52: 482–486.
- Sartor, F (2004) Surmortalité en Belgique au cours de l'été 2003. Institut Scientifique de Santé Republique Section d'Epidemiologie, Brussels.
- SBW (Sozialministerium Baden-Wuerttemberg) (2004) Gesundheitliche Auswirkungen der Hitzewelle im August 2003. SBW, Freiburg.
- Todisco, G (1987) Indagine biometeorologica sui colpi di calore verificatisi a Roma nell'estate del 1983 [Biometeorological Study of heat stroke in Rome during summer of 1983]. *Rivista di Meteorologia Aeronautica* XLVII: 189–197.
- Whitman, S et al. (1997) Mortality in Chicago attributed to the July 1995 heat wave. *American Journal of Public Health* 87: 1515–1518.

Potential Impact of Climate Change on Pandemic Influenza Risk

Daniela Curseu, Monica Popa, Dana Sirbu and Ioan Stoian

45.1 Introduction

Health problems related to the environment continue to be a major source of concern all over the world. Society needs to develop measures that will eliminate or considerably reduce hazardous factors from the environment that can result in health risk to humans.

There is scientific consensus worldwide through the Intergovernmental Panel on Climate Change, and National Academy of Sciences of USA, and other scientific professional associations, that the human modification of the global climate is occurring and that the climate is warming (Houghton et al., 2001; Oreskes 2004; Cicerone, 2005). Human activity is changing the climate by changing the chemical balance in the air. Certain gases in the atmosphere, called 'greenhouse gases,' absorb outgoing long wave radiation and re-emit back to the surface heat that would otherwise escape to space. The atmospheric concentrations of several greenhouse gases emitted by human activities, including carbon dioxide and methane, are increasing dramatically. Because these gases are causing the atmosphere to recycle heat and hold in more warmth, the average temperature at the surface of the planet is going up. The rate of increase has accelerated in the last 50 years, and significant further increases are expected in the next century and beyond. The global average surface temperature has increased over the twentieth century by about 0.6°C, and is projected to rise by an additional 1.4–5.8°C over the twenty-first century, depending on future emissions of greenhouse gases (Houghton et al., 2001).

A question that naturally arose is what effect will this have on human health, specifically on infectious diseases? This question has generated considerable public interest and stimulated the publication of numerous research and review papers. There is solid scientific evidence that increasing temperatures can lead to increased transmission of disease, through direct action on infectious agents (e.g., malarial parasites develop in the mosquito more rapidly in higher temperatures),

effects on vectors (e.g., greater geographic range and longer active season for mosquitoes, ticks, etc.), or changes in host behavior (e.g., shifts in migratory bird patterns). As noted by several researchers, climate change is partly responsible for the recent resurgence and re-emergence of some diseases, especially vector-borne diseases. Warmer temperatures and changes in rainfall have created ideal conditions for vectors and the pathogens to survive in some areas that were previously inhospitable to them. Tropical Africa is not the only area where deadly viruses have recently emerged. In Southeast Asia severe epidemics of dengue hemorrhagic fever started in 1954 and flu pandemics have originated from China such as the Asian flu (H2N2) in 1957, the Hongkong flu (H3N2) in 1968, and the Russian flu (H1N1) in 1977. However, it is especially during the last 10 years that very dangerous viruses for mankind have repeatedly developed in Asia, with the occurrence of Alkhurma hemorrhagic fever in Saudi Arabia (1995), avian flu (H5N1) in Hongkong (1997), Nipah virus encephalitis in Malaysia (1998), and, above all, the SARS pandemic fever from southern China (2002). The evolution of these viral diseases was probably not directly affected by climate change. In fact, their emergent success may be better explained by the development of large industry poultry flocks increasing the risks of epizootics, dietary habits, economic and demographic constraints, and negligence in the surveillance and reporting of the first cases.

Research on climate and infectious disease linkages inherently requires interdisciplinary collaboration. Studies that consider the disease host, the disease agent, the environment, and society as an interactive system require more interdisciplinary collaboration among climate modelers, meteorologists, ecologists, social scientists, and a wide array of medical and public health professionals. Encouraging such efforts requires strengthening the infrastructure within universities and funding agencies for supporting interdisciplinary research and scientific training. In addition, educational programs in the medical and public health fields need to include interdisciplinary programs that explore the environmental and socioeconomic factors underlying the incidence of infectious diseases.

A more pressing issue for the World Health Organization is pandemic flu. With 329 cases of avian influenza in humans, including 206 deaths, reported officially to World Health Organization, the experts agree that the next influenza pandemic is inevitable.

According to the UN Food and Agriculture Organization (FAO, 2005) climate change and globalization could promote the spread of avian influenza and create a global pandemic. As the climate becomes more unstable, its role increases. There are many ways that global warming could conceivably impact influenza transmission. For instance, warming may change bird migration patterns and thus patterns of interaction between humans and infected animals.

Avian flu and climate warming are questions which involve not just remote countries but the whole planet and which impose on us new attitudes and a new way of finding solutions. This chapter will therefore first discuss how climate change may influence the spread of highly pathogenic influenza. On the other hand, the paper performs several key messages and advice for people living in

areas affected by avian influenza to reduce its harm and to help limit the spread of a pandemic and prevent disease and death.

45.2 Climate Change, Migratory Birds, and Infectious Diseases

Several species of wild birds can act as biological or mechanical carriers of human pathogens as well as of vectors of infectious agents (Olsen et al., 1995; Klich et al., 1996; Gylfe et al., 2000; Friend et al., 2001; Niskanen et al., 2003; Rappole and Hubalek, 2003; Reed et al., 2003; Hubalek, 2004; Krauss et al., 2004). Many of these birds are migratory species that seasonally fly long distances through different continents (de Graaf and Rappole, 1995). Climate change has been implicated in changes in the migratory and reproductive phenology (advancement in breeding and migration dates) of several bird species, their abundance and population dynamics, as well as a northward expansion of their geographical range in Europe (Silllett et al., 2000; Parmesan and Yohe, 2003; Brommer, 2004; Both and Visser, 2005). Two possible consequences of these phenological changes in birds to the dispersion of pathogens and their vectors as follows:

1. Shifts in the geographical distribution of the vectors and pathogens due to altered distributions or changed migratory patterns of bird populations,
2. Changes in the life cycles of bird-associated pathogens due to the mistiming between bird breeding and the breeding of vectors, such as mosquitoes. One example is the transmission of St. Louis encephalitis virus, which depends on meteorological triggers (e.g., precipitation) to bring the pathogen, vector, and host (nestlings) cycles into synchrony, allowing an overlap that initiates and facilitates the cycling necessary for virus amplification between mosquitoes and wild birds (Day, 2001).

Wild water birds play an important role in the occurrence of both animal and human disease. They have been implicated as important carriers of poultry pathogens including Newcastle, paramyxovirus, and avian influenza viruses (Pederson et al., 2004; Jorgensen et al., 2004; Soares et al., 2005). These diseases are often subclinical in wild water birds but can cause devastating infections with high mortality and huge economic loss in domestic poultry. These viruses readily infect migratory water birds that disseminate them along migratory pathways.

45.2.1 Could climate change spread avian influenza and create a global pandemic?

Influenza A viruses have been isolated from many species including humans, pigs, horses, mink, felids, marine mammals and a wide range of domestic birds, but wild birds belonging to the orders Anseriformes (particularly ducks, geese, and swans) and Charadriiformes (particularly gulls, terns, and waders) are thought to form the virus reservoir in nature (Olsen et al., 2006). Climate change and alterations in the environment or animal breeding processes could be responsible for the mutations undergone by the virus and the jumps from one species to another. Ducks and other aquatic birds tend to congregate into flocks in the late fall and

winter, creating dense populations that are optimal for efficient influenza transmission. Because of their likely avian origin in ducks and other shorebird, the winter seasonal nature of influenza in humans may be a relic of avian influenza in bird species.

H5N1 avian influenza spread rapidly across Asia from east to west. The pathways by which the virus has and will spread between countries have been debated extensively, but have yet to be analyzed comprehensively and quantitatively. Despite intensive research, the means by which this spread was accomplished have remained extraordinarily controversial. Evidence is beginning to suggest that a combination of factors have all contributed to the persistence and spread of H5N1: movements by infected wild birds, transportation of infected domestic birds, and uncontrolled interactions between wild and domestic birds. To minimize the adverse effects of avian influenza, it is critical to detect its presence in a potential host population – whether wild bird or domestic poultry – early enough to mount an appropriate and effective response. Understanding the role of migratory birds in the spread of avian influenza viruses, the epidemiology of the avian influenza virus and its subtypes, and the exposure rates of various wild species are essential to future management of this disease.

The H5N1 virus has become established in bird populations of Southeast Asia and it has probably already reached the Arctic through migratory water birds. Avian flu virus can last indefinitely at a temperature dozens of degrees below freezing, as it is found in the northern most areas that migratory birds frequent. Influenza A viruses can survive over 30 days at 0°C (over 1 month at freezing temperature). Recently Scott Rogers from Bowling Green State University in Ohio and his colleagues found the influenza A virus genes in ice and water from high-latitude lakes that are visited by large numbers of migratory birds (Rogers et al., 2006). It shows that there is potential for a human virus to survive the freezing process. Imagine if older, more vicious strains, such as the virus responsible for the Spanish flu pandemic, which killed somewhere between 20 and 40 million people in 1918–1919, were to re-emerge. So if these viruses have been huddled in the ice for thousands of years, how did they get there in the first place? According to Rogers et al. one very effective way for viruses to travel the world is to hitch a ride in the guts of migrating birds. As the birds visit lakes along their paths they shed viruses into the lakes and onto the ice (when present) and drink water containing viruses discharged by other birds or released from the ice by thawing. Therefore, these lakes become abiotic mixing pools for the viruses, while the birds are the biotic vessels where mixing occurs (including replication and recombination). Since there are susceptible hosts along their migration path, they may pass the viruses to other birds as well as to swine, humans, or other animals.

Mixing and recombination of American and Eurasian influenza strains occurs in regions such as Alaska where these species mix and breed (Pederson et al., 2004). When birds migrate south they carry and disseminate these viruses along their migratory pathways.

Until recently, bird flu outbreaks mainly occurred in Indonesia, Vietnam, Thailand, Laos, Cambodia, and China. But in July, 2005, Russia and Kazakhstan confirmed H5N1 outbreaks in poultry and wild birds. Birds flying from Siberia

have carried the virus to the Greece, Turkey, and eastern Europe. Many scientists believe migrating wild fowl are responsible for carrying the virus from Asia and Siberia to Romania and Turkey. The scientists found that viruses from the most recently affected countries, all of which lie along migratory routes, were almost identical to viruses recovered from dead migratory birds at Qinghai Lake in China. The viruses from Turkey's first human cases were also virtually identical to the Qinghai Lake strain. In Romania, the outbreak was first detected in and around the remote Danube Delta, Europe's largest wetlands which also happen to lie on a major migratory route for wild birds.

Although some argue there is not enough evidence yet for firm conclusions, the theory is gaining ground. Kilpatrick et al. (2006) integrated data on phylogenetic relationships of virus isolates, migratory bird movements, and trade in poultry and wild birds to determine the pathway for 52 individual introduction events into countries and predict future spread. They showed that 9 of 21 of H5N1 introductions to countries in Asia were most likely through poultry, and 3 of 21 were most likely through migrating birds. In contrast, spread to most (20/23) countries in Europe were most likely through migratory birds. Spread in Africa was likely partly by poultry (2/8 introductions) and partly by migrating birds (3/8). Their analyses predict that H5N1 is more likely to be introduced into the Western Hemisphere through infected poultry and into the mainland United States by subsequent movement of migrating birds from neighboring countries, rather than from eastern Siberia. These results highlight the potential synergism between trade and wild animal movement in the emergence and pandemic spread of pathogens and demonstrate the value of predictive models for disease control (Kilpatrick et al., 2006).

It is increasingly acknowledged that migratory birds, notably waterfowl, play a critical role in the maintenance and spread of influenza A viruses. In order to elucidate the epidemiology of influenza A viruses in their natural hosts, a better understanding of the pathological effects in these hosts is required.

Wild birds were thought not to suffer from mild forms of avian influenza. But new data suggest that so-called 'low-pathogenic' avian influenza viruses do affect the lives of birds. According to scientist Jan van Gils from Netherlands Institute of Ecology, infected swans clearly suffer from their 'mild' disease. The late departure from the wintering grounds could lead to late arrival in the breeding grounds, and thus to a lost breeding season. All in all, these low-pathogenic viruses have a much greater impact than previously thought. Because of their slower migration, ill birds get in touch with many more healthy birds passing by them on migration. In this way the virus can spread itself more rapidly than previously thought (Van Gils et al., 2007).

Acquiring more knowledge about mild but illness-causing avian influenza viruses is very important. Van Gils suggests that these mild virus types always formed the origin of massive pandemics such as the Spanish Flu and that only such viruses that are non-lethal to birds can be spread easily by (wild or captive) birds, simply because the birds stay alive. Only after mixing with human flu can such a low-pathogenic avian flu cause the nightmare of a deadly pandemic among

humans. High-pathogenic avian flu that causes death among birds seems to originate from intensive poultry farms.

Biologists reported on the feeding and migratory performance of wild migratory Bewick's swans (*Cygnus columbianus bewickii* Yarrell) naturally infected with low-pathogenic avian influenza (LPAI) A viruses of subtypes H6N2 and H6N8. Using information on geolocation data collected from Global Positioning Systems fitted to neck-collars, they showed that infected swans experienced delayed migration, leaving their wintering site more than a month after uninfected animals. This was correlated with infected birds traveling shorter distances and fueling and feeding at reduced rates. The data suggest that LPAI virus infections in wild migratory birds may have higher clinical and ecological impacts than previously recognized (Van Gils et al., 2007). This contrasts previous ideas that mild forms of bird flu do not cause illness among wild birds. Moreover, these patterns can affect the rate of spread of avian influenza. Warming climate may be a factor in the population increase and expansion in distribution. Biologists believe that climate change is affecting living things worldwide, and the latest evidence suggests that warmer winters may mean fewer migratory birds. New research shows that as winter temperatures have risen in central Europe, the number of migratory birds has dropped. Ultimately, this may also decrease the number of migratory bird species there (Society for Conservation Biology, 2003).

