Juan Gabriel Segovia-Hernández
Adrián Bonilla-Petriciolet *Editors*

Process Intensification in Chemical Engineering

Design Optimization and Control

Springer

Process Intensification in Chemical Engineering

Juan Gabriel Segovia-Hernández
Adrián Bonilla-Petriciolet
Editors

Process Intensification in Chemical Engineering

Design Optimization and Control

Springer

Editors
Juan Gabriel Segovia-Hernández
Universidad de Guanajuato
Guanajuato, Mexico

Adrián Bonilla-Petriciolet
Instituto Tecnológico de Aguascalientes
Aguascalientes, Mexico

ISBN 978-3-319-28390-6 ISBN 978-3-319-28392-0 (eBook)
DOI 10.1007/978-3-319-28392-0

Library of Congress Control Number: 2016931878

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG Switzerland

Preface

Today, we are witnessing important new developments that go beyond traditional chemical engineering. Engineers and industrial researchers are working on novel equipment and techniques that potentially could transform our concept of chemical plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes. These developments share a common focus on "process intensification," an approach that has been around for quite some time but has truly emerged only in the past few years as a special and interesting discipline of chemical engineering.

Process intensification can be defined as: "Any engineering development that leads to a substantially smaller, cleaner, safer, and more energy-efficient technology." The application of this concept in process system engineering is most often characterized by a significant reduction in plant volume, production costs, waste generation, and also getting improvements, even in orders of magnitude, on process performance and efficiency including the reduction of environmental pollution problems. In recent years, process intensification has attracted considerable academic interest as a potential means for process improvement and to meet the increasing demands for a sustainable production. A variety of intensified operations developed in academia and industry creates a large number of options to potentially improve the process. However, the task for identifying the set of feasible solutions for process intensification in which the optimal can be found may take considerable resources. Hence, a synthesis tool to systematically achieve the process intensification would potentially assist in the generation and evaluation of process options.

Currently, several process design tools with a clear focus on specific process intensification tasks exist. Therefore, this book covers current topics for the design, optimization, and control in the context of process intensification. This book was motivated by the desire we and others have had to show the evolution and advances in this area. Chapters of this book cover a variety of concepts and aspects, involving a variety of processes as case of study and examples, related to process intensification in chemical engineering.

We are deeply indebted to the authors who have contributed to this book. Also, we acknowledge the anonymous reviewers for their time and effort in assisting us with the edition of this book.

Guanajuato, Mexico — Juan Gabriel Segovia-Hernández
Aguascalientes, Mexico — Adrián Bonilla-Petriciolet

Contents

Contributors

Ricardo Aguilar-López Centre of Research and Advanced Studies, Instituto Politécnico Nacional, Mexico City, Mexico

J. Rafael Alcántara-Avila Tokushima University, Tokushima, Japan

Paloma Andrade-Santacoloma Technical University of Denmark, Lyngby, Denmark

Deenesh K. Babi Department of Chemical & Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Adrián Bonilla-Petriciolet Instituto Tecnológico de Aguascalientes, Aguascalientes, Mexico

Irene Cano-Rodríguez Division de Ciencias Naturales y Exactas, Departamento de Ingenieria Quimica, Universidad de Guanajuato, Guanajuato, Mexico

Mauricio Sales Cruz Department of Chemical & Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Universidad Autónoma Metropolitana - Cuajimalpa, Delegacion Cuajimalpa de Morelos, Mexico, Denmark

Massimiliano Errico Department of Chemical Engineering, Biotechnology and Environmental Technology, University of Southern Denmark, Odense M, Denmark

Zeferino Gamiño-Arroyo Division de Ciencias Naturales y Exactas, Departamento de Ingenieria Quimica, Universidad de Guanajuato, Guanajuato, Mexico

Rafiqul Gani Department of Chemical & Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark

Fernando I. Gómez-Castro Department of Chemical Engineering, Biotechnology and Environmental Technology, Universidad de Guanajuato, Guanajuato, Mexico

Claudia Gutiérrez-Antonio Facultad de Química, Universidad Autónoma de Querétaro, Santiago de Querétaro, Mexico

Héctor Hernández-Escoto Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato, Mexico

Gladys Jiménez-García Instituto Tecnológico Superior de Pátzcuaro, Pátzcuaro, Mexico

Anton A. Kiss AkzoNobel Research, Development and Innovation, Process Technology Strategic Research Group, Deventer, The Netherlands

Faculty of Science and Technology, Sustainable Process Technology Group, University of Twente, AE, The Netherlands

Hao-Yeh Lee National Taiwan University of Science and Technology, Tapei, Taiwan

Rafael Maya-Yescas Faculty of Chemical Engineering, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, Morelia, Mexico

Paola A. Molano Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Sede Bogotá, Bogotá, Colombia

Ricardo Morales-Rodríguez Department of Chemical Engineering, Universidad de Guanajuato, Guanajuato, Mexico

Alvaro Orjuela Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Sede Bogotá, Bogotá, Colombia

José María Ponce-Ortega Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mexico

Oscar Andrés Prado-Rubio Department of Chemical Engineering, Universidad Nacional de Colombia - Manizales, Manizales, Colombia

Ben-Guang Rong University of Southern Denmark, Odense M, Denmark

Miguel A. Santaella Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia, Sede Bogotá, Bogotá, Colombia

Juan Gabriel Segovia-Hernández Universidad de Guanajuato, Guanajuato, Mexico

Chapter 1
Introduction

Juan Gabriel Segovia-Hernández and Adrián Bonilla-Petriciolet

Abstract This chapter provides an overview of process intensification in chemical engineering and summarizes the content of this book.

The chemical, pharmaceutical, and bio-based industries produce products that are essential for modern society. Nevertheless, these industries face considerable challenges because of the need to develop sustainable production methods for the future.

Process intensification (PI) targets dramatic improvements in manufacturing and processing by rethinking existing operation schemes into ones that are both more precise and efficient than existing operations. PI frequently involves combining separate unit operations such as reaction and separation into a single piece of equipment resulting in a more efficient, cleaner, and economical manufacturing process. At the molecular level, PI technologies significantly enhance mixing, which improves mass and heat transfer, reaction kinetics, yields, and specificity. These improvements translate into reductions in equipment numbers, facility footprint, and process complexity, and, thereby, minimize cost and risk in chemical manufacturing facilities.

In the frame of globalization and sustainability, the future of chemical engineering can be summarized in four main objectives:

1. Increase productivity and selectivity through intensification of intelligent operations and a multiscale approach to processes control (e.g., nano- or microtailoring of catalyst materials).
2. Design novel equipment based on scientific principles and new production methods: process intensification in using multifunctional reactors, microengineering, and microtechnology.

J.G. Segovia-Hernández (✉)
Deptamento de Ingenieria Quimica, Universidad de Guanajuato,
Noria Alta s/n, Guanajuato, Gto 36050, Mexico
e-mail: gsegovia@ugto.mx

A. Bonilla-Petriciolet
Instituto Tecnológico de Aguascalientes, Av. López Mateos 1801, Aguascalientes 20256,
Aguascalientes, Mexico
e-mail: petriciolet@hotmail.com

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_1

3. Design and engineering using the “triplet molecular Processes-Product-Process Engineering)” approach to manufacture end-use properties.
4. Implement multiscale application of computational chemical engineering modelling and simulation to real-life situations from the molecular scale to the production scale [1].

At the core of PI is the optimization of process performance by focusing on molecular level kinetics, thermodynamics, and heat and mass transfer. Gerven and Stankiewicz (2009) provide four guiding principles for PI [2]:

1. Maximize effectiveness of intramolecular and intermolecular events (e.g., dynamically changing conditions to attain kinetic regimes with higher conversion and selectivity).
2. Provide all molecules the same process experience (e.g., plug flow reactor with uniform, gradient-less heating).
3. Optimize driving forces at all scales and maximize the specific surface areas to which they apply (e.g., increase transfer surface area through microchannel designs).
4. Maximize synergistic effects from partial processes (e.g., affecting reaction equilibrium by removing products where and when they are formed).

PI designs that achieve all or some of these molecular-level optimal conditions are likely to be transformative. Reactors that enable precise control of the reactor environment could dramatically increase yields, conversions, and selectivity, which in turn would reduce material, energy, and carbon intensities, minimize purification needs, and reduce waste disposal burdens. Additionally, PI technologies could enable the manufacture of products that otherwise could not be safely or successfully made.

In general, process intensification consists of the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size/production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies. Or, to put this in a shorter form: any chemical engineering development that leads to a substantially smaller, cleaner, and more energy efficient technology is process intensification [3].

The whole PI field generally can be divided into two areas:

- Process-intensifying equipment, such as novel reactors, and intensive mixing, heat-transfer and mass-transfer devices.
- Process-intensifying methods, such as new or hybrid separations, integration of reaction and separation, heat exchange, or phase transition (in the so-called multifunctional reactors), techniques using alternative energy sources (light, ultrasound, etc.), and new process-control methods (like intentional unsteady-state operation). Obviously, there can be some overlap. New methods may

require novel types of equipment to be developed and vice versa, while novel apparatuses already developed sometimes make use of new, unconventional processing methods.

Commercial applications of PI date back to the 1970s. Static mixers, which are ubiquitous today, were early PI inventions. Other early PI technologies deployed reactive distillation, including Eastman Chemical Company's tower reactor, which integrated five processing steps in the production of methyl acetate from methanol, achieving an 80 % reduction in energy and a large reduction in capital costs. In the chemical industry, reactive distillation, divided wall column distillation, and reverse flow reactors have been commercialized each with more than 100 installations. Drivers for PI innovation include the potential for reduction in feedstock cost, capital expenditure, energy, and safety issues. Barriers to deployment include risk of failure, scale-up unknowns, unreliability of equipment, and uncertain safety, health, and environmental impacts [4].

In recent years, PI has attracted considerable academic interest as a potential means for process improvement to meet the increasing demands for sustainable production. Process intensification is gaining much attention as one of the key objectives in designing new plants and retrofitting existing units. Several drivers have contributed to this increasing attention. For instance, enhanced process safety and homeland security are tied to process intensification; as the inventory and flows of hazardous substances are lowered, the process risk is typically reduced. As many processes, particularly those in the chemicals, nuclear and oil industries, involve the production, handling, and use of hazardous substances, process intensification is one way in which the inventory of such substances, and the consequences of a process failure, may be significantly reduced. PI, therefore, has the potential to be a significant factor in the implementation of inherent safety. Additionally, conservation of natural resources (including better utilization of mass and energy), biotechnological applications, and new control methods may be linked to Process Intensification. Also, PI is a valuable approach in developing economical processes with a minimal global footprint which will require new infrastructure to be designed and built [5]. PI is in development and, as is often the case in the emergence of new areas, there is an ongoing discussion about its definition. Consensus has been reached that PI involves creative innovation and stimulates the engineering community to strive to real breakthroughs, aiming at plants that are more compact, cost-effective, and safer. An integrated (or holistic) approach is essential, resulting in a symbiosis with well-defined disciplines, in particular Process Systems Engineering [6].

This book gathers research from across the globe in the study of design, control, and optimization in process intensification. Topics discussed include process separation, bioprocess, heat and mass exchanger networks, industrial applications, etc.

Chapter 2 gives an overview of the fundamentals of process intensification from a process systems engineering point of view. The concept of process intensification, including process integration, is explained together with the drivers for applying process intensification, which can be achieved at different scales of size, that is, the unit operation scale, the task scale, and the phenomena scale.

In Chapter 3, a systematic methodology to generate different classes of distillation configurations is presented. The generation methodology is able to consider thermally coupled, thermodynamically equivalent structures and intensified alternatives with a less number of columns compared to the corresponding simple column sequences. The methodology described has the advantage to produce a complete set of alternatives, avoiding the trial-and-error procedure with random configurations picked up from the literature. Finally, the methodology described has the benefit to keep a clear connection between the simple column sequences and all the alternatives predicted. This aspect helps the designer in the definition of columns' configuration parameters.

Chapter 4 presents the use of process integration as a useful tool for intensifying processes. Particularly, mass and heat integration through the synthesis of mass and heat exchanger networks represent powerful tools that can be used for reducing the need of external agents such as fresh water and hot and cold utilities. Two optimization formulations are presented for mass and heat integration and the application to two case studies show significant savings of external utilities.

Heat integration between vapor and liquid streams has been widely used in chemical and petrochemical plants for conventional distillation processes as an alternative to reduce the energy consumption. However, with the advances that have been proposed in intensified distillation processes in the last couple of decades, heat-integrated alternatives that are more attractive than the typical condenser–reboiler heat integration have also been proposed. Therefore, intensified distillation processes also need a new approach methodology to implement optimal locations and heat load in heat-integrated distillation. Chapter 5 aims to cover the fundamentals, simulation and optimization approaches for heat-integrated intensified distillation processes for nonreactive and reactive systems.

Reactive distillation stands out as a successful example of a process intensification technology for enhanced chemical manufacture. After almost a century of development, it has achieved a high degree of maturity in terms of design capabilities, the availability of commercial suppliers of hardware and software, and a large variety of processes effectively implemented at the industrial scale. Based upon an extensive review of the classical and recent literature on reactive distillation.

Chapter 6 briefly describes the context in which the technology was developed, its current status, and the expected areas for progress in the near future. In addition, the intensification principles behind the operation, its fundamentals, constrains, design methodologies, the optimization approaches, and the control strategies are discussed with fair detail. Finally, a case study on the ethyl acetate production via esterification of acetic acid with ethanol by reactive distillation is presented. In this example, a complete process synthesis procedure is described, from the conceptual design all the way to the process optimization.

In Chapter 7, bioprocess intensification is explored mainly from the perspective of transforming biomass into chemicals as an integrated solution for bioprocessing. Then, bioprocess intensification is addressed within the biorefinery context.

Chapter 8 presents process intensification technologies used in industrial applications, for increasing the eco-efficiency of the chemical equipment with the benefit of lower capital costs, substantial energy saving, reduced footprint, and safety by design. The key topics cover compact heat exchangers, static mixers, green chemical reactors (e.g., micro-reactors), high-gravity (HiGee) technology, cyclic distillation, dividing-wall column, and reactive distillation.

Chapter 9 describes and discusses stochastic optimization methods for solving problems involved in process intensification, given an emphasis in multi-objective optimization due to its increasing importance in the chemical engineering community. A brief description of the multi-objective optimization strategies such as genetic algorithms, simulated annealing, tabu search, differential evolution, ant colony and particle swarm optimization is provided, including several applications of evolutionary optimization methods in the intensification of separation processes.

Process intensification is a branch of Chemical Engineering which has taken importance in the last decades because through its application it is possible to obtain alternative processes with smaller/multitask equipment and reduced energy requirements. Such reductions may have a positive benefit to the environment, since smaller equipment implies less use of material for its construction; while reductions on energy requirements implies lowering direct emissions of greenhouse gases to the atmosphere. In Chapter 10, examples of intensification alternatives recently proposed for enhancement of processes is presented. In particular, process intensification in the production of liquid biofuels is analyzed. The application of such tool in the production of biofuels, which are expected to reduce environmental impact when compared to the use of fossil fuel, has both energy savings and further reductions in terms of pollutant emissions.

The arts of design, optimize, and control of chemical processes should be considered simultaneously. Nevertheless, in the case of process intensification the most common situation is that design is performed as first stage (following mass/energy integration guidelines), secondly processes are optimized (costs, profit, environmental impact), and finally a control scheme is adopted. Additionally, it is necessary to consider that intensification generates new process dynamics (different responses and characteristic times) and reduces, notoriously, the number of manipulate variables available for control. Hence, the original difficult tasks of partial control and stability of both, process and control, becomes more complicated. Chapter 11 is devoted to the analysis of the problems mentioned above, which are inherent to any chemical process although more evident during process intensification. Some special features of the control are identified and some suggestions are given to enface problems that arise after the intensification of some separation and reaction/separation examples.

In this book, we have highlighted a variety of topics that should play a significant role in the intensification of chemical processes. This has not been a comprehensive cataloging, as new developments are regularly emerging from researchers worldwide. The usage of a knowledge base has been presented to provide data for various PI applications, chemical systems, conditions, etc.

Process intensification, although yet to fully emerge as an established technology in the process industries, offers significant opportunities in sectors ranging from chemicals to food. The possibility of increased level of production and the growing use of biological renewable feedstocks opens up new challenges and opportunities for those active in integration as well as intensification.

References

1. Charpentier JC (2005) Four main objectives for the future of chemical and process engineering mainly concerned by the science and technologies of new material production. Chem Eng J 107:3
2. Van Gerven T, Stankiewicz A (2009) Structure, energy, synergy, time: the fundamentals of process intensification. Ind Eng Chem Res 48:2465
3. Moulijn JA, Stankiewicz A, Grievink J, Górak A (2008) Process intensification and process systems engineering: a friendly symbiosis. Comput Chem Eng 32:3
4. Lutze P, Gani R, Woodley JM (2010) Process intensification: a perspective on process synthesis. Chem Eng Process 49:547
5. Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM (2012) Process intensification: new understanding and systematic approach. Chem Eng Process 53:63
6. Keil FJ (2007) Modeling of process intensification-an introduction and overview. In: Keil FJ (ed) Modeling of process intensification. Wiley-VCH, Weinheim, p 1

Chapter 2
Fundamentals of Process Intensification: A Process Systems Engineering View

Deenesh K. Babi, Mauricio Sales Cruz, and Rafiqul Gani

Abstract This chapter gives an overview of the fundamentals of process intensification from a process systems engineering point of view. The concept of process intensification, including process integration, is explained together with the drivers for applying process intensification, which can be achieved at different scales of size, that is, the unit operation scale, the task scale, and the phenomena scale. The roles of process intensification with respect to process improvements and the generation of more sustainable process designs are discussed and questions related to when to apply process intensification and how to apply process intensification are answered through illustrative examples. The main issues and needs for generation of more sustainable process alternatives through process intensification are discussed in terms of the need for a systematic computer-aided framework and the methods and tools that should be employed through it. The process for the production of methyl-acetate is used as an example to highlight the generation of more sustainable process alternatives through this framework. Perspectives, conclusions, and future work are proposed in order to further develop the field of process intensification using a systems approach.

2.1 Introduction

The objective of process synthesis is the selection of the best (optimal) process flowsheet from among numerous alternatives for converting specified raw materials into specific desired products, subject to predefined performance criteria [1]. More

---

D.K. Babi • R. Gani (✉)
Department of Chemical & Biochemical Engineering, Technical University of Denmark,
Bldg 229, DK 2800 Kgs Lyngby, Denmark
e-mail: rag@kt.dtu.dk

M.S. Cruz
Department of Chemical & Biochemical Engineering, Technical University of Denmark,
Bldg 229, DK 2800 Kgs Lyngby, Denmark

Universidad Autónoma Metropolitana - Cuajimalpa, Delegación Cuajimalpa de Morelos,
C.P. 05300 Mexico, Denmark
e-mail: asales@correo.cua.uam.mx

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_2

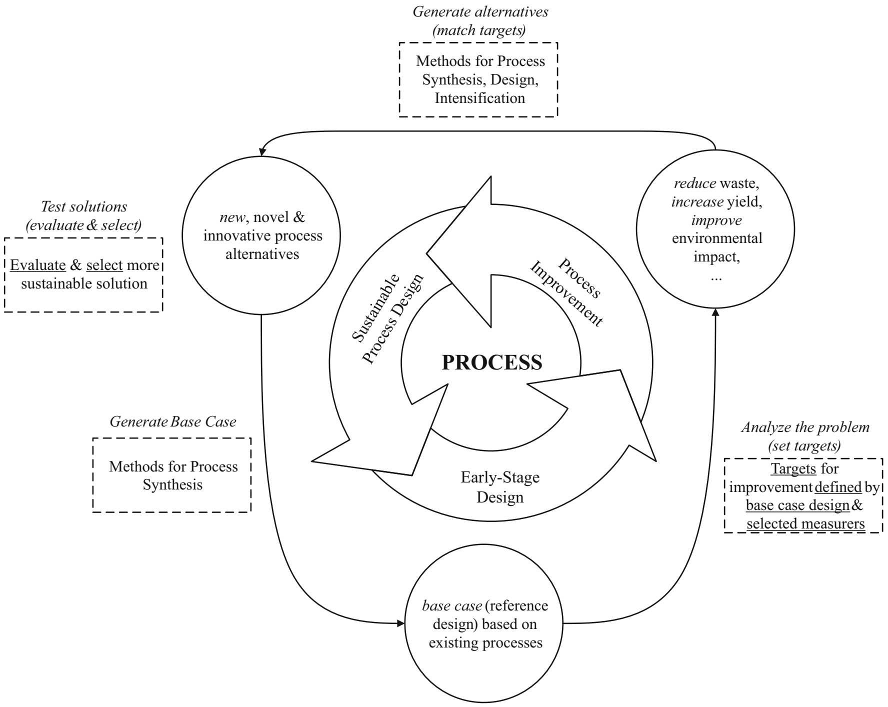


Fig. 2.1 Role of process intensification within sustainable process design

sustainable design is defined as the design of process flowsheets that correspond to lower values of a set of targeted performance criteria based on economical, operational, and environmental factors [2]. As shown in Fig. 2.1, the sustainable design is obtained through improvements with reference to the early stage design (also called reference design or base-case design). The role of process synthesis in finding the early stage design and/or the more sustainable design is to generate the feasible process alternatives. The generation of alternatives can be done in various ways, for example, trial and error, rule-based heuristics, process integration (mass and energy), process optimization, process intensification, and many more. In this chapter, process intensification, which also includes process integration, is presented. Through the improvements as shown in the middle layer of Fig. 2.1, the following improvements related to the physical system can be obtained through process intensification [3]:

- Catalysts—the screening and selection of novel catalysts for reactive systems
- Solvents—the generation, screening, and selection of environmentally friendly solvents for separation processes
- Materials—the design of new materials for the design of novel, innovative unit operations that combine reaction, separation, or reaction–separation systems

- Energy—the use of process integration concepts to generate more sustainable process alternatives with respect to reduced waste and environmental impact

Process intensification has been receiving increased attention and importance because of its potential to obtain innovative and more sustainable process design alternatives. But what is process intensification? Many definitions have been proposed for process intensification and a few are highlighted here. Stankiewicz and Moulijn [4] defined process intensification as the development of novel and sustainable equipment that compared to the existing state-of-the-art, produces dramatic process improvements related to equipment sizes, waste production, and other factors. Reay et al. [5] defined process intensification as process development that involves reduction in equipment (unit operation) sizes that lead to improvements in reaction kinetics, better energy efficiency, reduction in capital cost, and improvement in process safety. Ponce-Ortega et al. [6] defined process intensification as an activity characterized by five principles—reduced size of equipment, increased throughput of process, reduced equipment holdup or inventory, reduced usage of utilities and raw materials, and, increase efficiency of process equipment. The above definitions provide insights into the different scales at which process intensification can be employed.

With the exception of process integration, there are, however, not many published methods to determine the intensified solutions for processes, even though successful intensified solutions have been reported by many. Examples of process intensification methods have been proposed at unit operation scale by Bessling et al. [7], at task scale by Agreda et al. [8] and at phenomena/molecular scale by Freund and Sundmacher [9]. These methods however, mainly focus on the design of new/novel unit operations that enhances/integrates a particular set of tasks and/or phenomena within the process, but does not consider the interaction of the rest of the unit operations that constitute the final (total) process design. They are also specific to the characteristic of the unit operations studied.

With a systematic and generic method for find process intensification solutions, Lutze et al. [10] recently proposed a definition for process intensification that covers all three scales and consider the overall process. According to Lutze et al. [10], process intensification is defined as the targeted improvement of a process at the unit operations scale, the task scale, and/or the phenomena scale. With overall improvement as the objective, at the unit operations scale the individual equipment that constitute the final process design of any chemical or biochemical process is identified and/or designed; at the task scale, the functions (tasks) performed by each unit operation are identified and analyzed; and, at the phenomena scale, the phenomena that satisfies the tasks to be performed are identified and analyzed. In this way, links between the scales are established and allows the search in various scales to find the design of new, innovative, and sustainable processes. This method can be applied to the design of new processes as well as, the retrofitting of existing processes, in order to make them more sustainable. This concept of scales is illustrated through Fig. 2.2 where at the lower scales, a small set of tasks and phenomena are employed to represent various

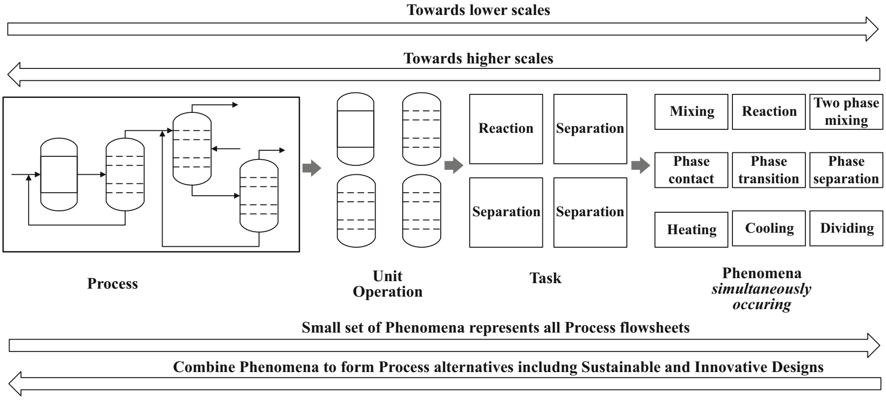


Fig. 2.2 Multiscale method for process intensification

process flowsheet alternatives. Moving from the higher to the lower scale increases the possibility for process innovation because of the following reasons:

- New alternatives that match the functions of unit operations can be generated through the combination of tasks, leading to new flowsheet alternatives.
- New ways to perform tasks can be generated by combining different phenomena, leading to the generation of novel and (more sustainable) flowsheet alternatives.

Therefore, if processes are designed at scales lower than the unit operation scale, there is an increased chance of finding a more sustainable overall process design. This is highlighted by the process intensification solutions reported by Agreda et al. [8] and Siirola [11] for the production of methyl-acetate from the reaction of methanol and acetic acid. Papalexandri and Pistikopoulos [12] proposed the idea of combination of phenomena to generate new unit operations. Peschel et al. [13], Lutze et al. [10, 14] and Babi et al. [2] illustrate the use of phenomena-based approaches to achieve process intensification.

Process integration can be considered as a special case of process intensification and is commonly defined as the design and analysis of the best (optimal) network for mass and energy utilization applied to the design (or retrofitting) and operation of new as well as existing processes [15]. Consequently, process integration is concerned with two integration concepts within a chemical (and biochemical) process—mass and/or energy integration [16, 17]. Mass integration is the efficient utilization of mass within the process (for example, minimization of fresh water use in a process) through the analysis and optimization of mass flows within the process. Analogously, energy integration is the efficient utilization of energy within the process (for example heat integration) through the analysis and optimization of energy needs within the process. As the use of water and energy are related to the performance criteria for more sustainable designs and are achieved through the integration of two or more operations, they are therefore also regarded as special cases of process intensification. Methods for performing process integration focus on the selection and combination of existing as well as novel process technologies in the best (optimal) manner for the efficient use and utilization of mass and/or energy. Therefore, in this chapter, unless otherwise indicated, PI includes process intensification as well as process integration.

The objective of this chapter is to present and discuss the fundamentals of process intensification. First, the concept of PI is introduced, followed by a discussion on when and how to employ PI? This includes a discussion on the role of process intensification in sustainable process design as well as the connection between process integration and process intensification. Also, examples of successful application of process intensification are given. Next, the methods and tools needed to determine process intensification solutions are presented in terms of a general mathematical problem formulation, a brief overview of the different solution techniques, the need for a systematic computer-aided framework, and the associated methods and tools. The application of this framework is highlighted through a case study involving the production of methyl-acetate by reaction of methanol with acetic acid. The chapter ends with a discussion of perspectives, conclusions, and future work on the role of process intensification in relation to the design of more sustainable and innovative processes as well as pointing out some of the recent achievements. Note that even though process integration is regarded as a special case of process intensification, it is only briefly covered in this chapter. Also, recent developments on process integration can be found in the review of the state-of-the-art by Klemes et al. [18].

2.2 When and How to Apply PI?

In the chemical and biochemical process industry, improvements in economic as well as environmental factors are required for new as well as existing processes [3, 19]. PI plays a major role in achieving the desired improvements in processing options through the design of processes that constitute more sustainable alternatives, that is, hybrid/intensified unit operations (equipment). A hybrid/intensified unit operation, is an operation that enhances the function of one or more unit operations for performing a task or a set of tasks through a new design of the unit operation or the combination of more than one unit operations. For example, reactive distillation is a combination of reaction and separation (see Fig. 2.3a) and a membrane reactor is a combination of reaction and in situ removal of a reactant or product (see Fig. 2.3b).

Process Integration can be applied in the following forms for achieving process improvement:

- Heat integration (heat exchanger networks) where energy efficiency is increased through energy consumption minimization. This was the first type of process integration, first developed by Linnhoff et al. [20] and further extended and

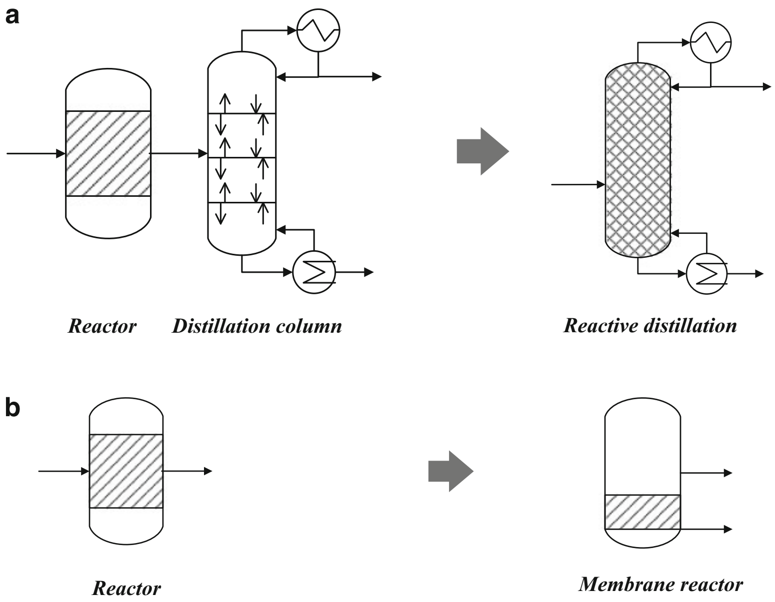


Fig. 2.3 Examples of hybrid/intensified unit operations: (**a**) reactive distillation (**b**) membrane reactor

solved using a mixed integer non-linear programming (MINLP) approach by Papoulias and Grossmann [21].

- Mass integration (mass exchanger networks) where the flow route of mass within the process is optimized, for example, through the use of concentration differences [16, 18].
- Supply-chain management where the total supply-chain cost (related to suppliers, storage, retailers, customers etc.), is minimized based on the concepts applied for heat and mass integration [18, 22].

The impact of process integration on cost reduction and environmental factors have been reported by numerous authors, see for example, Papoulias and Grossmann [21], Singhvi et al. [22] and Kazantzi and El-Halwagi [23] for overall capital cost and/or operating cost reduction through increased process integration. As the cost reduction due to more efficient use of energy and water resources is achieved, it also reduces the waste and has a positive impact on the environment, making the process thereby more sustainable.

Babi et al. [24] proposed a 3-stage sustainable process synthesis–design method (see Fig. 2.4) including the use of PI. According to this method, in the first stage, the optimal processing paths are synthesized to convert a set of raw materials into a desired set of products. In the second, the optimal processing path (flowsheet) is selected for further study that includes identification of the process bottlenecks or hot-spots. These hot-spots help to define targets for improvement, which when

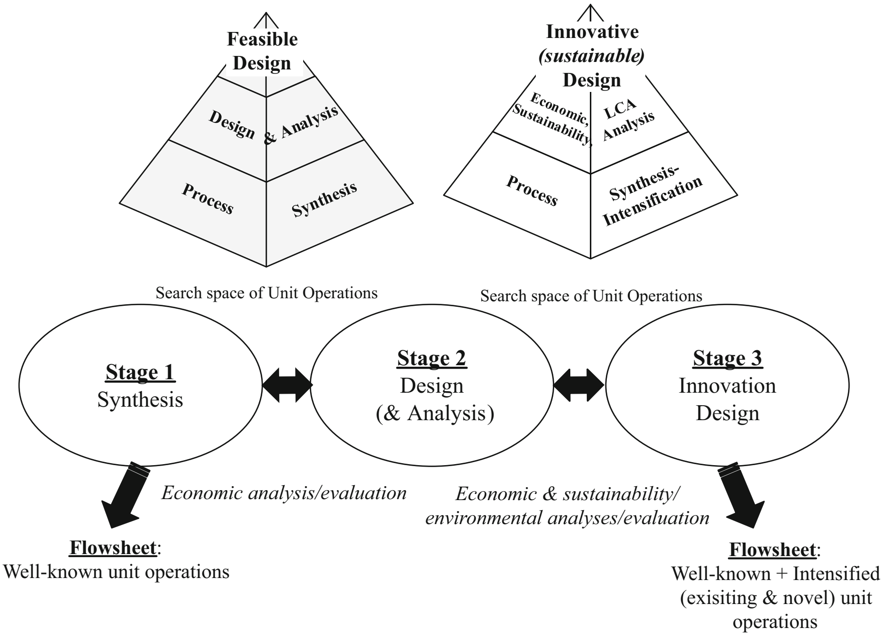


Fig. 2.4 Three-stage sustainable process design method that incorporates PI

matched would lead to more sustainable and innovative solutions. In the third-stage, methods with or without considering PI are applied to generate process alternatives that match the desired targets for process improvements. Here, applications of different PI methods are possible.

From Fig. 2.4, it can be noted that for existing processes with already identified hot-spots, entry to the 3-stage method is at stage 3. Alternatively, if the process exists but the hot-spots have not been identified, then the entry to the 3-stage method is at stage 2, while for a totally new process synthesis problem, the entry is at stage 1. Therefore, opportunities to apply PI exist whenever deficiencies (bottlenecks or hot-spots) in design and/or operation of a process are identified. A classic example is the flowsheet (see Fig. 2.5) for the production of methyl-acetate by reaction of methanol with acetic acid. Can the number of unit operations be decreased? Can the product yield and purity be increased? Can the process be made more sustainable? As Fig. 2.3b indicate, the answer is yes. Another classic example in the case of heat integration is the combination of a heat exchanger that needs to reduce the temperature of a stream with another that needs to increase the temperature of a stream. Integration in this case saves energy as well as cooling medium and thereby makes the process after integration more sustainable.

As the definition of PI implies, to apply PI, a combination of operations, tasks, and/or phenomena need to occur simultaneously subject to the specified objectives and constraints of the process. That is, which combination of operations, tasks,

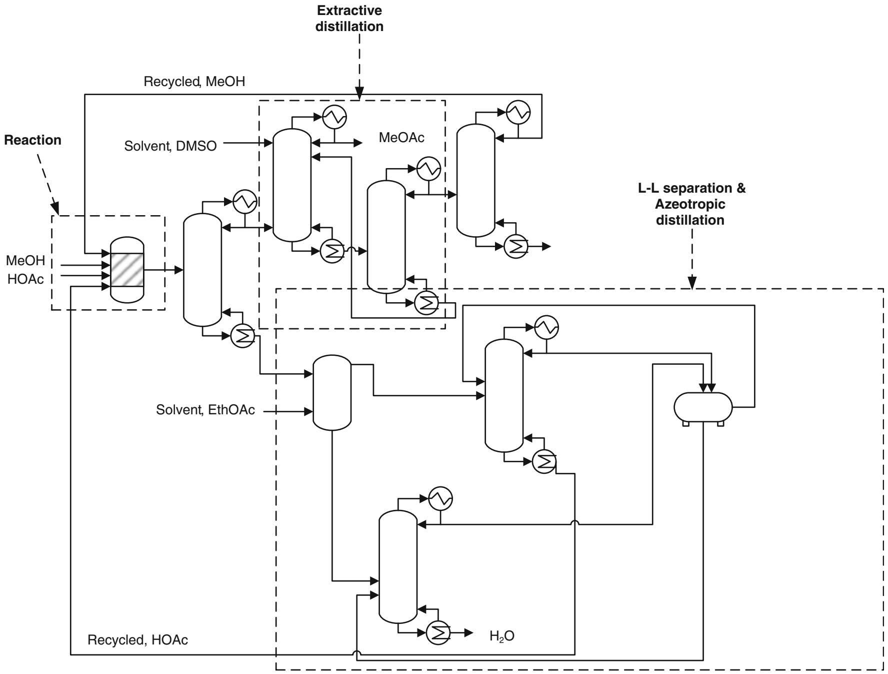


Fig. 2.5 When to apply PI—process flowsheet for the production of methyl-acetate

and/or phenomena would lead to an alternative that is better than the base-case design according to a set of performance criteria and subject to the principal requirements of PI? Siirola [11] proposed a combination of tasks that lead to the well-known intensified solution of a reactive distillation column for the production of methyl-acetate (see Fig. 2.5). Babi et al. [24] proposed a phenomena-based approach where combinations of a set of phenomena lead to a set of tasks, whose combinations lead to a set of new or existing unit operations that when combined give a final set of PI solutions. Babi et al. [24] also illustrated their method to the methyl-acetate production and reported same reactive distillation solution as well as other feasible PI solutions.

Through the use of intensification design concepts, novel hybrid/intensified unit operations (see Table 2.1) that exploit mechanisms (phenomena) related to, for example, heat and mass transfer are determined. Heat-transfer mechanisms are enhanced through the use of passive and active techniques, for example, rough surfaces (passive) and electrostatic fields (active). Mass transfer mechanisms are enhanced through the use and enhancement of three external physical characteristics, rotation (for example, use of a rotor), vibration (for example, high frequency ultrasound), and mixing (for example, inline mixers) [5]. In a reactive distillation, on the other hand, the phenomena of reaction and separation (for example, vapor–liquid equilibrium) take place simultaneously on every stage or transfer unit.

Table 2.1 List of reported hybrid/intensified unit operations

Unit operation (equipment)	Techniques for equipment intensification	Application	Reference
Compact heat exchanger	Channel size reduction	Power generation	[25]
Foam heat exchanger	Surface enhancement by metal-coated polymer foam	Micro-power generation	[26]
Micro-heat exchangers	Chemical etching	"Lab-on-a-chip"	[27]
Spinning disk reactor	Rotation and agitation of catalyzed disks	Pharmaceuticals-Darzen's reaction	[28]
Membrane reactors	Combination of reactor and membrane unit	Esterification reactions	[29]
Reactive distillation	Combination of catalyst (for reaction) and distillation	Esterification reactions	[11]
Divided-wall column	Thermal coupling of two adjacent columns into a single column	Extractive distillation	[30]
Deodorizer	Surface enhancement by metal-coated surface	Deodorization	[31]
HiGee (rotating disks)	Metal foam inside a rotating pack-bed	De-aeration	[32]
Inline mixers	Use of baffles	Polymer processing	[33]

Another similar example is a membrane reactor, which provides the opportunity for in situ product/by-product removal thereby simplifying the downstream processing steps [29, 34]. Table 2.1 lists various hybrid/intensified unit operations and their reported area of application.

The synthesis of heat exchanger networks using a pinch-based temperature interval method was first introduced by Linhoff and Flower [35] for energy (heat) integration. The method utilizes concepts based on thermodynamic and physical insights. The minimum utility requirements (heating and cooling) are identified first, followed by the design and analysis of an (heat) exchanger network. However, this method does not guarantee the best (optimal) solution to the energy integration problem, that is, the use of the minimum number of heat exchangers for the design of the integrated heat exchanger network. Therefore, the synthesis of heat exchanger networks was further developed using mathematical programming, see for example, Papoulias and Grossmann [21]. Here, the heat integration problem is defined as a MINLP problem that can be reduced to a mixed integer linear programming (MILP) problem for design and analysis of the optimal integrated heat exchanger network.

Similar concepts as proposed by Linhoff and Flower [35] have been extended to the design and analysis of mass exchanger networks; see for example, El-Halwagi and Manousiouthakis [36]. The minimum mass requirements, that is, the amount (mass) of a targeted species *p* that can be transferred into a lean process stream (above the mass pinch point) and the minimum amount (mass) of an external mass separating agent required for removal of the targeted species *p* (below the

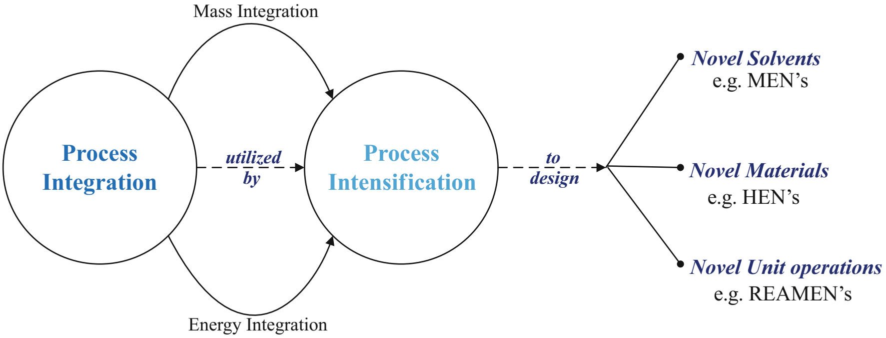


Fig. 2.6 The utilization of process integration in process intensification. Examples of process intensification that employ mass and energy integration are shown. *MEN* mass exchanger network, *HEN* heat exchanger networks, *REAMEN* reactive mass exchanger network

mass pinch point) are first identified followed by the design of the best (optimal) mass exchanger network.

Process intensification also utilizes the concepts from process integration in order to design hybrid/intensified unit operations that integrate mass and/or energy within a single-unit operation and/or reduce the number of unit operations, compared to a conventional process. This is shown in Fig. 2.6. As an example, consider a divided-wall column (single-unit operation) that integrates the separation of a ternary zeotropic mixture (mass) having a lower utility consumption (energy) compared to the conventional approach that uses a two-column sequence [24].

At whichever scale, process intensification is performed, the output is expected to be a better, more sustainable process compared to a selected reference (base-case) design. Stankiewicz and Moulijn [37] proposed that process intensification can be decomposed into two main classifications [9], intensified unit operations (hybrid/intensified equipment) and intensified methods. This is shown in Fig. 2.7. In each classification different subclassifications can be made with respect to intensified unit operations and available methods.

Since according to Fig. 2.7, multiple intensified unit operations exist, therefore, there is a need for the development of intensified methods that incorporate within their search space these unit operations for the design of (sustainable) chemical and biochemical processes. However, to go beyond the current search of these hybrid/intensified unit operations and to find truly predictive methods that also provide the opportunity to generate and design novel, innovative unit operations, these methods must operate at lower scales, for example, the phenomena/molecular scale [10, 38]. Table 2.2 provides examples of process intensification at the unit operations scale, task scale, and phenomena scale.

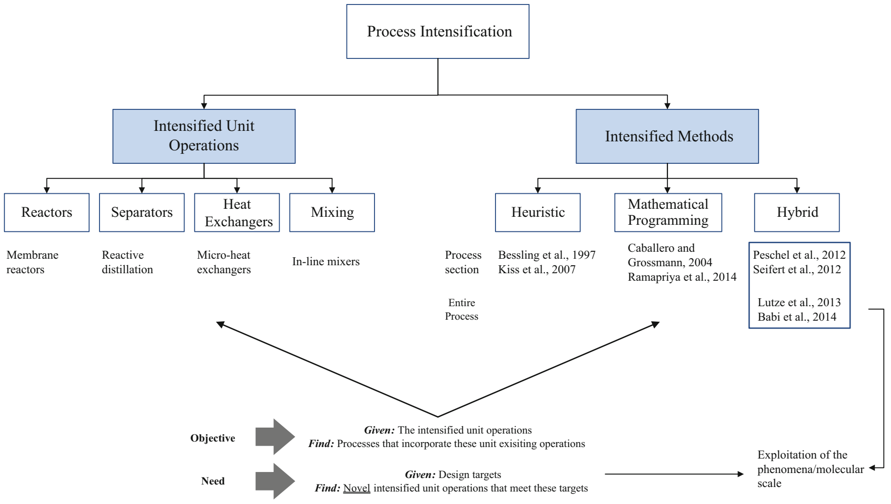


Fig. 2.7 Classification of PI operations

Table 2.2 List of PI solutions at different scales: unit operations, tasks, and phenomena

Process	Hybrid/ intensified unit operation	Remarks	Reference
	Unit operations		
Production of ethyl acetate	Pack-bed reactive distillation	Analysis of homogenous/heterogeneous catalysts and process operation conditions	[39]
Separation of acetone–butanol ethanol	PDMS/ceramic composite membrane	Analysis of molecular transport during pervaporation	[40]
Waste water treatment	Bioreactor	Kinetic study for the effect of oxidation processes	[41]
	Task (functional)		
Production of methyl-acetate	Reactive distillation	Integration of all reaction and process tasks	[8]
Crystallization	Crystallizer coupled with ultrasounds	Effect of paracetamol crystallization	[42]
Transesterification of DMC with ethanol	Microwave-assisted reactive distillation	Investigation of the impact of enhancing the reaction mechanism using microwave heating	[43]
	Phenomena/ Molecular		
Production of ethylene oxide	Membrane-based reactor	Analysis of a novel reactor design concept	[38]
Production of iso-propyl acetate	Plate-frame-flow reactor-pervaporator	Analysis of a novel reaction–separation reactor	[10]
Production of dimethyl-carbonate	Divided-wall column	Analysis of the effect on separation for dimethyl-carbonate and methanol	[24]

2.3 Methods and Tools for Achieving PI

The general sustainable process design problem highlighted in Fig. 2.3 can be formulated mathematically through (2.1)–(2.5)

$$\begin{aligned} &\min/\max F_{\text{obj}} = F_{\text{obj}}(x, y, d, z, \Theta) \\ &s.t. \end{aligned} \tag{2.1}$$

$$h_1(x, y, d, z, \Theta) = 0 \tag{2.2}$$

$$b^u \leq B_1 x + B_2 y \leq b^u \tag{2.3}$$

$$h_3{}^l \leq h_3(x, y) \leq h_3{}^u \tag{2.4}$$

$$g^l \leq g(x, y) \leq g^u \tag{2.5}$$

where

$$y_j = 0/1, j = 1, 2, \ldots n_y, x \geq 0 \tag{2.6}$$

The objective function to be minimized/maximized is defined by (2.1) and is subject to a set of design and optimization variables x; a set of binary decision integer variables y (0, 1); a set of equipment variables d; a set of thermodynamic variables z; and a set of process specifications Θ. Equation (2.2) represents a system of linear and/or non-linear process model equations. The process models are considered at steady state consisting of phenomena and, mass and energy balance equations. Note that in general, process models can be used for steady state, dynamic, or both. Equations (2.3) and (2.4) represent the process flowsheet physical constraints and equipment design specifications, for example, the process flowsheet structure and equipment design parameters. Equation (2.5) represents a set of intensification constraints, for example, intensified equipment design specifications and performance criteria (sustainability metrics and LCA factors) that the feasible (intensified) flowsheet alternatives must satisfy. Based on the mathematical formulation presented through (2.1)–(2.5), process synthesis-intensification is performed for the design of more sustainable processes that contain intensified/hybrid unit operations.

The process synthesis-intensification problem to be solved, (2.1)–(2.5), can be formulated as a MINLP problem when the objective function and/or constraints include both linear and non-linear equations and, binary integer variables (for the selection of phenomena, tasks, and/or unit operations). In order to manage the complexity for finding the best (optimal) solution to the synthesis-intensification problem, an efficient and systematic solution approach is required. One method is the decomposition-based solution strategy method where the problem is decomposed into a set of subproblems that are solved according to a predefined calculation order. Most of the subproblems require bounded solution of a subset of equations. The final subproblem is solved as a set of NLP or MILP.

Feasible, intensified flowsheet alternatives are identified as follows:

(a) First, the process model equations, (2.2), are solved subject to the constraints defined in (2.3) and (2.4) in order to generate a set of flowsheet alternatives.
(b) These alternatives are then evaluated using the intensification performance criteria, (2.5), in order to select a set of feasible (intensified) flowsheet alternatives.
(c) For the remaining flowsheet alternatives, the objective function value, (2.1), is calculated and ordered. The flowsheet alternative(s) that give the best (optimal) objective function value are selected as the more sustainable (innovative) designs.

Multiple performance criteria can be used in order to evaluate the opportunities for performing process intensification or process integration. A list of performance criteria [3, 10, 24] for the application of process intensification is given in Table 2.3 and are based on criteria defined at the unit operations scale, task scale, and phenomena scale.

2.3.1 Solution Approaches

Methods that have been developed for performing process intensification at the unit operations (process) scale, task scale, and phenomena scale, systematize the generation and selection of the best (more sustainable) intensified flowsheet design. In order to increase the efficiency of these methods, computer-aided tools have been developed in order to perform model-based analyses (for example, reactor analysis), environmental analyses (for example, LCA), etc.

The classification of methods for performing process synthesis can also be used for classifying the methods for process intensification. Process synthesis can be performed through the application of three types of methods, heuristic-based methods, mathematical programming and hybrid-based methods. In heuristic-based methods, knowledge-based methods that consist of sets of heuristic rules are applied [44–46]. In mathematical programming-based methods, an optimization problem is formulated and solved using a generated superstructure that contains a finite number of unit operations and their corresponding interconnections, commonly derived by making use of engineering judgement, heuristics, and/or thermodynamic considerations [21, 47, 48]. In hybrid-based methods the know-how of the previous two methods, heuristics and mathematical programming are utilized. These methods keep the simple structure of heuristic/knowledge-based methods, but replace the fixed rules with guidelines based on thermophysical insights, generated through the analysis of the behavior of the chemical system [49–51]. Hybrid methods move beyond the well-used unit operations scale and operate at different scales for performing process synthesis [11, 12].

For process intensification, unlike process synthesis, heuristic-based methods, and mathematical programming methods for the design of entire chemical and biochemical processes have not yet been proposed. However, methods for the

Table 2.3 Improvements and performance criteria for performing process intensification

	Improvements					
Performance criteria	Raw material utilization	Separation efficiency	Energy efficiency	Waste minimization	Process economics	Environment outlook
Effective use of resources (raw material)	*			*	*	*
New processing routes	*	*	*	*	*	*
Equipment capital investment		*	*		*	*
Utility consumption	*	*	*	*	*	
Sustainability metrics			*	*	*	
LCA factors			*	*	*	
Integration of unit operations (sustainable technologies	*	*	*	*	*	*
Integration of tasks	*	*	*	*	*	*
Integration of phenomena	*	*	*	*	*	*

*Indicates the performance criteria that are used as a measure of improvements intensification of specific parts (reaction and separation) of a process have been proposed. For heuristic-based methods, rule-based design decisions based on process know-how and thermophysical properties have been proposed for the use of reactive distillation [7] and reactive divided-wall columns [52]. For mathematical programming-based methods, methods for sequencing and selection of divided-wall columns [53, 54], for reactive distillation [55] and reactive distillation plus membrane separation [56], have been proposed.

Hybrid methods for process intensification have been proposed for intensification of an entire chemical and biochemical process and specific parts of a process. For intensification of specific parts of a process, Siirola [11] proposed the means–ends analysis that identifies tasks (based on expert knowledge) to satisfy a set of process specifications. Peschel et al. [13, 38] proposed a method for generating novel intensified reactor network designs based on elementary process functions and Seifert et al. [57] proposed a modular concept for process design where sections of a process are modularized in order to generate flexible process designs. For intensification of entire processes, Lutze et al. [10] and Babi et al. [2] proposed a phenomena-based method where the process phenomena are combined in order to fulfill tasks. Once these tasks are fulfilled, the combined phenomena are translated into unit operations. Such a method provides the opportunity to innovate because the generated unit operation from phenomena may either be novel (new, innovative) or existing.

2.3.2 Phenomena-Based Approach

A multi-level, multi-stage, computer-aided framework for process synthesis-intensification is highlighted. The framework offers process synthesis-intensification at the unit operations scale [58], at the task scale [11] and at the phenomena scales [10]. The framework is applied to the production of methyl-acetate (MeOAc) in order to generate intensified flowsheet alternatives inclusive of the well-known reactive distillation process proposed by Agreda et al. [8] using a phenomena-based synthesis method.

Concept of phenomena-based synthesis: This concept is similar to computer-aided molecular design methods [59] where molecules (similar in concept to unit operations) are designed subject to a set of target (desired) properties and using functional groups (different combinations of atoms, which are similar in concept to tasks) and/or atoms (similar in concept to phenomena) as the building blocks. Consider, for example, atoms that can be combined to form functional groups, in the same manner phenomena building blocks (PBBs) can be combined to form simultaneous phenomena building blocks (SPBs). These SPBs are combined to form operations in the same way that groups are joined together to form molecules. By combining building blocks at lower scales (molecules or PBBs), new molecules and/or new process flowsheets are in principle obtained. Also, a small set of building blocks are used for representing multiple molecules and flowsheets.

Phenomena-based process flowsheet representation: The PBBs involved in a process need to be identified. This is done through the analysis of a knowledge-base of unit operations, the tasks that they perform and the phenomena that they employ. Based on a study of multiple chemical (and biochemical) processes, it was found that most processes can be represented by using the following eight PPBs: mixing (M) (including two-phase-mixing (2phM)), heating (H), cooling (C), reaction (R), phase contact (PC), phase transition (PT), phase separation (PS) and dividing (D).

Combination of PBBs to represent tasks, unit operations and flowsheets: One or more PBBs are combined to form SPBs, subject to a set of combination rules that fulfill the objectives of any task. Two examples of these combination rules for combining PBBs are: (1) H and C PBBs cannot be combined to form SPBs because this combination is thermodynamically not feasible; (2) R and PT PBBs can be combined to form SPBs because the energy from an exothermic reaction can be used to drive simultaneous reaction–separation tasks. Note that other involved phenomena are then added to the SPB in order to complete the free connections. As an example of the final SPB for the R = PT combination, consider combining the following PBBs, M, 2phM, PC and PS, to fulfill the requirement of simultaneous reaction-reparation task, M = 2phM = R = PC(VL) = PT(VL) = PS(VL), where PT (VL) is a PBB representing a VL-separation task. A combination of SPBs forms operations that are translated to known or new (novel) unit operations that constitutes the final (more sustainable) flowsheet alternatives. An example of the representation of a reactive distillation (RD) column using SPBs having a reactive section is shown in Fig. 2.8.

The multi-level computer-aided synthesis-intensification framework: The multi-level framework is presented in Fig. 2.9. The input and output of each stage is highlighted together with the different computer-aided tools used at the different levels of the synthesis-intensification framework. The computer-aided tools are available in the updated version of ICAS version 17 [60], except for the commercial process simulators (PROII and ASPEN).

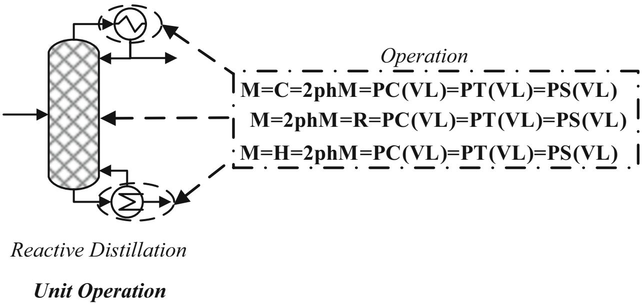


Fig. 2.8 Combination of SPBs to form an operation that fulfill a task (for example, a reaction-separation task)

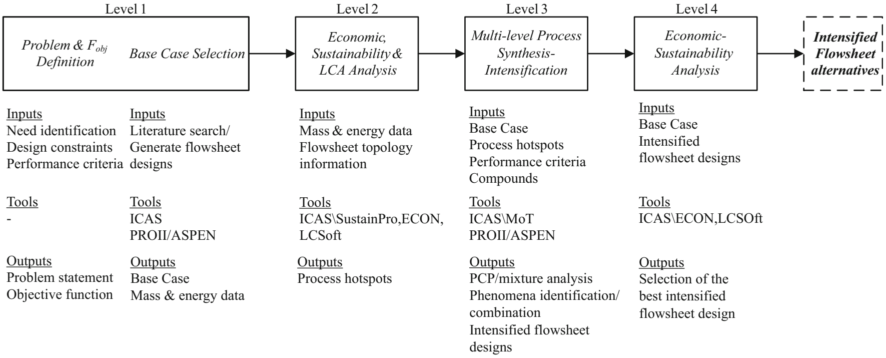


Fig. 2.9 Systematic process synthesis-intensification framework (adopted from Babi et al. [2])

The first level of the framework defines the problem, the objective function to be minimized (or maximized) and a selection/generation (if not available) of base-case design at the unit operations scale. The second level performs economic sustainability and LCA analyses to systematically and logically identify process hot-spots that are translated into intensification (design) targets/constraints for process improvements/design. The inputs to the analyses are detailed mass and energy balance data and the base-case process flowsheet information. The third level performs process synthesis-intensification at the three different scales (unit operations, tasks, phenomena) subject to the following condition: the new synthesized (intensified) flowsheets must have a reduction in the number of unit operations compared to the base-case design.

The base-case design at the unit operations scale is translated to the task-based flowsheet that is further translated to the phenomena-based flowsheet. All identified PBBs from the base-case design and additional (desirable) PBBs obtained from analysis of the chemical system, constitute the final PBB search space. All possible combination of the PBBs are calculated and screened using the combination rules for obtaining a feasible set of SPBs. Next, SPBs are combined to form operations that fulfill tasks that are translated to unit operations. Only those operations and their combination to flowsheets are retained if they satisfy all constraints and move the objective function in the desired direction.

2.3.3 Computer-Aided Tools

Different computer-aided tools can be employed for performing and evaluating process intensification at the three different scales and in the three different stages (see Fig. 2.4). Examples of these tools and their application are presented in Table 2.4.

Table 2.4 Tools for performing process intensification. Adopted from Babi et al. [2]

Method	Tool-name/ tool-type	Features	Intensification remarks
Property model-based	ICAS-utility[a] /Analysis	Group contribution-based property models used for VLE, LLE, SLE, distillation boundary, residue curve, etc., calculations	Use of phase diagrams for reaction, separation, and/or reaction–separation understanding
CAMD; Database search	ProCAMD[a]/ Selection	Search and selection of solvents for various types of solvent based separation processes	Selection of environmentally friendly solvents that affect the separation of compounds
Driving force-based; Equilibrium-based	PDS[a]/ Design, Analysis	Generation of phase and driving force diagrams for design of distillation columns	Use of driving force diagrams for the optimal design of hybrid/intensified unit operations
Model/Heuristic-based	ECON[a]/ Analysis	Economic calculation and evaluation based on the models from Peters et al. [61]	Economic evaluation of processes for identifying economic design targets for achieving process intensification
Model-based	SustainPro[a]/ Analysis	Indicator-based method [62]	Environmental evaluation of processes for identifying sustainability design targets for achieving process intensification
Model-based	LCSoft[a]	Indicator-based method using cradle to the gate concept for LCA analysis [63]	
Model-based	CAPSS[a]/ Analysis	Pure component property analysis [58]	Pure compound property evaluation for identifying feasible hybrid/intensified unit operations
Model-based	ProPred[a]	Group contribution-based property models [64]	Pure compound property prediction
Equation-oriented problem solution	MoT[a], Aspen Custom Modeller/ Analysis	Process and property models can be generated and solved for evaluation.	Model-based evaluation and design of intensified/hybrid unit operations
Model-based calculations	Aspen Plus, PROII/ Analysis	Models for well-known and hybrid/intensified unit operations	Model-based simulation and analysis of multiple intensified process alternatives

[a] Part of ICAS [60]

The tools listed in Table 2.4 are computer-aided and therefore, provide the opportunity for rapid investigation of alternatives at the different stages of process design. At the core of process simulation/investigation of the intensified flowsheet alternatives, are the property models that must accurately predict the properties of the pure compounds and mixtures present in the chemical (and biochemical) system. If the property models are accurate, then their coupling to the process models produce accurate and reliable process designs.

Many intensified solutions may need the use of an appropriate solvent or process fluid. For generation of alternative solvents and/or process fluids that are environmentally acceptable as well as easy to operate and inexpensive, model-based tools such as ProCAMD are used. For the selection of intensification design targets, model-based economic and sustainability indicator-based environmental evaluations are performed.

2.4 Case Study: Production of Methyl-Acetate

Application of the systematic synthesis-intensification framework is illustrated through the well-known production process for methyl-acetate (MeOAc). The objective here is to highlight the fundamental concepts of PI as well as to illustrate how intensified flowsheet alternatives inclusive of the well-known reactive distillation process proposed by Agreda et al. [8] can be generated using the phenomena-based method. The key steps of the framework are highlighted through the production of methyl-acetate (MeOAc) from an equilibrium-limited reaction between methanol (MeOH) and acetic acid (HOAc) with water (H_2O) as a by-product. The reaction is a liquid phase reaction catalyzed by Amberlyst 15. A molar feed ratio of 2:1 for the base-case design for MeOH and HOAc are used respectively with a total production of 122×10^3 t/year [65].

2.4.1 Level 1

The synthesis-intensification problem is defined as follows [2]: Find intensified process design alternatives for the production of MeOAc having a conversion of HOAc $\geq 92\ \%$ by maximizing the profit (objective function) defined by (2.7).

$$F_{\mathrm{obj}}(C_{\mathrm{Prod}}, C_{\mathrm{RM}}, C_{\mathrm{Ut}}) = \mathrm{Opt}\left\{ \left(\sum m_j C_{\mathrm{Prod},j} - \sum m_j C_{\mathrm{RM},j} - \sum E_j C_{\mathrm{Ut},j} \right) \Big/ \mathrm{kg\ \ Prod} \right\} \tag{2.7}$$

In (2.7), C, m, and E represent the costs, mass, and energy flows, respectively. The following constraints are specified compared to the base-case design: the use of solvents is to be minimized; the number of unit operations in the intensified flowsheet alternatives must be less; sustainability metrics and LCA factors must be the same or better. From a literature survey a base-case design (see Fig. 2.5) is available [8]. The base-case design consists of ten unit operations (one reactor, five distillation columns, one liquid–liquid extractor and decanter). It should be noted that if a base-case design does not exist, the framework has the option to generate one. The base-case design is then simulated to obtain detailed mass and energy balance data.

2.4.2 Level 2

Economic, sustainability, and LCA analyses are performed. Two potential process hot-spots are identified. These are limited equilibrium (the reaction does not go to full completion), which means high flow of raw material in the reactor outlet, and high energy consumption for solvent recovery in the extractive distillation section (see, Fig. 2.5). These process hot-spots are then translated into intensification (design) targets that must be matched through the design of a more sustainable intensified process. Two criteria to be considered could be: reduce process energy demand and improve sustainability and LCA factors.

2.4.3 Level 3

Identification of desirable tasks and phenomena: Using the appropriate computer-aided tools (see Table 2.4), the chemical system pure compound and mixture properties are analyzed. The following minimum boiling binary azeotropes are found: HOAc/H_2O (slightly pressure-dependent), MeOH/MeOAc (pressure-dependent), and MeOAc/H_2O (slightly pressure-dependent). Next, the base-case design is represented in terms of tasks and then in terms of phenomena. The selected PBBs obtained from representation of the base-case design at the phenomena level are R, M (assuming four types of mixing: ideal, flow, rectangular, vapor), 2phM, PC(VL), PS(VL), PT(VL) H, C and dividing (D) PBBs. The additional (desirable/beneficial) PBBs that are added based on thermodynamic insights [58] are PS(VV), PT(PVL), PT(VV) (key PBBs for pervaporation and vapor permeation membranes, respectively). Considering all possible combinations of the identified PBBs, 16278 SPBs are obtained, out of which 64 are found to be feasible using the combination rules of PBBs to SPBs.