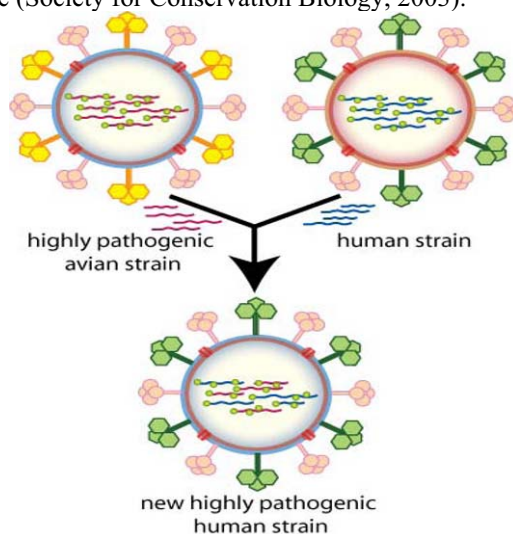


Fig. 45.1 Reassortment of viral RNA genome segments (genetic mixing or recombination) creating a new viral strain.

Wild aquatic water birds are the primary reservoir of influenza A viruses and bird influenza viruses serve as a genetic reservoir for other animal influenza strains including those that infect humans (Widjaja et al., 2004; Webster et al., 2002). The past influenza pandemics of the twentieth century are all of avian origin (Horimoto et al., 2005), including the 1918 influenza pandemic (Taubenberger et al., 2005). According to Taubenberger, the Spanish flu virus that killed up to 50

million people in 1918–1919 was “...avian like virus that adapted to humans”. The researchers believe the two other major flu pandemics of the twentieth century – in 1957 and 1968 – were caused by human flu viruses which acquired two or three key genes from bird flu virus strains. The greatest concern is that the H5N1 virus will recombine with a human virus that will give the new strain the capacity to become readily transmitted from person to person (Fig. 45.1). In places with high concentrations of domestic pigs and chickens, pigs may serve as a “mixing vessel” for the virus because of their genetic similarity to humans.

In 1997, the new avian influenza virus (H5N1 avian flu) emerged in Hong Kong killing six people. This was the first time that an avian influenza virus was shown to be transmitted directly from birds to humans. The virus persisted in the region, and has since spread to a number of 60 countries in Asia, Europe, and Africa (Fig. 45.2). Twenty-six countries have experienced outbreaks in 2007. Except for a few outbreaks in wild birds, most of the confirmed outbreaks have been in domestic poultry, including chickens, turkeys, geese, ducks, and quails.

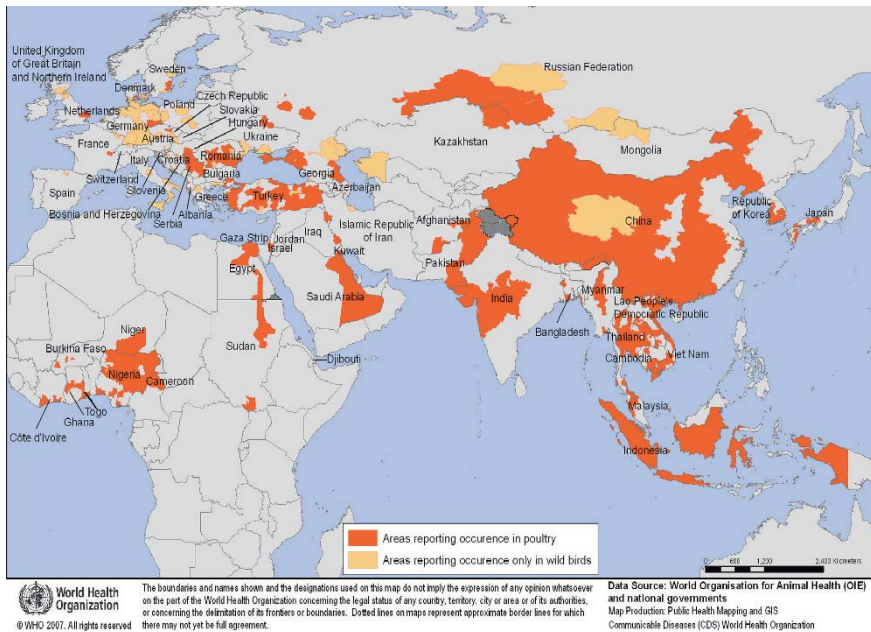


Fig. 45.2 Areas reporting confirmed occurrence of H5N1 avian influenza in poultry and wild birds since 2003.

The World Health Organization says there have been 329 cases of human avian influenza, including 206 deaths, with the highest number of cases reported in Indonesia and Vietnam. The avian H5N1 strain is highly virulent to people with a mortality rate of over 60% (Marshall et al., 2005). The case distribution upon age groups is different in avian influenza as compared to seasonal flu. For the latter,

the casualties are usually the very young and the very old, as exemplified by a V-shaped graph. For the pandemic flu, it is inverse with the youth with being the victims (Fig. 45.3). As of February 2008, the median age of patients influenza A (H5N1) virus infection is approximately 18 years. The overall case fatality proportion is 61%. The primary pathologic process that causes death is fulminant viral pneumonia (WHO, 2008). Handling of sick or dead poultry during the week before the onset of illness is the most commonly recognized risk factor. Although the A (H5N1) virus is at present poorly adapted to humans, limited human-to-human transmission continues to occur.

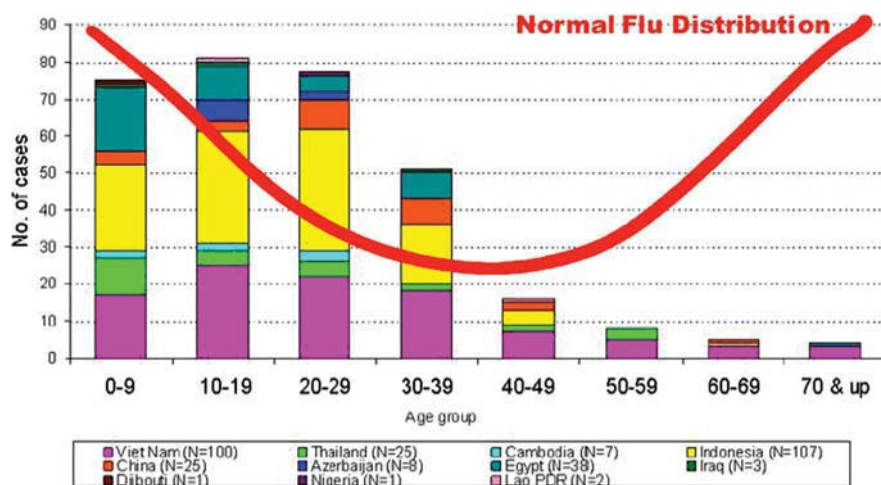


Fig. 45.3 Human avian influenza A (H5N1) cases by age group and country.

45.3 Key Messages and Advice

Health officials who are alerted to a location where poultry (chicken, ducks, and other farmed birds) have been found to be dying of bird flu or avian influenza (H5N1 virus) will need to take immediate steps to ensure that the disease does not spread. With a good plan, one that includes effective communication measures, the spread of bird flu can be successfully arrested.

The first objective is to identify the people and communities that are most at risk. The Food and Agriculture Organization estimates that 70% of poultry is raised in backyard farms. It is critical, therefore, that health authorities provide basic information on prevention and control of avian influenza to these people as

they are at greatest risk of being exposed to the disease. Several countries have adopted preventive measures like placing roofs or nets over chicken pens to keep domestic fowl from coming into contact with migratory birds. It is also advisable that this information could be disseminated through other communication channels such as the media, community leaders, nongovernmental organizations, and policy-makers. The second objective is to adopt and adapt the following key messages and information for local dissemination and use.

45.3.1 Advice of World Health Organization for people living in areas affected by bird flu or avian influenza

- **The spread of bird flu in affected areas can normally be prevented.**
- People should avoid contact with chickens, ducks, or other poultry unless absolutely necessary. This is the best way to prevent infection with the bird flu virus.
- Children are at high risk because they may play where poultry are found. Teach the children the following basic guidelines:
 - Avoid contact with any birds, their feathers, faeces, and other waste.
 - Do not keep birds as pets.
 - Wash hands with soap and water after any contact.
 - Not to sleep near poultry.
- Do not transport live or dead chickens, ducks or other poultry from one place to another even if you think the birds are healthy.
- Handling of poultry in affected areas should be done within the area without transporting them to other areas.
- Do not prepare poultry from affected areas as food for family or animals. The slaughter and preparation of such birds for food is dangerous.
- If you unintentionally come into contact with poultry in an affected area, such as touching the bird's body, touching its faeces or other animal dirt, or walking on soil contaminated with poultry faeces:
 - Wash the hands well with soap and water after each contact.
 - Remove the shoes outside the house and clean them of all dirt.
 - Check your temperature for 7 days at least once daily. If you develop fever ($>37.5^{\circ}\text{C}$), visit a doctor or the nearest health care facility immediately.
- **Proper handling of poultry that are ill, suspected of having bird flu or dead is an important control measure to prevent the spread of the disease.**
- Make sure to keep children away from dead or sick poultry.
- If you need to handle dead or sick poultry, make sure you are protected. Wear protective clothing such as a mask, goggles, gown, rubber boots, and gloves. If these are not available, cover your mouth with a piece of cloth, wear glasses, use plastic bags to cover hands and shoes and fix these tightly around wrists and ankles with a rubber band or string. Wear overalls that can be washed.

- If you encounter sick and dead poultry for the first time and are unsure of the situation, inform the authorities immediately and leave the handling of the poultry to experienced personnel (cullers, clean-up personnel, etc.).
- **Decontamination of the yard or chicken pen will help control the spread of the disease.**
- If possible, ask experienced personnel to help you decontaminate the yard or chicken pen.
- If this is not possible and you have to do it yourself, wear protective gear to protect your eyes, hands, feet, and other exposed parts of your body as described above.
- Dead birds should be buried safely.
- Effective cleaning results in no visible feathers or faeces remaining in the shed.
- Influenza viruses can survive for some time in organic material, so thorough cleaning with detergents is an important step in decontamination. All organic matter must be removed from poultry houses as much as possible.
- As outdoor areas used by poultry can be difficult to clean or disinfect, poultry should be excluded from these areas for a minimum of 42 days to allow natural ultraviolet radiation to destroy any residual virus. The period of exclusion should be longer in cold weather.
- Spraying of disinfectants on vegetated outdoor areas or soil is of limited value due to the inactivation of these chemicals by organic material. Removal of surface soil is not normally recommended unless it is heavily contaminated with faeces.
- **Dead birds and their feces should be buried or burnt.**
- As much as possible, seek assistance from your local agriculture authority on how to bury dead animals safely.
- When burying dead birds or their faeces, try to avoid generating dust. Spray or sprinkle water to dampen the area first. Bury bird carcass and faeces at a depth of at least 1 m.
- When the dead birds and their faeces have been properly disposed, clean all areas very well with detergent and water. Influenza viruses are relatively susceptible to a variety of detergents and disinfectants.
- **Contaminated protective clothing should be properly handled or disposed.**
- After the area has been cleaned, remove all the protective materials and wash your hands with soap and water.
- Wash clothes in hot or warm soapy water. Hang them in the sun to dry.
- Put used gloves and any other disposable materials in a plastic bag for safe disposal.

- Clean all reusable items such as rubber boots and glasses/goggles with water and detergent, but always remember to wash your hands after handling these items.
- Items that cannot be cleaned properly should be destroyed.
- Shower/wash body using soap and water. Wash your hair.
- Take care not to re-contaminate yourself or the cleaned area by avoiding contact with dirty, contaminated clothes and items.
- Most importantly, wash your hands every time after handling any contaminated items.
- **Footwear should also be decontaminated.**
- After walking around areas that may be contaminated (such as farms, markets, or backyards with poultry), clean your shoes as carefully as possible with soap and water.
- When cleaning shoes, make sure that you do not flick any particles into your face or on your clothes. Wear a plastic bag over your hands, shield your eyes by wearing glasses or goggles, and cover your mouth and nose with a cloth.
- Leave dirty boots and shoes outside the home until they have been thoroughly cleaned.
- **People who have flu-like illness should take additional precautions.**
- World Health Organization believes it is very important to prevent human influenza from spreading in areas affected by bird flu. Where the avian influenza viruses and human influenza viruses come in contact with each other, there is a risk that genetic material will be exchanged and a new virus could emerge.
- Anyone with flu-like illnesses should therefore be careful with secretions from the nose and mouth when around other people, especially small children, in order not to spread human influenza viruses.
- Cover your nose and mouth when coughing or sneezing. Use a tissue and throw it away once used. Teach children to do this as well.
- Always wash your hands with soap and water after any contact with secretions from nose or mouth as these can carry a virus.
- Children are especially prone to touching their face, eyes, and mouth with unwashed hands. Teach children the importance of hand washing after coughing, sneezing, and touching dirty items.
- Inform the health authorities immediately and seek medical advice from a health professional if you develop signs of illness, such as fever and/or flu-like symptoms.
- **Precautions can be taken when visiting friends or relatives in health-care facilities.**
- If you visit a patient who has bird flu, follow the advice from the hospital staff to wear protective clothing, including a mask, gown, gloves, and goggles.