Generation of sustainable intensified alternatives: Starting with the first reaction task and using thermodynamic insights [58], HOAc is removed from the reactor effluent containing MeOH/MeOAc. Since H_2O is present in the reactor effluent and also forms an azeotrope with MeOAc, H_2O is also found in the top and bottom of the first separation task (see Fig. 2.10a). The first separation task is achieved by a VL-separation, that is, using a PT(VL) PBB. In order to reduce the number of azeotropes in the mixture of H_2O, MeOAc, and MeOH, H_2O is removed using an SPB that contains a PT(PVL) PBB, which translates into a pervaporation membrane. Two VL-separation tasks operating at different pressures are employed next to separate HOAc/H_2O and MeOAc/MeOH mixtures, thereby avoiding the use of solvents (see Fig. 2.10a). Flowsheet alternative 2 (see Fig. 2.10b) is generated by a priori removal of H_2O before the HOAc separation, thereby further reducing the size of flowsheet alternative 1.

Flowsheet alternative 3 (see Fig. 2.10c) is generated by combining the first reaction and separation PBBs, thereby making it feasible to combine the first

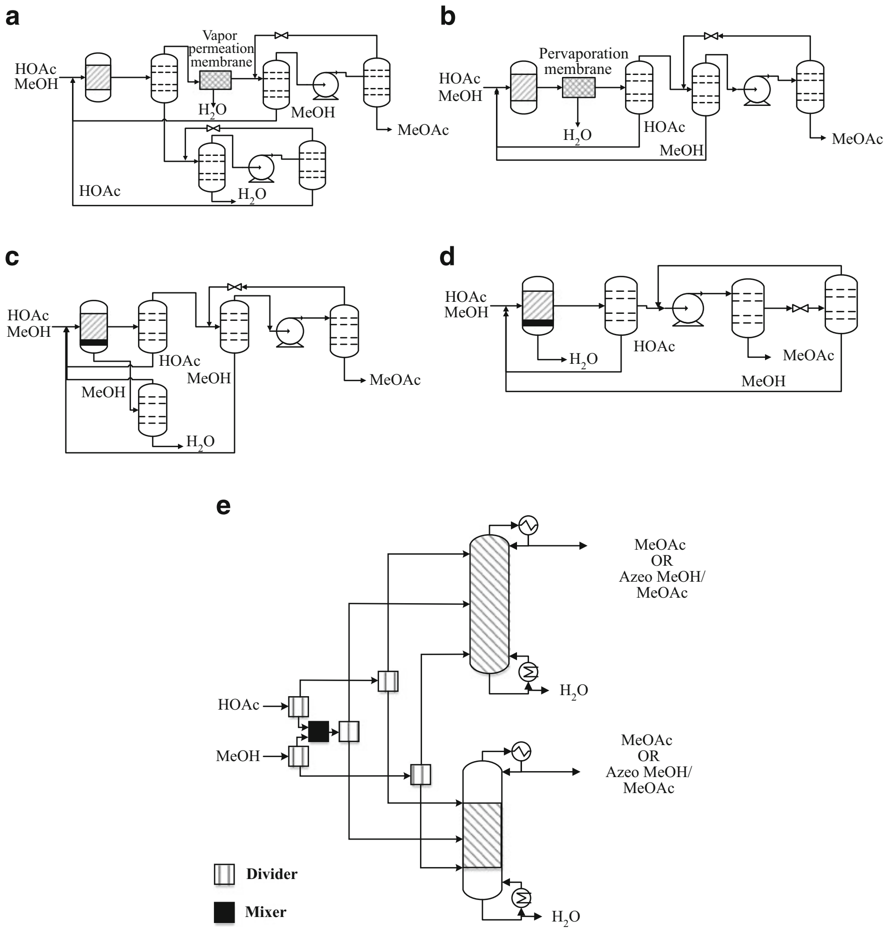


Fig. 2.10 The generated flowsheet alternatives for the production of MeOAc [2]. (**a**) Flowsheet alternative 1, (**b**) Flowsheet alternative 2, (**c**) Flowsheet alternative 3, (**d**) Flowsheet alternative 4 (**e**) Flowsheet alternatives 6–9

reaction and separation tasks for the in situ removal of water using a R = PT(PVL) SPB. The reactor outlet contains some H_2O because of the raw material feed molar ratio that affects the membrane behavior. The rest of the flowsheet is similar to flowsheet alternative 1 (see Fig. 2.10a). Flowsheet alternative 4 (see Fig. 2.10d) is generated by changing the MeOH–HOAc feed ratio resulting in an easier and lesser separation tasks after the membrane reactor. Flowsheet alternative 5 is not shown in Fig. 2.10 for reasons of confidentiality.

Flowsheet alternative 6–9 are generated through the combination of the remaining reaction and separation tasks, thereby producing a reactive distillation superstructure [2] that consists of reactive stages only, reactive and separation stages, single- and double-feed configurations (see Fig. 2.10e). It should be noted

Table 2.5 Values of selected performance criteria for the base-case design and 4 intensified (and more sustainable) alternatives

Performance metrics	Base-case	Alternatives			
		3	4	5	9
Feed ratio	2:1	2:1	2:1	1:1	1:1
Energy usage (MJ/kg MeOAc)	21.9	20.6	19.1	3.6	2.2
Raw material (kg/kg MeOAc)	0.88	0.87	0.87	0.87	0.88
Utility cost ($/kg MeOAc)	0.1	0.09	0.08	0.01	0.01
Carbon footprint (eq. kg of CO_2)	0.92	0.56	0.52	0.09	0.05
Fobj, (2.6)	2.06	2.08	2.09	2.16	2.16

that among the different SPBs that can be generated, only those that have the potential to overcome the process hot-spots are considered in order to identify the more sustainable flowsheet alternatives.

2.4.4 Level 4

Selection of the best, intensified alternative is dependent on economic factors, sustainability metrics, and LCA factors in addition to the objective function value and constraints. Table 2.5 gives values of a selected set of performance criteria for the base-case design and four selected alternative (intensified) designs from the 9 generated alternatives. For each alternative, the conversion of HOAc ≥ 92 % has been achieved, no solvents have been used and the number of unit operations have been reduced from 10 (the base-case) to 1 (alternative 9).

The finding of non-trade-off-intensified designs that offer improvements in economic, sustainability/LCA factors is shown in Fig. 2.11 where the ratios of different performance criteria with respect to the base-case (multiplied by 100) have been plotted. Not that for profit, the inverse has been taken. The base-case design is at the boundary while the more sustainable alternatives are all within the boundary, indicating clearly that these alternatives are more sustainable than the base-case. Alternatives 5 and 9 give the best results.

2.5 Perspectives, Conclusions, and Future Work

The design of novel, innovative, more sustainable equipment (unit operations) and methods for the selection and design of the best (optimal) innovative process are required for successful achievement of PI. Research and development in intensified equipment design, overall PI solutions, and methods–tools to identify them will continue to remain an active area as,

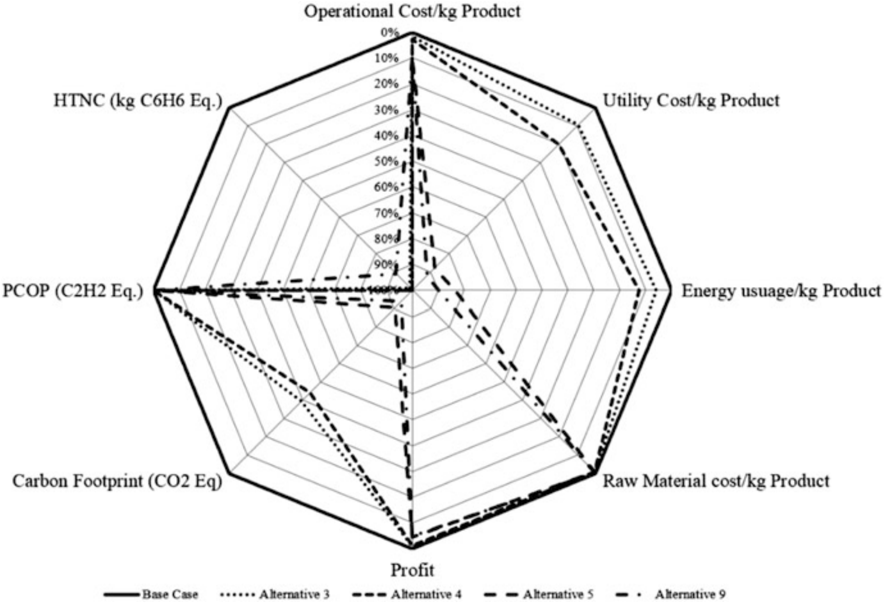


Fig. 2.11 Economic and LCA improvements relative to the base-case design. *PCOP* photochemical oxidation potential, *HTNC* human toxicity (non-carcinogenic impacts)

- New design concepts for unit operations for multiple applications in the chemical and biochemical industry will need to be developed
- Accurate models are needed for a better understanding of the complex behavior of reacting, separating and reacting–separating mixtures in hybrid/intensified unit operations
- Suitable (novel) materials need to be found for construction of these hybrid/intensified unit operations for pilot scale testing
- Methods for chemical (and biochemical) process design and optimization need to be further extended or developed for the selection of a wider range of hybrid/intensified unit operations that are more flexible and versatile from a sustainable point of view

Other challenges to application of PI also need to be addressed, for example, the controllability of hybrid/intensified unit operations, because it is well-known that the combination of phenomena, that lead to the combination of tasks and unit operations, also lead to a reduction in the degrees of freedom available for process control. Therefore, finding/developing the best, more sustainable control strategies need to be investigated. This can be addressed by integration of process design and process controller design and by making a priori design decisions that correspond to the best control strategy.

Process intensification can be performed at different scales (unit operations, task, and phenomena) and performing PI at each scale increases process innovation.

Process intensification improves the performance of an existing process as well as improves the design of a new process in terms of economic and environmental improvements. It is imperative that chemical and biochemical manufacturers remain competitive through the design of economically viable, innovative, more sustainable processes. Therefore, PI plays an important role in identifying the more sustainable and innovative process designs. In this respect the three-stage approach of process synthesis stage, process design (and analysis) stage, and innovation stage (process intensification) where new (or novel) hybrid/intensified unit operations could be generated, could become an important tool.

References

1. Gani R, Babi DK (2014) Systematic computer aided framework for process synthesis, design and intensification. In: Letcher T, Scott J, Darrell PA (eds) Chemical processes for a sustainable future. Royal Chemical Society, Cambridge, pp 698–752
2. Babi DK, Lutze P, Woodley JM, Gani R (2014) A process synthesis-intensification framework for the development of sustainable membrane-based operations. Chem Eng Process 86:173–195. doi:10.1016/j.cep.2014.07.001
3. Moulijn JA, Stankiewicz A, Grievink J, Górak A (2008) Process intensification and process systems engineering: a friendly symbiosis. Comput Chem Eng 32(1–2):3–11. doi:10.1016/j.compchemeng.2007.05.014
4. Stankiewicz A, Moulijn JA (2000) Process intensification: transforming chemical engineering. Chem Eng Prog 96(1):22–24
5. Reay D, Ramshaw C, Harvey A (2008). In: Reay D, Ramshaw C, Harvey A (eds) Process intensification. IChemE, Rugby.
6. Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM (2012) Process intensification: new understanding and systematic approach. Chem Eng Process 53:63–75. doi:10.1016/j.cep.2011.12.010
7. Bessling B, Schembecker G, Simmrock KH (1997) Design of processes with reactive distillation line diagrams. Ind Eng Chem Res 36(8):3032–3042. doi:10.1021/ie960727p
8. Agreda VH, Partin LR, Heise WH (1990) High-purity methyl acetate via reactive distillation. Chem Eng Prog 86(2):40–46
9. Freund H, Sundmacher K (2008) Towards a methodology for the systematic analysis and design of efficient chemical processes. Chem Eng Process 47(12):2051–2060. doi:10.1016/j.cep.2008.07.011
10. Lutze P, Babi DK, Woodley JM, Gani R (2013) Phenomena based methodology for process synthesis incorporating process intensification. Ind Eng Chem Res 52(22):7127–7144. doi:10.1021/ie302513y
11. Siirola JJ (1996) Strategic process synthesis: advances in the hierarchical approach. Comput Chem Eng 20:S1637–S1643. doi:10.1016/0098-1354(96)85982-5
12. Papalexandri KP, Pistikopoulos EN (1994) A multiperiod MINLP model for the synthesis of flexible heat and mass exchange networks. Comput Chem Eng 18(11–12):1125–1139. doi:10.1016/0098-1354(94)E0022-F
13. Peschel A, Jörke A, Freund H, Sundmacher K (2012) Model-based development of optimal reaction concepts for plant wide process intensification. Comput Aided Chem Eng 31:150–154. doi:10.1016/B978-0-444-59507-2.50022-6
14. Lutze P, Román-Martinez A, Woodley JM, Gani R (2012) A systematic synthesis and design methodology to achieve process intensification in (bio) chemical processes. Comput Chem Eng 36:189–207. doi:10.1016/j.compchemeng.2011.08.005

15. El-Halwagi MM (1997) Pollution prevention through process integration: systematic design tools. Academic, San Diego
16. El-Halwagi MM (2006) Process systems engineering- process integration. Elsevier
17. Smith R (2005) Chemical process: design and integration. WILEY-VCH Verlag GmbH, Weinheim
18. Klemeš JJ, Varbanov PS, Kravanja Z (2013) Recent developments in process integration. Chem Eng Res Des 91(10):2037–2053. doi:10.1016/j.cherd.2013.08.019
19. Harmsen J (2010) Process intensification in the petrochemicals industry: drivers and hurdles for commercial implementation. Chem Eng Process 49(1):70–73. doi:10.1016/j.cep.2009.11.009
20. Linnhoff B, Townsend DW, Boland D, Hewitt GF, Thomas BEA, Guy AR, Marsland RH (1982) A user guide on process integration for the efficient use of energy. IChemE, Rugby
21. Papoulias SA, Grossmann IE (1983) A structural optimization approach in process synthesis—II. Comput Chem Eng 7(6):707–721. doi:10.1016/0098-1354(83)85023-6
22. Singhvi A, Madhavan KP, Shenoy UV (2004) Pinch analysis for aggregate production planning in supply chains. Comput Chem Eng 28(6–7):993–999. doi:10.1016/j.compchemeng.2003.09.006
23. Kazantzi V, El-Halwagi MM (2005) Targeting material reuse via property integration. Chemical Engineering Progress 101(8), 28–37. http://www.scopus.com/inward/record.url?eid=2-s2.0-27844440901&partnerID=tZOtx3y1
24. Babi DK, Holtbruegge J, Lutze P, Gorak A, Woodley JM, Gani R (2015) Sustainable process synthesis–intensification. Comput Chem Eng 81:218–244. doi:10.1016/j.compchemeng.2015.04.030
25. Oxley P, Brechtelsbauer C, Ricard F, Lewis N, Ramshaw C (2000) Evaluation of spinning disk reactor technology for the manufacture of pharmaceuticals. Ind Eng Chem Res 39 (7):2175–2182. doi:10.1021/ie990869u
26. Lutze P, Gorak A (2013) Reactive and membrane-assisted distillation: recent developments and perspective. Chem Eng Res Des 91(10):1978–1997. doi:10.1016/j.cherd.2013.07.011
27. Asprion N, Kaibel G (2010) Dividing wall columns: fundamentals and recent advances. Chem Eng Process 49(2):139–146. doi:10.1016/j.cep.2010.01.013
28. Alfa Laval (2015) A new degree of deodorization control. http://local.alfalaval.com/de-de/wichtige-industrien/lebensmittel-molkerei-getraenke/oele/Documents/Desodorierung_Alfa%20Laval%20SoftFlex%E2%84%A2%20semi-continuous.pdf
29. Alfa L (2015) Gasketed plate-and-frame heat exchangers. Heat Exchangers. http://www.alfalaval.com/products/heat-transfer/plate-heat-exchangers/Gasketed-plate-and-frame-heat-exchangers/
30. Ramshaw C (1993) The opportunities for exploiting centrifugal fields. Heat Recovery Syst CHP 13(6):493–513. doi:10.1016/0890-4332(93)90003-E
31. Al Taweel AM, Yan J, Azizi F, Odedra D, Gomaa HG (2005) Using in-line static mixers to intensify gas–liquid mass transfer processes. Chem Eng Sci 60(22):6378–6390. doi:10.1016/j.ces.2005.03.011
32. Babi DK, Gani R (2014) Hybrid distillation schemes: design, analysis, and application. In: Gorak A, Sorensen E (eds) Distillation. Elsevier, London, pp 357–381. doi:10.1016/B978-0-12-386547-2.00009-0
33. Linnhoff B, Flower JR (1978) Synthesis of heat exchanger networks: I. Systematic generation of energy optimal networks. AIChE J 24(4):633–642. doi:10.1002/aic.690240411
34. Zhao CY, Lu W, Tassou SA (2006) Thermal analysis on metal-foam filled heat exchangers. Part II: tube heat exchangers. Int J Heat Mass Transf 49(15–16):2762–2770. doi:10.1016/j.ijheatmasstransfer.2005.12.014
35. Osakada K, Shiomi M (2006) Flexible manufacturing of metallic products by selective laser melting of powder. Int J Mach Tool Manuf 46(11):1188–1193. doi:10.1016/j.ijmachtools.2006.01.024

36. El-Halwagi MM, Manousiouthakis V (1989) Synthesis of mass exchange networks. AIChE J 35:1233–1244. doi:10.1002/aic.690350802
37. Stankiewicz A, Moulijn JA (2004) Re-engineering the chemical processing plant. Marcel-Dekker, New York
38. Peschel A, Karst F, Freund H, Sundmacher K (2011) Analysis and optimal design of an ethylene oxide reactor. Chem Eng Sci 66(24):6453–6469. doi:10.1016/j.ces.2011.08.054
39. Calvar N, González B, Dominguez A (2007) Esterification of acetic acid with ethanol: reaction kinetics and operation in a packed bed reactive distillation column. Chem Eng Process 46 (12):1317–1323. doi:10.1016/j.cep.2006.10.007
40. Liu G, Gan L, Liu S, Zhou H, Wei W, Jin W (2014) PDMS/ceramic composite membrane for pervaporation separation of acetone–butanol–ethanol (ABE) aqueous solutions and its application in intensification of ABE fermentation process. Chem Eng Process 86:162–172. doi:10.1016/j.cep.2014.06.013
41. Leyva-Díaz JC, López-López C, Martín-Pascual J, Muñío MM, Poyatos JM (2015) Kinetic study of the combined processes of a membrane bioreactor and a hybrid moving bed biofilm reactor-membrane bioreactor with advanced oxidation processes as a post-treatment stage for wastewater treatment. Chem Eng Process 91:57–66. doi:10.1016/j.cep.2015.03.017
42. Jordens J, Gielen B, Braeken L, Van Gerven T (2014) Determination of the effect of the ultrasonic frequency on the cooling crystallization of paracetamol. Chem Eng Process 84:38–44. doi:10.1016/j.cep.2014.01.006
43. Werth K, Lutze P, Kiss AA, Stankiewicz AI, Stefanidis GD, Górak A (2015) A systematic investigation of microwave-assisted reactive distillation: influence of microwaves on separation and reaction. Chem Eng Process 93:87–97. doi:10.1016/j.cep.2015.05.002
44. Douglas JM (1985) A hierarchical decision procedure for process synthesis. AIChE J 31 (3):353–362. doi:10.1002/aic.690310302
45. Bayer B, Schneider R, Marquardt W (2000) Integration of data models for process design—first steps and experiences. Comput Chem Eng 24(2–7):599–605. doi:10.1016/S0098-1354(00)80002-2
46. Gernaey KV, Gani R (2010) A model-based systems approach to pharmaceutical product-process design and analysis. Chem Eng Sci 65(21):5757–5769. doi:10.1016/j.ces.2010.05.003
47. Hostrup M, Gani R, Kravanja Z, Sorsak A, Grossmann I (2001) Integration of thermodynamic insights and MINLP optimization for the synthesis, design and analysis of process flowsheets. Comput Chem Eng 25(1):73–83. doi:10.1016/S0098-1354(00)00634-7
48. Grossmann IE (2012) Advances in mathematical programming models for enterprise-wide optimization. Comput Chem Eng 47:2–18. doi:10.1016/j.compchemeng.2012.06.038
49. Siirola JJ, Powers GJ, Rudd DF (1971) Synthesis of system designs: III. Toward a process concept generator. AIChE J 17(3):677–682. doi:10.1002/aic.690170334
50. Kobus A, Kuppinger F-F, Meier R, Düssel R, Tuchlenski A, Nordhoff S (2001) Improvement of conventional unit operations by hybrid separation technologies—a review of industrial applications. Chem Ing Tech 73(6):714. doi:10.1002/1522-2640(200106)73:6<714::AID-CITE7142222>3.0.CO;2-S
51. d'Anterroches L, Gani R (2005) Group contribution based process flowsheet synthesis, design and modelling. Fluid Phase Equilib 228–229:141–146. doi:10.1016/j.fluid.2004.08.018
52. Kiss A, Pragt H, van Strien C (2007) Computer aided chemical engineering. In: 17th European Symposium on Computer Aided Process Engineering, vol 24, Elsevier, Amsterdam, pp 467–472. doi:10.1016/S1570-7946(07)80101-5
53. Caballero JA, Grossmann IE (2004) Design of distillation sequences: from conventional to fully thermally coupled distillation systems. Comput Chem Eng 28(11):2307–2329. doi:10.1016/j.compchemeng.2004.04.010
54. Madenoor Ramapriya G, Tawarmalani M, Agrawal R (2014) Thermal coupling links to liquid-only transfer streams: a path for new dividing wall columns. AIChE J 60(8):2949–2961. doi:10.1002/aic.14468

55. Urselmann M, Barkmann S, Sand G, Engell S (2011) Optimization-based design of reactive distillation columns using a memetic algorithm. Comput Chem Eng 35(5):787–805. doi:10.1016/j.compchemeng.2011.01.038
56. Amte V (2011) Computer aided chemical engineering, vol 29. doi:10.1016/B978-0-444-53711-9.50144-9
57. Seifert T, Sievers S, Bramsiepe C, Schembecker G (2012) Small scale, modular and continuous: a new approach in plant design. Chem Eng Process 52:140–150. doi:10.1016/j.cep.2011.10.007
58. Jaksland C, Gani R, Lien K (1995) Separation process design and synthesis based on thermodynamic insights. Chem Eng Sci 50:511–530. doi:10.1016/0009-2509(94)00216-E
59. Harper PM, Gani R (2000) A multi-step and multi-level approach for computer aided molecular design. Comput Chem Eng 24(2–7):677–683. doi:10.1016/S0098-1354(00)00410-5
60. Gani R, Hytoft G, Jaksland C, Jensen AK (1997) An integrated computer aided system for integrated design of chemical processes. Comput Chem Eng 21(10):1135–1146. doi:10.1016/S0098-1354(96)00324-9
61. Peters MS, Timmerhaus KD, West RE (2003) Sign and economics for chemical engineers. In: Peters MS, Timmerhaus KD, West RE (eds) 5th edn. Mc Graw Hill, New York. http://catalogs.mhhe.com/mhhe/viewProductDetails.do?isbn=0072392665
62. Carvalho A, Matos HA, Gani R (2013) SustainPro—a tool for systematic process analysis, generation and evaluation of sustainable design alternatives. Comput Chem Eng 50:8–27. doi:10.1016/j.compchemeng.2012.11.007
63. Kalakul S, Malakul P, Siemanond K, Gani R (2014) Integrated of life cycle assessment software with tools for economic and sustainability analyses and process simulation for sustainable process design. J Clean Prod 71:98–109. doi:10.1016/j.jclepro.2014.01.022
64. Marrero J, Gani R (2001) Group contribution based estimation of pure component properties. Fluid Phase Equilib 183–184:183–208. doi:10.1016/S0378-3812(01)00431-9
65. Huss RS, Chen F, Malone MF, Doherty MF (2003) Reactive distillation for methyl acetate production. Comput Chem Eng 27(12):1855–1866. doi:10.1016/S0098-1354(03)00156-X

Chapter 3
Systematic Synthesis of Intensified Distillation Systems

Massimiliano Errico and Ben-Guang Rong

Abstract The choice of the optimal configuration for the separation of multicomponent mixtures represents one of the prevailing problems in the process industry. Simple distillation column sequences have been the favorite choice for long time, until the increase of the energy price makes these configurations no more competitive from an economic point of view. The research of alternative arrangements is an evergreen topic in the Chemical Engineering community. In this chapter a systematic methodology to generate different classes of distillation configurations is presented. The generation methodology is able to consider thermally coupled, thermodynamically equivalent structures and intensified alternatives with a less number of columns compared to the corresponding simple column sequences. The methodology described has the advantage to produce a complete set of alternatives, avoiding the trial and error procedure with random configurations picked up from the literature. Finally, the methodology described has the benefit to keep a clear connection between the simple column sequences and all the alternatives predicted. This aspect helps the designer in the definition of columns' configuration parameters.

3.1 Introduction

Distillation is for sure an old art; it was initially developed batchwise and then extend to the modern continuous equipment currently used. It is difficult to define who was the first to apply the distillation physical principles. Going back in history, from ancient Greek to Egypt and China, to philosophers and Napoleon, an

---

M. Errico (✉)
Department of Chemical Engineering, Biotechnology and Environmental Technology,
University of Southern Denmark, Campusvej 55, DK 5230, Odense M, Denmark
e-mail: maer@kbm.sdu.dk

B.-G. Rong
University of Southern Denmark, Campusvej 55, DK 5230, Odense M, Denmark
e-mail: bgr@kbm.sdu.dk

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_3

interesting historical review was reported by Forbes [1]. Nowadays distillation is for sure one of the most used separation methods in the chemical process industry, proved by the fact that the number of operative distillation columns was quantified in 40,000 units only in the USA [2]. As the distillation technology evolves, also the research's focus have been changed along the years. Around the 20s and the 50s the developing of short-cut methods was the main interest in order to obtain a fast design without an excessive mathematical effort [3, 4]. Later, the definition of heuristic rules, to prompt the removal order for the different components in multicomponent mixtures, took up most of the 70s and 80s [5–7]. The availability of more powerful mathematical tools opened the age of optimization and the developing of different control strategies [8–10]. Anyway, the energy crisis changed the way distillation was considered.

Even if so widely diffused, distillation is recognized for the generally low thermodynamic efficiency and its resulting high-energy consumption. The necessity to reduce the energy load, together with the resulting impact of its production in terms of environmental sustainability, moves part of the research focus in developing new distillation arrangements. Considering multicomponent mixtures, it is easy to imagine that once the intended individual splits are identified, it is possible to obtain different separation orders corresponding to different separation sequences. The identification of all the possible alternatives is usually referred as a synthesis problem.

The importance of this step can be condensate in the sentence from Kaibel and Shoenmakers [11]: "If the optimum alternative is not predefined it will not be found." In other words, it is of fundamental importance to define a method able to predict all the possible alternatives for a defined separation task. The quality of the method, expressed by its ability in the generation of a complete set of alternatives, is directly related to the possibility of selecting the best option.

As evidenced by Thompson and King [5] "Process synthesis is regarded, for the most part, as an intuitive art" but a subjective approach to the synthesis can lead to explore only part of the possibilities, resulting in the selection of a non-global optimal solution. From this consideration, the necessity to define a systematic synthesis methodology becomes of paramount importance in the generation of alternative distillation structures. The synthesis comes to light as an independent research topic and many authors contributed in defining different methods and different approaches to increase the number of distillation structures available with the aim to reduce the energy consumption and the capital costs.

A complete review is out of the scope of the present book chapter, but it is right and proper to recall at least some relevant contributions in the synthesis of distillation alternatives.

Also, in terms of synthesis, here it is important to recognize the difference between ternary distillations and distillations for four or more component separations. For ternary mixtures, the various configurations have been coming into light gradually in a somewhat chaotic, evolutionary process [12]. Unlike ternary mixtures, it is impossible to obtain all feasible distillation configurations by chaotic activities for four or more component mixtures. The differences are that: first, the number of possible distillation configurations is becoming explosive with increasing the number of components in the mixtures. Second, there are distinct subspaces of different types of distillation configurations for four or more component mixtures, each distinct subspace also includes a large number of feasible configurations [13]. For example, for the single Petlyuk configuration for a four or more component mixture, Rong and Turunen [14] demonstrated that it is impossible to draw all the possible thermodynamically equivalent structures (TES) by the inventive activities, rather, a systematic procedure is needed to obtain all the TES structures.

In the literature, there are different synthesis methodologies presented to synthesize multicomponent distillation configurations (four or more component). Agrawal [15] presented a methodology to draw distillation configurations with $n-1$ columns through modifying a network-superstructure for a multicomponent mixture. Later on a six-step matrix method was described to generate all the basic configurations [16]. The six-step matrix method was then extended to an eight-step matrix method to include also configurations with less than $n-1$ columns [17].

Caballero and Grossmann [18] presented a state-task-network superstructure methodology to mathematically formulate the alternatives space of multicomponent distillation configurations. This superstructure was evolutionarily extended to include different types of distillation configurations in order to search the optimal configuration for specific applications [19, 20].

Differently from the superstructure methodologies, Rong et al. [13] developed a methodology which can synthesize all possible distillation configurations with equal to $n-1$ or more than $n-1$ columns for an n-component mixture. This methodology was based on formulating all the feasible distinct separation sequences (DSS) for a n-component mixture a priori, which consisted of both sharp and nonsharp sequences. During the development of the methodology, mechanisms and methods to synthesize different types of distillation configurations were developed. First, for the subspace of the sharp separation sequences, the method was developed for synthesis of the thermally coupled configurations for the five-component mixtures [21, 22]. Then, a method to synthesize the distillation configurations from both sharp and nonsharp sequences was developed [13], where the method has explored all the possible subspaces of the multicomponent distillation configurations, including the DSS, the traditional distillation configurations (TDC), the original thermally coupled configurations (OTC), and the thermodynamically equivalent structures. Later on, methods and systematic procedures for synthesis of different subspaces of distillation configurations were presented, including the heat-integrated thermally coupled configurations [23, 24], the TES [24, 25]. Recently, new methods and systematic procedures were developed for the synthesis of intensified distillation systems with less than $n-1$ columns for an n-component distillation, including the intensified sidestream columns for sharp sequences [26], the DWC columns [27], the intensified simple column (ISC) configurations [28], and the intensified sidestream columns for nonsharp sequences [29].

It is clear that the synthesis of a complete searching space including the highest number of distillation alternatives represents an essential point to proceed in the selection of the configuration that satisfy a predefined objective function.

In this chapter, some of the recent progress on the synthesis of intensified distillation systems for multicomponent distillations are summarized. The objective is that, with the specific cases illustrated, the designers are helped to design the intensified distillation systems step-by-step. In this way, the designers can systematically modify the structures and determine the connections of the column sections. More importantly, the structural derivation and design can later on give the designers the hints and steps for parametrically design and optimize the obtained intensified distillation systems.

3.2 The Simple Column Distillation Sequences: The Reference for Any Alternative Structure

A simple distillation column is defined as a column with a single feed, equipped with a condenser and a reboiler. Considering a column section as a column's portion not interrupted by mass and/or energy flows, a simple column contains only two sections.

When the process involves the separation of a n-component mixture, there are different possibilities in the component separation order, each possibility corresponds to a different column sequence. The number of simple column sequences can be predicted by the formula of Thompson and King [5] reported in (3.1):

$$S_n = \frac{[2(n-1)]!}{n!(n-1)!} \tag{3.1}$$

The subspace that includes all the simple column sequences represents the simplest class of distillation alternatives. For many years the research of the best distillation configuration was limited to this subspace. The reason is that most of the available design methods were developed for simple columns and also searching criteria as heuristic rules were based on this class of configurations. Reliable design methods, together with trustworthy control systems, made simple columns sequences the preferred choice in the process industrial practice. This is the motivation because the set of simple columns sequences represents the term of comparison with all the alternatives predicted. This point will be of essential importance in the synthesis procedure described as follow: at the beginning of the alternatives generation procedure the designer has already defined the simple columns sequences parameters.

3.3 Sharp, Nonsharp Splits and Number of Columns in the Sequence

The case discussed in the previous paragraph and the equation (3.1) reported is valid when only sharp splits are considered. A sharp split can be realized when each stream is enriched in one component while the concentration of the other ones is kept below an acceptable limit. In this case, from a n-component mixture, if n products are obtained, it is necessary to connect $n - 1$ simple columns. Since to each rectifying section is associated a condenser and to each stripping section is connected a reboiler, $n - 1$ condensers and $n - 1$ reboilers are needed. The column's number in the simple column sequence is often mentioned as the minimum number of simple distillation columns required for the separation.

Anyway sharp splits are not the only possibility to perform a separation. In some cases one or more middle boiling components can be allowed to distribute in a significant amount between the distillate and the bottom stream. The kind of separation is referred as nonsharp or sloppy split. In general the separation sequence with nonsharp splits contains a number of columns higher than $n - 1$. If a three-component mixture ABC is considered, from the equation (3.1), two possible simple column sequences are predicted. Since there is only one middle component, then only one sequence with sloppy split is possible. The alternatives are reported in Fig. 3.1.

In the sequences reported in Fig. 3.1a, b there is a net separation between adjacent key components and the resulting configurations are composed by two columns. Simple column sequences for three-component separations were extensively studied in the literature [30–32] and applied in many industrial processes like the separation of benzene, toluene, and xylenes [33] or the production of enriched ethane, propane, and butane from crude distillation, naphtha reformation, and naphtha cracking processes [34].

When the middle component is distributed between the distillate and the bottom stream, as reported in Fig. 3.1c, the corresponding sequence has three columns. It is

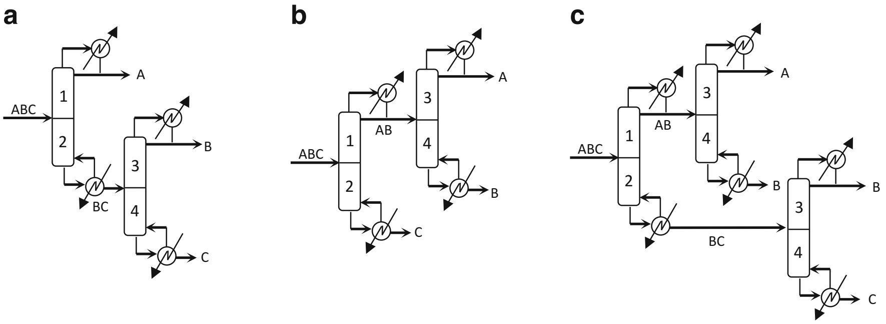


Fig. 3.1 (**a**, **b**) Sharp split sequences, (**c**) sloppy split sequence

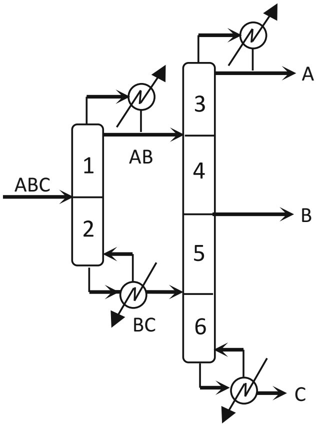


Fig. 3.2 Three component sloppy sequence with a reduced number of columns

already known that, in order to reduce the capital costs, configurations with a number of columns equal to simple column sequences are usually suggested. By observation of the sloppy sequence of Fig. 3.1c it is possible to notice that B is co-produced in the reboiler of the second column and also in the condenser of the third one. Integrating the second and the third column is possible obtain a two-column sequence as reported in Fig. 3.2.

In this case the resulting configuration can not be considered as a simple column sequence since the second column has more than two sections, two feeds and also a side stream.

From this example emerges that configurations with sloppy splits give the flexibility to consider cases with more than $n - 1$ columns, less than $n - 1$, or with exactly $n - 1$ columns.

The simple column sequences together with the configurations obtained introducing also sloppy splits are called TDC.

3.4 Synthesis of Alternative Distillation Configurations

Before to proceed with the description of the methodology followed to derive the set of distillation alternatives, it is interesting to define the motivation to dispose of such alternative configurations. The main reason is the necessity to reduce the energy consumption associated to the production, moreover also the reduction of the capital costs is emerging as an important driver in the design of new plants or retrofit of existing ones.

These new trends are condensed in the Process Intensification that recently emerges in the chemical engineering community as a new design philosophy.

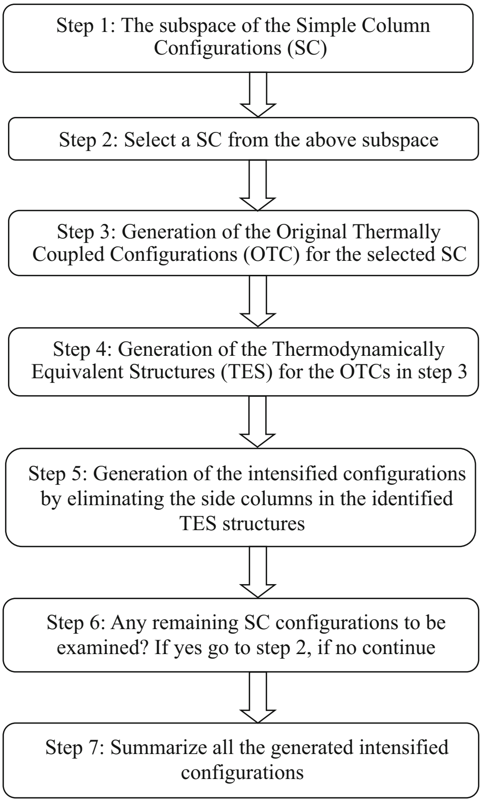
Stankiewicz and Moulijn [35] defined Process Intensification as: “any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology.”

Moreover, talking about distillation, another important point to add to the Process Intensification principles is to prefer distillation alternatives with a simple design that somehow resembles the simple column sequences. Potential in energy reduction, intensification of the process by reduction of the number of columns and design simplicity are the main points inspiring the generation of alternative distillation configurations.

The searching space should be defined keeping in mind two important aspects discussed in details by Giridahar and Agrawal [36]. The former regards the necessity to dispose of a set of configurations that includes all the configurations that could be potentially optimal for a feed composition case. The latter is the needing in a reduced searching space that theoretically includes only the most promising configurations, decreasing in this way the efforts in screening all the alternatives.

For this reason a systematic and general method to generate all the alternatives is presented first, and then, by the analysis of alternatives with specific features, the synthesis method is improved to directly produce specific alternatives.

The systematic methodology, based on the introduction of thermal couplings and on the column section reorganization, is summarized in Fig. 3.3 and here is applied, as an example, for a four-component mixture ABCD.



Step 1: The subspace of the Simple Column Configurations (SC)

Step 2: Select a SC from the above subspace

Step 3: Generation of the Original Thermally Coupled Configurations (OTC) for the selected SC

Step 4: Generation of the Thermodynamically Equivalent Structures (TES) for the OTCs in step 3

Step 5: Generation of the intensified configurations by eliminating the side columns in the identified TES structures

Step 6: Any remaining SC configurations to be examined? If yes go to step 2, if no continue

Step 7: Summarize all the generated intensified configurations

Fig. 3.3 Systematic procedure to generate intensified configurations from simple column sequences

Table 3.1 The simple column sequences for a four-component separation

Sequence no.	Simple column sequence
1	ABC/D(1) AB/C(2) A/B(3)
2	ABC/D(1) A/BC(2) B/C(3)
3	AB/CD(1) A/B(2) C/D(3)
4	A/BCD(1) B/CD(2) C/D(3)
5	A/BCD(1) BC/D(2) B/C(3)

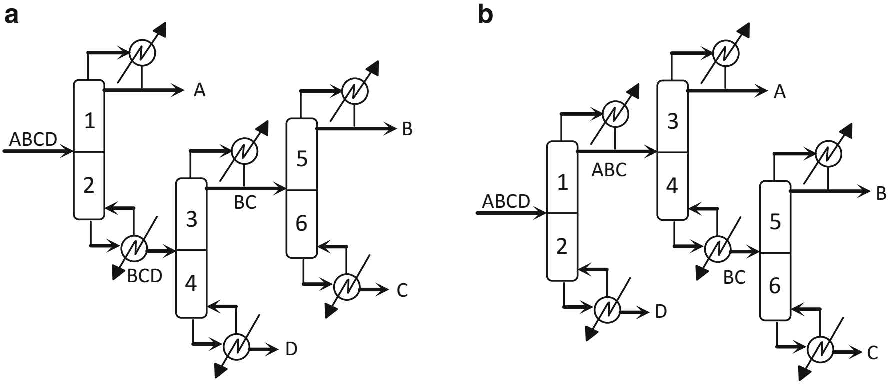


Fig. 3.4 (**a**) Direct–indirect and (**b**) indirect–direct simple column sequence

Step 1: Considering sharp splits, according to the King's formula, five simple column sequences are possible. The direct, the indirect, the direct–indirect, the indirect–direct, and the symmetric sequence.

The five sequences are reported in Table 3.1. Each sequence includes three individual splits numbered in brackets.

Step 2: Among all the sequences, the direct–indirect and the indirect–direct are here considered and reported in Fig. 3.4. The name of the sequences is derived by the component separation order, in Fig. 3.4a the lightest separation is removed first and then the heaviest one, in Fig. 3.4b instead the heaviest component is removed first followed by the lightest one.

Step 3: OTC configurations are obtained by substitution of a condenser and/or a reboiler associated to submixture by a bidirectional vapor and liquid stream [13]. Thermally coupled configurations were extensively studied and successfully applied because of the possibility in energy saving compared to the correspondent simple column sequences from which are derived [37–39]. In Fig. 3.5 the OTCs are reported.

Step 4: The presence of a thermal coupling makes the stripping or rectifying section of the subsequent columns movable. The number of movable sections equals the number of thermal couplings introduced. The configurations obtained are

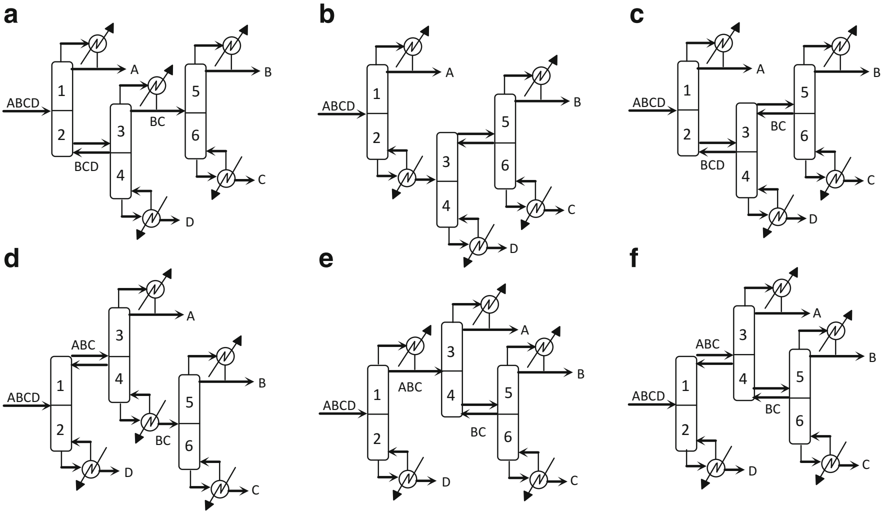


Fig. 3.5 OTC configurations corresponding to the direct–indirect (**a**–**c**) and to the indirect–direct sequence (**d**–**f**)

reported in Fig. 3.6 and are called TES [13, 25]. It is possible to notice that the TES have at least one single column section that can be a single rectifying or stripping section or in some cases can be a single section included between two columns. In this case is called "transport section" as its function is to transfer a submixture between one column to another.

Step 5: To generate the Intensified Configurations (IS), the single column sections, identified in step 4, are eliminated and substituted by a side stream. The resulting configurations, reported in Fig. 3.7, have the same feature of a reduced number of columns. This subspace of alternatives is called "distillation configurations with less than $n-1$ columns" or more briefly "Intensified Configurations" to highlight the cohesion with the Process Intensification principles.

Step 6: The remaining simple column sequences identified in step 1 are considered and the methodology repeated.

Step 7: For a four-component mixture it is possible to obtain 31 intensified sequences summarized by Errico et al. [26].

One of the objectives in the generation of the alternative distillation configurations is to associate the possibility in energy and capital costs reduction together with a simple design. A simple design is here considered as a configuration that has structural similarities with the simple column sequences.

Screening all the intensified configurations, the ones reported in Fig. 3.7a, c, f, h are associated by the fact that each column has two products, one distillate from the top condenser and the other from the bottom reboiler. All the products are obtained as distillates and bottoms streams, never as side withdrawn. They have the same

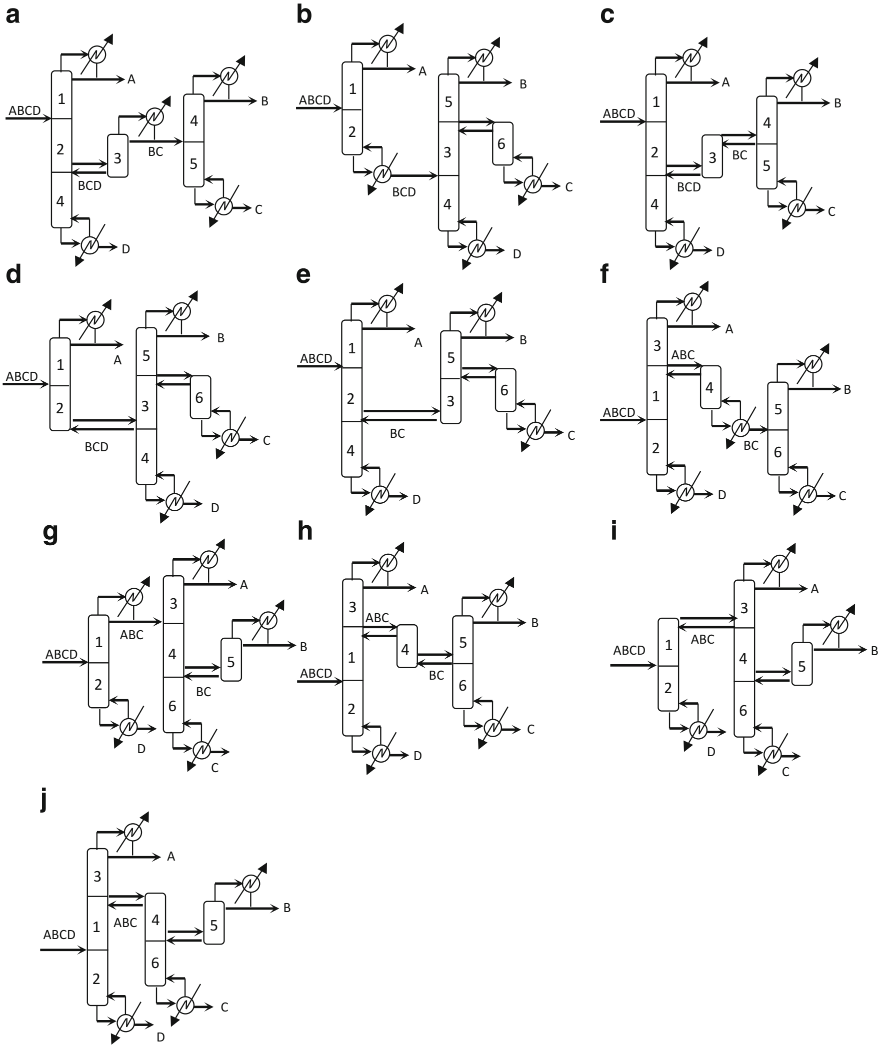


Fig. 3.6 TESs derived from the OTC configurations of Fig. 3.5

structural simplicity as the simple column sequences but with a reduced number of columns and heat exchangers. Taking into account this similarity, this particular sub-space of alternatives was called ISC configurations.

The structural features of ISC configurations derived from simple column sequences are here summarized:

(a) Any ISC configuration uses less than $n - 1$ columns for an n-component distillation.

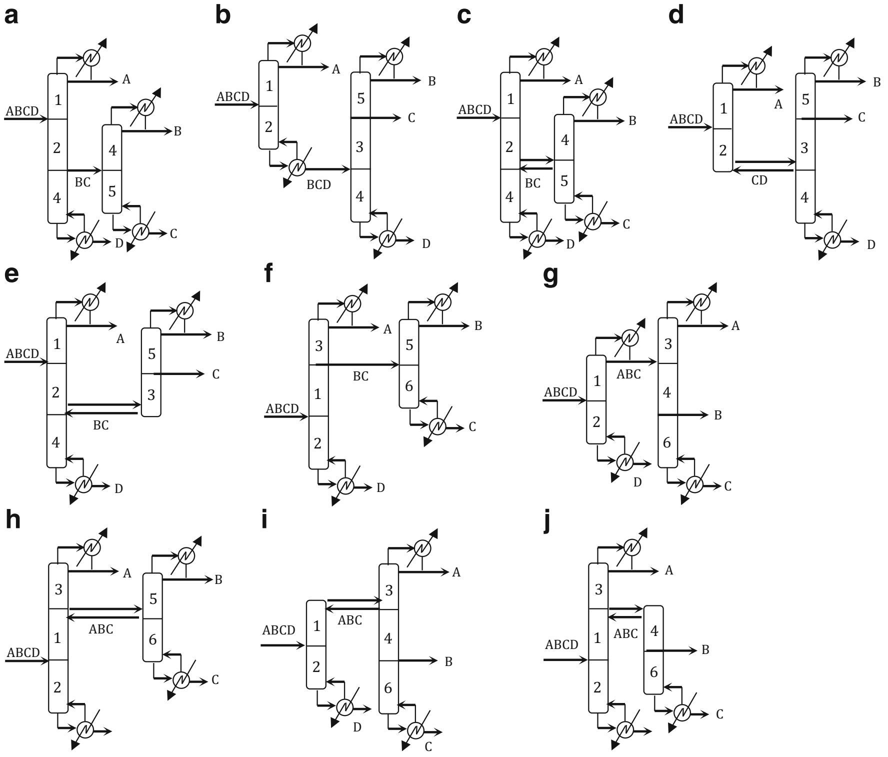


Fig. 3.7 Intensified configurations derived from the direct–indirect (**a**–**e**) and indirect–direct SC sequences (**f**–**j**)

(b) Each column has an overhead condenser and a bottom reboiler.
(c) There exist submixtures transferring between intermediate locations of columns. An intermediate submixture can transport between two columns in one-way (like in Fig. 3.7a, f) or in two-way (like in Fig. 3.7c, h).
(d) A column in an ISC configuration can have more than two sections.
(e) Each product is obtained once in the sequence.

For some composition cases, considering four-component mixtures, it was already proved that ISC configurations are valid alternatives to simple column sequences [40] for this reason is useful to dispose of a direct generation method for their prediction, particularly when the number of components in the feed is higher than 4.

3.5 A Systematic Generation Method to Synthesize Intensified Simple Column Configurations

It is clear that the ISC configurations are obtained from the TES by elimination of a single column section.

It is possible to identify different kinds of single sections:

- Product-side-rectifier-column (Fig. 3.6g, i, j): a single column section equipped with a condenser associated to a product stream
- Product-side-stripping section (Fig. 3.6b, d, e): a single column section equipped with a reboiler associated to a product stream
- One-way transport-side-rectifier (TSR1) like the one in Fig. 3.6a, where the single rectifier section has the main function of transportation of a intermediate submixture between columns
- Two-way transport-side-rectifier (TSR2) as the one reported in Fig. 3.6c, where the side rectifier transfers the submixture though a two-way thermal coupling streams
- One-way transport-side-stripper (TSS1) like the one in Fig. 3.6f, where the single stripping section has the main function of transportation of an intermediate submixture between columns
- Two-way transport-side-stripper (TSS2) as the one reported in Fig 3.6h, where the side stripper transfers the submixture though a two-way thermal coupling streams

Single column section's type plays an essential role in the generation of intensified simple column configurations. It is possible to define two criteria that the TES must satisfy in order to finally lead to ISC configurations [40].

Criterion 1: The TES must contain the single-section transport side columns.
Criterion 2: Except the transport side columns, each of the other columns in the TES must keep the simple column features that each column produces an overhead product with a condenser and a bottom product with a reboiler.

By examinations of the TES reported in Fig. 3.6 it is possible to identify four different cases for the single-section transport side columns that fulfill these two criteria:

Case 1: A TES structure with TSR1
Case 2: A TES structure with TSR2
Case 3: A TES structure with TSS1
Case 4: A TES structure with TSS2

The systematic method for the synthesis of intensified simple column configurations can be summarized in an eight-step procedure as reported in Fig. 3.8.

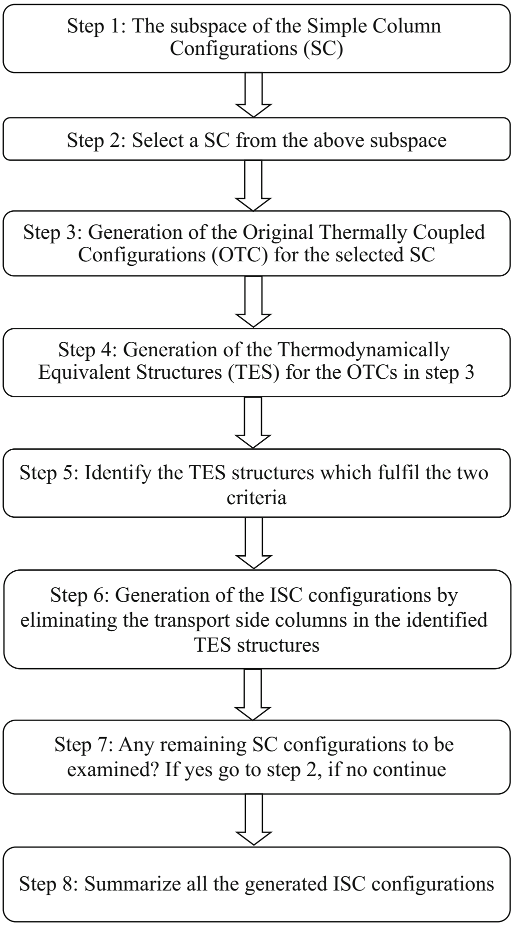


Fig. 3.8 The systematic procedure to synthesize intensified simple column configurations from SC sequences

3.6 Example: Intensified Simple Column Configurations for a Five-Component Mixture

The systematic procedure to generate ISC configurations is now applied to a five-component mixture ABCDE where the A is the most volatile component and E is the least one.

Step 1: The number of simple column sequences can be calculated by equation (3.1). For $n = 5$, 14 different sequences are possible. Each sequence consists in four individual splits which are numbered in brackets and reported in Table 3.2.

Step 2: Among all the 14 simple column sequences listed in Table 3.2, the sequence 11 was selected as example. This configuration is reported in Fig. 3.9.

Step 3: To generate the OTC configurations is necessary to replace the heat exchangers associated to submixture by thermal couplings. For the selected

Table 3.2 The 14 simple column sequences for a five-component separation

Sequence no.	Simple column sequence
1	ABCD/E(1) ABC/D(2) AB/C(3) A/B(4)
2	ABCD/E(1) ABC/D(2) A/BC(3) B/C(4)
3	ABCD/E(1) AB/CD (2) A/B(3) C/D(4)
4	ABCD/E(1) A/BCD(2) B/CD(3) C/D(4)
5	ABCD/E(1) A/BCD(2) BC/D(3) B/C(4)
6	ABC/DE(1) D/E(2) A/BC(3) B/C(4)
7	ABC/DE(1) D/E(2) AB/C(3) A/B(4)
8	AB/CDE(1) A/B(2) CD/E(3) C/D(4)
9	AB/CDE(1) A/B(2) C/DE(3) D/E(4)
10	A/BCDE(1) BCD/E(2) BC/D(3) B/C(4)
11	A/BCDE(1) BCD/E(2) B/CD(3) C/D(4)
12	A/BCDE(1) BC/DE (2) B/C(3) D/E(4)
13	A/BCDE(1) B/CDE(2) CD/E(3) C/D(4)
14	A/BCDE(1) B/CDE(2) C/DE(3) D/E(4)

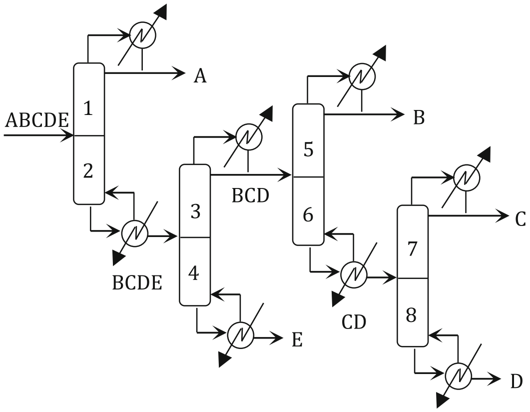


Fig. 3.9 The selected SC sequence for a five-component separation

configuration it is possible to substitute the reboiler associate to the mixture BCDE, the BCD condenser and the CD reboiler. The substitution can be individual or following different combinations. Globally, seven thermally coupled configurations are obtained as showed in Fig. 3.10.

Step 4 and 5: For any OTC configuration identified in step 3, there are a certain number of movable column sections due to the thermal couplings introduced. By recombining the movable column sections individually or combinatorially, all of the TES structures can be generated. For the 7 OTC configurations in Fig. 3.10, totally 19 TES are generated, among which there are 4 TES structures, presented in Fig. 3.11, which fulfill the 2 criteria for the generation of the ISC configurations.

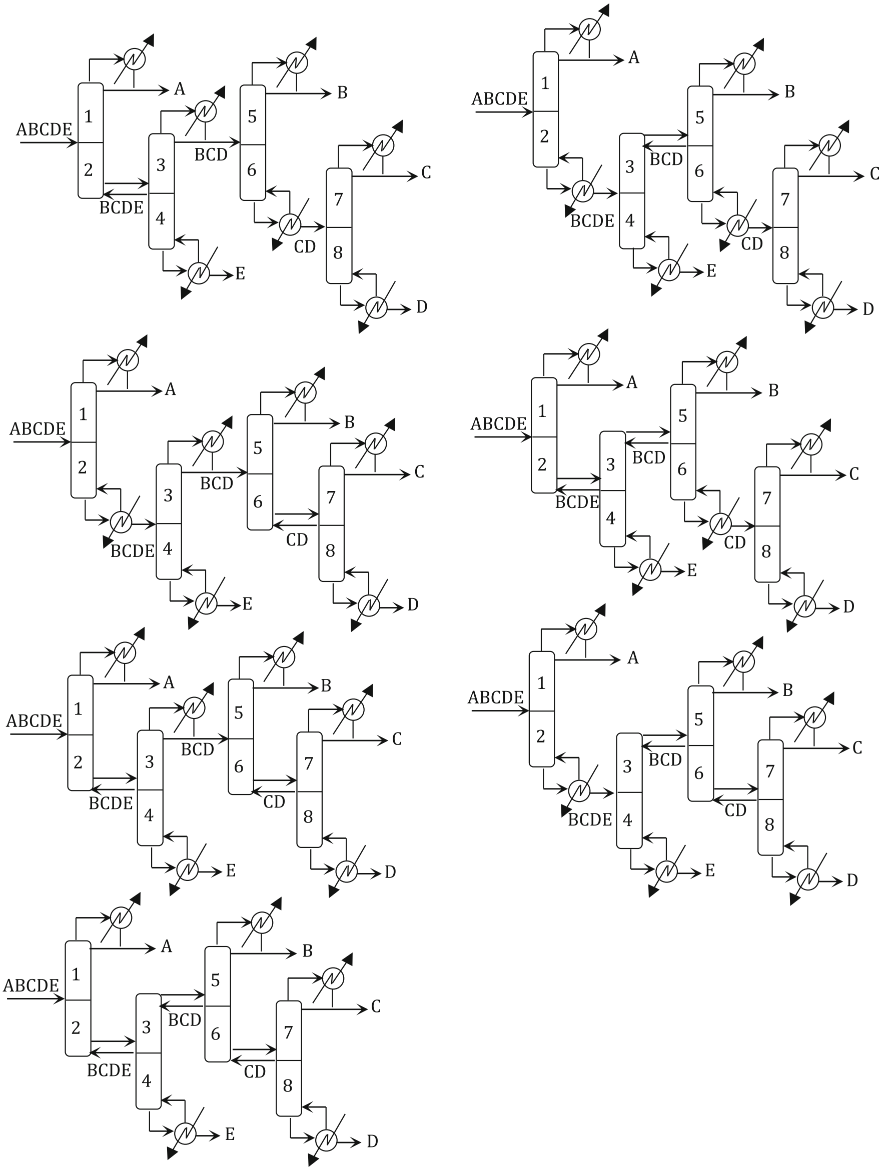


Fig. 3.10 Original thermally coupled configurations derived from the SC of Fig. 3.9

Step 6: Each thermodynamic equivalent structure identified in step 5 already contains the single transport section required for the generation of ISC sequences. In particular Fig. 3.11a has a one-way transport-side-rectifier, Fig. 3.11b has a TSS1, Fig. 3.11c has a two-way transport-side-rectifier and Fig. 3.11d has a TSS2. The corresponding ISC configurations are reported in Fig. 3.12.

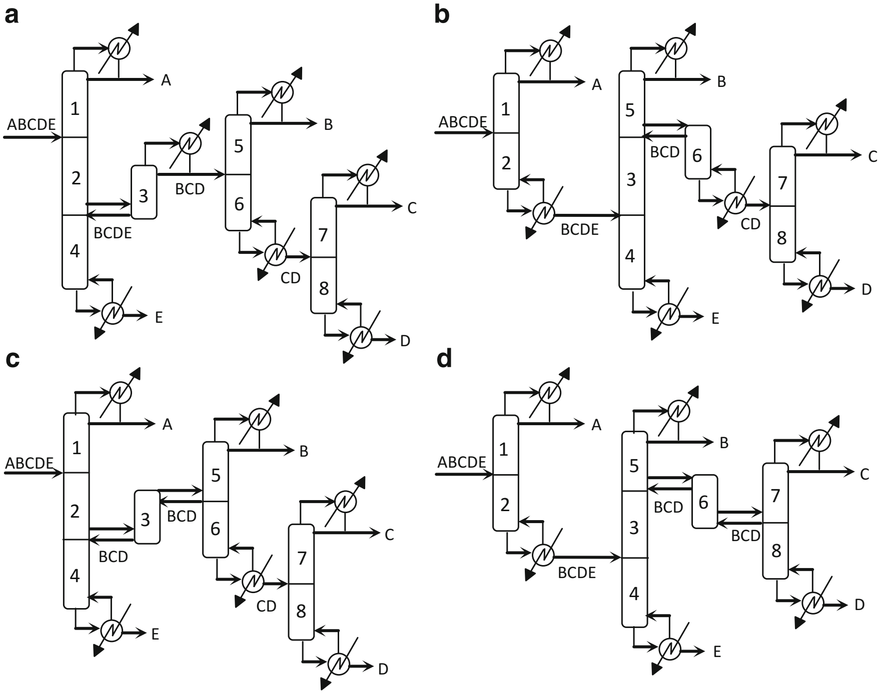


Fig. 3.11 Thermodynamically equivalent structures satisfying the two criteria for the ISCs generation

Step 7: Selecting another simple column sequences from Table 3.2 it is possible to repeat the steps from 3 to 6.

Step 8: For a five-component mixture all the possible ISC sequences were reported by Rong and Errico [28]. In particular 24 alternatives were obtained.

By examination of the ISC configurations of Fig. 3.12 it is possible to notice there is a correspondence between configurations in Fig. 3.12a, c and between Fig. 3.12b, d. These configurations have exactly the same structure with the same individual columns except the difference in one-way or two-way transport of the same submixture. Anyway should be considered that all the configurations were obtained from distinct thermally coupled configurations. If, for example, a one-way transport side-rectifier is considered, the submixture is transported by means of a condenser, this condenser can always be replaced by a thermal coupling obtaining a two-way transport side-rectifier. Similarly for the one-way transport side-stripper the reboiler can be always substituted with another thermal coupling to obtain a two-way transport side-stripper.