- Such special protective clothing is required when you have direct contact with the patient and/or the patient's environment.
- It is important that the protective mask fits properly. If it does not, seek advice from the hospital staff.
- When you leave the patient's room you must remove these items and wash your hands with soap and water.
- **In affected areas where the presence of bird flu has been confirmed, do not eat poultry meat that comes from dead or sick animals.**
- In affected areas it is advisable not to use dead and sick chicken or other poultry for preparing food for humans and/or animals. Even healthy-looking poultry of any kind from a bird flu affected area should not be used for food.
- **In neighboring areas (next to the bird flu affected area) some precautions need to be taken.**
- In general, only apparently healthy poultry should be prepared for food.
- For killing, use a method that does not contaminate you or the environment of your household with blood, dust, faeces, and other animal dirt. Seek advice from the agriculture authority about the proper procedure.
- For plucking, use a method that does not contaminate you or the environment of your household with dust, faeces, and other animal dirt. It is best to put poultry in boiling water before plucking feathers.
- For degutting, use a method that does not contaminate you or the environment of your household with blood, dust, faeces, and other animal dirt.
- Do not touch other items or your face (e.g., rubbing your eyes) during the procedure, unless you have washed your hands with soap and water.
- **Take all precautionary measures to ensure that poultry and poultry products are properly prepared and safe to eat.**
- Chicken prepared hygienically and cooked thoroughly, i.e., no pink juices should be observed, can be considered safe to eat. However, remember, if the bird has a transmittable disease, such as bird flu, the person preparing the food is at risk of becoming infected and the environment may become contaminated.
- Eggs, too, may carry pathogens, such as the bird flu virus inside or on their shells. Care must be taken in handling raw eggs and shells. Wash shells in soapy water and wash hands afterward. Eggs, cooked thoroughly (hard boiled, 5 minutes, 70°C) will not infect the consumer with bird flu.
- In general, all food should be thoroughly cooked to an internal temperature of 70°C or above.

45.4 Conclusions

- The past influenza pandemics of the twentieth century were all of avian origin. The natural reservoir for influenza is suspected to be aquatic birds (ducks, geese) because they commonly exhibit no ill effects to low-pathogenic avian influenza.
- Climate changes that influence wild water bird habitat, migration, and stopover sites could be a factor in global distribution of avian virus agents and possibly the emergence of a new pandemic influenza strain.
- Climate change as well as globalization could promote the spread of avian influenza and create a global pandemic. However, for global warming, there has not been any evidence to show that it makes human influenza pandemics more likely. Alarmist statements blaming migrants for the spread of an emerging disease with pandemic potential and ignoring or underplaying the role of the poultry industry do not do justice to the complexity of the issues involved.
- With avian influenza prevention and control measures, many countries have been able to contain or even eradicate the disease. Pandemics might be stopped at the very start, but it does not look like the current situation can be stopped; just delayed and slowed down.

Acknowledgment

This study was realized in frame of National Research Project CEEX 128/2006, SIMONPAN.

References

- Both, C, Visser, ME (2005) The effect of climate change on the correlation between avian life-history traits. *Global Change Biology* 11: 1606–1613.
- Brommer, JE (2004) The range margins of northern birds shift pole wards. *Annales Zoologici Fennici*. 41: 391–397.
- Cicerone RJ (2005) Current state of climate science: recent studies from the National Academies, Statement before the Committee on Energy and Natural Resources, U.S. Senate, July 21, 2005. (www7.nationalacademies.org/ocga/testimony/ClimateChange_Science_and_Economics.asp)
- Day, JF (2001) Predicting St. Louis encephalitis virus epidemics: lessons from recent, and not so recent, outbreaks. *Annual Review of Entomology* 46: 111–138.
- De Graaf, R, Rappole, J (1995) Neotropical migratory birds: natural history, distribution and population change. Cornell University Press, Ithaca, New York, pp. 676.
- Food and Agriculture Organization of the United Nations (FAO) (2005) A global strategy for the progressive control of highly pathogenic avian influenza (HPAI). FAO, World Organization for Animal Health and World Health Organization, pp. 55.
- Friend, M, McLean, RG, Dein, FJ (2001) Disease emergence in birds: challenges for the twenty-first century. *Auk* 118: 290–303.
- Gylfe, A, Bergstrom, S, Lunstrom, J, Olsen, B (2000) Epidemiology: reactivation of *Borrelia* infection in birds. *Nature* 403: 724–725.

- Horimoto, T, Kawaoka, Y (2005) Influenza: lesson from past pandemics, warnings from current incidents. *Nature* 3: 591–600.
- Houghton, JT, Ding, Y, Griggs, DJ, Nogueira, M, van der Linden, PJ, Xiaogu, D (2001) Climate change 2001: the scientific basis. contribution of working group I to the third assessment report of the intergovernmental panel on climatic change (IPCC). Cambridge: Cambridge University Press.
- Hubalek, Z (2004) An annotated checklist of pathogenic microorganisms associated with migratory birds. *Journal of Wildlife Diseases* 40: 639–659.
- Jorgensen, PH, Handberg, KJ, Aherns, P, Therkildsen, OR, Manvell, RJ, Alexander, DJ (2004) Strains of avian paramyxovirus type I of low pathogenicity for chickens isolated from poultry and wild birds in Denmark. *Veterinary Record* 154: 497–500.
- Kilpatrick, AM, Chmura, AA, Gibbons, DW, Fleischer, RC, Marra, PP, Daszak, P (2006) Predicting the global spread of H5N1 avian influenza. *Proceedings of the National Academy of Sciences of the United States of America* 103:19368–19373.
- Klich, M, Lankester, MW, Wu, KW (1996) Springmigratory birds (Aves) extend the northern occurrence of blacklegged tick (Acari: Ixodidae). *J. Medical Entomology* 33: 581–585.
- Krauss, S, Walker, D, Pryor, SP, Niles, L, Li, CH, Hinshaw, VS, Webster, RG (2004) Influenza A viruses of migrating wild aquatic birds in North America. *Vector-Borne Zoonotic* 4: 177–189.
- Marshall, SJ (2005) Governments in a dilemma over bird flu. *Bulletin of the World Health Organization* 83: 325–326.
- Niskanen, T, Waldenstrom, J, Fredriksson-Ahomaa, M, Olsen, B, Korkeala, H (2003) virF-positive *Yersinia pseudotuberculosis* and *Yersinia enterocolitica* found in migratory birds in Sweden. *Applied and Environmental Microbiology* 69: 4670–4675.
- Olsen, B, Munster, VJ, Wallensten, A, Waldenström, J, Osterhaus, A (2006) Global patterns of influenza A virus in wild birds. *Science* 312: 384–388.
- Olsen, B, Duffy, DC, Jaenson, TGT, Gylfe, A, Bonnedahl, J, Bergstrom, S (1995) Trans-hemispheric exchange of Lyme-disease spirochetes by seabirds. *Journal of Clinical Microbiology* 33: 3270–3274.
- Oreskes, N (2004) The scientific consensus on climate change. *Science* 306(5702):1686.
- Parnesan, C, Yohe, G (2003) Globally coherent fingerprint of climate change impacts across natural systems. *Nature* 421: 37–42.
- Pederson, JC, Senne, DA, Woolcock, PR (2004) Phylogenetic relationships among virulent Newcastle disease virus outbreaks from 2002–2003 outbreak in California and other recent outbreaks in North America. *Journal of Clinical Microbiology* 42:2329–2334.
- Rappole, JH, Hubalek Z (2003) Migratory birds and West Nile virus. *Journal of Applied Microbiology* 94: 47–58.
- Reed, KD, Meece, JK, Henkel, JS, Shukla, SK (2003) Birds, migration and emerging zoonoses: West Nile virus, Lyme disease, influenza A and enteropathogens. *Clinical medicine & research* 1(1):5–12.
- Rogers, SO, Zhang, G, Shoham, D, Gilichinsky, D, Davydov, S, Castello, JD (2006) Evidence of Influenza A Virus RNA in Siberian Lake Ice. *Journal of Virology* 80(24):12229–12235.
- Sillett, TS, Holmes, RT, Sherry, TW (2000) Impacts of a global climate cycle on population dynamics of a migratory songbird. *Science* 288: 2040–2042.
- Soares, PB, Demetrio, C, Sanfilippo, L, Kawanoto, AH, Brentano, L, Durigo, EL (2005) Standardization of a duplex RT-PCR for the detection of influenza A and Newcastle disease viruses in migratory birds. *Journal of virological methods* 123: 125–130.
- Society For Conservation Biology (2003) Climate change linked to migratory bird decrease. *Science Daily*. Retrieved February 13, 2008, from <http://www.sciencedaily.com/releases/2003/03/030326073630.html>.

- Taubenberger, J, Reid, A, Lourens, R, Wang, R, Jin, G, Fanning, T (2005) Characterization of the 1918 influenza virus polymerase genes. *Nature* 437: 889–893.
- Van Gils, JA, Munster, VJ, Radersma, R, Liefhebber, D, Fouchier, RA (2007) Hampered foraging and migratory performance in swans infected with low-pathogenic avian influenza A virus. *PLoS ONE* 2(1): e184. doi:10.1371/journal.pone.0000184 (<http://dx.doi.org/10.1371/journal.pone.0000184>).
- Webster, RG (2002) The importance of animal influenza for human disease. *Vaccine Suppl.* 2: 16–20.
- Widjaja, LS, Krauss, L, Webby, RJ, Xie, T, Webster, RG (2004) Matrix gene of influenza viruses isolated from wild aquatic birds: ecology and emergence of influenza A viruses. *Journal of virology* 78: 8771–8779.
- Writing Committee of the Second World Health Organization Consultation on Clinical Aspects of Human Infection with Avian Influenza A (H5N1) Virus, (2008) Update on avian influenza A (H5N1) virus infection in humans. *The New England journal of medicine* 358: 261–273.

Index

Note: Locators followed by *f* and *t* refer to figures and tables respectively.

A

Absorption Cooling Systems (ACS),
147
considered for building in Bigadic,
152*f*
Acidimetric titration method, 488
Acid rain, 73, 585
ACS, *see* Absorption Cooling Systems
(ACS)
Acute and chronic health problems,
580
Ad hoc working group (AWG), 413
Advanced gas reactor (AGR), 131
Advanced high-temperature reactor
(AHTR), 131–132
Agricultural solar water pumping
stand-alone system, 78*f*
Agro-environmental science, 591
Agronomic crops and weeds
phenology, 601
Air pollutants and meteorological
parameters in Erzurum, Turkey,
485
data analysis, 489
evaluation of SO₂ and TSP
concentrations/meteorological
parameters, 490
materials and methods, 487
description, 487
SO₂ and TSP monitoring, 487
regression analysis, 494
relationship between SO₂, TSP, and
meteorological factor, 493
Air pollution, 485
and environmental concerns in
Turkey, 227–229
Air pollution control (APC) equipment,
212
Algerian bentonite, 621
Alkaline fuel cell (AFC), 162
Alkhurma hemorrhagic fever/Saudi
Arabia/1995, 644
Alzheimer's disease, 583–584
Amagat model for ideal gas mixtures,
182

American Society for Testing and
Materials (ASTM), 349
Ammonia (NH₃), 110
cost correlation for hydrogen
obtained from, 116*f*
vs. decomposition temperature,
cooling effect of, 120*f*
features in comparison with other
fuels, 111
hydrogen source, comparison with
other options, 117*t*
prior its use as fuel on vehicle, 121*f*
reasons for storage and distribution of
H₂, 110–111
specific/volumetric energy densities
of various fuels *vs.*, 118
storage advantages, 115
toxicity, 110
“*An Inconvenient Truth*,” 26
Anthropogenic pollutant, 485
APC, *see* Air pollution control (APC)
equipment
Asian flu (H2N2) in 1957, 644
Asthma, by aerosols in local levels, 609
ASTM, *see* American Society for
Testing and Materials (ASTM)
Atmosphere and warming phenomena, 8
Auger analysis, 318
Australia's “Big Dish,” 93
Avian flu (H5N1)/Hongkong/1997, 644
prevention and control of, 650
AWG, *see* Ad hoc working group
(AWG)

B

Basic shipyard processes, 581*f*
BAU, *see* Business as usual (BAU) level
Benzo(a) pyrene-equivalent (BaPE)
carcinogenic power, 615
Best Management practice (BMP) study
in Turkish shipyard, 587
control for waste reduction, 587
tin-free, TBT-free, or low-VOC paint,
587
Beta gauge instrument (KS-301-F), 488

BHM, *see* Boiler hardware model (BHM)

Bigadic Geothermal District Heating System, 148–150
 environmental benefits of, 157
 reduced emission values for house in summer season, 158*f*
 flowchart, 150*f*
 used for, 157

Biochemical oxygen demand (BOD), 548

Biogenic/anthropogenic origin, 609

Biogenic emission and essential oils of some eucalyptus species, 357
 atmospheric emission, mass spectrometer, 359
 enantiomeric distribution of monoterpenes, 363
 materials and methods
 essential oils, 358–359
 oil isolation, 358–359
 physicochemical indices, 358–359
 plant materials, Bainem forest, 358–359

Biological pump, 284
 See also Ocean sequestration

Biomass, electricity generation from, 75–76

BOD, *see* Biochemical oxygen demand (BOD)

Boiler hardware model (BHM), 457

“Breathalyzer test,” 8

Broccoli drying, 267–274
 composition of broccoli florets, 269*i*
 drying procedure and measurements, 269–270
 vacuum-oven method, 269–270
 effects of drying air temperature, 274–277
 energy and exergy balance equations, 272–274
 exergy balance equation, conveyor dryer was, 273
 exergy efficiency, 274
 ‘improvement potential rate,’ 272–274
 thermal properties of food and drying air, 270–272

Bunsen reaction, 135

Business as usual (BAU) level, 419

C

Ca–Br cycle, 137
 schematic of modified, 138*f*

Carbon capture
 chemical absorption through solvent, 282–283
 diethelamine (DEA), 282–283
 gas separation films, 283
 low-temperature distillation, 283
 methyldiethelamine (MDEA), 282–283
 monoethelamine (MEA), 282–283
 physical absorption on solids, 283

Carbon cycle and chemistry models, 513

Carbon energy, usage, 3–4

Carbon fuel dependency syndrome (CFDS), 10

Carbon preference Index (CPI), 614

Carbon sequestration, 281, 282*f*, 292–293*t*
 biological processes, 290
 emission of carbon, 281, 282*f*, 292–293*t*

Carcinogenic/mutagenic compounds, 610

Carlo Erba Gas Chromatograph, 358–359

Carnot cycle, 51*f*
 development of, 55*f*

Carnot principle, 53–54

Carnot refrigerator, 52

Caspian sea level rise/climate change in north of Iran, impacts of, 501
 global sea level rise predictions, 502
 paleoclimatic warming, 502
 semi-empirical model, 502
 materials and methods, 504
 planning responses, 507
 two-tier approach, 507
 protection responses, 507
 existing natural protection systems, maintenance of, 507
 longer term physical engineering works, 507
 regional and local scales sea level rise predictions, 503