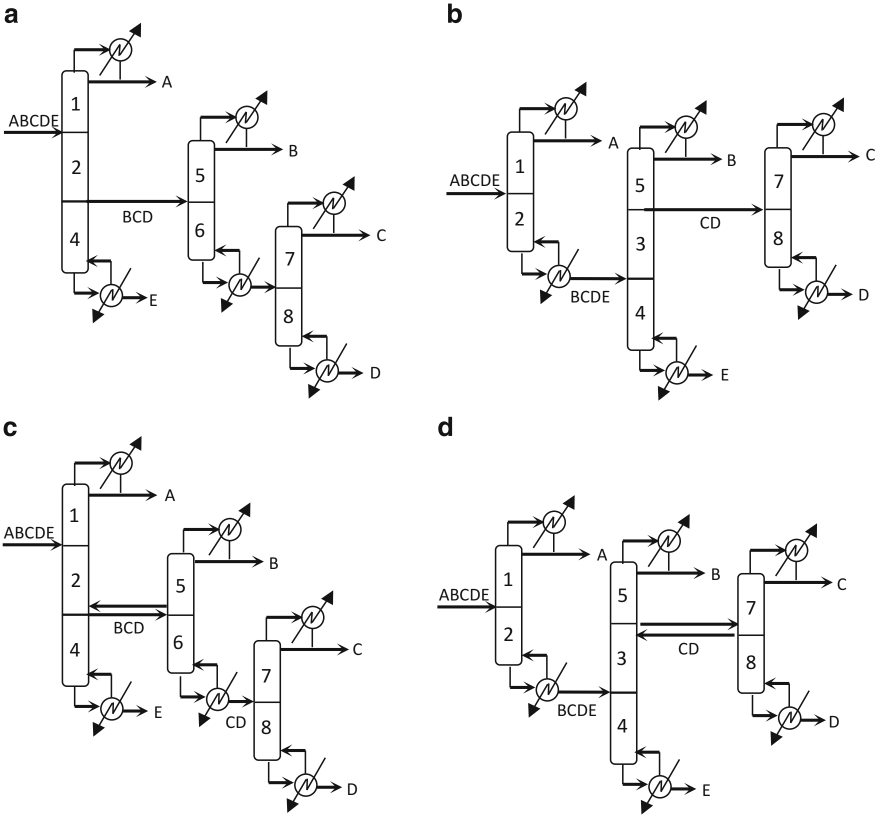


Fig. 3.12 Intensified simple column configurations derived from the SC sequence of Fig. 3.9

3.7 Generalization of the Synthesis Generation Method for Any Traditional Distillation Configuration

As discussed at the beginning of the chapter, sharp splits are not the only possible way to perform a separation. Multicomponent mixture can be separated using also sloppy splits. At this point, considering the interest in ISC configurations, it is very convenient to generalize their systematic synthesis starting from any TDC. The methodology is here extended considering a five-component mixture as an example.

For a five-component separation task Rong and Kraslawski [41] identified 719 functionally DSS and, depending on the way to combine the individual columns, the TDC can contain more than $n-1$ columns, exactly $n-1$ columns, or less than $n-1$. If the separation sequence ABCD/E(1) → ABCD(2) → A/BC (3) → BC/D(4) → B/C(5) is considered, there are five individual splits, correspondingly, five individual columns, each with a condenser and a reboiler, are needed:

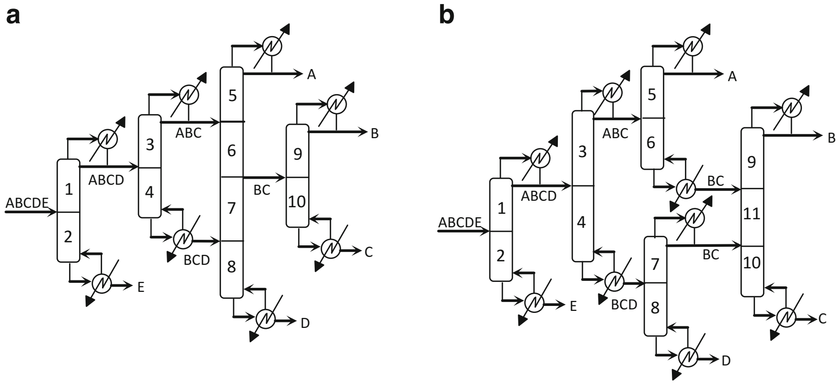


Fig. 3.13 Initial traditional distillation configurations: (**a**) four columns, (**b**) five columns

column 1 for ABCD/E, column 2 for ABCD, column 3 for A/BC, column 4 for BC/D, and finally column 5 for B/C. Depending on how the individual columns are combined it is possible to have different initial TDC. Two possibilities are reported in Fig. 3.13.

Fig. 3.13a contains exactly $n-1$ columns since column three and four are combined in a single column with the submixture BC obtained as side stream. Fig. 3.13b instead contains five columns, thus more than $n-1$, since all the columns are standing alone.

If the configuration reported in Fig. 3.13a is considered to initialize the synthesis procedure to obtain intensified distillation configurations, the corresponding thermally coupled and the thermodynamically equivalent structures are reported in Fig. 3.14a, b and Fig. 3.14c, d, respectively. The reported configurations do not represent all the possible alternatives but only the ones respecting the two criteria defined for the single-section transport column and the restriction for the other columns to obtain the products by the condenser and the reboiler.

The corresponding ISC configurations are reported in Fig. 3.14e, f. If the configuration of Fig. 3.13b is considered as a starting point it is possible to generate the thermally coupled configurations reported in Fig. 3.15, the TES fulfilling the two-criteria of Fig. 3.16 and finally the eight ISC configurations of Fig. 3.17.

For all the obtained configurations three columns are employed, it means less than $n-1$. This is a very important conclusion; starting from a TDC with more than $n-1$ columns there is still the possibility to generate intensified alternatives.

The TDC with more than $n-1$ columns should not be prematurely excluded, rather they are the preferred alternatives to generate the ultimate intensified distillation systems with fewer columns. The reason is undoubtedly that they have kept the flexibility to rearrange the column sections in their subsequent TES structures, which can create more opportunities to produce the intensified distillation systems with fewer columns.

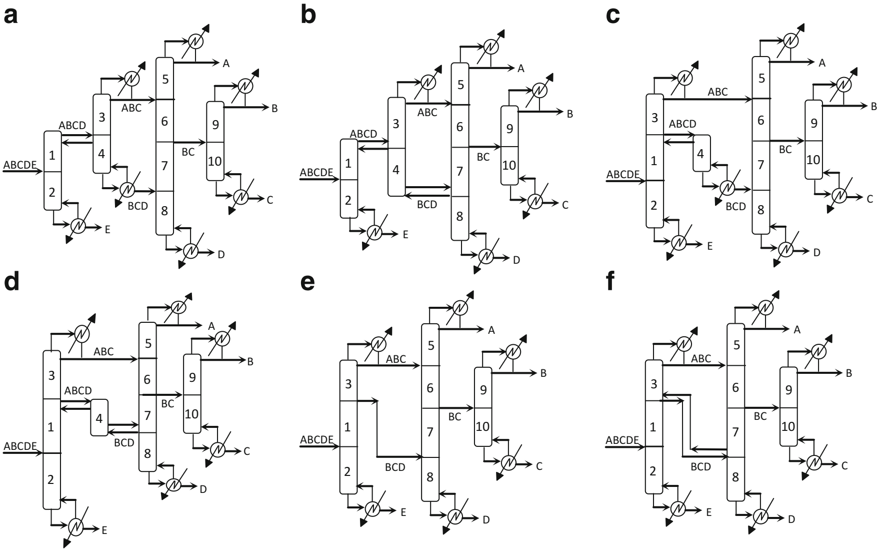


Fig. 3.14 (**a**, **b**) Thermally coupled configurations, (**c**, **d**) thermodynamically equivalent structures, (**e**, **f**) intensified simple column configurations

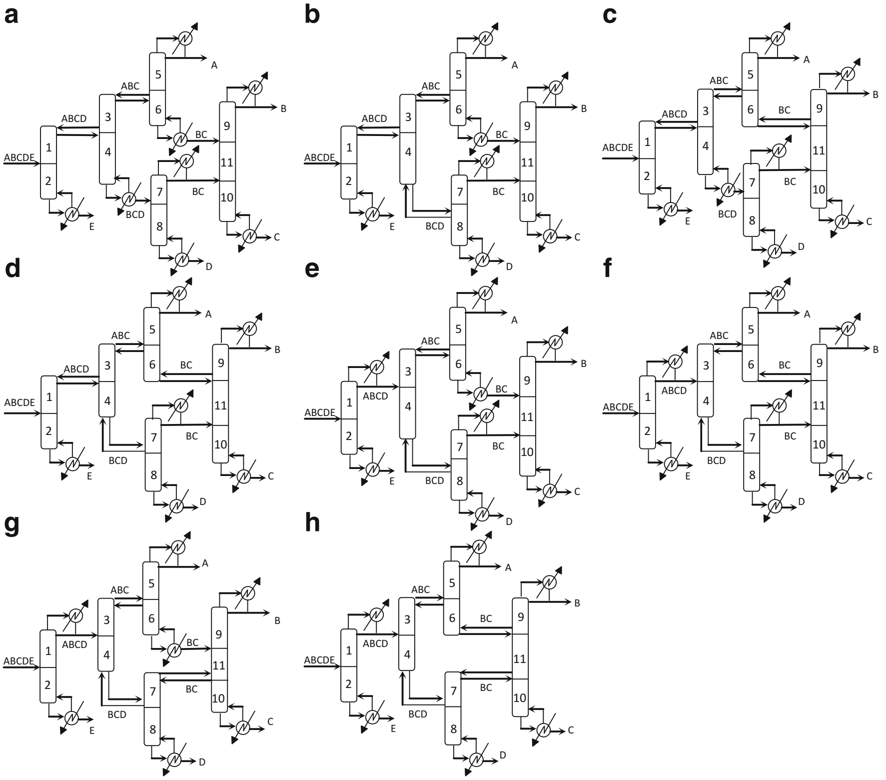


Fig. 3.15 Thermally coupled configurations derived from Fig. 3.13b

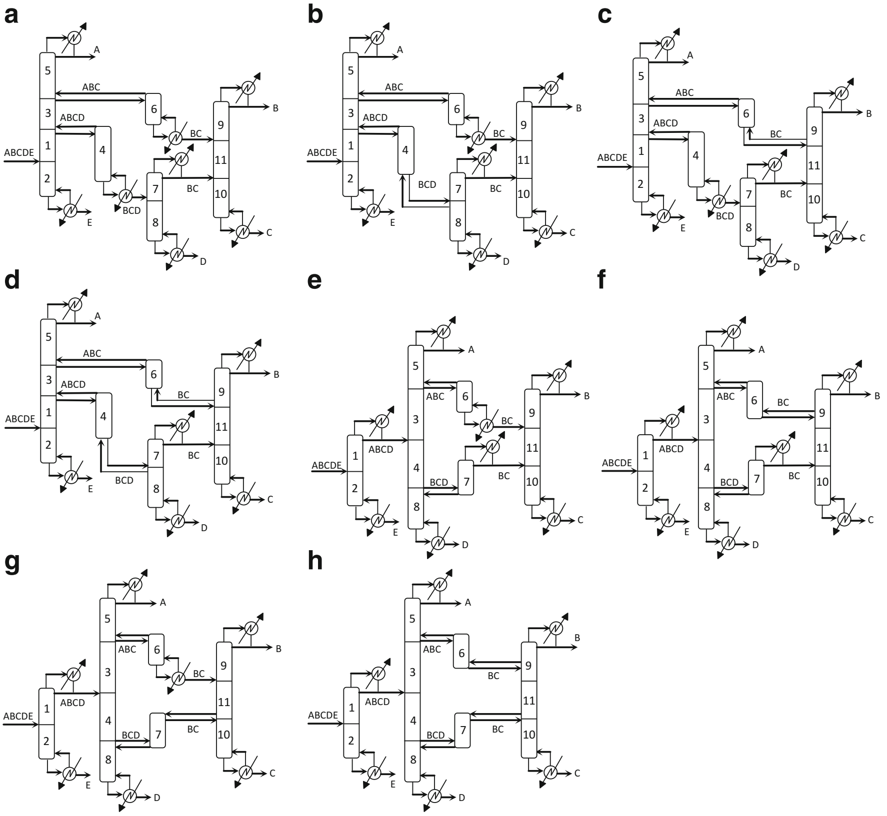


Fig. 3.16 Selected thermodynamically equivalent structures derived from Fig. 3.15

The synthesis procedure can be generalized in the flowchart reported in Fig. 3.18.

Should be emphasized that the synthesis methodology generalized in the flowchart of Fig. 3.18 is focused on the generation of ISC configurations. These configurations represent only one part of the intensified configurations with less then $n - 1$ columns. If the designer is interested to the whole sub-space of intensified configurations, then should not apply the two criteria used to select the TES and proceed considering all the alternatives [29].

3.8 Extension of the Synthesis Methodology: The Divided Wall Column Configurations

In the discussed synthesis methodology one fundamental step is the elimination of one or more single column sections to generate intensified configurations. Considering a four-component mixture, in the TES the single side rectifying section of

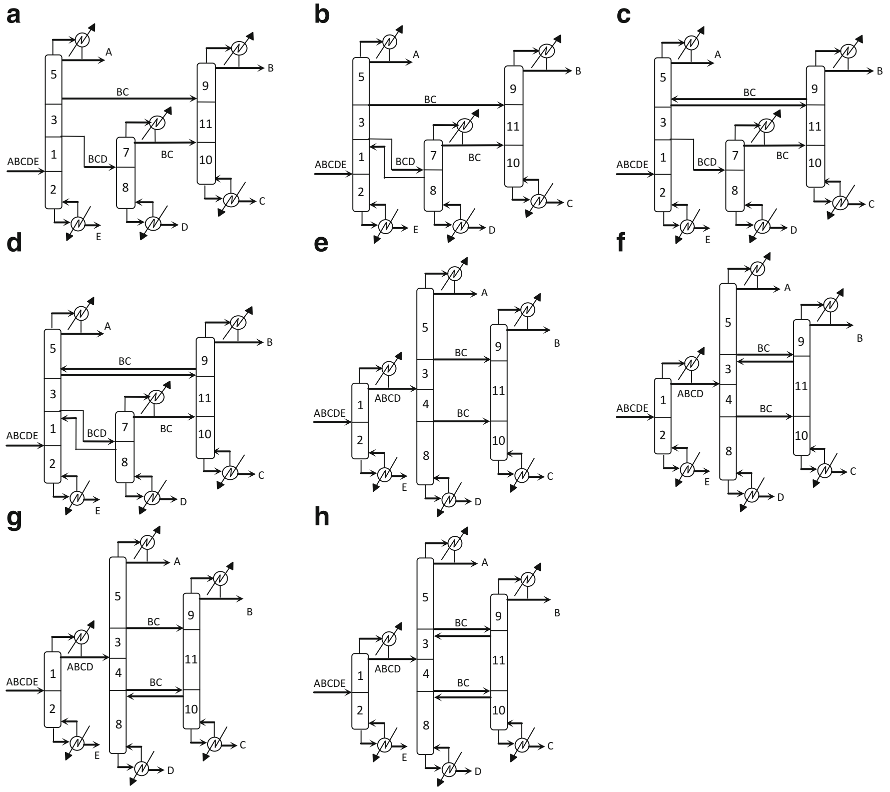
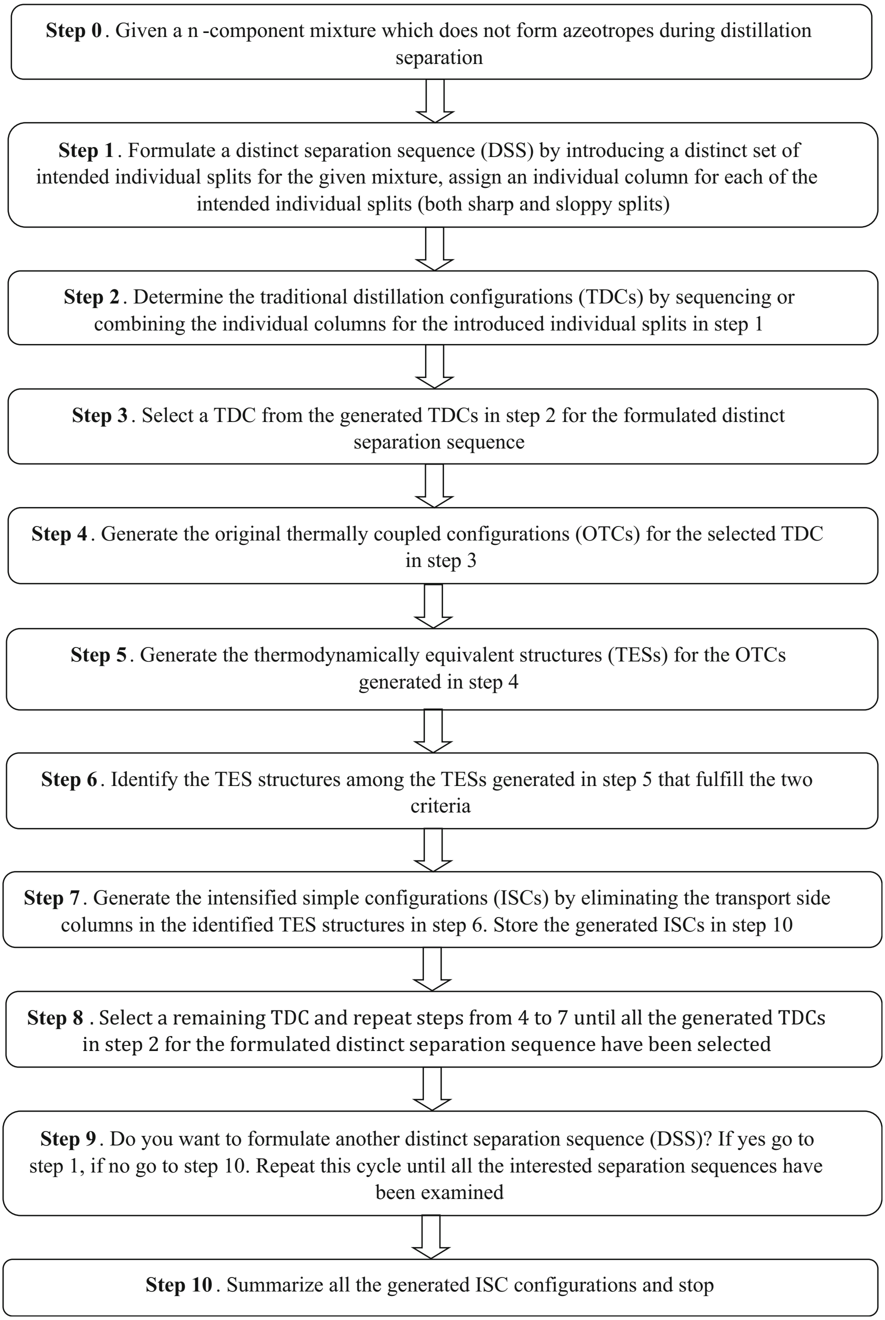


Fig. 3.17 Intensified simple column configurations derived from Fig. 3.13b

Fig. 3.6a, c is used to separate component D so that a mixture with only intermediate components B and C is transported to the next column. However, depending on the relative volatilities of the feed components and product purity requirements, when the relative volatility between C and D is large and separation between C and D is easy, a mixture with only B and C can be withdrawn and the side column can be eliminated. Similarly, the side strippers in Fig. 3.6f, h are for the further stripping the lightest component A so that a mixture with only intermediate components B and C is transported to the next column. Also, depending on the relative volatilities of the feed components and product purity requirements, when the relative volatility between A and B is large and separation between A and B is easy, a mixture with only B and C can be withdrawn and the side column can be eliminated. Anyway when the single column section does not have only a transportation function but realizes an effective separation function, then its elimination is not possible and the synthesis methodology can not proceed through the generation of intensified sequences in the way defined since now.

Considering the sloppy separation sequence for a four-component mixture reported in Fig. 3.19, it is possible to introduce one or more thermal couplings



Step 0. Given a n -component mixture which does not form azeotropes during distillation separation

Step 1. Formulate a distinct separation sequence (DSS) by introducing a distinct set of intended individual splits for the given mixture, assign an individual column for each of the intended individual splits (both sharp and sloppy splits)

Step 2. Determine the traditional distillation configurations (TDCs) by sequencing or combining the individual columns for the introduced individual splits in step 1

Step 3. Select a TDC from the generated TDCs in step 2 for the formulated distinct separation sequence

Step 4. Generate the original thermally coupled configurations (OTCs) for the selected TDC in step 3

Step 5. Generate the thermodynamically equivalent structures (TESs) for the OTCs generated in step 4

Step 6. Identify the TES structures among the TESs generated in step 5 that fulfill the two criteria

Step 7. Generate the intensified simple configurations (ISCs) by eliminating the transport side columns in the identified TES structures in step 6. Store the generated ISCs in step 10

Step 8 . Select a remaining TDC and repeat steps from 4 to 7 until all the generated TDCs in step 2 for the formulated distinct separation sequence have been selected

Step 9. Do you want to formulate another distinct separation sequence (DSS)? If yes go to step 1, if no go to step 10. Repeat this cycle until all the interested separation sequences have been examined

Step 10. Summarize all the generated ISC configurations and stop

Fig. 3.18 The systematic procedure to synthesize intensified simple column configurations from any TDCs

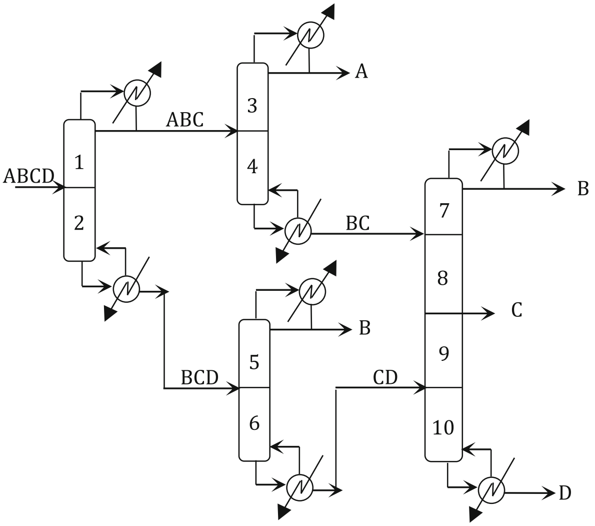


Fig. 3.19 Sloppy split configuration for a four-component separation

corresponding to the submixture streams transferred between the columns. Limiting the analysis only to the thermally coupled configurations obtained removing the condenser and/or the reboiler associated to the first column, the resulting configurations are reported in Fig. 3.20.

The introduction of one or more thermal coupling gives the flexibility to move one or more column sections generating the TES reported in Fig. 3.21.

At this point if the single column section in the thermodynamically equivalent structures performs a separation task it is not possible to proceed through its elimination in order to generate intensified configurations. Anyway, in this case, the single column section can be included in the column to which is connected to realize an intensified configuration with a divided wall column.

For the case considered all the alternatives are reported in Fig. 3.22.

Once again it is possible to notice that starting with a sloppy configuration with more than $n - 1$ column is still possible to generate intensified alternatives with less than $n - 1$ columns.

For some composition cases, the new alternatives predicted were able to decrease the energy consumption and the capital costs compared to the traditional configurations [42].

In general it is possible to assert that the single column sections have a fundamental role in the synthesis methodology. When their function is related only to transportation it is possible to directly move to intensified sequences, whereas if a separation function is realized, then the single section can be used to generate divided wall column sequences. The feed properties dictate which alternative is the best.

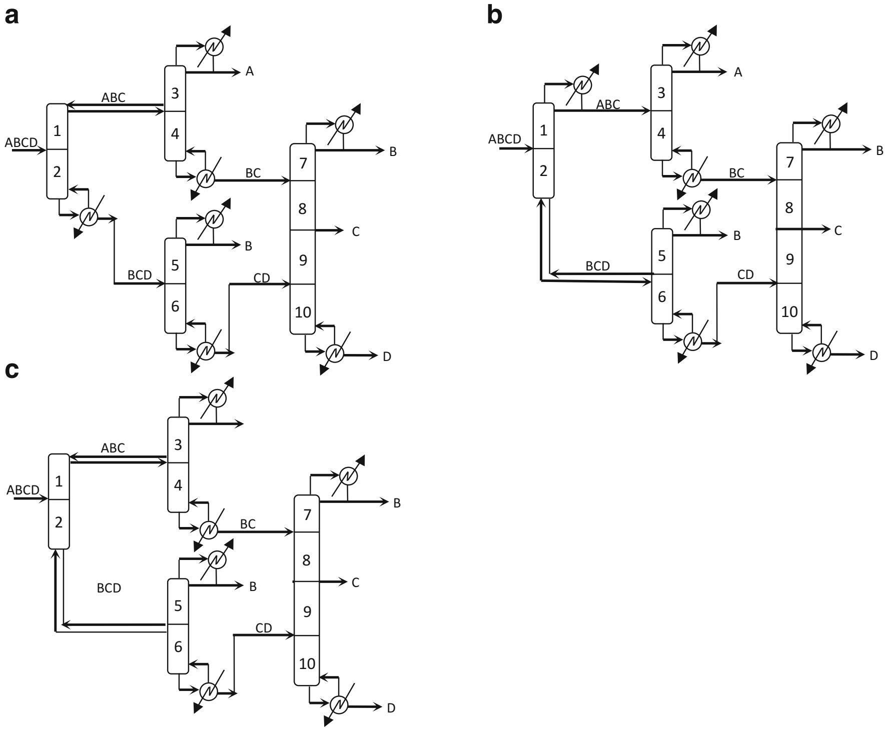


Fig. 3.20 Thermally coupled configurations generated from Fig. 3.19

3.9 Synthesis and Design: A New Common Approach

The definition of the optimal alternative to perform a specified separation task passes through five fundamental steps:

1. Definition of the separation method
2. Generation of the alternatives
3. Design of the alternatives
4. Screening of the alternatives by means of an objective function
5. Selection of the best alternative

The first point regards the definition of a suitable separation method. The choice is mainly related to the analysis of the physical properties of the components in the feed. Separation indexes like the relative volatility help the designer to define an appropriate method. Considering the cases where distillation can be applied, the second point was the object of the previous paragraphs where a systematic method was used to generate as much as possible a complete set of alternative configurations. The third point regards the definition of the structural and operative

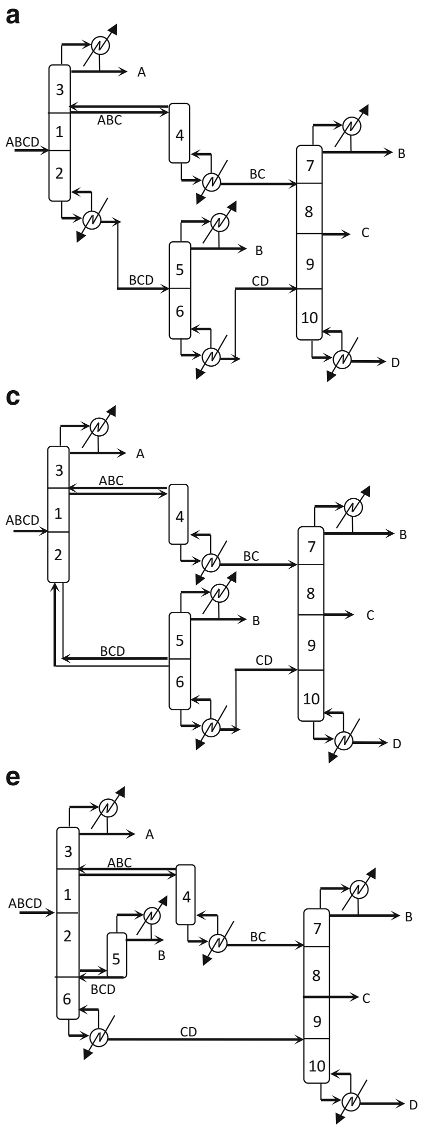


Fig. 3.21 Thermodynamically equivalent structures corresponding to the thermally coupled configurations of Fig. 3.20

parameters for the design of the distillation columns. Points four and five are related to the definition of the objective function used to select the final option.

Among all these points for sure the third one requires particular efforts in terms of time when the set of alternatives to design includes many options.

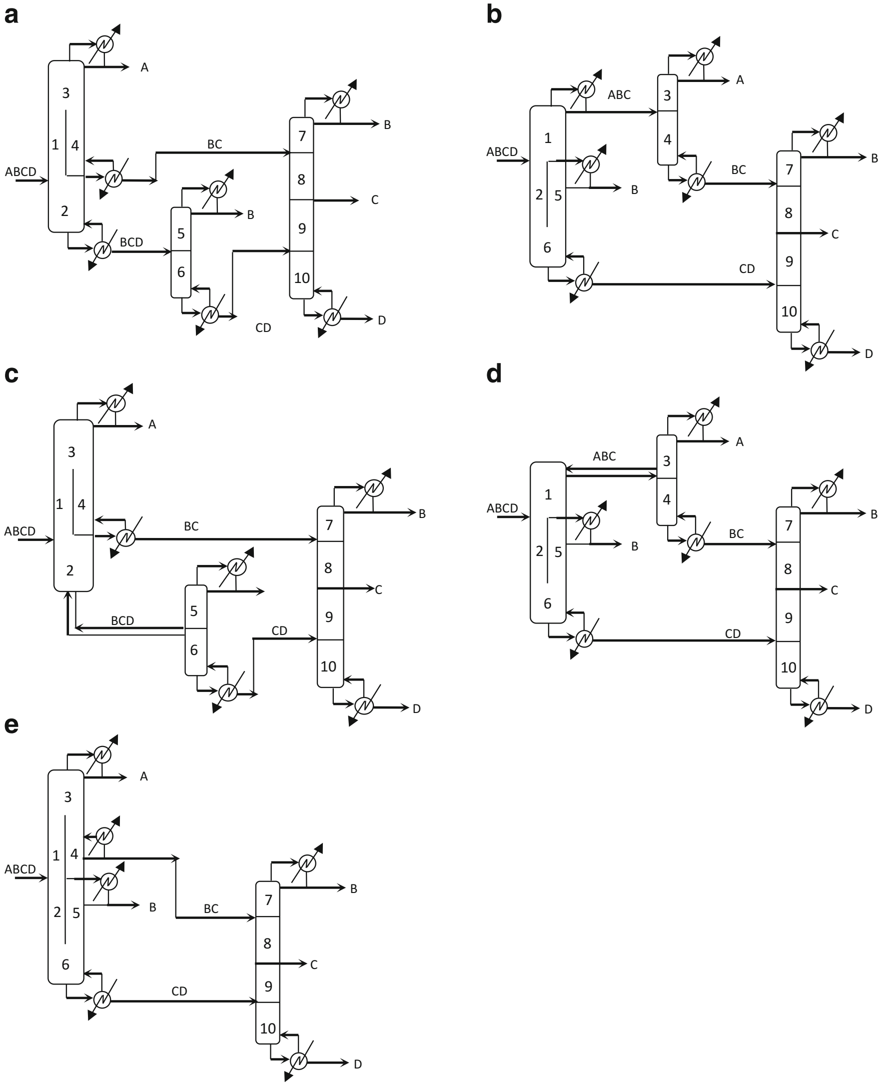


Fig. 3.22 Intensified divided wall column configurations

Anyway in the systematic methodology presented for the synthesis of alternative distillation arrangements, the step-by-step procedure moves the designer from the different sub-spaces introducing thermal couplings and rearranging column sections. The starting point can be any of the TDC and it is possible to define a clear connection from the root configuration and all the alternatives generated from it. It means that there is a correspondence in the column sections function between the root configuration and the derived alternatives. If the

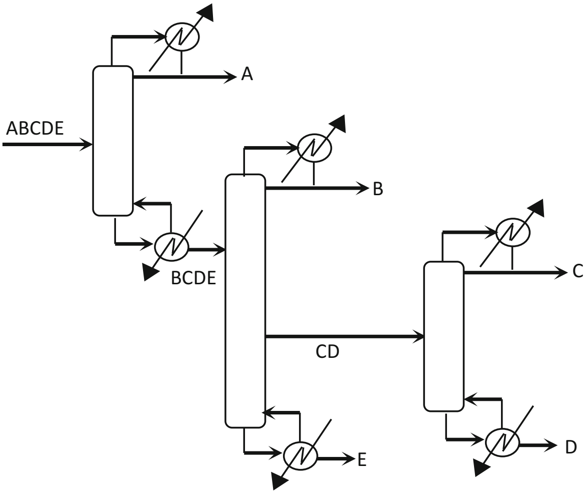


Fig. 3.23 Intensified simple column sequence for a five-component separation

column section still performs the same separation task, then it's possible to transfer the number of stages, the reflux ratio, and the feed locations from the root to the alternative considered. This new approach links the synthesis method used to derive the alternatives with their design and represents an important tool to speed up the screening of the research space. The method described was called Sequential Design Method (SDM) [43].

If the sequence in Fig. 3.23 is considered as a promising alternative for a five-component mixture separation, its design is related to the classical two-step approach based on short-cut and rigorous design. If this sequences is now related to the systematic procedure as showed in Fig. 3.24 it's possible to make some considerations. Now the alternative is related though the systematic method to the corresponding simple column sequence. Since the design of this sequence is already available because it represents the term of comparison, the alternative sequence can be designed transposing the corresponding column section parameters. The reliability of this method was evidenced for both non-azeotropic and azeotropic separations [44] and represents an effective tool in the design of the alternative distillation configurations.

In conclusion the synthesis methodology developed has the benefit to generate different class of alternatives keeping at the same time a strict connection among all the alternatives. This connection represents an useful tool during the design stage, helping the designer to obtain the final result in a reasonable time.

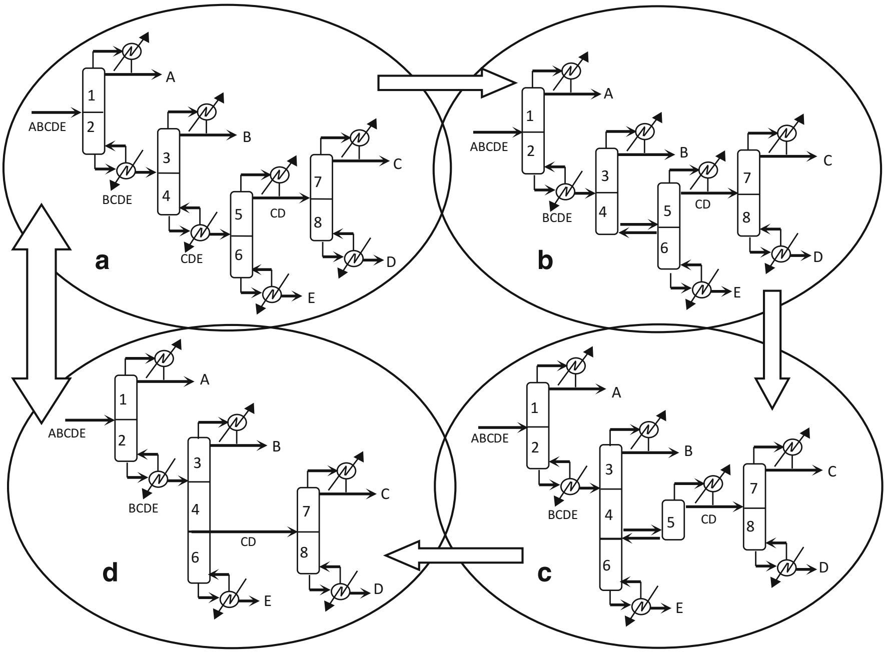


Fig. 3.24 Synthesis procedure to obtain the configuration of Fig. 3.23

References

1. Forbes RJ (1970) A short review history of the art of distillation. EJ Brill, Leiden
2. Humphrey JL, Seibert AF (1992) New horizons in distillation. Chem Eng 99(12):86–98
3. McCabe WL, Thiele EW (1925) Graphical design of fractionating columns. Ind Eng Chem 17 (6):605–611
4. Underwood AJV (1949) Fractional distillation of multicomponent mixtures. Ind Eng Chem 41 (12):2844–2847
5. Thompson RW, King CJ (1972) Systematic synthesis of separation schemes. AIChE J 18 (5):941–948
6. Nath R, Motard RL (1981) Evolutionary synthesis of separation processes. AIChE J 27 (4):578–587
7. Malone MF, Glinos K, Marquez FE, Douglas JM (1985) Simple, analytical criteria for the sequencing of distillation columns. AIChE J 31(4):683–689
8. Moore CF (1992) Selection of controlled and manipulated variables in practical distillation control. Van Nostrand Reinhold, New York, pp 140–177, Chapter 8
9. Hori ES, Skogestad S (2007) Selection of control structure and temperature location for two-product distillation columns. Chem Eng Res Des 85(3):293–306
10. Skogestad S (2007) The dos and don’ts of distillation column control. Chem Eng Res Des 85 (1):13–23
11. Kaibel G, Schoenmakers H (2002) Process synthesis in industrial practice. In: 12th European symposium on computer aided process engineering, The Hague, May 26–29, 2002, pp 9–22
12. Fidkowski ZT (2006) Distillation configurations and their energy requirements. AIChE J 52 (6):2098–2106

13. Rong B-G, Kraslawski A, Turunen I (2003) Synthesis of functionally distinct thermally coupled configurations for quaternary distillations. Ind Eng Chem Res 42:1204–1214
14. Rong B-G, Turunen I (2006) A new method for synthesis of thermodynamically equivalent structures for Petlyuk arrangements. Chem Eng Res Des 84:1095–1116
15. Agrawal R (2003) Synthesis of multicomponent distillation column configurations. AIChE J 49(29):379–401
16. Shah VH, Agrawal R (2010) A matrix method for multicomponent distillation sequences. AIChE J 56(7):1759–1775
17. Shenvi AA, Shah VH, Zeller JA, Agrawal R (2012) A synthesis method for multicomponent distillation sequences with fewer columns. AIChE J 58(8):2479–2494
18. Caballero JA, Grossmann IE (2004) Design of distillation sequences: from conventional to fully thermallly coupled distillation systems. Comput Chem Eng 28:2307–2329
19. Caballero JA, Grossmann IE (2006) Structural considerations and modeling in the synthesis of heat-integrated-thermally coupled distillation sequences. Ind Eng Chem Res 45:8454–8474
20. Caballero JA, Grossmann IE (2012) Synthesis of complex thermally coupled distillation systems including divided wall columns. AIChE J 59:1139–1159
21. Rong B-G, Kraslawski A (2002) Optimal design of distillation flowsheets with a lower number of thermal couplings for multicomponent separations. Ind Eng Chem Res 41:5716–5726
22. Rong B-G, Kraslawski A (2003) Partially thermally coupled distillation systems for multicomponent separations. AIChE J 49(5):1340–1347
23. Rong B-G, Kraslawski A, Turunen I (2003) Synthesis of heat-integrated thermally coupled distillation systems for multicomponent separations. Ind Eng Chem Res 42:4329–4339
24. Rong B-G, Turunen I (2006) Synthesis of new distillation systems by simultaneous thermal coupling and heat integration. Ind Eng Chem Res 45:3830–3842
25. Rong B-G, Kraslawski A, Turunen I (2004) Synthesis and optimal design of thermodynamically equivalent thermally coupled distillation systems. Ind Eng Chem Res 43:5904–5915
26. Errico M, Rong B-G, Tola G, Turunen I (2009) A method for systematic synthesis of multicomponent distillation systems with less than N-1 columns. Chem Eng Process: Process Intensif 48(4):907–920
27. Rong B-G (2011) Synthesis of dividing wall columns (DWC) for multicomponent distillations—a systematic approach. Chem Eng Res Des 89(8):1281–1294
28. Rong B-G, Errico M (2012) Synthesis of intensified simple column configurations for multicomponent distillations. Chem Eng Process: Process Intensif 62:1–17
29. Rong B-G (2014) A systematic procedure for synthesis of intensified nonsharp distillation systems with fewer columns. Chem Eng Res Des 92:1955–1968
30. Scully DB (1976) Interpretation of distillation of a three-component mixture on a ternary diagram. Ind Eng Chem Fundam 15(4):344–346
31. Tedder DW, Rudd DF (1978) Parametric studies in industrial distillation. Part I. Design comparison. AIChE J 24(2):303–315
32. Tedder DW, Rudd DF (1978) Parametric studies in industrial distillation. Part II. Heuristic optimization. AIChE J 24(2):316–323
33. Lee JY, Kim YH, Hwang KS (2004) Application of a fully thermally coupled distillation column for fractionation process in naphtha reforming plant. Chem Eng Process: Process Intensif 43:495–501
34. Lee JY, Kim YH, Hwang KS (2002) Design of gas concentration process with thermally coupled distillation column using HYSYS simulation. J Control Autom Syst Eng 8:842–846
35. Stankiewicz A, Moulijn JA (2000) Process intensification: transforming chemical engineering. Chem Eng Prog 96:22–34
36. Giridhar A, Agrawal R (2010) Synthesis of distillation configurations: I. Characteristics of a good searching space. Comput Chem Eng 34:73–83
37. Calzon-McConville CJ, Rosales-Zamora MB, Segovia-Hernandez JG, Hernandez S, Rico-Ramirez V (2006) Design and optimization of thermally coupled distillation schemes for the separation of multi-component mixtures. Ind Eng Chem Res 45(2):724–732

38. Segovia-Hernandez JG, Hernandez-Vargas EA, Marquez-Munoz JA (2007) Control properties of thermally coupled distillation sequences for different operating conditions. Comput Chem Eng 31(7):867–874
39. Errico M, Rong B-G, Tola G, Turunen I (2008) Process intensification for the retrofit of a multicomponent distillation plant—an industrial case study. Ind Eng Chem Res 47:1975–1980
40. Errico M, Rong B-G (2012) Modified simple column configurations for quaternary distillations. Comput Chem Eng 36:160–173
41. Rong B-G, Kraslawski A (2002) Synthesis of thermodynamically efficient distillation schemes for multicomponent separations. In: 12th European symposium on computer aided process engineering The Hague, May 26–29, 2002, pp 319–324
42. Torres-Ortega CE, Errico M, Rong B-G (2015) Design and optimization of modified non-sharp column configurations for quaternary distillations. Comput Chem Eng 74:15–27
43. Errico M, Rong B-G, Torres-Ortega CE, Segovia-Hernandez JG (2014) The importance od the sequential synthesis methodology in the optimal distillation sequences design. Comput Chem Eng 62:1–9
44. Errico M, Pirellas P, Torres-Ortega CE, Rong B-G, Segovia-Hernandez JG (2014) A combined method for the design and optimization of intensified distillation systems. Chem Eng Process: Process Intensif 85:69–76

Chapter 4
Process Intensification in Heat and Mass Exchanger Networks

José María Ponce-Ortega

Abstract This chapter presents the use of process integration as a useful tool for intensifying processes. Particularly, mass and heat integration through the synthesis of mass and heat exchanger networks represent powerful tools that can be used for reducing the need of external agents such as fresh water and hot and cold utilities. Two optimization formulations are presented for mass and heat integration and the application to two case studies shows significant savings of external utilities.

4.1 Introduction

In recent years, when unified processes are required to be competitive in the global market, process intensification has become a very exciting topic [1]. In this way, process intensification has been defined by Ponce-Ortega et al. [2] as any activity that involves one of the following points:

(a) Smaller equipment for given throughput.
(b) Higher throughput for given equipment size or given process.
(c) Less holdup for equipment or less inventories for process of certain material for the same throughput.
(d) Less usage of utility material and feedstock for a given throughput and given equipment size.
(e) Higher performance for given unit size.

On the other hand, process integration has been recognized as a useful tool for intensifying processes; see, for example, Lutze et al. [3], El-Halwagi [4], and Gopalakrishnan et al. [5]. Particularly, energy and mass integration have been identified as powerful tools for improving processes. Energy integration allows reducing the energy consumption in industrial processes through intensifying the

---

J.M. Ponce-Ortega (✉)
Universidad Michoacana de San Nicolás de Hidalgo, Edificio V1, Ciudad Universitaria, Morelia, Michoacan, 58060, Mexico
e-mail: jmponce@umich.mx

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_4

use of the available energy in the processes. A special approach for energy integration in the industrial processes is through the synthesis of heat exchanger networks (HEN), where process streams exchange energy to reduce the consumption of hot and cold utilities. Several options can be identifying for the synthesis of HEN, and the optimal solution depends on the selected objective. For example, if the objective is to select the solution for the minimum utility consumption [6], the minimum heat transfer area [7], the minimum number of heat transfer units [8], the minimum total annual cost [9, 10], the minimum environmental impact [11] or the maximum social benefit [12, 13].

In the same way, the synthesis of mass exchanger networks (MEN) allows reducing the consumption of external agents such as solvents and raw materials. A special way of mass integration is the synthesis of water networks, where substantial reductions of fresh water consumption can be achieved. Similarly as the HEN, in the synthesis of MEN different objective functions can be identified, including the minimum consumption of fresh resources [14], the minimum cost [15–20], the minimum number of mass transfer units [21], the minimum environmental impact [22, 23], social objectives [24], between others.

Recently, there has been highlighted the importance to consider different or contradictory objective functions in designing intensified HEN and MEN, because the economic point of view must trade-off other important objectives. Therefore, this chapter presents a description of the application of synthesis of HEN and MEN for process intensification since the optimization point of view.

4.2 Synthesis of Heat Exchanger Networks for Process Intensification

The problem for the synthesis of HEN can be stated as follows: Given a set of hot process streams that need to be cooled and a set of cold process streams that need to be heated, then the problem consists in determining the solution that satisfies the energy needs intensifying a specific objective function. Considering as example the superstructure proposed by Yee and Grossmann [25] as it is shown in Fig. 4.1, where the hot process streams go from left to right and the cold process streams go from right to left. The problem then is divided in stages, and in each stage there is proposed the potential exchange between any pair of hot and cold process streams and the existence of each exchanger is an optimization variable; this way the temperatures between stages are also optimization variables. The optimization formulation for this superstructure is summarized as follows, see [8, 9]:

$$(\mathrm{TIN}_i - \mathrm{TOUT}_i)\mathrm{FCp}_i = \sum_{k \in \mathrm{ST}} \sum_{j \in \mathrm{CPS}} q_{ijk} + \mathrm{qcu}_i, \quad i \in \mathrm{HPS1} \tag{4.1}$$

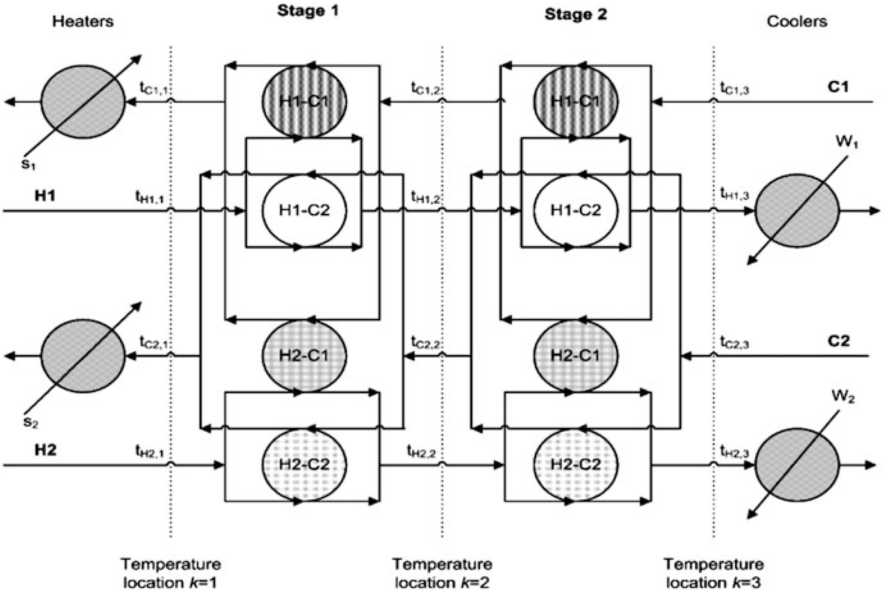


Fig. 4.1 Superstructure for HEN synthesis [25]

$$F\lambda_i^{\text{cond}} = \sum_{k\in \text{ST}} \sum_{j\in \text{CPS}} q_{ijk} + \text{qcu}_i, \quad i \in \text{HPS2} \tag{4.2}$$

$$\begin{aligned}&\left(\text{TIN}_i - T_i^{\text{cond}}\right)\text{FCp}_i + F\lambda_i^{\text{cond}} + \left(T_i^{\text{cond}} - \text{TOUT}_i\right)\text{FCp}_i\\ &= \sum_{k\in \text{ST}} \sum_{j\in \text{CPS}} q_{ijk} + \text{qcu}_i, \quad i \in \text{HPS3}\end{aligned} \tag{4.3}$$

$$\left(\text{TOUT}_j - \text{TIN}_j\right)\text{FCp}_j = \sum_{k\in \text{ST}} \sum_{i\in \text{HPS}} q_{ijk} + \text{qhu}_j, \quad j \in \text{CPS1} \tag{4.4}$$

$$F\lambda_j^{\text{evap}} = \sum_{k\in \text{ST}} \sum_{i\in \text{HPS}} q_{ijk} + \text{qhu}_j, \quad j \in \text{CPS2} \tag{4.5}$$

$$\begin{aligned}&\left(\text{TOUT}_j - T_j^{\text{evap}}\right)\text{FCp}_j + F\lambda_j^{\text{evap}} + \left(T_j^{\text{evap}} - \text{TIN}_j\right)\text{FCp}_j\\ &= \sum_{k\in \text{ST}} \sum_{i\in \text{HPS}} q_{ijk} + \text{qhu}_j, \quad j \in \text{CPS3}\end{aligned} \tag{4.6}$$

$$(t_{i,k} - t_{i,k+1})\text{FCp}_i = \sum_{j\in \text{CPS}} q_{ijk}, \quad k \in \text{ST}, \;\; i \in \text{HPS1} \tag{4.7}$$

$$(t_{i,k} - t_{i,k+1})\mathrm{FCp}_i + q^{\Lambda}_{i,k} = \sum_{j \in \mathrm{CPS}} q_{ijk}, \quad k \in \mathrm{ST}, \ i \in \mathrm{HPS3} \tag{4.8}$$

$$\left(t_{j,k} - t_{j,k+1}\right)\mathrm{FCp}_j = \sum_{i \in \mathrm{HPS}} q_{ijk}, \quad k \in \mathrm{ST}, \ j \in \mathrm{CPS1} \tag{4.9}$$

$$\left(t_{j,k} - t_{j,k+1}\right)\mathrm{FCp}_j + q^{\Lambda}_{j,k} = \sum_{i \in \mathrm{HPS}} q_{ijk}, \quad k \in \mathrm{ST}, \ j \in \mathrm{CPS3} \tag{4.10}$$

$$\mathrm{TIN}_i = t_{i,1}, \quad i \in \mathrm{HPS} \tag{4.11}$$

$$\mathrm{TIN}_i = t_{j,\mathrm{NOK}+1}, \quad j \in \mathrm{CPS} \tag{4.12}$$

$$t_{i,k} \geq t_{i,k+1}, \quad k \in \mathrm{ST}, \ i \in \mathrm{HPS1} \quad \text{or} \quad i \in \mathrm{HPS3} \tag{4.13}$$

$$t_{i,k} = \mathrm{TIN}_i, \quad k \in \mathrm{ST}, \ i \in \mathrm{HPS2} \tag{4.14}$$

$$t_{j,k} \geq t_{j,k+1}, \quad k \in \mathrm{ST}, \ j \in \mathrm{CPS1} \quad \text{or} \quad j \in \mathrm{CPS3} \tag{4.15}$$

$$t_{j,k} = \mathrm{TIN}_j, \quad k \in \mathrm{ST}, \ j \in \mathrm{CPS2} \tag{4.16}$$

$$\mathrm{TOUT}_i \leq t_{i,\mathrm{NOK}+1}, \quad i \in \mathrm{HPS1} \quad \text{or} \quad i \in \mathrm{HPS3} \tag{4.17}$$

$$\mathrm{TOUT}_j \geq t_{j,1}, \quad j \in \mathrm{CPS1} \quad \text{or} \quad j \in \mathrm{CPS3} \tag{4.18}$$

$$(t_{i,\mathrm{NOK}+1} - \mathrm{TOUT}_i)\mathrm{FCp}_i = \mathrm{qcu}_i, \quad i \in \mathrm{HPS1} \tag{4.19}$$

$$(t_{i,\mathrm{NOK}+1} - \mathrm{TOUT}_i)\mathrm{FCp}_i + q_i^{\Lambda,\mathrm{cu}} = \mathrm{qcu}_i, \quad i \in \mathrm{HPS3} \tag{4.20}$$

$$\left(\mathrm{TOUT}_j - t_{j,1}\right)\mathrm{FCp}_j = \mathrm{qhu}_j, \quad j \in \mathrm{CPS1} \tag{4.21}$$

$$\left(\mathrm{TOUT}_j - t_{j,1}\right)\mathrm{FCp}_j + q_j^{\Lambda,\mathrm{hu}} = \mathrm{qhu}_j, \quad j \in \mathrm{CPS3} \tag{4.22}$$

$$F\lambda_i^{\mathrm{cond}} = \sum_{k \in \mathrm{ST}} q^{\Lambda}_{i,k} + q_i^{\Lambda,\mathrm{cu}}, \quad i \in \mathrm{HPS2} \quad \text{or} \quad i \in \mathrm{HPS3} \tag{4.23}$$

$$F\lambda_j^{\mathrm{evap}} = \sum_{k \in \mathrm{ST}} q^{\Lambda}_{j,k} + q_j^{\Lambda,\mathrm{hu}}, \quad j \in \mathrm{CPS2} \quad \text{or} \quad j \in \mathrm{CPS3} \tag{4.24}$$

$$\begin{pmatrix} Y^1_{i,k} \\ t_{i,k+1} \geq T_i^{\mathrm{cond}} + \delta \\ q^{\Lambda}_{i,k} = 0 \end{pmatrix} \bigvee \begin{pmatrix} \neg Y^1_{i,k} \\ t_{i,k+1} \leq T_i^{\mathrm{cond}} \\ q^{\Lambda}_{i,k} \geq 0 \end{pmatrix} \tag{4.25}$$

$$\begin{pmatrix} Y_{i,k}^{2} \\ t_{i,k} \le T_i^{\text{cond}} - \delta \\ q_{i,k}^{\Lambda} = 0 \end{pmatrix} \bigvee \begin{pmatrix} \neg Y_{i,k}^{2} \\ t_{i,k} \ge T_i^{\text{cond}} \\ q_{i,k}^{\Lambda} \ge 0 \end{pmatrix} \tag{4.26}$$

$$\begin{pmatrix} Y_{i}^{3} \\ t_{i,\text{NOK}+1} \le T_i^{\text{cond}} - \delta \\ q_{i}^{\Lambda,\text{cu}} = 0 \end{pmatrix} \bigvee \begin{pmatrix} \neg Y_{i}^{3} \\ t_{i,\text{NOK}+1} \ge T_i^{\text{cond}} \\ q_{i}^{\Lambda,\text{cu}} \ge 0 \end{pmatrix} \tag{4.27}$$

$$\begin{pmatrix} Y_{j,k}^{5} \\ t_{j,k+1} \ge T_j^{\text{evap}} + \delta \\ q_{j,k}^{\Lambda} = 0 \end{pmatrix} \bigvee \begin{pmatrix} \neg Y_{j,k}^{5} \\ t_{j,k+1} \le T_j^{\text{evap}} \\ q_{j,k}^{\Lambda} \ge 0 \end{pmatrix} \tag{4.28}$$

$$\begin{pmatrix} Y_{j}^{6} \\ t_{j,1} \ge T_j^{\text{evap}} + \delta \\ q_{j}^{\Lambda,\text{hu}} = 0 \end{pmatrix} \bigvee \begin{pmatrix} \neg Y_{j}^{6} \\ t_{j,1} \le T_j^{\text{evap}} \\ q_{j}^{\Lambda,\text{hu}} \ge 0 \end{pmatrix} \tag{4.29}$$

$$\begin{aligned} &\text{if} \quad T_i^{\text{cond}} - T_j^{\text{evap}} < \Delta T_{\text{MIN}} \\ &\qquad q_{i,k}^{\Lambda} = 0 \qquad\qquad i \in \text{HPS3},\ j \in \text{CPS3},\ k \in \text{ST} \\ &\qquad q_{j,k}^{\Lambda} = 0 \end{aligned} \tag{4.30}$$

$$q_{ijk} - Q_{i,j}^{\max} z_{ijk} \le 0, \quad i \in \text{HPS},\ j \in \text{CPS},\ k \in \text{ST} \tag{4.31}$$

$$\text{qcu}_i - Q_i^{\max} \text{zcu}_i \le 0, \quad i \in \text{HPS} \tag{4.32}$$

$$\text{qhu}_j - Q_j^{\max} \text{zhu}_j \le 0, \quad j \in \text{CPS} \tag{4.33}$$

$$\text{dt}_{ijk} \le t_{ik} - t_{jk} + \Delta T^{\max}\left(1 - z_{ijk}\right), \quad i \in \text{HPS},\ j \in \text{CPS},\ k \in \text{ST} \tag{4.34}$$

$$\text{dt}_{i,j,k+1} \le t_{i,k+1} - t_{j,k+1} + \Delta T^{\max}\left(1 - z_{ijk}\right),\ i \in \text{HPS},\ j \in \text{CPS},\ k \in \text{ST} \tag{4.35}$$

$$\text{dtcu}_i \le t_{i,\text{NOK}+1} - \text{TOUT}_{\text{cu}} + \Delta T^{\max}(1 - \text{zcu}_i), \quad i \in \text{HPS} \tag{4.36}$$

$$\text{dthu}_j \le \text{TOUT}_{\text{hu}} - t_{j,1} + \Delta T^{\max}\left(1 - \text{zhu}_j\right), \quad j \in \text{CPS} \tag{4.37}$$

$$\begin{aligned} &\text{if} \quad \text{TIN}_i - \text{TIN}_j < \Delta T_{\text{MIN}} \\ &\qquad \Delta T_{i,j}^{\max} = \text{abs}\left[\text{TIN}_i - \text{TIN}_j\right] + \Delta T_{\text{MIN}} \\ &\text{else} \\ &\Delta T_{i,j}^{\max} = \max\left\{0, \text{TIN}_i - \text{TIN}_j, \text{TOUT}_j - \text{TOUT}_i\right\} \end{aligned} \tag{4.38}$$

$$\left(\begin{array}{c} Y^{7}_{i,j,k} \\ \mathrm{lmtd}_{i,j,k} = f\left(\mathrm{dt}_{i,j,k}, \mathrm{dt}_{i,j,k+1}, \mathrm{dt}^{\mathrm{sat}}_{i,j}\right) \\ q^{\Lambda}_{i,k} \geq \delta \\ q^{\Lambda}_{j,k} \geq \delta \end{array}\right) \bigvee \left(\begin{array}{c} \neg Y^{7}_{i,j,k} \\ \mathrm{lmtd}_{i,j,k} = f\left(\mathrm{dt}_{i,j,k}, \mathrm{dt}_{i,j,k+1}\right) \end{array}\right) \tag{4.39}$$

$$\begin{aligned} \mathrm{lmtd}_{i,j,k} \leq & \left\{\left(\mathrm{dt}_{i,j,k}\right)\left(\mathrm{dt}_{i,j,k+1}\right)\left(\mathrm{dt}^{\mathrm{sat}}_{i,j}\right)\left(\frac{\mathrm{dt}_{i,j,k} + \mathrm{dt}_{i,j,k+1} + \mathrm{dt}^{\mathrm{sat}}_{i,j}}{3}\right)\right\}^{1/4} \\ & + \mathrm{lmtd}^{\max}_{i,j}\left(1 - y^{7}_{i,j,k}\right), \quad i \in \mathrm{HPS3}, \ j \in \mathrm{CPS3}, \ k \in \mathrm{ST} \end{aligned} \tag{4.40}$$

$$\begin{aligned} & \mathrm{lmtd}_{i,j,k} \leq \left\{\left(\mathrm{dt}_{i,j,k}\right)\left(\mathrm{dt}_{i,j,k+1}\right)\left(\frac{\mathrm{dt}_{i,j,k} + \mathrm{dt}_{i,j,k+1}}{2}\right)\right\}^{1/3} + \mathrm{lmtd}^{\max}_{i,j} y^{7}_{i,j,k}, \\ & i \in \mathrm{HPS}, \ j \in \mathrm{CPS}, \ k \in \mathrm{ST} \end{aligned} \tag{4.41}$$

$$\left.\begin{array}{l} y^{1}_{i,k} + y^{7}_{i,j,k} \leq 1 \\ y^{2}_{i,k} + y^{7}_{i,j,k} \leq 1 \\ y^{4}_{i,k} + y^{7}_{i,j,k} \leq 1 \\ y^{5}_{i,k} + y^{7}_{i,j,k} \leq 1 \end{array}\right\} \quad i \in \mathrm{HPS3}, \ j \in \mathrm{CPS3}, \ k \in \mathrm{ST} \tag{4.42}$$

$$y^{1}_{i,k} + y^{2}_{i,k} + y^{4}_{j,k} + y^{5}_{j,k} + y^{7}_{i,j,k} \geq 1, \quad i \in \mathrm{HPS3}, \ j \in \mathrm{CPS3}, \ k \in \mathrm{ST} \tag{4.43}$$

$$h_{i,k} = h^{\mathrm{suph}}_{i} y^{1}_{i,k} + h^{\mathrm{subc}}_{i} y^{2}_{i,k} + h^{\mathrm{mean}}_{i}\left(1 - y^{1}_{i,k} - y^{2}_{i,k}\right), \quad i \in \mathrm{HPS3}, \ k \in \mathrm{ST} \tag{4.44}$$

$$h^{\mathrm{cu}}_{i} = h^{\mathrm{subc}}_{i} y^{3}_{i} + h^{\mathrm{mean}}_{i}\left(1 - y^{3}_{i}\right), \quad i \in \mathrm{HPS3} \tag{4.45}$$

$$h^{\mathrm{mean}}_{i} = \frac{h^{\mathrm{suph}}_{i}\mathrm{FCP}_{i}\left(\mathrm{TIN}_{i} - T^{\mathrm{cond}}_{i}\right) + h^{\mathrm{subc}}_{i}\mathrm{FCP}_{i}\left(T^{\mathrm{cond}}_{i} - \mathrm{TOUT}_{i}\right) + h^{\mathrm{cond}}_{i} F\lambda^{\mathrm{cond}}_{i}}{\mathrm{FCP}_{i}\left(\mathrm{TIN}_{i} - T^{\mathrm{cond}}_{i}\right) + \mathrm{FCP}_{i}\left(T^{\mathrm{cond}}_{i} - \mathrm{TOUT}_{i}\right) + F\lambda^{\mathrm{cond}}_{i}}, \quad i \in \mathrm{HPS3} \tag{4.46}$$

$$h_{j,k} = h^{\mathrm{suph}}_{j} y^{5}_{j,k} + h^{\mathrm{subc}}_{j} y^{4}_{j,k} + h^{\mathrm{mean}}_{j}\left(1 - y^{4}_{j,k} - y^{5}_{j,k}\right), \quad j \in \mathrm{CPS3}, \ k \in \mathrm{ST} \tag{4.47}$$

$$h^{\mathrm{hu}}_{j} = h^{\mathrm{suph}}_{j} y^{6}_{j} + h^{\mathrm{mean}}_{j}\left(1 - y^{6}_{j}\right), \quad j \in \mathrm{CPS3} \tag{4.48}$$

$$h_j^{\text{mean}} = \frac{h_j^{\text{suph}}\text{FCP}_j\left(\text{TOUT}_j - T_j^{\text{evap}}\right) + h_j^{\text{subc}}\text{FCP}_j\left(T_j^{\text{evap}} - \text{TIN}_j\right) + h_j^{\text{evap}}F\lambda_j^{\text{evap}}}{\text{FCP}_j\left(\text{TOUT}_j - T_j^{\text{evap}}\right) + \text{FCP}_j\left(T_j^{\text{evap}} - \text{TIN}_j\right) + F\lambda_j^{\text{evap}}},\quad j \in \text{CPS3} \tag{4.49}$$

$$\begin{aligned}
\text{TAC} = {} & \sum_{i\in\text{HPS}} \text{CCUqcu}_i + \sum_{j\in\text{CPS}} \text{CHUqhu}_j \\
& + \sum_{i\in\text{HPS}}\sum_{j\in\text{CPS}}\sum_{k\in\text{ST}} \text{CF}_{i,j}z_{,j,k} + \sum_{i\in\text{HPS}} \text{CF}_{i,\text{cu}}\text{zcu}_i + \sum_{j\in\text{CPS}} \text{CF}_{\text{cu},j}\text{zhu}_j \\
& + \sum_{i\in\text{HPS}}\sum_{j\in\text{CPS}}\sum_{k\in\text{ST}} C_{i,j}\left\{\frac{q_{i,j,k}\left(\frac{1}{h_{i,k}} + \frac{1}{h_{j,k}}\right)}{\text{lmtd}_{i,j,k} + \delta}\right\}^{\beta} \\
& + \sum_{i\in\text{HPS}} C_{i,\text{cu}}\left\{\frac{\text{qcu}_i\left(\frac{1}{h_i^{\text{cu}}} + \frac{1}{h_{\text{cu}}}\right)}{\left[(\text{dt}_{i,\text{cu}})(\text{TOUT}_i - \text{TIN}_{\text{cu}})\left(\frac{\text{dt}_{i,\text{cu}} + \text{TOUT}_i - \text{TIN}_{\text{cu}}}{2}\right) + \delta\right]^{1/3}}\right\}^{\beta} \\
& + \sum_{j\in\text{CPS}} C_{\text{hu},j}\left\{\frac{q_{\text{hu},j}\left(\frac{1}{h_{\text{hu}}} + \frac{1}{h_j^{\text{hu}}}\right)}{\left[\left(\text{dt}_{\text{hu},j}\right)\left(\text{TIN}_{\text{hu}} - \text{TOUT}_j\right)\left(\frac{\text{dt}_{\text{hu},j} + \text{TIN}_{\text{hu}} - \text{TOUT}_j}{2}\right) + \delta\right]^{1/3}}\right\}^{\beta}
\end{aligned} \tag{4.50}$$