Caspian Sea level rise (CSLR), 501
 effect of, 505

CC, *see* Cloud cover (CC)

- CDM, *see* Clean development mechanism (CDM)
- Center for Climate Prediction and Research, 513
- Central Hungarian Institution, 630
- Central Hungarian Region (CHR), 629
- Central region climate fields, 519, 519*t*
- Central Statistical Office, 637
- Centre for Environment, Technology and Development, Malaysia (CETDEM), 390
- CER, *see* Certified emission reduction (CER)
- Certified emission reduction (CER), 410
- CETDEM, *see* Centre for Environment, Technology and Development, Malaysia (CETDEM)
- CGE, *see* Computable general equilibrium (CGE) analysis
- Cgw model, 432*f*
- Chemical equilibrium, 48
- Chlorofluorocarbons (CFC), 585
- CHP, *see* Cogeneration, or combined heat and power production (CHP)
- CIDB, *see* Construction Industry Development Board (CIDB)
- Clausius–Clapeyron equation, 63–64
- Clausius statement
- development and entropy, 55*f*
 - graphical explanation, 53*f*
 - second law of thermodynamics, 52–53
- Clay, characterization of, 622
- Clean Air Act (CAA), 164, 170
- Clean development mechanism (CDM), 407
- See also* Kyoto protocol (KP)
- “Clean energy,” 74
- Climate change
- consequence, decision-making, 2
 - issue, 1–3
 - measures reflecting, 9, 10*t*
- Climate modeling system, 513
- See also* Providing Regional Climates for Impact Studies ‘PRECIS’
- Climatic policy department, 471
- Closed system, thermodynamics, 47
- exergy, 58
 - first law of thermodynamics, 49
- Cloud cover (CC), 469–470
- research, 469
 - weather stations, 469
- Cloud cover radiation model (CRM), 471–472
- global and diffuse horizontal irradiances, 471
- CO₂ absorption in mini-module
- membrane reactor, 307
 - ambient temperature and pressure, 310–311*f*
 - coal upgrading process, 307–308
 - energy-efficient devices, 307–308
 - experimental
 - contactor characteristics, 308*t*
 - isothermal condition, 308–309
 - gas–liquid membrane contactors, 307
 - selectivity process, 307–308
- CO₂ (atmospheric) and temperature fluctuates, 5
- Coal-based hydrogen production with clean coal
- energy information administration, 295
 - experimental procedure and materials
 - chromatographic method settings, 298
 - hydrogen-rich gas production, tests of, 296–299
 - gas composition obtained in gasification, 302–303*f*
 - process
 - Boudouard reaction, 296
 - steam gasification of coal to hydrogen-rich gas, 296*t*
 - integrated gasification combined cycle system, 296
 - steam coal gasification tests, 300*t*, 301*f*
 - steam gasification process, 299–304
- Coalition formation theory, post-Kyoto and, 413–415
- effects of stocks pollutants utilizing dynamic programming, 413–420
 - renegotiation proofness, 415
 - subgame perfectness, 415
- CO₂ and SO₂ capture capability
- carbonation of sorbents
 - carbonation–calcination, 336*f*

- effect of reaction time and temperature, 338–340
- florina limestone, 335–340
- megapolis limestone, 335–340
- particle size effect, 337–338
- CO-capture capability of sorbents
 - sequential carbonation/sulfation cycles, 343–345
- experimental
 - apparatus and procedure, 331–332
 - materials, 330–331
- limestone properties
 - Ca-based sorbents, 332–334
 - X-ray mapping of epoxy-embedded, 333*f*
- sequential carbonation and sulfation, 343–345
- sulfation of sorbents, 340–341
- CO₂ emissions, 8
 - distribution in various sectors in North America, 109*f*
- CO₂ emissions reduction, partial
 - gasification for, 179–181
- partial gasification-based IGCC system
 - partial gasification process, 181
 - proposed IGCC system with supplementary firing, 181
- system performance analysis, 185
 - effect of feedstock on, 190–191
 - effect of gasification on combined cycle performance, 185–186
 - effect of gasifier-operating conditions, 189–190
 - effect of operating temperatures, 188–189
 - combined cycle performance, 186–187
 - validation of current results with published results, 191–192
- thermodynamic analysis, 182
 - combined cycle performance, 184
 - gas cycle performance, 183–184
 - gasification and combustion reactions, 182–183
 - mass and energy balance, 183
 - steam cycle performance, 184
- Cogeneration, 174
 - or combined heat and power production (CHP), 225
- CO₂ hydrogenation to methanol, 315
- CO₂ hydrogenation, reactivity in, 322
- copper-based catalysts, 315
 - experimental
 - catalysts preparation, 316–317
 - catalytic CO₂ hydrogenation, 317*t*
 - catalytic isoprene hydrogenation, 316
 - hydrogen species titration, 322–325
 - CO₂ active site modeling, 325*f*
 - heterolytic dissociation, 322–325
 - solid solution (SS), 323–325
 - isoprene hydrogenation in helium, reactivity in, 320–322
 - catalysts modeling, 322*f*
 - isoprene hydrogenation products distribution, 320–322, 321*t*, 324*f*
 - physico-chemical characterizations, 316
- Combustion processes, 610
- Comparative analysis, 291–293
- Compressed natural gas (CNG), 117
- Computable general equilibrium (CGE) analysis, 409
- Construction Industry Development Board (CIDB), 389
- Cooling capacity factor profiles, 155*f*
- Cooling load and electricity requirement, 156*f*
- Coordinatively unsaturated sites (CUS), 315
- COP, *see* Coefficient of performance (COP)
- Copper–chlorine cycle, *see* Cu–Cl hydrogen production cycle
- Correlation analysis, 570
 - correlation coefficient, 570
 - positive/negative correlation, 570
 - temperature and rainfall, 574
- Correlation coefficient, 570
- CPI, *see* Carbon preference Index (CPI)
- CRM, *see* Cloud cover radiation model (CRM)
- Crude mortality data, 637
- Crustal deformation, 502
- Cu–Cl hydrogen production cycle, 137–143
 - exergy efficiencies of steps associated with Cu–Cl cycle, 140, 141*t*

- key steps of, 138*t*
 - relation between overall exergy
 - efficiency and temperature of, 143*f*
 - thermochemical, 139*f*
 - variation of overall energy efficiency
 - based on cycle temperature, 142*f*
 - variation of reaction heat with
 - reaction temperature, 140*f*
 - Cu²⁺ and Ni²⁺ from aqueous solution by
 - Algerian clay materials, removal of, 621
 - Algerian bentonite, 621
 - characterization of clay, 622
 - effect of shaking time, 624–625
 - Infrared Spectroscopy study, 622–624
 - FT-IR Spectrometer, 622
 - hydration OH stretching, 624
 - infrared spectra of clay material
 - untreated and treated with HCl, 623*f*
 - infrared spectra of natural and treated with HCl bentonite clays, 624*t*
 - Perkin Elmer Spectrum model, 622
 - X-ray diffraction patterns of
 - bentonite clay, 623*f*
 - mass of clay, effect of
 - clay–metal interactions, 627
 - material clays as adsorbents, 621
 - materials and experimental methods, 621–622
 - Algerian clay, characterization of, 622
 - flame atomic absorption
 - spectrometer, 621
 - mechanical shaker of type Janke, 622
 - pH meter, Cyber Scan pH 500, 622
 - reagent and solutions, 622
 - Varian type SAA-110, 621
 - pH, effect of, 625*f*
 - Algerian clay on removal of Cu²⁺ and Ni²⁺, 626*f*
 - pH on removal of Cu²⁺ and Ni²⁺, 626*f*
 - shaking time, effect of, 625
 - removal of Cu²⁺ and Ni²⁺, 625*f*
 - SAA method, 625
 - XRD study, 622
 - “Cure,” defined, 5–6
 - Curves of nonlinear association, 636
 - CUS, *see* Coordinatively unsaturated sites (CUS)
- ## D
- Daily crude mortality data, 630
 - Daily mean temperature, 639
 - Darwin’s principles, 243
 - Data for model software, 515–516
 - DEFRA, *see* UK Department for Environment, Food and Rural Affairs (DEFRA)
 - Degree days of species, 603
 - Degree-hours, geothermal-based
 - absorption cooling systems, 153
 - Degree of swelling (DS), 558
 - Dengue hemorrhagic fever, 644
 - Department for Pest Prevention, 528
 - DEPC, *see* Diesel engine-powered cogeneration (DEPC)
 - Designated national authorities (DNA), 420
 - Designated operational entities (DOE), 420
 - Diesel engine-powered cogeneration (DEPC), 225
 - electricity consumer, 225–226
 - emission characteristics of, 225
 - emission difference analysis, 235–238
 - exhaust flow in DEPC plant,
 - description of
 - denitrification unit (DeNO_x), 229–232, 231*t*, 233*t*, 235*t*, 236*t*
 - desulfurization unit (DeSO_x), 232
 - diesel engine-actuated generator, 229–232
 - fuel savings analysis
 - heat efficiency η_e , 232–235
 - thermodynamic calculations, 232–235
 - Direct/indirect forcing, by aerosols in
 - global scale, 609
 - Direct reforming, 162–163, 166
 - “Dirty energy,” 74

DNA, *see* Designated national authorities (DNA)
DOE, *see* Designated operational entities (DOE)
Downsian model, 418
DPPS, *see* Planning and National Development Doctrine (DPPS)
Drying (food process), 267
DS, *see* Degree of swelling (DS)

E

Earth's atmosphere, increasing temperature, 4
Eastern Mediterranean Basin, warming tendency and its influence on West Nile fever outbreaks, 525–532
daily temperature, 528
department for pest prevention, 528
Eastern Mediterranean (EM) basin, 525
Israeli Ministry of environmental protection, 528
Israel Ministry of health, epidemiology department, 528
methods, 528–529
geographic information system (GIS), 528
mean monthly temperatures, 528
Pearson cross-correlations, 529
perennial monthly averages, 528
Spearman correlation, 529
results and discussion, 529–532
lag correlation analysis using Z-test, 530
Mediterranean climate type, 532
mosquito repellent, 531
pest control systems use, 531
population dispersion, 529
spearman correlation calculation between WNF, 532*t*
temperature anomalies, 531*f*
urban and suburban areas, 532
2-week lag (result of multinomial logistic regression), 529
WNF cases distribution in Israel, 530*f*
study aim, 528
 C. pipiens mosquito population, 528
 WNF frequency in humans, 528
West Nile virus
 Culex pipiens, 526
 fatal human meningitis or encephalitis, 526
 vector-borne zoonotic disease, 526
 West Nile fever (WNF), 526
 WNV, 526
WNF outbreaks, 527–528
 frequency of heat waves, 527
 goose flocks in summer, 527
 WNV encephalitis in humans, 527
WNV and heat conditions, 527
 high temperatures, speed up replication of WNV, 527
 mosquito-to-vertebrate transmission rates, 527
 WNV activity, 527
 WNV outbreaks, 527
Eastern Mediterranean (EM) basin, 525
Eastern province, 518
 eastern region climate fields, 518*t*
EBGA, *see* Elitism-based genetic algorithm method (EBGA)
Electricity generation from renewables
 biomass, 75–76
 geothermal, 76
 hydro, 74–75
 others, 76
 solar, 75
 wind, 76
Electrothermochemical water-splitting process for H₂ production, 135*f*
Elitism-based genetic algorithm method (EBGA), 243
EM, *see* Eastern Mediterranean (EM) basin
Embodied carbon, 367
 energy and pollutant emissions, embodied, 368
 manufacturing release non-fuel-related carbon, 381
 meeting needs for future generations, 367–368
 method, 368–374
 energy analysis, 368–370
 life cycle thinking, 369–371
 pyramid of representation, 369*f*
 system boundaries, 374
 rule of thumb, 369

- second-order effects, 368
- umbrella concepts of sustainability, 397
- Embodied energy to embodied carbon, 373*f*
- Emission difference analysis, 235–238, 237*f*
 - heat–power ratios, 236*t*
 - load variation, 238*f*
- Emission market at end of commitment period, 399
- under Kyoto Protocol, 399
- equilibrium
 - decision making of nations, 403–405
 - decision making of private brokers, 402–403
 - linear equilibrium, 402–403
 - normal distributions, 402–403
- model, 401–402
 - emissions trading market, 401–402
- numerical examples, 405–406
- presumptions, 400
- ratifying Kyoto Protocol, 399–400
- trueup period, 399–400
- Emission reduction units (ERU), 410
- Emissions
 - carbon and CO₂, and their
 - projections, 28*f*
 - history of for EU, 33
 - increase due to energy use, 9
 - from industrial and transport activity, 8
 - under Kyoto Protocol, 399
 - linear relationship between world economic growth and, 31*f*
 - for power generation from differing sources, 37*t*
 - reduced, for house in summer season, 158*f*
 - steps to reduce, 34
 - worldwide CO₂, into atmosphere from various energy sources, 72*f*
- Empty quarter climate fields, 520, 520*t*
- Energy
 - consumption points and process flows
 - during food supply chain, flowchart of, 201*f*
 - and exergy efficiencies of PV and PV/T systems, 83*f*
 - production through Municipal Solid Waste (MSW), 162
 - utilization strategy plan, 22–23
 - world primary sources
 - consumption, 10
 - projection, 11
 - variation of actual and projected consumption, 11*f*
- Energy–environment technologies, 2
- Energy-resource utilization
 - environmental impact and, 38
- Energy sources for nuclear-based hydrogen production
 - advanced gas reactor (AGR), 131
 - advanced high-temperature reactor (AHTR), 131–132
 - high-temperature gas-cooled reactor (HTGR), 131
 - modular helium reactor (MHR), 132
- Energy use
 - economic growth and CO₂ emissions, 9
 - efficient energy use, 20–21
 - growth in Canada, 18*f*
 - increase in global warming with
 - increase in, 5
 - intensity reduction for New Zealand, 19*f*
 - population and increased dependency, 11
 - right to, 4
- Enhanced oil recovery (EOR), 291
- Enterprise Risk Management (ERM), 423–424
 - risk management process, 431–436
 - risks–reward paradigm, 428–431
- Enterprise risk management strategies, 427
- Enthalpy, 48
 - cooling effect of ammonia, 119
 - of drying air, 271
- Entropy, 54–58
 - change of universe, 57
 - development of Clausius’ statement, 55*f*
 - generation, 57
 - irreversibility of, 58
 - reversible cycle, 56*f*
- Environmental impact
 - energy-resource utilization and, 38
 - factor, 170