The used nomenclature in the model formulation is described as follows: A is the heat transfer area, C is the area cost coefficient, CCU is the unit cost of cold utility, CHU is the unit cost of hot utility, CF is the fixed charge for exchangers, Cp is the specific heat capacity, CPS $\{j|j$ is a cold process stream$\}$, CPS1 $\{j|j$ is a non-isothermal cold process stream$\}$, CPS2 $\{j|j$ is an isothermal cold process stream$\}$, CPS3 $\{j|j$ is a stream that exchanges latent and sensible heat$\}$, CU is the cold utility, $\text{dt}_{i,j,k}$ is temperature approach difference for match (i, j) at temperature location k, dtcu_i is temperature approach difference for match between hot stream i and cold utility, dthu_j is temperature approach difference for match between cold stream j and hot utility, $\text{dt}_{i,j}^{\text{sat}}$ is temperature difference between saturated streams, F is the flow rate, FCp is the heat capacity flow rate, h is fouling heat transfer coefficient, h^{cond} is the fouling heat transfer coefficient for condensation, h^{evap} is the fouling heat transfer coefficient for evaporation, h^{mean} is the mean fouling heat transfer coefficient, h^{suph} is the fouling heat transfer coefficient for superheated part of a stream, h^{subc} is the fouling heat transfer coefficient for subcooled part of a stream, HPS $\{i|i$ is a hot process stream$\}$, HPS1 $\{i|i$ is a non-isothermal hot process stream$\}$, HPS2 $\{i|i$ is an isothermal hot process stream$\}$, HPS3 $\{i|i$ is a stream that exchanges latent and sensible heat$\}$, HU is the hot utility, $\text{lmtd}_{i,j,k}$ is the log-mean temperature difference, $\text{lmtd}_{i,j}^{\max}$ is the upper limit for the lmtd for match i, j, NOK is the total number of stages, $q_{i,j,k}$ is the heat exchanged between hot process stream i and cold stream j in stage k, qcu_i is the heat exchanged between cold utility and hot stream i, qhu_j is the heat exchanged between hot utility and cold stream j, $Q^{\max}$ is the upper bound for heat exchange, ST $\{k|k$ is a stage in the superstructure, $k=1,\ldots,\text{NOK}\}$, $t_{i,k}$ is the temperature of hot stream i at the hot end of stage k, $t_{j,k}$ is the temperature of cold stream j at the hot end of stage k, $t_{i,k}^{n}$ is the disaggregated variables used to model disjunctions, TAC is the total annual cost, $t_{j,k}^{n}$ is the disaggregated variables used to model disjunctions, T_i^{cond} is the condensation temperature for hot stream i, T_j^{evap} is the evaporation temperature for cold stream j, TIN is the inlet temperature of a process stream, TOUT is the outlet temperature of a process stream, $\Delta T^{\max}$ is the upper bound for temperature difference, ΔT_{MIN} is the minimum approach temperature difference, Y is the boolean variables used to model disjunctions, y is the binary variable used to model disjunctions, $z_{i,j,k}$ is the binary variable for match (i, j) in stage k, zcu_i is the binary variable for match between cold utility and hot stream i, zhu_j is the binary variable for match between hot utility and cold stream j, λ is the unit latent heat, $F\lambda_i^{\text{cond}}$ is the condensation heat load for hot stream i, $F\lambda_j^{\text{evap}}$ is the evaporation heat load for cold stream j, $q_{i,k}^{\Lambda}$ is the condensation heat load of hot stream i exchanged at stage k, $q_{j,k}^{\Lambda}$ is the evaporation heat load of cold stream j exchanged at stage k, $q_i^{\Lambda,\text{cu}}$ is the condensation heat load that is exchanged with the cold utility, $q_j^{\Lambda,\text{hu}}$ is the evaporation heat load exchanged with a hot utility, β is the exponent for area in cost equation, δ is a small number, i is a hot process stream, j is a cold process stream, and k is an index for stage $(1,\ldots,\text{NOK})$ and temperature location $(1,\ldots,\text{NOK}+1)$, respectively.

The intensification of such process can be observed through the considered objective function. For example, one objective can be stated as minimizing the TAC, and other can be considered as minimizing the total heat transfer area, the number of heat transfer units, the associated greenhouse gas emissions, etc. And the results of such intensified process can be different depending on the considered objective. Therefore, there is needed to account for a proper method that trade-offs different objectives. The application of the intensification concept is described in the next section for the case study presented.

4.2.1 Case Study for Synthesizing Intensified HEN

The problem consists of two hot and one cold process streams, with high, medium, and low pressure steam available as hot utilities, and cold water as a cold utility. This problem was also solved by Shenoy et al. [26] and Isafiade and Fraser [27]. The streams data are shown in Table 4.1. To determine the capital cost for the heat exchanger units, the cost model $\text{Cexc} = 800[\text{Area}(\text{m}^2)]$ was used, with an annualization factor of 0.298/year [26]. The problem consists of 511 constraints,

Table 4.1 Data for the example for synthesizing HEN

Stream	TIN [°C]	TOUT [°C]	FCp [kW K^{-1}]	h [kW/(m^2 K)]	Cost ($/(kW year))
H1	105	25	10	0.5	–
H2	185	35	5	0.5	–
HPS[a]	210	209	–	5.0	160
MPS[b]	160	159	–	5.0	110
LPS[c]	130	129	–	5.0	50
C1	25	185	7.5	0.5	–
CW[d]	5	6	–	2.6	10

[a] High pressure steam
[b] Medium pressure steam
[c] Low pressure steam
[d] Cooling water

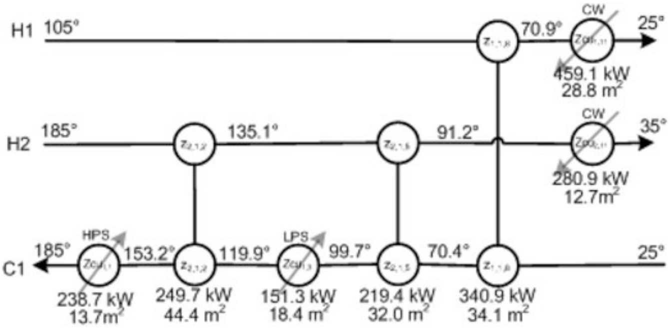


Fig. 4.2 Optimal solution for the HEN

501 continuous variables, and 120 binary variables. Applying the optimization approach and taking as objective function the minimization of the total annual cost, see (4.50), the solution obtained is shown in Fig. 4.2. It should be noted that for solving this problem there are needed three stages in the superstructure. The network requires three heat exchangers. There are also two coolers and two heaters, one that uses 238.7 kW of high pressure steam and the other one 151.3 kW of the low pressure steam. Notice that there is a heater in stage three of the superstructure, situation not allowed in the original model by Yee and Grossmann [25]. The network reported in Fig. 4.2 has a total investment cost of $43,922/year and a total utility cost of $53,157/year to yield a total annual cost of $97.079/year. Table 4.2 shows a result comparison between different solutions obtained for this problem. It should be noticed that the solution obtained in this work uses the highest amount of high pressure steam but has the lowest number of units, and it shows savings in total annual cost of 1.22 and 0.14 % with respect to the solutions reported by Shenoy et al. [26] and Isafiade and Fraser [27].

Table 4.2 Results comparison for the example of synthesizing a HEN

Solution method	This chapter	Shenoy et al. [26]	Isafiade and Fraser [27]
HPS load [kW]	238.7	203	244.6
MPS load [kW]	0	53	1
LPS load [kW]	151.3	119.5	143.7
CW load [kW]	740.0	725.5	739.3
Number of units	7	9	9
TAC [$/year]	97,079	98,263	97,211

4.3 Synthesis of Intensified Water Networks

The problem of synthesizing a water network is defined as follows: Given a set of water sources that discharge wastewater with specific characteristics (properties), also there is a set of process units (sinks) that need water with given characteristics (properties), then the problem consists in determining the network that satisfies the water demands for the process sinks using the wastewater available and fresh sources considering as objective function different criteria, for example minimizing the fresh water consumption, minimizing the number of treatment units, minimizing the total annual cost, minimizing the wastewater discharge to the environment, minimizing the network complexity, minimizing the environmental impact, between others.

A very common superstructure for synthesizing water networks is the one reported by Ponce-Ortega et al. [21] and shown in Fig. 4.3. The corresponding model formulation is the following:

$$F_r = \sum_{j \in \mathrm{NSINKS}} f_{r,j}, \quad r \in \mathrm{FRESH} \tag{4.51}$$

$$W_i = \sum_{\mathrm{int}^1 \in \mathrm{INT}^1} w_i^{\mathrm{int}^1}, \quad i \in \mathrm{NSOURCES} \tag{4.52}$$

$$w_i^{\mathrm{int}^1} = \sum_{\mathrm{int}^2 \in \mathrm{INT}^2} w_i^{\mathrm{int}^1,\mathrm{int}^2}, \quad i \in \mathrm{NSOURCES}, \ \mathrm{int}^1 \in \mathrm{INT}^1 \tag{4.53}$$

$$w_i^{\mathrm{int}^1,\mathrm{int}^2,\ldots,\mathrm{int}^{N-1}} = \sum_{\mathrm{int}^N \in \mathrm{INT}^N} w_i^{\mathrm{int}^1,\mathrm{int}^2,\ldots,\mathrm{int}^N}, \quad i \in \mathrm{NSOURCES}, \ \mathrm{int}^1 \in \mathrm{INT}^1, \ldots, \mathrm{int}^{N-1} \in \mathrm{INT}^{N-1} \tag{4.54}$$

$$w_i^{\mathrm{int}^1,\ldots,\mathrm{int}^N} = \sum_{j \in \mathrm{SINKS}} g_{i,j}^{\mathrm{int}^1,\ldots,\mathrm{int}^N} + g_{i,\mathrm{waste}}^{\mathrm{int}^1,\ldots,\mathrm{int}^N}, \quad i \in \mathrm{NSOURCES}, \ \mathrm{int}^1 \in \mathrm{INT}^1, \ldots, \mathrm{int}^N \in \mathrm{INT}^N \tag{4.55}$$

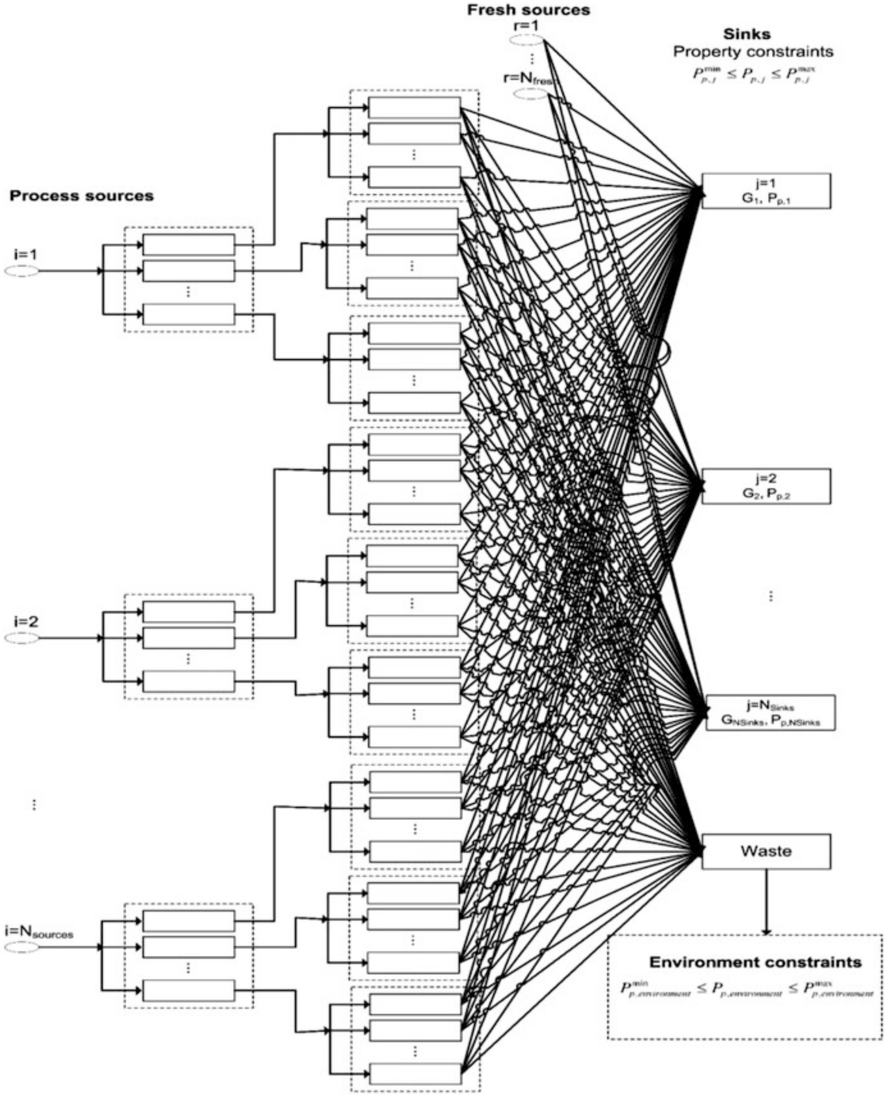


Fig. 4.3 Superstructure for synthesizing water networks by Ponce-Ortega et al. [21]

$$G_j = \sum_{i\in \mathrm{NSOURCES}} \sum_{\mathrm{int}^1} \cdots \sum_{\mathrm{int}^N} g_{i,j}^{\mathrm{int}^1,\ldots,\mathrm{int}^N} + \sum_{r\in \mathrm{FRESH}} f_{r,j}, \quad j \in \mathrm{NSINKS} \qquad (4.56)$$

$$\psi_p\left(P_{j,p}^{\mathrm{InSink}}\right)G_j = \sum_{i\in \mathrm{NSOURCES}} \sum_{\mathrm{int}^1} \cdots \sum_{\mathrm{int}^N} \left[\psi_p\left(P_{i,p}^{\mathrm{OutPIN},\mathrm{int}^1,\ldots,\mathrm{int}^N}\right) g_{i,j}^{\mathrm{int}^1,\ldots,\mathrm{int}^N}\right] + \sum_{r\in \mathrm{FRESH}} \left[\psi_p\left(P_{r,p}^{\mathrm{InFresh}}\right) f_{r,j}\right], \quad j \in \mathrm{NSINKS},\ p \in \mathrm{NPROP} \qquad (4.57)$$

$$\mathrm{waste} = \sum_{i \in \mathrm{NSOURCES}} \sum_{\mathrm{int}^1} \cdots \sum_{\mathrm{int}^N} g_{i,\mathrm{waste}}^{\mathrm{int}^1,\ldots,\mathrm{int}^N} \tag{4.58}$$

$$\psi_p\left(P_{\mathrm{waste},p}\right)\mathrm{waste} = \sum_{i \in \mathrm{NSOURCES}} \sum_{\mathrm{int}^1} \cdots \sum_{\mathrm{int}^N} \left(\psi_p\left(P_{i,p}^{\mathrm{OutPIN},\mathrm{int}^1,\ldots,\mathrm{int}^N}\right) g_{i,\mathrm{waste}}^{\mathrm{int}^1,\ldots,\mathrm{int}^N}\right), \quad p \in \mathrm{NPROP} \tag{4.59}$$

$$\psi_p\left(P_{j,p}^{\mathrm{min,\,Sink}}\right) \le \psi_p\left(P_{j,p}^{\mathrm{in,\,Sink}}\right) \le \psi_p\left(P_{j,p}^{\mathrm{max,\,Sink}}\right), \quad j \in \mathrm{NSINK}, \ \ P \in \mathrm{NPROP} \tag{4.60}$$

$$\psi_p\left(P_{j,p}^{\mathrm{min,\,Env}}\right) \le \psi_p\left(P_{\mathrm{waste},p}\right) \le \psi_p\left(P_{j,p}^{\mathrm{max,\,Env}}\right), \quad P \in \mathrm{NPROP} \tag{4.61}$$

$$\begin{aligned}\mathrm{TAC} = {} & H_{\mathrm{Y}} \sum_{r \in \mathrm{FRESH}} \mathrm{Cost}_r^{\mathrm{Fresh}} F_r \\ & + H_{\mathrm{Y}} \sum_{i \in \mathrm{NSOURCES}} \left(\sum_{\mathrm{int}^1 \in \mathrm{INT}^1} \left(\mathrm{Cost}_p^{\mathrm{int}^1} w_i^{\mathrm{int}^1} + \cdots \sum_{\mathrm{int}^N \in \mathrm{INT}^N} \left(\mathrm{Cost}_p^{\mathrm{int}^N} w_i^{\mathrm{int}^1,\ldots,\mathrm{int}^N} \right) \right) \right)\end{aligned} \tag{4.62}$$

The nomenclature used in previous formulation is the following: AER is the aeration process, Bp is linearization for the bilinear term, C is the concentration (ppm), COD is the chemical oxygen demand, Color is the property color, $\mathrm{Cost}^{\mathrm{Fresh}}$ is the unit cost for fresh utility, $\mathrm{Cost}^{\mathrm{int}N}$ is the unit cost for interceptor N, H_{Y} is the operating time of the plant (hour per year), int^n is the interceptor for property n, INT^n is the set for the property interceptor n, F_r is the total flow rate for fresh source r, $f_{r,j}$ is the segregated flow rate from fresh source r to sink j, G_j is the total flow rate for process sink j, $g_{i,j}^{\mathrm{int}1,\ldots,\mathrm{int}N}$ is the segregated flow rate from interceptors, int1,…, int$N$ to process sink j for process source i, $g_{i,\mathrm{waste}}^{\mathrm{int}1,\ldots,\mathrm{int}N}$ is the segregated flow rate from interceptor, int1,…,int$N$ to waste for source i, MW is the molecular weight, NFresh is the total number of fresh sources, NSinks is total number of sinks, NSources is the total number of process sources, NEU is the neutralization process, NFRESH set for the fresh sources $\{r|r=1,\ldots,\mathrm{NFresh}\}$, NPROP is the set for the properties intercepted $\{p|p=1,\ldots,\mathrm{NProp}\}$, NSINKS is the set for the sinks $\{j|j=1,\ldots,\mathrm{NSinks}\}$, NSOURCES is the set for the process sources $\{i|i=1,\ldots,\mathrm{NSources}\}$, Odor is the property odor, pH is the potential of hydrogen, R is the electric resistivity, P represents any property, $R\infty$ is the paper reflectivity, REC is the recovery of a hazardous component, RVP is the Reid vapor pressure, TAC is total annual cost, Tox or TOX is the toxicity, W_i is the total flow rate for the process sources i, $w_i^{\mathrm{int}1}$ is the segregated flow rate from process source i to interceptor int1, $w_i^{\mathrm{int}1,\ldots,\mathrm{int}N}$ is the segregated flow rate from process source i to interceptors int1,…, int$N$, waste total is the flow rate for the waste stream discharged to the environment, x is the fractional contribution (mass/volume), Y is the lethal response, z is the composition or concentration, $\alpha_p^{\text{int1},\ldots,\text{int}N}$ is the efficiency of property interceptor for property p, Ψ_p is the property operator for the mixing rule for property p, ρ is the density, μ is the viscosity, Env is the environment, i is the process source, In is inlet, j is sink, LO is lower value, max is maximum, min is the minimum, Out is out, p is property, PIN is property interceptor network, r is fresh source, Sink is sink, Source is source, UP is upper value, and Waste is the waste discharged to the environment, respectively.

4.3.1 *Case Study for Synthesizing Intensified Water Networks*

This problem consists in the production of phenol from cumene peroxide. Wastewater streams are taken as a basis for the mass integration process. Notice that such streams may contain several components (such as phenol, acetone, cumene, isopropane, dymethyleter, methyleter, ethylene, oxygen, nitrogen, sulfur, and sodium); therefore, the properties of the streams depend on all of the components as well as their pressure and temperature. Phenol is taken as the major hazardous component; therefore, the model for the mass integration considers constraints based on the concentration of the phenol in addition to the constraints based on the properties that are affected by all of the streams components. Table 4.3 shows the main characteristics for these streams, where the inlet property values for the sources are included. Two fresh sources are available, fresh source 1, water with high purity, and fresh source 2, water slightly contaminated. The unit costs for the fresh sources 1 and 2 are \$0.02/kg and \$0.013/kg, respectively. Table 4.4 shows the constraints for the process sinks, and Table 4.5 gives the efficiency and cost data for each of the interceptors considered.

This problem is a mixed-integer nonlinear programming problem and it involves 2168 variables with 574 constraints, and the optimal solution was obtained in 0.682 s of CPU time.

Table 4.3 Process and fresh sources characteristics for Example 1

Sources i	F (kg/h)	z_{phenol} (ppm)	Tox (%)	pH	COD (kg O_2/m^3) × 10^3	ρ (kg/m^3)	μ (cP)
Process sources							
1	3666	0.016	0.3	5.4	0.187	907.19	1.256
2	1769	0.024	0.5	5.1	48.850	1001.53	1.220
3	1487	0.220	1.5	4.8	92.100	1065.94	1.201
Fresh sources							
1	–	0.000	0	7.0	0.000	999.72	1.002
2	–	0.010	0.1	7.1	0.010	1001.99	0.992

Table 4.4 Process sinks constraints for Example 1

Sink$j$	G (kg/h)	$z_{\text{phenol}}^{\text{MaxSink}}$ (ppm)	$\text{pH}^{\text{MinSink}}$	$\text{pH}^{\text{MaxSink}}$	ρ^{MinSink} (kg/m^3)	ρ^{MaxSink} (kg/m^3)	μ^{MinSink} (cP)	μ^{MaxSink} (cP)
1	2721	0.013	5.3	8.0	816	1270	0.900	1.202
2	1995	0.011	5.4	7.8	771	1113	0.905	2.230
3	1129	0.100	5.2	8.2	839	1315	0.903	1.260

Table 4.5 Efficiency and unit cost for interceptors

Property	Interceptor	Conversion factor (α)	Unit cost ($/kg)
Composition	REC^1	0.02	0.0143
	REC^2	0.15	0.0073
Toxicity	TOX^1	0	0.0216
	TOX^2	0.10	0.0165
COD	AER^1	0.20	0.0143
	AER^2	0.45	0.0071
pH	NEU^1	0.50	0.1389
	NEU^2	0.70	0.0397
	NEU^3	1.50	0.1433
	NEU^4	1.30	0.0419

Figure 4.4 shows the optimal solution for this problem and Table 4.6 shows a summary of results and other obtained solutions. For the simplified case without integration, the solution shows a total annual cost of $2,244,805/year, which is 388 % higher than the optimal solution with mass and property integration. The simplified solution uses only fresh source 2 (the cheapest choice), and the total waste discharged to the environment is 478 % higher than the optimal solution; as a consequence, the associated cost to treat this waste yields a significant higher total cost. Therefore, it should be clear that there is an incentive to consider the environmental regulations simultaneously as part of the mass and property integration process.

4.4 Conclusions

This chapter has shown that process integration through heat and mass integration is a powerful tool for process intensification. Particularly, heat integration through the synthesis of HEN allows reducing significantly the utility consumption; whereas mass integration through the synthesis of water networks allows reducing the fresh water consumption. Accounting for an objective function that involves the total annual costs allows to consider the trade-offs between several issues like the number of transfer units, the network complexity, the size for the transfer units and the use of external agents such as mass and energy.

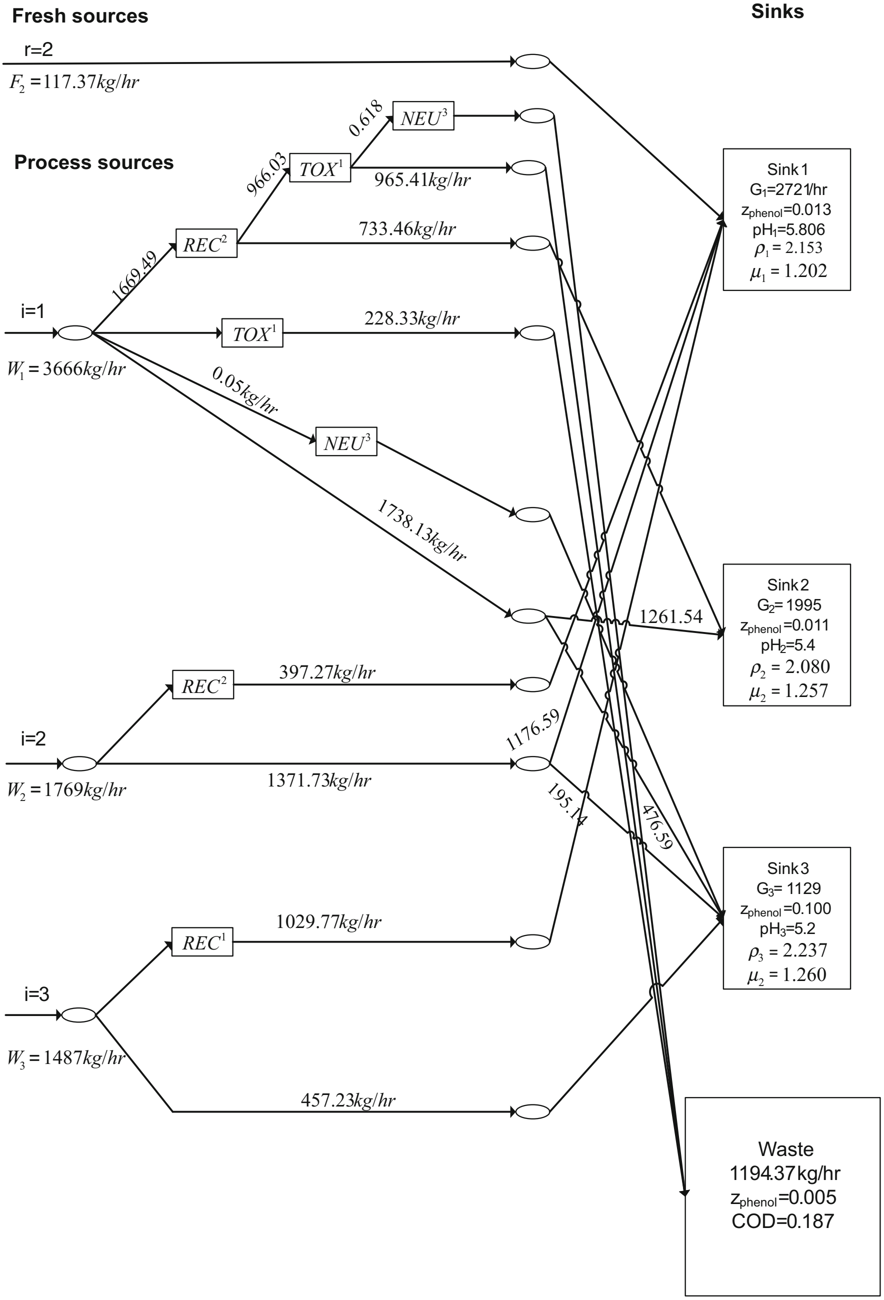


Fig. 4.4 Optimal solution for the example of synthesizing a MEM

Table 4.6 Result comparison for Example 1

Concept	Optimal solution	Without integration
F1 (kg/h)	0	0
F2 (kg/h)	117	5845
waste (kg/h)	1194	6922
Fresh sources cost ($/year)	12,206	607,880
Recovery cost ($/year)	240,256	432,121
Toxicity cost ($/year)	206,387	1,196,122
Aeration cost ($/year)	0	0
Neutralization cost ($/year)	762	8682
Total annual cost ($/year)	459,611	2,244,805

References

1. Stankiewicz A, Moulijn J (eds) (2004) Process intensification: history, philosophy, principles. Marcel Dekker, New York
2. Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM (2012) Process intensification: new understanding and systematic approach. Chem Eng ProcessProcess Intensif 53(3):63–75
3. Lutze P, Gani R, Woodley JM (2010) Process intensification: a perspective on process synthesis. Chem Eng ProcessProcess Intensif 49(6):57–558
4. El-Halwagi MM (2012) Sustainable design through process integration: fundamentals and applications to industrial pollution prevention, resource conservation and profitability enhancement. Butterworth Heinemann, Oxford
5. Gopalakrishnan M, Ponce-Ortega JM, El-Halwagi MM (2012) A systems approach for process simplification through process integration. Chem Eng Technol 35(7):1262–1272
6. Serna-González M, Jiménez-Gutiérrez A, Ponce-Ortega JM (2007) Targets for heat exchanger networks synthesis with different heat transfer coefficients and non-uniform exchanger specifications. Chem Eng Res Des 85(A10):1447–1457
7. Serna-González M, Ponce-Ortega JM (2011) Total cost target for heat exchanger networks considering simultaneously pumping and area effects. Appl Therm Eng 31(11–12):1964–1975
8. Ponce-Ortega JM, Serna-González M, Jiménez-Gutiérrez A (2008) Synthesis of multipass heat exchanger networks using genetic algorithms. Comput Chem Eng 32(10):2320–2332
9. Ponce-Ortega JM, Jiménez-Gutiérrez A, Grossmann IE (2008) Optimal synthesis of heat exchanger networks involving isothermal streams. Comput Chem Eng 32(8):1918–1942
10. Ponce-Ortega JM, Serna-González M, Jiménez-Gutiérrez A (2010) Synthesis of heat exchanger networks with optimal placement of multiple utilities. Ind Eng Chem Res 49 (6):2849–2856
11. López-Maldonado LA, Ponce-Ortega JM, Segovia-Hernández JG (2011) Mutiobjective synthesis of heat exchanger networks minimizing the total annual cost and the environmental impact. Appl Therm Eng 31(6–7):1099–1113
12. Lira-Barragán LF, Ponce-Ortega JM, Serna-González M, El-Halwagi MM (2014) Optimal design of process energy systems integrating sustainable considerations. Energy 76:139–160
13. Lira-Barragán LF, Ponce-Ortega JM, Serna-González M, El-Halwagi MM (2014) Sustainable integration of trigeneration systems with heat exchanger networks. Ind Eng Chem Res 53 (7):2732–2750
14. Ponce-Ortega JM, Hortua AC, El-Halwagi MM, Jiménez-Gutiérrez A (2009) A property-based optimization of direct recycle networks and wastewater treatment processes. AIChE J 55 (9):2329–2344

15. Nápoles-Rivera F, Ponce-Ortega JM, El-Halwagi MM, Jiménez-Gutiérrez A (2010) Global optimization of mass and property integration networks with in-plant property interceptors. Chem Eng Sci 65(15):4363–4377
16. Rojas-Torres MG, Ponce-Ortega JM, Serna-González M, Nápoles-Rivera F, El-Halwagi MM (2013) Synthesis of water networks involving temperature-based property operators and thermal integration. Ind Eng Chem Res 52(1):442–461
17. Rubio-Castro E, Ponce-Ortega JM, Serna-González M, El-Halwagi MM, Pham V (2013) Global optimization in property-based inter-plant water integration. AIChE J 59(3):813–833
18. Sotelo-Pichardo C, Ponce-Ortega JM, Nápoles-Rivera F, Serna-González M, El-Halwagi MM, Frausto-Hernández S (2014) Optimal reconfiguration of water networks base on properties. Clean Technol Environ Policy 16(2):303–328
19. Sotelo-Pichardo C, Bamufleh H, Ponce-Ortega JM, El-Halwagi MM (2014) Optimal synthesis of property-based water networks considering growing demand projections. Ind Eng Chem Res 53(47):18260–18272
20. Jimenez-Gutierrez A, Lona-Ramírez J, Ponce-Ortega JM, El-Halwagi MM (2014) An MINLP model for the simultaneous integration of energy, mass and properties in water networks. Comput Chem Eng 71:52–66
21. Ponce-Ortega JM, El-Halwagi MM, Jiménez-Gutiérrez A (2010) Global optimization of property-based recycle and reuse networks including environmental constraints. Comput Chem Eng 34(3):318–330
22. Ponce-Ortega JM, Mosqueda-Jiménez FW, Serna-González M, Jiménez-Gutiérrez A, El-Halwagi MM (2011) A property-based approach to the synthesis of material conservation networks with economic an environmental objectives. AIChE J 57(9):2369–2387
23. López-Villareal F, Lira-Barragán LF, Rico-Ramírez V, Ponce-Ortega JM, El-Halwagi MM (2014) An MFA optimization approach for pollution treading considering the sustainability of the surrounding watershed. Comput Chem Eng 63:140–151
24. El-Halwagi A, Rosas C, Ponce-Ortega JM, Jiménez-Gutiérrez A, Mannan MS, El-Halwagi MM (2013) Multi-objective optimization of biorefineries with economic and safety objectives. AIChE J 59(7):2427–2434
25. Yee TF, Grossmann IE (1990) Simultaneous optimization models for heat integration-II. Heat exchanger network synthesis. Comput Chem Eng 14(10):1165–1184
26. Shenoy UV, Sinha A, Bondyopadhyay S (1998) Multiple utilities targeting for heat exchanger networks. Chem Eng Res Des 76(Part A):259–272
27. Isafiade AJ, Fraser DM (2008) Interval-based MINLP superstructure synthesis of heat exchange networks. Chem Eng Res Des 86(A3):245–257

Chapter 5
Heat-Integrated Intensified Distillation Processes

J. Rafael Alcántara-Avila and Hao-Yeh Lee

Abstract Heat integration between vapor and liquid streams has been widely used in chemical and petrochemical plants for conventional distillation processes as an alternative to reduce the energy consumption. However, with the advances that have been proposed in intensified distillation processes in the last couple of decades, heat-integrated alternatives that are more attractive than the typical condenser–reboiler heat integration have also been proposed. Therefore, intensified distillation processes also need a new approach methodology to implement optimal locations and heat load in heat-integrated distillation. This chapter aims to cover the fundamentals, simulation and optimization approaches for heat-integrated intensified distillation processes for nonreactive and reactive systems. Conventional distillation can result in an intensified process if heat integration is allowed at locations other than the condenser and reboiler. Although thermally coupled distillation and Heat-Integrated Distillation (HIDiC) are already intensified processes, they can attain higher energy reduction by rearranging their heat load distribution. For reactive systems, at the location subject to heat integration, vapor–liquid equilibrium and reaction kinetic conditions are modified simultaneously, which results in a very challenging problem. Reactive system via multi-effect and thermally coupled configuration is also covered in this chapter for the methyl acetate hydrolysis and esterification of isopropyl alcohol. The applications of heat-integrated intensified distillation show feasible solutions with improved energy efficiency and total annual cost reduction for new designs.