- for different scenarios, 175*f*
- reducing, 1
- Environmental Protection Agency, 435
- EOR, *see* Enhanced oil recovery (EOR)
- EOR method, 287–288*f*
- Equilibrium, emission market
 - decision making of nations, 403–405
 - decision making of private brokers, 402–403
 - linear equilibrium, 402–403
 - normal distributions, 402–403
- Equilibrium constant of reaction, 310
- ERM, *see* Enterprise Risk Management (ERM)
- ERU, *see* Emission reduction units (ERU)
- Eucalyptus* essential oils, 360–362*t*
 - E. globulus*, 357
- Exergy, 58–59
 - closed system, 58
 - efficiency, 81–82
 - with Cu–Cl cycle, 140, 141*t*
 - of PV and PV/T systems, comparison of, 84*f*
 - of PV and PV/T systems, energy and, 83*f*
 - variation of sustainability index (SI) with, 85*f*
 - emptying system, 59
 - filling system, 59
 - open system, 58
- Exhaust flow in DEPC plant, description of, 229–232, 230*f*

F

- Fan pressure ratio–bypass, 248–249
- Fan pressure ratio (II*f*), 251–252
- Fatal human meningitis or encephalitis, 526
- FBC, *see* Fluidized bed combustion (FBC)
- FFM, *see* Fuel forwarding module (FFM)
- Filling/emptying system, thermodynamics, 47–48
 - exergy, 58–59
 - first law of thermodynamics, 49–50
- Five-person agreement, 416*f*
- Flame atomic absorption spectrometer, 621
- Flame ionization detector, 612
- Flowering species, 603
 - P. aviculare*, 603
 - Scolymus hispanicus*, 603
- Fluidized bed combustion (FBC), 330
- Flu pandemics, 644
- Food chain, acidity in water affecting, 5
- Food drying processes, exergy analysis of, 267
- Food industry
 - alternative solution to reduce greenhouse gas emissions from, 206*f*
 - possible strategies for reducing greenhouse gas emissions produced by, 204*f*
 - process steps in, 200*f*
 - strategic program for food industry, 205*f*
- Food products
 - energy demand and global warming potentials, 202
- Food supply chain and global warming in terms of raw material and fossil fuel use, relationship between, 199*f*
- Fossil fuel
 - consumption/green energy consumption, 13
 - emissions, 157*t*
 - utilization ratio, 91
- Freezing process, 646
- FT-IR Spectrometer, 622
- Fuel cell, 39
 - See also individual fuel cells*
- Fuel forwarding module (FFM), 230
- Fuel saving analysis (FSA), 226
- Fuel utilization efficiency, 226
 - See also* Fuel saving analysis (FSA)

G

- Game analysis of Kyoto and Post-Kyoto schemes, 407
 - flexibility mechanisms, 408
 - Kyoto mechanisms, 408–413
 - bottom-up method, 412–413
 - clean development mechanism, 410

- emission trading (ET), 408–409
- issues concerning baseline setting
 - methods and additionality, 410–412
- joint implementation (JI), 409–410
- post-Kyoto, 413–420
 - coalition formation, 413–415
 - negotiation, 413–415
 - post-Kyoto and coalition formation theory, 413–415
 - role of CDM, 418–420
- Gas and steam cycles, comparison of
 - CO₂ emission, 189*f*
 - four different solid fuel types, 191*f*
- Gaseous precursor emissions, 486
- Gas-phase reactions, 617
- Gas turbine (GT), 165–166
- Gas turbine combustion chamber (GTCC), 181–182
- GC-FTIR analysis
 - Aldrich-vapor phase (Library spectrum), 358–359
- GC-MS analysis, 358–359
- GC retention times, 612
- Generalized additive regression model (GAM), 630
- Genetic algorithms (GA), 243
- Geographic Information System (GIS), 528
- Geothermal, electricity generation from, 76
- Geothermal district heating systems (GDHS), 148
 - in Turkey, 148
- Geothermal field in Bigadic, 149*f*
- GHG, *see* Greenhouse gas (GHG)
- GHG emissions, 265, 408
 - analysis of, 167
 - comparison of LFG utilization technologies, 170
 - electricity generation technologies from LFG, 168–169
 - flaring, 167–168
 - landfill site with/without active collection system, 167
 - from food industry, alternative solution to reduce, 206*f*
 - mean price, efficiency of electricity generation, and average, expressed as CO₂, 73*t*
 - produced by food industry, possible strategies for reducing, 204*f*
 - reducing, from waste, 162
 - reduction
 - assumed contributions to, 36*t*
 - as proposed by NRTEE, 26*f*
 - reduction ratio for different scenarios, 174*f*
 - routes in landfill site with LFG collection system, 165*f*
 - specific lifetime, 170
 - for different scenarios, 175*f*
 - for various LFG utilization methods, 173*f*
- GHG reduction ratio, 170
- GIO, *see* Greenhouse Gas Inventory Office (GIO)
- GIS, *see* Geographic Information System (GIS)
- GIS technology, 515
- Glacial isostatic adjustment, 502
- Global average temperatures, instrumental record of, 4*f*
- Global climate changes, 606
- Global climate models (GCM), 512
- Global horizontal irradiance, 468, 471
 - See also* Cloud cover radiation model (CRM)
- Global positioning systems, 648
- Global radiation, 472, 482
- Global solar radiation, 481
 - based on cloud data for major cities of South Korea, calculation of, 467
 - cloud amount and solar altitude for global radiation, function of, 472
 - cloud cover radiation model (CRM), 471–472
 - measured and calculated data, comparison of, 480
 - Hamburg coefficients, 480
 - measured data, 469–471
 - cloud cover (CC), 469–470
 - solar radiation, 471
- Global temperature, increasing
 - causes, 7
 - remedy/symptoms, 5
 - short term solution, ineffective, 13–14
 - steps to reduce, 6
- Global warming

- advice from advisors: suffering from “wedgemia,” 23–26
 - assessing alternative or substitution value, 36–38
 - cure, 5–7
 - defined, 161
 - diagnosis of cause, 7–8
 - cure alls, 15–17
 - green energy and its effectiveness, 14–15
 - panaceas, painkillers, and procrastination, 13–14
 - carbon fuel dependency, 9–12
 - second opinion confirms fears, 8–9
 - truly disabling treatments, 17–19
 - doctor, 3–4
 - feeling good: lifestyle changes and spa treatments, 33–36
 - health of planet, 1–2
 - hydrogen cure, 38–41
 - many values of carbon, 28–30
 - valuing emissions: carbon trading business, 31–33
 - world value of carbon emissions, 30–31
 - efficiency improvement, 19–23
 - planetary patient/planet
 - suffering, 2–3
 - plethora of ineffective and costly therapies, 26–28
 - pollution, 268
 - sustainability, and risk management, 430
 - symptoms, 4–5
 - Global warming, effect of shipyards on, 585
 - halogenated volatile organic compound, 585
 - chlorofluorocarbons (CFC), 585
 - hydrochlorofluorocarbons (HCFC), 585
 - trichloroethane, 585
 - non-methane (NM) VOC, 585
 - photochemical smog, 585
 - ‘Global warming potential’ (GWP), 161
 - Green energy
 - to compensate conventional resources shortages, 11
 - expected consumption increase, 12
 - quotes encouraging, 14–15
 - usage and efficiency, 14
 - Greenhouse effect, 307–308
 - Greenhouse gas emissions from food industry, strategic program to reduce, 197–198
 - analysis, 198
 - energy demand and global warming potentials, 202
 - energy use in food supply steps, 200–201
 - food supply chain, 198
 - general processes in food industry, 198–200
 - results and discussion, 202–203
 - alternative solution, 205–208
 - some key drivers and strategies, 203
 - strategic program, 203–205
 - Greenhouse gas emissions from landfill site using various thermal systems, reducing, 161–163
 - analysis of greenhouse gas emissions, 167
 - comparison of LFG utilization technologies, 170
 - electricity generation technologies from LFG, 168–169
 - flaring, 167–168
 - landfill site with/without active collection system, 167
 - landfill processes, 163
 - calculation of landfill gas generation, 163–164
 - collection, 164
 - thermal systems considered, 164
 - gas turbine (GT), 165–166
 - internal combustion engine (ICE), 165
 - solid oxide fuel cell (SOFC), 166
 - Greenhouse gas (GHG), 7, 28, 71, 329–330, 643
 - harms of, 73
 - released due to human activity, 161
 - Greenhouse Gas Inventory Office (GIO), 591
 - “Green Market,” 15
- ## H
- Haber–Boch process, 113
 - Habitat, alterations in species, 5

- Hadley Center's global atmospheric model, 513
- Halogenated volatile organic compound, 585
- chlorofluorocarbons (CFC), 585
 - hydrochlorofluorocarbons (HCFC), 585
 - trichloroethane, 585
- "Harvesting" effect, 630
- Hazards of SO₂, 485
- Health-care system, 640
- Health impacts of heat waves of 2007 in Hungary, 629–630
- central Hungarian region (CHR), 629
 - characterization of temperature, 630–631
 - daily mean temperature, 631
 - heat waves, 631
 - outskirt (Pestszentlorinc), 631
 - summer temperature and related data in Budapest, 631*t*
 - comparison/previous, present
 - associations/of daily mortality and temperature, 636–640
 - association of daily mean temperature and mortality in Budapest, 636*f*
 - central statistical office, 637
 - crude mortality data, 637
 - curves of nonlinear association, 636
 - daily mean temperature, 639
 - health-care system, 640
 - heat health-warning system, 640
 - heat-wave events and attributed mortality in Europe, 638*t*
 - heat wave mortality, 639
 - national excess mortality, 639
 - optimal or threshold temperature, 636
 - quasi-linear in higher temperature, 640
 - real time data, 639
 - short-, middle- and long term measures, 640
 - temperature-mortality association, 640
- EuroHeat, by Public Health Program/EC, 629
- mortality rates/excess mortality, extreme high temperature, 632–636, 633*f*, 634*f*
- association of daily temperature and, in CHR, 632*f*
 - Central Hungarian region, 636
 - daily in/out of hospital death counts and daily mean temperature in CHR, 634*f*
 - daily mortality in CHR, 632*f*
 - heat wave mortality, 632–636
 - mean daily mortality, 632
 - mean mortality, 633
 - minimum and maximum values of mortality, 634
 - mortality and temperature values, 635
 - mortality displacement (harvesting), 635
 - rate of mortality, 633
 - risk factor of mortality, 632
 - seasonal variation, 632
- mortality-temperature relationship, 630
- PHEWE, by EC FP6 framework program, 629
- University of Birmingham, 629
- Heat health-warning system, 640
- Heating, ventilation, and air conditioning system (HVAC system), 439
- Heat pump conveyor dryer system, 270*f*, 275–277*f*
- Heat pump-driven conveyor dryer, 268
- Heat pumps (HP), 268
- Heat wave, 629
- mortality, 632–636, 639
- Henry's law of utilizing solvents, 282–283
- H₂ICE Ford Focus to Ammonia fuel, conversion of, 124*t*
- High-bypass ratio turbofan engines, 242, 244*f*
- High-bypass turbofan engine modeling, 244–245
- High-pathogenic avian flu, 648
- High-pressure gas turbine (HPGT), 181
- High-resolution data, 505
- High-temperature gas-cooled reactor (HTGR), 131
- H5N1 avian influenza, 646
- H5N1 virus, 646
- Hollow fiber membrane contactors, 307–308, 309*f*

- Hongkong flu (H3N2)/1968, 644
 8760 hour-by-hour method, 151
 Human flu viruses, 649
 HVAC system, *see* Heating, ventilation, and air conditioning system (HVAC system)
 Hybrid photovoltaic solar water heater, 80*f*
 Hybrid photovoltaic/thermal (PV/T) system, 81
 Hybrid solar still, 81
 Hybrid sulfur cycle, 136, 138*f*
 Hydration OH stretching, 624
 Hydro, electricity generation from, 74–75
 Hydrochlorofluorocarbons (HCFC), 585
 Hydrogen
 from ammonia economy for transportation, 113*f*
 economy for transportation, 112*f*
 electrothermochemical water-splitting process, 135*f*
 energy
 criteria essential to achieving sustainable development, 38–39
 improved energy efficiency, 39
 major R&D activity areas for pathway to, 42*f*
 role in meeting future energy needs, 39–40
 scientific and technical challenges for, 41
 system, 130
 membrane reformer, principle of, 134*f*
 obtained from ammonia, cost correlation for, 116*f*
 technology options for nuclear hydrogen production, 134*f*
 thermochemical process for producing, 133–134
 Hydrogen production from ammonia for vehicles, environmentally benign, 109–112
 driving range and its cost, 122–124
 energetic and cost parameters, 117–119
 hydrogen production from ammonia, 112–117
 onboard refrigeration with ammonia, 119–122
 Hydrogen production systems, 132–133
 Ca–Br Cycle, 137
 copper–chlorine cycle, 137–143
 hybrid sulfur cycle, 136
 iodine–sulfur cycle, 135–136
 ISPRA Mark 9 Cycle, 136
 steam conversion of methane, 133
 thermochemical and thermoelectrochemical cycles, 133–135
 Hydrologic models, 513
- ## I
- ICE, *see* Inventory of Carbon and Energy (ICE)
 ICE domestic building model, 374–380, 375*f*, 377–378*f*
 benchmark results, 376–380
 embodied energy and embodied carbon, 376*t*
 English dwellings, 379–380*t*
 ICP-AES, *see* Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)
 IFIAS, *see* International Federation of Institutes for Advanced Study (IFIAS)
 IGCC configuration
 CO₂ emission among different temperature conditions for, 188*f*
 relative net work output among different temperature conditions for, 187*f*
 variation in values of parameters under investigation for given, 186*f*
 IMF, *see* International Monetary Fund (IMF)
 Incheon observatory, 471
 Independent variables, 490
 Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), 332
 Industrial revolution, cause for global warming, 8
 Influenza A viruses, 645
 INRF, *see* Institut National de la Recherche Forestière (INRF)
 Insolation (INcident SOLar radiATion energy flux), 89

Institute National de la Recherche Forestière (INRF), 358
 Integrated gasification combined cycle (IGCC), 179
 partial gasification-based, 181
 with supplementary firing, 181
 power plant, 180*f*
 Interdisciplinary research and scientific training, 644
 Intergovernmental panel on climate change, 643
 Internal combustion engine (ICE), 165
 International energy agency (IEA), 227
 International federation of institutes for advanced study (IFIAS), 368
 International monetary fund (IMF), 213
 Inventory of carbon and energy (ICE), 371
 Iodine–sulfur cycle, 135–136
 process for thermochemical
 production of H₂, 136*f*
 ISPR Mark 9 cycle, 136
 hydrogen production process, 137*f*
 Israeli Ministry of Environmental Protection, 528
 Israel Ministry of Health, epidemiology department, 528

J

Jacobians, method of, 59
 Janke, mechanical shaker of type, 622
 JISC, *see* JI supervisory committee (JISC)
 JI supervisory committee (JISC), 410

K

Kelvin–Planck statement
 graphical explanation, 53*f*
 second law of thermodynamics, 52
 Kerosene jet fuel, 247*t*
 Kerosene usage chain, 250*f*
 Kinetic energy, 319
 KMA, *see* Korea Meteorological Administration (KMA)
 Korea, changing fuel type as energy resource, 211
 conversion into coal, 220–221

 CO₂ emissions, 220*t*
 conversion to high-sulfur fuel, 218–219, 219*t*
 methods, 212–213
 national-scale industrial complexes (IC), 211
 natural gas and nuclear power options, 222
 SO_x levels in major cities, comparison, 213–214, 214*f*
 desulfurization facilities (DSF), 213–214
 SO_x levels with change of sulfur content, 214–218, 215*f*
 Korea Meteorological Administration (KMA), 469
 Korean solar radiation observatory, 471
 Kuwait Institute for Scientific Research, 448
 Kyoto protocol (KP), 407
 emissions under, 399

L

Laboratory-scale fixed bed reactor, 296–299, 297*f*
 reactor with resistance furnace, 298–299*f*
 Lag correlation analysis using Z-test, 530
 Land ecosystem sequestration
 carbon content techniques
 increase of carbon density in soil, 286
 increase of mass and depth of trees roots, 286
 minimization of decay rate, 286
 ecosystem administration, 286
 ecosystems protection and maintenance, 286
 stabilization of photosynthesis, 286
 Land fill gas (LFG), 162, 163
 collection, 164
 greenhouse gas emission routes in landfill site, 165*f*
 electricity generation technologies from
 gas turbine, 168–169
 internal combustion engine, 168
 solid oxide fuel cell, 169
 generation, calculation of, 163

Landfill processes, 163
 calculation of landfill gas generation, 163–164
 landfill gas collection, 164
 LFG composition in landfill site (case study), 170–176
 annual gas generation of LFG and its components, 172*f*
 collected and uncollected amount of LFG and its components, 173*f*
 environmental impact factor for different scenarios, 175*f*
 GHG reduction ratio for different scenarios, 174*f*
 input data for case studies, 171*t*
 specific lifetime GHG emission for different scenarios, 175*f*
 total GHG emissions for various LFG utilization methods, 173*f*
 LandGEM, 163
 Large combustion plants (LCP), 229
 “Law of unintended consequences,” 16
 LCA, *see* Life cycle assessment (LCA)
 LCP, *see* Large Combustion Plants (LCP)
 LCS, *see* Life cycle savings (LCS)
 Least squares regression analysis, 570
 Leukoencephalopathy, 583–584
 LFG, *see* Land fill gas (LFG)
 LFG and its components
 annual gas generation of, 172*f*
 collected and uncollected amount of, 173*f*
 Life cycle assessment (LCA), 370
 Life cycle for species
 Setaria viridis (L)/*Echinochloa crus-galli* (L), 601
 Life cycle savings (LCS), 441
 “Limestone-gypsum” process, 232
 Liquefied natural gas (LNG), 216
 Liqui-Cel Mini-Module, 308–309
 See also Membrane gas absorption
 LNG, *see* Liquefied natural gas (LNG)
 Locations for spread effects of climate change, 516–517
 PRECIS simulation weighted area daily values, 517*t*
 6 regions with 37 locations, 517*f*
 LPAI virus infections, 648

M

Machining and metalworking process and wastes, 584
 metal cutting processes, types of, 584
 MAD, 481
 MAFF, *see* Ministry of Agriculture, Forestry, and Fisheries (MAFF)
 Malaysian Science and Technology Information Centre (MASTIC), 389
 Malnutrition, due to energy poverty, 4
 Marnoch performance for multiple pressure vessel, 255, 259*f*, 265*f*
 absorbs heat from higher temperature source, 255–257
 Carnot efficiency, 255
 conservation of mass/ Bernoulli’s equation, 260
 operating parameters, 260–261*t*
 heat exchangers, data for, 261*t*
 modeling/analysis of engine performance, 257–262
 renewable energy resources, 265
 Marnoch power device, 256*f*
 Marnoch prototype engine, 258*f*
 Marnoch thermal energy conversion device, 266
 MASTIC, *see* Malaysian Science and Technology Information Centre (MASTIC)
 Maximum takeoff weight (MTOW), 243
 Maxwell relations, 59
 Mean of absolute deviations (MAD), 481
 Mechanical equilibrium, 48
 Megalopolis limestone, 314*f*, 338*f*
 Membrane gas absorption, 307–308, 308*t*
 Meteorological equipment
 modernization plan, 471
 Meteorological parameters, 467, 487
 cloud cover, 467
 sunshine duration, 467
 Meteorology, role of, 485
 Methane, steam conversion of, 133
 Method of Jacobians, 59
 Methyl *tert*- Butyl Ether (MTBE)-contaminated water/wastewater, 555–561

- experimental pervaporation setup, 559*f*
- membrane preparation, 558
- solution casting method, 558
- MTBE/water mixtures separation by pervaporation, 557*t*
- PEBA 2533
 - hydrophilic PEBA materials, 557
 - hydrophobic PEBA materials, 557
 - manufactured by Elf-Atochem, 557
 - polyamide and polyether segment (block), 557
- pervaporation, 556
 - characteristics of, 556
 - vacuum and sweep gas pervaporation, 556
- pervaporation experiments, 558–559
 - refractometer, 558
 - separation factor (selectivity), 558
- pervaporation results, 560–562
 - flux in mixtures of MTBE/water for PEBA, 561*f*
 - permselective for MTBE, 560
 - relationship between compositions for MTBE/water mixtures through PEBA, 560*f*
 - separation factor in mixtures of MTBE/water for PEBA, 561*f*
 - solution–diffusion model, 561
- sorption experiments, 558
 - degree of swelling (DS), 558
- sorption results, 559–560
 - MTBE/water for PEBA, 559*f*
 - pervaporation flux, 560
 - pervaporation selectivity, 560
- Mini-module membrane reactor, CO₂
 - absorption in, 307
 - ambient temperature and pressure, 310–311*f*
 - coal upgrading process, 307–308
 - energy-efficient devices, 307–308
 - experimental
 - contactor characteristics, 308*t*
 - isothermal condition, 308–309
 - gas–liquid membrane contactors, 307
 - selectivity process, 307–308
- Ministry of Agriculture, Forestry, and Fisheries (MAFF), 592
- Modular Helium Reactor (MHR), 132
- Molten carbonate fuel cell (MCFC), 162
- MSW, *see* Municipal Solid Waste (MSW)
- MTBE, *see* Methyl *tert*-Butyl Ether (MTBE)
- MTOW, *see* Maximum takeoff weight (MTOW)
- Multimedia pollutant, sources/effects on, 579–580
 - acute and chronic health problems, 580
 - best management practice (BMP)
 - study in Turkish shipyard, 587
 - control for waste reduction, 587
 - tin-free, TBT-free, or low-VOC paint, 587
- chlorinated solvents, 585
 - global warming or acid rain, 585
- current situation, 588–589
- definition/characterization/prevention, 580
- global warming, effect of shipyards on, 585
 - halogenated volatile organic compound, 585
 - non-methane (NM) VOC, 585
 - ‘photochemical smog,’ 585
- machining and metalworking process and wastes, 584
 - metal cutting processes, types of, 584
- painting and coating process and wastes, 583–584
 - copper-based and tributyltin (TBT), antifouling paints, 583
 - halogenated and nonhalogenated solvents, 583
 - organic solvents, hazardous chemicals, 583–584
 - VOC, special category for air pollutants, 583
- pollutants and wastes, 581
 - particulates matter (PM), 581
 - volatile organic compounds (VOC), 581
- potential environmental and human health hazardous wastes, 580
- previous situation, 587–588
 - safety issues, threats to workers, 588

- separation of process wastes, 588
 - training of managers, employers
 - about waste management, 587
 - waste material description
 - according to color codes, 588*f*
 - recycling, 587
 - aerobic and anaerobic treatment, 587
 - reformulation or redesign of products, 586–587
 - shipbuilding industry, 579
 - shipyard processes and pollutant sources, 580–581
 - basic shipyard processes, 581*f*
 - solid, liquid, gaseous pollutants, 581
 - shipyard production processes,
 - studies of, 580
 - contaminants, 580
 - human health and environment, effects on, 580
 - management of wastes in shipyards, 580
 - shipyards, 579
 - new shipbuilding division, 579
 - ship repairing division, 579
 - solvent cleaning and degreasing
 - process and wastes, 584
 - cold cleaning and vapor degreasing, 584
 - VOC and HAP/air emissions, 584
 - source reduction, 586
 - waste management hierarchy, 586*f*
 - surface preparation process and wastes, 581–583
 - common surface preparation methods, 581–582
 - VOC, wastes and pollutants
 - particulates, 579
 - waste management in shipyards, 586
 - welding and cutting process and wastes, 584–585
 - mechanical or thermal hot metal cutting operations, 584–585
 - on-site/off-site treatment, 585
 - Multiple sclerosis, 583–584
 - Multi-staged enthalpy extraction technology (MEET) system, 179
 - Municipal Solid Waste (MSW), 456
 - energy production through, 162
 - as fuel, 456
 - landfill gas generation, 163
 - production plant, 460*f*
- N**
- N*-alkenes, of organic aerosols, 613
 - airborne particles, 614
 - carbon preference index (CPI), 614
 - evolution of meteorology dominating Algiers region, 613
 - motor vehicular exhaust emissions, 614
 - plant wax contribution vs. petroleum-derived fuels, 614
 - seasonal average *n*-alkenes concentrations, 613*t*
 - Nash bargaining solution, 417
 - National Academy of Sciences of USA, 643
 - National excess mortality, 639
 - National Institute of Environmental Health in Budapest, 630
 - National Meteorological Service, 630
 - National Public Health and Medical Officers' Service, 630
 - National Toxicological Committee, 616
 - National University of Malaysia (UKM), 389
 - Natural disasters, 502
 - Natural resources, usage/exhaustion, environmental problem, 1
 - Neurobehavioral disorders, 583–584
 - Nigeria, temperature variations and their effects on rainfall
 - analysis of rainfall and temperature trends, 574
 - climatic regions, 566
 - correlation analysis
 - correlation coefficient, 570
 - positive/negative correlation, 570
 - temperature and rainfall, 574
 - data analysis, 567–569
 - annual rainfall average, 569
 - annual temperature average, 568
 - rainfall situation, 568
 - temperature situation, 567
 - data used
 - discrepancy in duration of Nigeria/locations, population, and duration, 567*t*

- Nigerian Institute of Meteorological Agency (NimetAg), 566
 six geo-political zones, 566
 global scale sea-surface temperature anomalies/rainfall characteristics, 571
 least squares regression analysis
 'least square,' 570
 least squares line method, 570
 least squares regression plots
 for north central zone, 571*f*
 for northeast zone, 571*f*
 for northwest zone, 573*f*
 for southeast zone, 573*f*
 for south-south zone, 572
 for southwest zone, 572*f*
 locations and climatic conditions, 565-566
 rainfall against temperature for geo-political zones, 575*t*
 rainfall and temperature variations in Nigeria, 574-575*t*, 574*t*
 rainfall and sequential version of Mann-Kendall, 576*f*
 regression analysis results of rainfall/temperature variations, 574*t*
 southern Nigeria, 566
 temperature and sequential version of Mann-Kendall, 577*f*
 temperature average for Nigeria, 567*f*
 trend analysis, 569-570
 least squares regression analysis, 570
 Mann-Kendall rank statistics, 569
 parametric and non-parametric tests, 569
 Nigerian Institute of Meteorological Agency (NimetAg), 566
 NimetAg, *see* Nigerian Institute of Meteorological Agency (NimetAg)
 Nipah virus encephalitis/Malaysia/1998, 644
 Nitro-polycyclic aromatic hydrocarbons (NPAH), 616-619
 formation mechanisms of nitrated PAH, 618
 gas-phase reactions, 617
 Mean 2-nitrofluoranthene (2-NFA) and 2-nitropyrene (2-NPY) concentrations, 617*t*
 oxidative capacity, 616
 2-nitrofluoranthene (2-NFA), 616
 2-nitropyrene (2-NPY), 616
 Nitrous Oxide emission from
 agricultural practices in Japan, 591-598, 593-594
 activities and emission factors data for livestock husbandry, 594*t*
 activity data and emission factors for crop production, 594*t*
 agriculture, direct and indirect emissions from, 594-596
 direct/indirect N₂O emission, from crop production/livestock husbandry, 595*f*
 Japanese emission factor, 595
 N₂O emissions from each kind of agricultural sector, 596*f*
 N volatilization rates of Mishima, 594
 significant environmental implications, 595
 agriculture, global N₂O emissions, sources of
 agricultural land, 591
 crop residue burning, 591
 manure handling, 591
 agriculture in relation to, 597-598
 agricultural practices to global warming, 597
 deodorization during composting, 598
 reduction in N inputs, 598
 data sources/N₂O emissions
 association of livestock production, 592
 chemical fertilizer nitrogen (N), 592
 MAFF cost of livestock products, 592
 MAFF questionnaires and production environment statistics, 592
 data validation/N₂O emissions, 594
 differences/uncertainties of, 597
 chemical N fertilizer application, 597
 chemical N fertilizer demand, 597

- GIO and N infiltration, 597
 - IPCC default emission factor, 597
 - Japan livestock technology association, 597
 - N deposition, 597
 - N excreta-related N_2O emissions, 597
 - N volatilization rate, 597
 - residual N as manure, 597
 - direct/indirect N_2O emission, 593–594
 - framework, N_2O emissions associated with agricultural N flow, 592*f*
 - N_2O emissions/calculation for estimation of, 592–593
 - crop production part, 593
 - livestock husbandry part, 593
 - N_2O emissions from each sector and their trends, 596–597
 - crop production, 596
 - livestock husbandry, 596
 - Nitrous oxide (N_2O), 591
 - NMHC, *see* Non-methane hydrocarbons (NMHC)
 - Non-conventional sources of energy, *see* Renewable energy sources
 - Non-methane hydrocarbons (NMHC), 357
 - Non-methane (NM) VOC, 585
 - Non-methane organic compound (NMOC), 163
 - Northern region climate fields, 519, 520*r*
 - Nuclear-based hydrogen production, environmentally benign, 129–131
 - energy sources for nuclear-based hydrogen production
 - advanced gas reactor (AGR), 131
 - advanced high-temperature reactor (AHTR), 131–132
 - high-temperature gas-cooled reactor (HTGR), 131
 - modular helium reactor (MHR), 132
 - hydrogen production systems, 132–133
 - Ca–Br Cycle, 137
 - copper–chlorine cycle, 137–143
 - hybrid sulfur cycle, 136
 - iodine–sulfur cycle, 135–136
 - ISPR Mark 9 Cycle, 136
 - steam conversion of methane, 133
 - thermochemical and thermoelectrochemical cycles, 133–135
 - Nuclear energy-driven thermochemical cycle, 130
 - Nuclear hydrogen production, technology options for, 134*f*
- O**
- Ocean sequestration
 - direct injection, 284–285*f*
 - Gigatons Carbon (GtC), 284–285
 - iron fertilization, 284–285
 - reinforcement of natural sequestration
 - iron fertilization, 285
 - fish cultivation industries, 285
 - phosphorus minimization technique, 285
 - OECD, *see* Organization for Economic Co-Operation and Development (OECD)
 - Olson, collective-action problem of, 412
 - Open-air Brayton cycle engines, 95
 - Open system, thermodynamics, 48
 - exergy, 58
 - first law of thermodynamics, 49
 - Optimal or threshold temperature, 636
 - Organic aerosols, analysis of, 612
 - co-injected standards, 612
 - flame ionization detector, 612
 - GC retention times, 612
 - selected ion monitoring (sim) modality, 612
 - trace GC gas chromatograph, 612
 - trace Q mass spectrometer, 612
 - Organic aerosols, chemical characteristics/source reconciliation, 609–610
 - asthma, by aerosols in local levels, 609
 - biogenic/anthropogenic origin, 609
 - carcinogenic/mutagenic compounds, 610
 - combustion processes, 610
 - direct/indirect forcing, by aerosols in global scale, 609
 - sample extraction and clean-up, 612

- column chromatography on neutral alumina, 612
- non-polar aliphatic compounds, 612
- sampling procedure, 611
- PM₁₀ aerosols, 611
- sampling protocol and rationale, 610–611
 - aerosol, composition of, 610
 - dirty fogs, formation of, 610
 - global emission budget, 610
 - Oued Smar waste landfill, 611
 - particulate organic matter (POM), 610–611
 - Urban POM, 611
- Organic Rankine Cycles (ORC), 94
- Organization for Economic Co-Operation and Development (OECD), 227
- Original coefficient, 481
- Oxidative medium on removal of sulfur and mineral matter from can lignites, 347
- acidic medium deduction of sulfur ratio, 355
- background, 347
 - silopi harput asphaltite, 348
- experimental study, 348–354
 - ash and demineralization variation, 349*t*
 - bomb calorimeter, 349–350
 - calorific values of can lignite, 350*t*
 - FTIR spectrum, 350–352*f*
 - oxidative medium, 348–349
 - proximate analyses (%) of can lignite, 348*t*
 - total sulfur % values of can lignite, 349*t*
 - X-ray spectrum of Can lignite, 353–354*f*
- Ozone layer depletion, 73
- P
- PAH, *see* Polycyclic aromatic hydrocarbons (PAH)
- PAH indicator, 615
- Painting and coating process and wastes, 583–584
 - copper-based and tributyltin (TBT), antifouling paints, 583
 - halogenated and nonhalogenated solvents, 583
 - organic solvents, hazardous chemicals, 583–584
 - Alzheimer's disease, 583–584
 - leukoencephalopathy, 583–584
 - multiple sclerosis, neurobehavioral disorders, 583–584
 - VOC, special category for air pollutants, 583
- Paleoclimatic warming, 502
- Pandemic influenza risk, potential impact of climatic change, 643–654
 - climate change, migratory birds, and infectious diseases
 - phenological changes in birds, 645
 - wild water birds, 645
 - climate change spread avian influenza, 645–650
 - avian origin, 648
 - bird flu outbreaks, 646
 - Bowling Green State University in Ohio, 646
 - freezing process, 646
 - Global Positioning Systems, 648
 - High-pathogenic avian flu, 648
 - H5N1 avian influenza, 646
 - H5N1 virus, 646
 - Human avian influenza A (H5N1)
 - cases by age group and country, 650*f*
 - human flu viruses, 649
 - influenza A viruses, 645
 - limited human-to-human transmission, 650
 - low-pathogenic avian influenza (LPAI) A viruses, 648
 - mixing and
 - recombination/American and Eurasian influenza strains, 646
 - 'mixing vessel' for virus, 649
 - phylogenetic relationships of virus, 647
 - potential synergism, 647
 - reassortment of viral RNA genome segments, 648*f*
 - reservoirs of viruses, 648
- Partial gasification process, 181
- Pearson cross-correlations, 529

- PEBA, *see* Polyether block amide (PEBA) membranes
- PEBA 2533, 557
- Perkin–Elmer 8500 gas chromatograph, 309
- Perkin–Elmer spectrometer, 350–351
- Perkin Elmer spectrum model, 622
- Pervaporation, 556
- flux, 560
 - selectivity, 560
 - factor, 558
- See also* Pervaporation selectivity
- Pest control systems use, 531
- Phenological adaptation of cereal weeds
- to climate variations
 - materials and methods, 602–603
 - BBCH scale, 602
 - climatic characteristics of 5 years of observations, 602*t*
 - degree-days accumulation by phenological stages of each species, 604*t*
 - “Nouvelle flore d’Algérie” of Quezel and Santa, 602
 - phenological cereal weeds/climatic variations, determined by equation, 602
 - phenological aspects/events, 601
 - warming accelerates plant development, 606
- Phenological stages of major cereal weeds in Setif region, 605*t*
- Phenology, 601
- abundant species, 603
- pH meter, Cyber Scan pH 500, 622, 625
- Phosphoric acid fuel cell (PAFC), 162
- ‘Photochemical smog,’ 585
- Photovoltaic systems, 76–77
- applications, 77–79
 - agricultural solar water pumping stand-alone system, 78*f*
 - grid-connected PV systems, 78
 - hydrogen production, 78–79
 - space applications, 77
 - stand-alone systems, 77–78
 - energy and exergy efficiencies of, 82, 83*f*
- PV vs. PV/T systems, exergy
- efficiency of, 84
 - thermal (PV/T) applications, 79–81
 - energy efficiency of, 81
 - hybrid photovoltaic solar water heater, 80*f*
 - PV/T air collector, 79–80
 - PV/T water collector, 80–81
- Photovoltaic technology, 71
- Phylogenetic relationships of virus, 647
- Piston-cylinder arrangement, *see* Closed system, thermodynamics
- Planning and National Development Doctrine (DPPS), 390
- Plasma-atomic emission spectroscopy, 331–332
- Pneumatic rotary actuator, 257
- Pollutants and wastes, 581
- particulates matter (PM), 581
 - volatile organic compounds (VOC), 581
- Polycyclic aromatic hydrocarbons (PAH), 614–616
- air parcels holding particulates, 616
 - benzo(a) pyrene-equivalent (BaPE) carcinogenic power, 615
 - ‘diagnostic ratios’ between selected PAH congeners (DRPAH), 616
 - influence of automobile source, 616
 - National Toxicological Committee, 616
 - PAH-associated carcinogenicity, 615
 - PAH indicator, 615
 - seasonal average PAH concentrations, 615*t*
 - tailpipe emission, 616
 - TCDD-equivalence index, 615
 - total PAH concentrations, 615
- Polycyclic aromatic hydrocarbons (PAH), 609
- Polyether block amide (PEBA) membranes, 563
- Population dispersion, 529
- Potential environmental and human health hazardous wastes, 580
- Potential synergism, 647
- Power stroke, 262
- Power systems for vehicles, comparative performance analysis, 123*f*
- Precipitation, 503
- ‘PRECIS,’ *see* Providing Regional Climates for Impact Studies ‘PRECIS’
- Pressure swear absorption (PSA), 283

Presumptions, 400
 Prisoners dilemma, 413*f*
 Providing Regional Climates for Impact
 Studies 'PRECIS,' 513
 PSA, *see* Pressure swear absorption
 (PSA)

Q

Quadratic zirconia phase, 320
 Quartz wool, better temperature
 distribution, 296–299

R

Ratifying Kyoto Protocol, 399–400
 REACH, *see* Registration, Evaluation,
 and Authorization of Chemicals
 framework (REACH)
 Reagent and solutions, 622
 Real Estate and Housing Developers'
 Association (REHDA), 391
 "Refining margin," 30
 Reflectometric method, 488
 Regional climate model (RCM), 512
 Registration, Evaluation, and
 Authorization of Chemicals
 framework (REACH), 426
 Regression analysis, 486
 REHDA, *see* Real Estate and Housing
 Developers' Association
 (REHDA)
 Reheat combustor (RHC), 181–182
 Renewable energy in sustainable
 development, role of, 71–72
 electricity generation from renewables
 biomass, 75–76
 geothermal, 76
 hydro, 74–75
 others, 76
 solar, 75
 wind, 76
 environmental impact, 72–74
 photovoltaic systems, 76–77
 applications, 77–79
 thermal (PV/T) applications, 79–81
 Renewable energy sources, 71, 84
 advantages, 73
 electricity generation from, 74
 biomass, 75–76
 geothermal, 76

hydro, 74–75
 solar, 75
 'fundamental' sources, 89
 sustainability indicators for some,
 73*t*, 74

Restriction of hazardous substances
 directive (RoHS), 426

Reynolds' transport theorem, 48–49

Risk factor of mortality, 632

Risk management process, 428*f*
Auto Wars, 431

RoHS, *see* Restriction of hazardous
 substances directive (RoHS)

Russian flu (H1N1)/1977, 644

S

SACS, *see* Saline Aquifer Carbon
 Dioxide Storage (SACS)

SAIC/STM SunDish, 95

Saline Aquifer Carbon Dioxide Storage
 (SACS), 289*f*

SARS pandemic fever/southern
 China/2002, 644

Saudi Arabia, climate change on water
 resources in

plan developing, 513

basic analysis, 514–515

carbon cycle and chemistry models,
 513

center for climate prediction and
 research, 513

central region climate fields, 519,
 519*t*

climate fields averaged over all six
 regions, 521*t*

climate modeling system, 513

data for model software, 515–516

eastern province, 518

empty quarter climate fields, 520,
 520*t*

geological/meteorological/
 hydrological characteristics,
 516

GIS technology, 515

global climate models (GCM), 512

Hadley Center's global atmospheric
 model, 513

hydrologic models, 513

localized changes in soil water
 balance, 522*f*

- locations for spread effects of climate change, 516–517
- northern region climate fields, 519, 520*t*
- PRECIS (Providing Regional Climates for Impact Studies), 513
- regional changes in soil moisture balance, 522*f*
- regional climate model (RCM), 512
- setting up and running PRECIS, 513–514
- southern region climate fields, 519–520, 520*t*
- UK Department for Environment, Food and Rural Affairs (DEFRA), 513
- UK Department of International Development, 513
- UN Framework Convention on Climate Change (UNFCCC), 511
- United Nations Development Program (UNDP), 513
- United Nations Organizations, 513
- validation of daily mean temperature and precipitation, 511–522, 518*f*
- water cycle and greenhouse effects, 511
- western region climate fields, 519, 519*t*
- SBR, *see* Sequencing batch reactor methods (SBR)
- Science University of Malaysia (USM), 389
- SCR, *see* Selective catalytic reduction (SCR) process
- Sea ice in Arctic, variation in, 7
- Sea level rise, 430, 501–508
 - issue, 501
 - response, 501
 - scenarios, 501
- Sea levels, rising, 5
- Seasonal variation, 632
- Second International Polar Year, 471
- Selected ion monitoring (sim) modality, 612
- Selective catalytic reduction (SCR) process, 231
- SEM image, 335*f*
- Separate power heat systems (SPHS), 226
- Sequencing batch reactor methods (SBR), 551
- Sequestration in geological repositories
 - active or depleted oil and gas reservoirs, 287–288*t*
 - geological repositories, 286–287*t*
 - high-depth carbon plunge and coal-bed methane formation, 289
 - high-depth liquid formations and saline formations, 288–289
- Setaria viridis* (L)/*Echinochloa crus-galli* (L), life cycle for, 601
- Setting up and running PRECIS, 513–514
 - linux operation system, 513
- SFC, *see* Specific fuel consumption (SFC)
- SGDBS, *see* Steam Generation at Different levels via Biomass and Solar (SGDBS)
- Shipbuilding industry, 579
- Shipyards, 579
 - new shipbuilding division, 579
 - ship repairing division, 579
- Shoreline designation, 501
- Shoreline erosion, 502
- Shortest cycle species, 604
 - R. arvensis* and *V. hederifolia*, 604
- Short-term limit (STL), 490
- Sinapis arvensis* L. growth stages, 601
- Site-fitted coefficient, 481
- “Snake oil,” 6
- Snowfall pH, 485
- Snowpack, 503
- Solar collector
 - characteristics, 97*t*
 - concentrating, 93
 - geometry, optimization of, 103*f*
- Solar dish system, parabolic, 99–102
 - definition of parameters used for system modeling, 100*t*
- Solar-driven heat engine system, residential, 101*f*
- Solar-driven Rankine cycle systems, 95
- Solar energy
 - application
 - passive solar design, 467
 - photovoltaics, 467
 - solar thermal systems, 467

- characteristics, 90–91
 - technologies, 90
- electricity generation from, 75
- and environment, 90–92
- heating and cooling system, 442*f*
- performance of large-scale systems, 97*f*
- sustainability ratio, 91*f*
- utilization ratio comparison, 91*f*
- Solar generators, 98
- Solar heating and cooling systems in
 - Kuwait Climate, 439
 - Arkla chiller, 441
- CO₂ emission variation with collector area, 450*f*
- economic analysis, 444–445
 - FORTRAN program, 444–445
 - TRNSYS, money savings, 444–445
- environmental life cycle assessment, 446–447
 - baseline, 446–447
- lithium bromide–water absorption chiller, 439
- solar fraction variation with collector area, 449*f*
- system description and control
 - strategy, 441–443
 - control strategy for room thermostat, 443*t*
 - single-effect lithium bromide water absorption chiller, 442
 - vapor compression air conditioner, 441–443
- system parameters and data, 447–448*f*
- theoretical analysis, 444
- variation of system parameters with collector area, 449*f*
- Solar power
 - CO₂ mitigation induced by, and investment costs, 99*f*
 - generation systems, types of, 92*f*
 - generation systems for better
 - environment, residential, 89–90
 - parabolic solar dish system, 99–102
 - solar energy and environment, 90–92
 - solar power generation systems, 92–99
- Solar power generation systems, 92–99
- Solar radiation
 - data, 468
 - silver-disk pyrheliometer, 471
- Solar receiver temperature, 102
- Solar stills, 80–81
- Solar systems, leveled electricity cost (LEC) for large-scale, 98*f*
- Solar thermal applications, 76
- Solar thermal power systems, parabolic dish concentrators for, 93
- Solar tower, 96
- Solar trough power plant, 30 MW
 - hybrid, 96*f*
- Solid oxide fuel cell (SOFC), 166, 169
 - advantages, 162–163
- Solution casting method, 558
- Southern region climate fields, 519–520, 520*t*
- Spearman correlation, 529
- Specific fuel consumption (SFC), 241
- Speed of sound, 65
- SPHS, *see* Separate power heat systems (SPHS)
- Spring–summer species, 603
- SPSS, *see* Statistical packages for social sciences (SPSS)
- Standard Gear Pump (ISM446 BVP-Z), 309
- Statistical packages for social sciences (SPSS), 391
- Steam generation at different levels via biomass and solar (SGDBS), 462
- Steam network optimization by utilizing biomass and solar energy sources in oil refinery, 455
 - capital cost comparison of discussed scenarios, 463*f*
 - elements of typical energy system by biomass integration, 460*f*
 - integrated solar plant schematic diagram, 459*f*
 - integration of solar energy, 459*t*
 - optimization methods
 - Linear Programs (LP), 460
 - Nonlinear Programs (NLP), 460
 - pinch technology, 456
 - process description, 460–462
 - scenarios, 462*t*
 - Tehran oil refinery steam network, 461*f*

- solar and biomass integration to steam network, 458–460
- steam network description, 456–458
 - boiler hardware model, 456–458
 - Boiler T – H diagram, 458*f*
 - turbine hardware model, 456–458
- Tehran oil refinery, 456
- Sustainable construction practices in Malaysia, 385, 393*f*
- moving toward sustainable construction in Malaysia, 387*f*, 389–390
 - ‘Malaysia’s Vision 2020,’ 387*f*, 389–390
- survey, 390–391
- sustainability in construction, 386–388
 - green construction, 386–388
 - principles of sustainable, 388*i*
- Sustainable development process, 429*f*
- Sustainability practices, implementation of
 - enforcement on existing legislation, 393*f*, 394*f*
 - cost factor, 394
 - education vs. experience, 394
 - government intervention, 393
 - lack of enforcement, 393
 - passive culture, 394
 - pointing fingers, 393
 - urgency factor, 393
- System effectiveness, 122
- System operation parameters, optimization of, 104*f*
- T**
- TCDD-equivalence index, 615
- TCPD, *see* Town and Country Planning Department (TCPD)
- Technological Research Council of Turkey (TUBITAK), 277
- Temperature–mortality association, 640
- Thermal equilibrium, 48
- Thermal power plants, 74
- Thermal swear absorption (TSA), 283
- Thermal systems considered, 164
 - gas turbine (GT), 165–166
 - internal combustion engine (ICE), 165
 - solid oxide fuel cell (SOFC), 166
- Thermochemical and thermoelectrochemical cycles, 133–135
- Thermochemical water-splitting process, simple coupling of, 135*f*
- Thermodynamic cycle, 48
- Thermodynamic equilibrium, 48
- Thermodynamic process, 48
- Thermodynamics, 47
 - Carnot principle, 53–54
 - conservation equations, 48–50
 - design of experiments, 63–65
 - entropy, 54–58
 - exergy, 58–59
 - first law of, 49
 - and global warming, 47
 - literature errors, 65–66
 - non-measurable thermodynamic properties, 59–63
 - performance characteristics of devices, 51–52
 - second law of thermodynamics, 52
 - Clausius statement, 52–53
 - Kelvin–Planck statement, 52
 - sign convention in, 50–51
 - state principle, 48
 - properties, 48
- Thermogravimetric analyzer, 331, 331*f*
- Thermogravimetry, 318
- THM, *see* Turbine hardware model (THM)
- TOE, *see* Ton of oil equivalent (TOE)
- Ton of oil equivalent (TOE), 216
- Total suspended material (TSP), 485
- Town and Country Planning Department (TCPD), 390
- Trace GC gas chromatograph, 612
- Trace Q mass spectrometer, 612
- Trichloroethane, 585
- TSA, *see* Thermal swear absorption (TSA)
- TSP concentration, 494
- Turkey air pollution/environmental concerns in
 - CO₂ emissions and greenhouse gases, 227
 - emission standards for power plants, 229*f*
 - NO_x and SO_x emissions, 227–228, 228*f*, 237–238*f*

particulate matter (PM) emissions, 228–229

power sector, emissions is, 227–229

Turbine hardware model (THM), 456

Turbofan engine-II, genetic algorithm, 246*t*, 251*f*

Turbofans on Global Warming, Fuel Consumption, 241

Aerothermodynamic models, 243

bypass ratio (α), 248–249*f*, 251–252

elitism-based genetic algorithm, 241–244, 245–246*t*

Rolls-Royce, 242

Turan TURBOGENf (turbofan genetic fan), 243

TURBOGENf (turbofan genetic fan), 243, 245–249

Two-person pure bargaining problem, 416

Two-tier approach, 507

U

UiTM, *see* University Technology of Mara (UiTM)

UK Department for Environment, Food and Rural Affairs (DEFRA), 513

UK Department of International Development, 513

UKM, *see* National University of Malaysia (UKM)

Ulsan

air pollution in, 211–212, 221*t*

annual oil consumption, 216*t*

improvement in SO_x levels, 214

SO_x and TSP levels, correlation, 218*f*

success of industries, 212

TSP or PM₁₀ concentrations, 217*f*

Ultraviolet fluorescence (AF 21M), 488

UNDP, *see* United Nations Development Program (UNDP)

UNFCCC, *see* UN Framework Convention on Climate Change (UNFCCC)

UN Food and Agriculture Organization (FAO, 2005), 644

UN Framework Convention on Climate Change (UNFCCC), 511

United Nations Development Program (UNDP), 513

United Nations Framework Convention on Climate Change (UNFCCC), 407

United Nations Organizations, 513

University of Birmingham, 629

University Technology of Mara (UiTM), 389

UN's Intergovernmental Panel on Climate Change (IPCC), 8–9

Urban heat islands, causes of, 497

Urbanization, 497

USM, *see* Science University of Malaysia (USM)

V

Vacuum and sweep gas pervaporation, 556

Varian type SAA-110, 621

VCDAT, *see* Visual Climate Data Analysis Tool (VCDAT)

Vector-borne diseases, 644

Vector-borne zoonotic disease, 526

see also West Nile Virus (WNV)

Vectors, effects on, 644

Very high-temperature reactor, 132

Virtual world vs. actual world, 371*f*

Visual Climate Data Analysis Tool (VCDAT), 517

VOC, *see* Volatile organic compounds (VOC)

VOC, wastes and pollutants particulates, 579

Volatile organic compounds (VOC), 211, 555, 581

W

WAJ, *see* Water authority of Jordan (WAJ)

Waste Electrical and Electronic Equipment Directive (WEEE), 426

Waste management in shipyards, 586

Wastewater management in

North–South gap (Germany/Jordan), 545–553

comparisons according to discharge regulations, 552–553

German standard for treated wastewater, 552

- Jordanian and German standards for treated wastewater discharge, 553*t*
- Jordan standard for treated wastewater, 552
- comparisons according to treatment efficiency, 548–549
- eutrophication phenomenon, 548
- flow parameters, 549
- removal efficiencies on average of all plants, 549*f*
- comparisons according to used technologies, 549–552
- BOD removal efficiency, 550*f*
- COD removal efficiency, 550*f*
- mechanical treatment plants, 550
- membrane or multi-treatment stages, 551
- municipal wastewater treatment in Jordan, 549
- sequencing batch reactor methods (SBR), 551
- treatment plants in Germany, 551*t*
- wastewater treatment in Germany, 552*t*
- wastewater treatment in Jordan, 551*t*
- comparisons according to wastewater characteristics, 548
- ammonium (NH_4), 548
- biochemical oxygen demand (BOD), 548
- chemical oxygen demand (COD), 548
- total phosphorus (TP), 548
- total suspended solid (TSS), 548
- wastewater characteristics in Germany and Jordan, 548*t*
- Hashemite Kingdom of Jordan
- international water poverty line, 545
- semi-arid climate, 545
- water reuse, 545
- wastewater characteristics
- BOD and COD, parameters, 547
- Closed reflux method, 547
- standard methods for Examination of Water and Wastewater, 547
- TSS and TDS concentrations, 547
- wastewater treatment plants, 546
- water authority of Jordan (WAJ), 547
- wastewater management system, in Germany, 545
- Wastewater treatment plants, 546
- Water authority of Jordan (WAJ), 547
- Water course management
- and water users on minimum runoff, 541–542
- on flood, 542–543
- Feernic flood wave hydrograph in 2005 at SimoneMti, 543*f*
- on monthly mean discharge, 539–541
- Bălăușeri and Târnăveni hydrostations, 539
- highest rate of runoff, 540
- monthly average discharges in 1990 at Târnăveni, 541*f*
- monthly discharges variation at Mihalp hydrometric station, 540*f*
- water management works, 540
- water training works, 541
- Water cycle and greenhouse effects, 511
- Water gas shift reaction (WGS), 296
- Water management works in Tarnave river basin, Romania, 535–543
- changes in annual mean runoff, 538–539
- Blaj hydrometric station, 539
- DQ correction discharge, 538
- Mihalt hydrometric station, 538
- modifying factors of natural flow, 539
- methods and techniques, 537–538
- hydrometric stations, 538
- reconstruction into riverbeds, 538
- and water users on minimum runoff, 541–542
- long intervals of drought, 541
- negative influence of water users, 541
- on flood, 542–543
- feernic flood wave hydrograph in 2005 at SimoneMti, 543*f*
- flood protection works, 542
- heavy rainfalls and melting snow, 542
- hydrometrical station from Topa/Sarateni, 542
- Odorhei hydrometric station, 542

- Simone^oti hydrometric station, 543
 on monthly mean discharge,
 539–541
 in 1990 at Târnăveni, 541*f*
 variation at Mihălp hydrometric
 station, 540*f*
 in Târnave river basin, 536–537
 detention reservoirs, 537
 storage reservoirs, 536–537
 water users within Târnave basin,
 537
 Water management works in Târnave
 river basin, 536–537
 detention reservoirs, 537
 non-permanent storage reservoirs,
 537
 Vânători storage reservoir, 537
 storage reservoirs, 536–537
 bezid storage reservoir, 536
 zetea storage reservoir, 537
 water users within Târnave basin, 537
 fresh water supplies, 537
 industrial water/irrigation systems,
 537
 irrigation canals, 537
 Weed species, ecological factors, 601
 WEEE, *see* Waste Electrical and
 Electronic Equipment Directive
 (WEEE)
 Welding and cutting process and wastes,
 584–585
 mechanical or thermal hot metal
 cutting operations, 584–585
 on-site/off-site treatment, 585
 Western region climate fields, 519,
 519*t*
 West Nile fever (WNF), 526
 West Nile virus (WNV)
 Culex pipiens, 526
 fatal human meningitis or
 encephalitis, 526
 vector-borne zoonotic disease, 526
 WGS, *see* Water gas shift reaction
 (WGS)
 Winter–spring species, 603
 WNF, *see* West Nile fever (WNF)
 WNV, *see* West Nile virus (WNV)
 World Health Organization, 644
 advice to people living in areas
 affected by bird flu/avian
 influenza, 651
 contaminated protective
 clothing/properly handled or
 disposed, 652
 dead birds, feces/buried or burnt,
 652
 decontamination/yard or chicken pen,
 652
 footwear/decontaminated, 653
 people, flu-like illness/take additional
 precautions, 653
 precautionary measures/poultry and
 poultry products/properly
 prepared and safe to eat, 654
 precautions/when visiting friends or
 relatives/in health-care facilities,
 653–654
 presence of bird flu/confirmed, do not
 eat poultry meat, 654
 proper handling of poultry, 651
 spread of bird flu/in affected
 areas/prevented, 651
 World's natural resources, 1
- ## X
- XPS characterization
 Leybold-hereaus LHS 10
 spectrometer, 316
 XPS and Auger analysis, 320*t*
 XRD characterization
 Siemens D5000 diffractometer, 316,
 318*f*
 XRD study, 622
- ## Z
- Zero energy office building (ZEO), 390