J.R. Alcántara-Avila (✉)
Tokushima University, 2-1 Minami Josanjima-cho, Tokushima 770-8506, Japan
e-mail: jrafael.alcantara@tokushima-u.ac.jp

H.-Y. Lee
National Taiwan University of Science and Technology, Taipei City, Taiwan

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_5

5.1 Fundamentals in Heat Integration

Distillation is a process that repetitively boils liquid streams and condensates vapor streams from bottom to top at each stage for the separation of components with different vapor pressures. Components with lower vapor pressure are concentrated at the top of the column while components with higher vapor pressure are concentrated at the bottom of the column. Pressure and temperature gradients at each stage inside the column result in changes in the vapor–liquid proportion among components, therefore, separation is possible. The vapor leaving at the top of the distillation column is at the lowest temperature, and it is condensed by exchanging heat with a cooling utility (e.g., water) in a device called condenser. Contrarily, the liquid leaving at the bottom of the distillation column is at the highest temperature, and it is boiled by exchanging heat with a heating utility (e.g., steam) in a device called reboiler.

To reduce the necessary amount of cooling and heating utilities in distillation, one possibility is to use the column streams to provide cooling or heating; therefore, vapor streams above the feed stage (i.e., rectifying section) can be regarded as vapor heat sources and liquid streams below the feed stage (i.e., stripping section) can be regarded as liquid heat sinks [1]. However, the necessary condition to realize heat integration in distillation columns is that the temperature of heat sources must always be higher than that of heat sinks by at least a specified minimum temperature difference $\Delta T_{\min}$. To satisfy this condition, the pressure and/or the temperature of only the top vapor stream or the entire rectifying section must be increased.

5.1.1 *Heat-Integrated Distillation*

Although condenser–reboiler heat exchange has been widely used in the last couple of decades, the pressure difference between the condenser and reboiler must be at its maximum value to satisfy a given $\Delta T_{\min}$.

The heat-integrated distillation processes presented in this chapter exploit the idea of removing heat from stages in the rectifying section, which are at a temperature higher than that in the condenser, and supplying heat to stages in the stripping section, which are at a temperature lower than that in the reboiler. Thus, the search space for optimal distillation processes is expanded by including the heat integration possibilities between stages in rectifying and stripping sections in the same column or in different columns.

Figure 5.1 shows a representative temperature profile for the separation of 100 kmol/h a benzene-toluene equimolar mixture into two products with 99 % mol purity. The vertical axes show the temperature profile for heat sources in the rectifying section at the left and that for heat sinks in the stripping section at the right, respectively, and the horizontal axis shows the stage number. In addition, stages are numbered from the top condenser (stage 1) to bottom reboiler (stage 20).

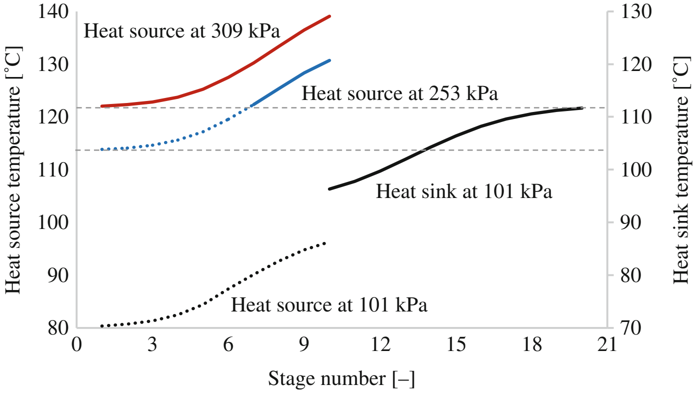


Fig. 5.1 Rectifying and stripping section temperature profile for a benzene/toluene separation

The solid lines in Fig. 5.1 represent feasible heat integrations while the dotted lines represent infeasible heat integrations with the reboiler. Additionally, the assumed value of ΔT_{min} is 10 °C. To realize heat integration between the vapor stream at stage 1 and the liquid stream at stage 20, the pressure must be equal or higher than 309 kPa. If heat sources are at a lower pressure (253 kPa), the condenser–reboiler heat integration becomes infeasible, but it is still possible to exchange heat between vapor streams in the condenser and liquid streams from stage 10 to stage 13, and vapor streams from stage 7 to stage 9 and the liquid stream in the reboiler.

5.1.2 Problems in Simulation and Optimization of Heat-Integrated Distillation

There are three main differences between conventional condenser–reboiler heat integration (i.e., external heat integration) and heat integration between stages (i.e., internal heat integration) [2]. Because of these differences, simulation and optimization problems have been limited for the heat integration between two sections in the same column or between two different columns for the separation binary and multicomponent mixtures [1–4].

5.1.2.1 Combinatorial Problem

There is a remarkable increase of heat integration possibilities when stages are considered as candidates for heat integration, and it is represented in Fig. 5.2. The typical case of heat integration is the one between condenser and reboiler (Fig. 5.2a). In the case of heat integration between stages, heat can be supplied from all the *M* stages in a rectifying section to all the *N* stages in a stripping section.

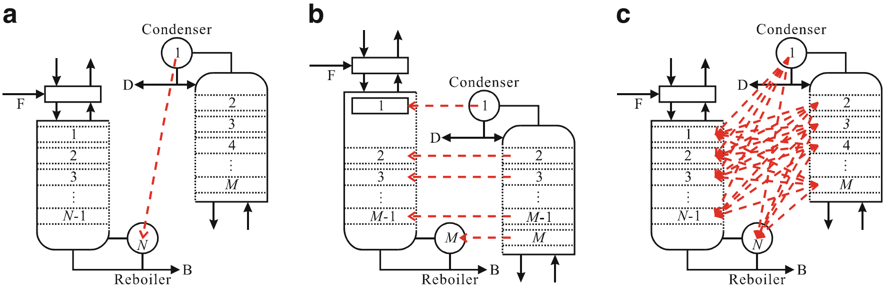


Fig. 5.2 Heat integration possibilities between rectifying and stripping sections. (**a**) Condenser–reboiler. (**b**) Internal heat integration one to one. (**c**) Internal heat integration one to all

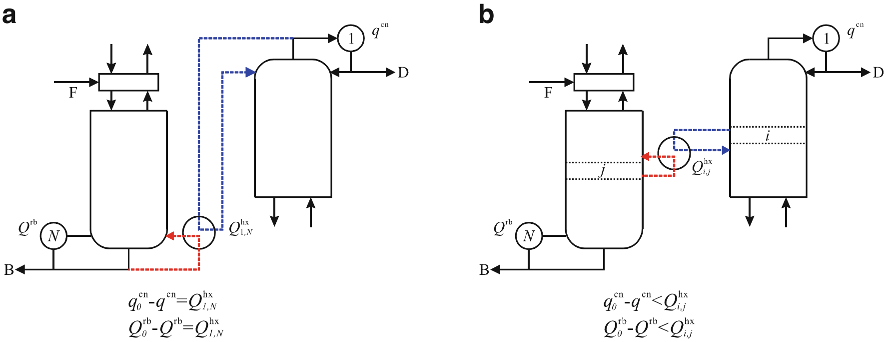


Fig. 5.3 Changes in heat duty after heat integration. (**a**) Between condenser and reboiler. (**b**) Between stages

In Fig. 5.2b, heat integrations can be done from one stage in the rectifying section to one stage in the stripping section while in Fig. 5.2c heat integrations can be done from one stage in the rectifying to all stages in the stripping section, and vice versa. It can be seen that all combinations in Fig. 5.2a, b are included in Fig. 5.2c. Additionally in Fig. 5.2, F denotes the feed, D the distillate product, and B the bottoms product.

To illustrate how the combinatorial problem increases, consider that the rectifying section consists of ten stages ($M = 10$) and the stripping section consists of ten stages ($N = 10$), the possible matches in Fig. 5.2a–c are 1, 10, and 100, respectively, when one heat integration is enforced. If more heat integrations are enforced, the number of possible combinations also increases.

5.1.2.2 Changes in Heat Duty

There are changes in the condenser and reboiler heat duties after heat integration, and it is represented in Fig. 5.3. In the case of heat integration between a condenser and reboiler, their energy reduction is equal to the energy exchanged between them (Fig. 5.3a). Contrarily, in the case of internal integration at stages, the energy reduction at a condenser and at a reboiler is not equal to the energy exchanged by the stage-stage heat integration (Fig. 5.3b).

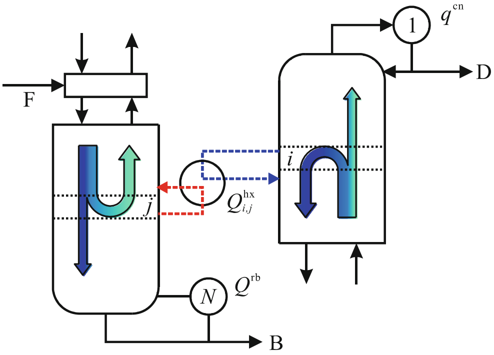
In Fig. 5.3, q_0^{cn} and Q_0^{rb} are the condenser and reboiler heat duty before any heat integration, q^{cn} and Q^{rb} are the condenser and reboiler heat duty after heat integration, and $Q_{i,j}^{\mathrm{hx}}$ is the amount of heat exchanged between stages i and j. When heat is exchanged between the condenser ($i = 1$) and reboiler ($j = N$), the amount of heat reduced at the condenser and reboiler is equal to the amount of heat transferred $Q_{1,N}^{\mathrm{hx}}$. Contrarily, when heat is exchanged between stages i and j, the amount of heat reduced at the condenser and reboiler is less than the amount of heat transferred $Q_{i,j}^{\mathrm{hx}}$. Furthermore, the reduction in condenser and reboiler heat duties depends on two factors: the locations i and j subject to heat integration and the amount of heat transferred $Q_{i,j}^{\mathrm{hx}}$.

5.1.2.3 Changes in Temperature Profile

The installation of heat exchangers in rectifying and stripping sections results in changes of the stage temperature due to the partial condensation and evaporation of components with higher and lower boiling points, respectively.

Figure 5.4 shows a conceptual representation of the partial evaporation and condensation of components in stages with heat integration. The degradation of arrows from dark to light represents the composition changes of components from higher to lower boiling point. In the rectifying section, while the components with a higher boiling point are partially condensed, the components with low boiling point move towards the top of the column. As a consequence, the stage temperature decreases because the composition of lower boiling point components increases. Contrarily in the stripping section, while the components with a lower boiling point are partially evaporated, the components with high boiling point move towards the bottom of the column. As a consequence, the stage temperature increases because the composition of higher boiling point components increases.

Fig. 5.4 Partial evaporation and condensation in heat-integrated stages



These temperature changes are difficult to estimate and to calculate because changes in the composition and temperature depend on the locations i and j subject to heat integration and the amount of heat transferred $Q_{i,j}^{\mathrm{hx}}$.

Because of the aforementioned differences between typical condenser–reboiler heat integration and heat integration at stages, the design, simulation, and optimization of intensified distillation processes through heat integration become more difficult. In the following sections, simulation and optimization approaches are proposed and validated through case studies in which the heat-integrated alternatives are better from the energy and economic viewpoints.

5.2 Simulation and Optimization of Heat-Integrated Intensified Distillation

Simulations can readily be done by process simulators or numerical analysis software. In process simulators, the governing equations for chemical processes and equipment are embedded in an object-oriented or equation-oriented environment while in the numerical analysis software, the process and equipment model must be programmed by the user. Similarly, optimization can be done by using built-in tools in process simulators, built-in tools in optimization software, or by programming an optimization algorithm.

Recent developments in process simulation and optimization techniques have facilitated its combined application to solve complex problems. However, in most cases, the use of built-in optimization tools in process simulators are limited to the solution of nonlinear constrained or unconstrained problems involving only continuous variables. In addition, convergence is difficult and usually fails to find feasible solutions.

This section presents a simulation-based optimization to find optimal heat-integrated intensified distillation processes by combining a mixed integer linear programming (MIP) optimization algorithm that can deal with all combinatorial problems (Sect. 5.1.2.1) and a process simulator that can deal with all the inherent nonlinearities and nonconvexities in distillation (Sects. 5.1.2.2 and 5.1.2.3) to find the optimal heat-integrated distillation process for nonreactive and reactive systems. The presented approaches in the next sections can effectively substitute trial-and-error approaches based on extensive simulations and complex mixed integer nonlinear programming problems (MINLP).

5.2.1 Simulation and Optimization for Nonreactive Systems

It is necessary to determine the objective function. When well-known equipment is used, or there is reliable data to estimate the cost, economic minimization should be preferred. However, when nonstandard equipment is used, or there is a high

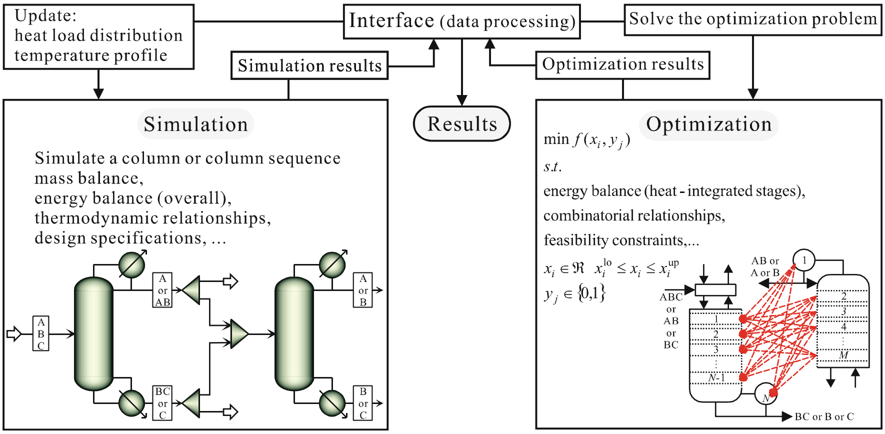


Fig. 5.5 Simulation-based optimization approach for nonreactive systems

uncertainty in their cost, energy minimization should be preferred. Although the minimization of economic and energy criteria is dominant, entropy production, environmental impact, or another criterion can be chosen without any major changes in the optimization procedure.

In Sect. 5.3.1 the objective function is to minimize the cost and energy requirement, the continuous variables are the vapor flow rate and its pressure and temperature at the compressor outlet and at each heat-integrated stage, and the integer variables are the locations and the number of compressors and heat-integrated stages. In Sects. 5.3.2, 5.3.3, and 5.4.2, the objective function is to minimize the energy, the continuous variables are the pressure at each section, the vapor flow rate to the compressor, and the heat distribution in heat-integrated distillation column (HIDiC), and the integer variables are the locations and the number of heat-integrated stages (Sects. 5.3.3 and 5.4.2).

The optimization approaches to design HIDiC in Sect 5.3 use extensive simulations or graphical methods for the separation of binary or multicomponent mixtures into two product streams. The proposed optimization approach in this chapter to find heat-integrated intensified distillation is described in Fig. 5.5. It takes the advantages from mixed integer linear optimization to find the locations of heat-integrated stages and the robustness of process simulation to deal with all the inherent nonlinearities and nonconvexities in distillation.

In Fig. 5.5 a column simulation can be a HIDiC or one with vapor recompression while a column sequence simulation can be a conventional sequence or a thermally coupled configuration for the separation of multicomponent mixtures. The simulation and optimization variables are solved iteratively until they converge to the final results. The involved variables in the simulation are continuous (e.g., pressure, temperature, molar flow, liquid or vapor composition) and integer (number of stages, feed stage) while in the optimization x_i are the continuous variables (e.g., heat load distribution) and y_j are the integer variables (e.g., number of heat exchangers, location(s) of heat-integrated stages). x_i^{lo} and x_i^{up} are the lower and upper bounds for continuous variables. Microsoft Excel can be used as an interface to handle the data between the simulation and optimization.

5.2.2 *Simulation and Optimization for Reactive Systems*

For reactive systems, the simulation and optimization approach is similar to the one in Fig. 5.5; however, there are some important features that must be considered in reactive systems. Unlike for nonreactive systems, the conversion is the most important factor when the stream leaves the reactive distillation. Otherwise, the whole system will not meet the composition specifications and even some of the continuous variables (e.g., reflux ratio, reboiler duty) will be used to adjust the product compositions. Therefore, the number of reactive stages and the holdup in the reactive stage need to be considered carefully before the optimization procedure.

A large reactive holdup is required to initialize the reactive system simulation. After this, the column diameter can be calculated in the process simulator. By using this diameter and the setting of the weir height, the holdup of each stage can be determined. As for the reactive section of the column, the catalyst volume in each tray is assumed to occupy half of the total holdup.

The proposed optimization approach in this chapter to find heat-integrated intensified reactive distillation is described in Fig. 5.6. It assumes complete conversion of reactants to products. It can also be seen that reactive holdup and number of trays can be updated and solved iteratively until it converges.

The simulation of reactive systems is not easy to converge to feasible results because of the complexity of reaction kinetics and thermodynamics. Due to the

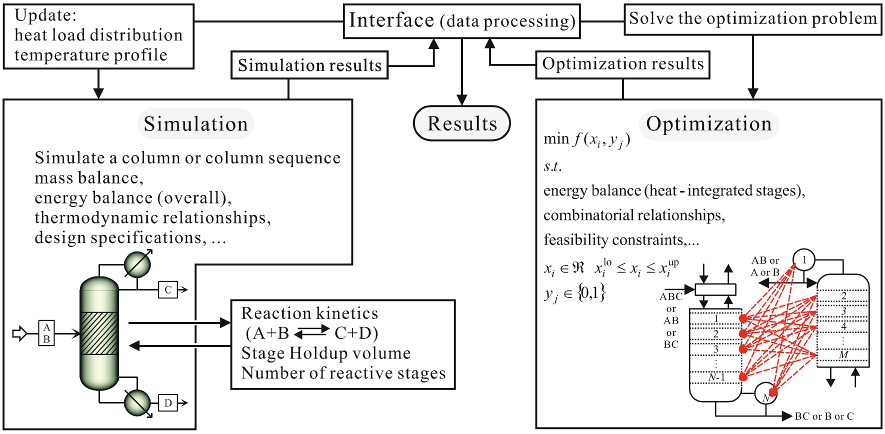


Fig. 5.6 Simulation-based optimization approach for reactive systems

complexity of reactive system characteristics, the optimization of these kinds of reactive distillation with heat integration is usually determined by sequential iterative methods. It means that the design variables need to be analyzed first and then run the simulations one at a time to find the optimal result.

5.3 Heat Pump-Assisted Distillation

Heat pump-assisted distillation processes have been proposed to reduce the energy consumption is distillation by increasing the pressure and temperature of the vapor streams in the rectifying section to exchange heat with the liquid streams in the stripping section. The vapor recompression is used to upgrade the heat by compressing the vapor distillate or a working fluid while the internally HIDiC enhances both heat and mass transfer [5]. In this section, the aforementioned applications and their working principles are covered.

5.3.1 Vapor Recompression Columns (VRC)

Conventional mechanical vapor recompression and vapor compression columns (MVR and VC) require either work input or external driving thermal energy to remove the heat from a low-temperature source and to transform it to a higher temperature level [6]. Figure 5.7 shows the working principle for MVR and VC in which a liquid boils or a vapor condenses at a higher temperature if its pressure is increased. In the figure, the low-pressure vapor passes through the compressor where it is compressed to a higher pressure by the application of work.

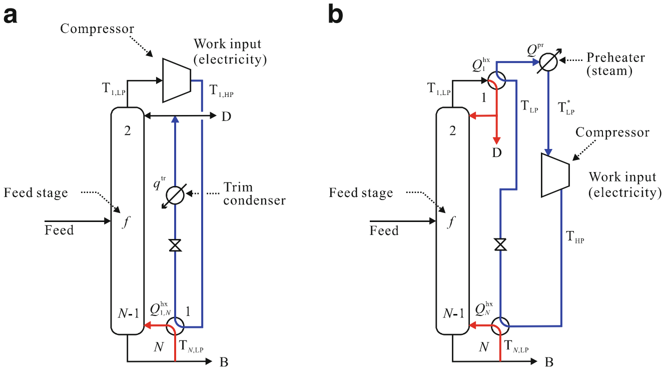


Fig. 5.7 Vapor recompression columns. (**a**) MVR. (**b**) VC

The resulting high-temperature vapor gives its latent heat at a high temperature to the low-pressure liquid causing it to boil. Then, the condensed liquid passed through a throttle valve and expands back to a low-pressure liquid. Figure 5.7a uses its own vapor streams while Fig. 5.7b uses an external fluid in the vapor compression cycle.

In Fig. 5.7a, the vapor leaving the column at low temperature ($T_{1,\mathrm{LP}}$) is recompressed to reach an outlet temperature ($T_{1,\mathrm{HP}}$) that must be higher than the liquid inlet temperature ($T_{N,\mathrm{LP}}$) in the bottom stage to generate the heat integration $Q_{1,N}^{\mathrm{hx}}$. After decompression of the reflux liquid stream a trim condenser (q^{tr}) is used to returned the stream as a saturated or subcooled liquid.

In Fig. 5.7b, the vapor and liquid streams leaving the column at low temperature ($T_{1,\mathrm{LP}}$ and $T_{N,\mathrm{LP}}$) are condensed and boiled, respectively, by means of an external vapor compression cycle. In this case, the vapor temperature after compression (T_{HP}) must be higher than the liquid inlet temperature ($T_{N,\mathrm{LP}}$) and the liquid temperature after the throttling valve (T_{LP}) must be lower than the vapor inlet temperature ($T_{1,\mathrm{LP}}$) to generate the heat integrations Q_1^{hx} and Q_N^{hx}, respectively. After Q_1^{hx}, a preheater (Q^{pr}) is used to return the working fluid to the compressor as a saturated or superheated vapor at a temperature T_{LP}^{*}.

Economic and/or energy savings have been reported for MVR to recover chemicals in wastewater streams [7] and the separation of binary mixtures [3, 8], and for VC to the separation of binary mixtures [9]. In MVR and VC, the vapor stream is compressed until it reaches a temperature higher than that in the reboiler and cooled down at a temperature lower than that in the condenser; therefore, the compressor temperature and pressure differences are at their highest values ($T_{1,\mathrm{HP}} - T_{1,\mathrm{LP}}$ for MVR, and $T_{\mathrm{HP}} - T_{\mathrm{LP}}{}^{*}$ for VC), which can result in high compression work duty, thus high electricity cost. In the following subsections, heat-pump distillation processes with two-staged recompression and heat-integrated stages are covered in detail.

5.3.1.1 MVR with Heat-Integrated Stages

By reducing the temperature and pressure difference in the inlet and outlet streams in the compressor, savings in work duty and electricity can be attained. Figure 5.8a shows the heat integration possibilities between the top vapor stream leaving the column and stages in the rectifying section. For MVR with heat-integrated stages, it is necessary to use a trim reboiler (Q^{tr}) to provide the remaining heat duty to achieve the desired product purity. Equation (5.1) shows the temperature relations between MVR and MVR with heat-integrated stages in the left and right side, respectively.

$$T_{N,\mathrm{HP}} - T_{1,\mathrm{LP}} > T_{j,\mathrm{HP}} - T_{1,\mathrm{LP}} \quad j \in f+1, \ldots, N-1 \tag{5.1}$$

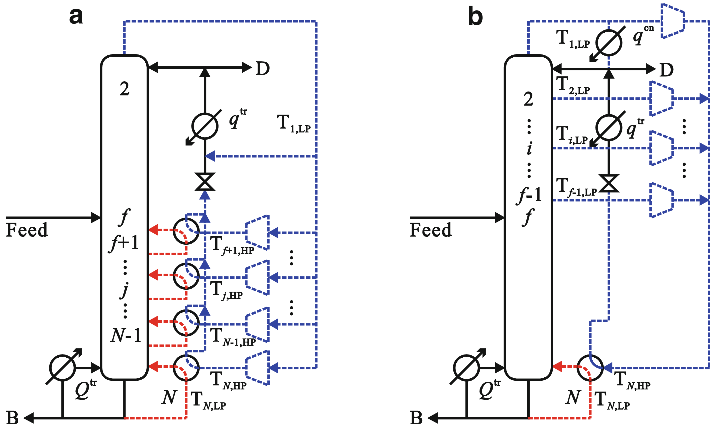


Fig. 5.8 Vapor recompression with heat-integrated stages. (**a**) Stripping section. (**b**) Rectifying section

Assuming an ideal, isentropic, diabatic expansion the compressor outlet temperature can be calculated as shown in Eqs. (5.2) and (5.3) for MVR and MVR with heat-integrated stages in the stripping section

$$T_{N,\mathrm{HP}} = T_{1,\mathrm{LP}}(P_{N,\mathrm{HP}}/P_{1,\mathrm{LP}})^{(\gamma-1)/\gamma} \tag{5.2}$$

$$T_{j,\mathrm{HP}} = T_{1,\mathrm{LP}}\left(P_{j,\mathrm{HP}}/P_{1,\mathrm{LP}}\right)^{(\gamma-1)/\gamma} \quad j \in f+1, \ldots, N-1 \tag{5.3}$$

where $P_{N,\mathrm{HP}}$, $P_{j,\mathrm{HP}}$, and $P_{1,\mathrm{LP}}$ are the high pressure at stage N, j and the low pressure at stage 1, respectively. $\gamma = Cp/Cv$ is called isentropic exponent. By combining Eqs. (5.1)–(5.3), it can be demonstrated that $P_{N,\mathrm{HP}} > P_{j,\mathrm{HP}}$.

Figure 5.8b shows the heat integration possibilities between vapor streams at stages in the rectifying section and the bottom liquid stream. Equation (5.4) shows the temperature relations between MVR and MVR with heat-integrated stages in the left and right side, respectively.

$$T_{N,\mathrm{HP}} - T_{1,\mathrm{LP}} > T_{N,\mathrm{HP}} - T_{i,\mathrm{LP}} \quad i \in 2, \ldots, f-1 \tag{5.4}$$

For MVR with vapor streams at stages in the rectifying section, the compressor outlet pressure can be calculated as shown in Eq. (5.5)

$$T_{N,\mathrm{HP}} = T_{i,\mathrm{LP}}(P_{N,\mathrm{HP}}/P_{i,\mathrm{LP}})^{(\gamma-1)/\gamma} \quad i \in 2, \ldots, f-1 \tag{5.5}$$

where $P_{i,\mathrm{LP}}$ is the low pressure at stage i. By combining Eqs. (5.2), (5.4), and (5.5), it can be demonstrated that $P_{i,\mathrm{LP}} > P_{1,\mathrm{LP}}$.

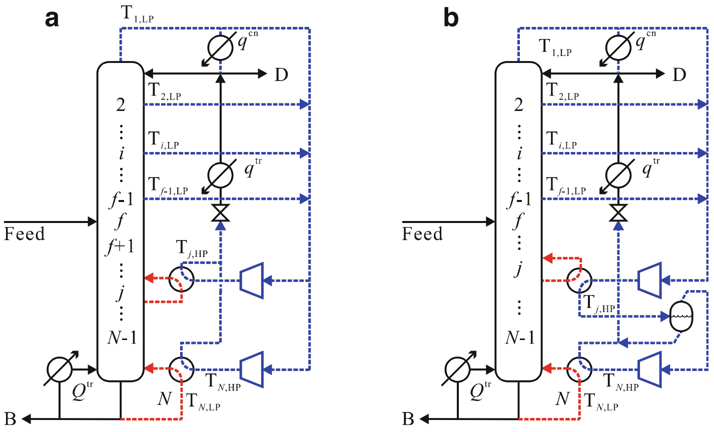


Fig. 5.9 Two-staged vapor recompression with heat-integrated stages. (**a**) Parallel. (**b**) series

Table 5.1 Simulation conditions for the n-heptane/benzene separation

Feed molar flow (kmol/h)	100
Feed composition n-heptane/benzene (mol%)	50/50
Feed condition	Saturated liquid
Condenser pressure (kPa)	100
Product purity n-heptane/benzene (mol%)	99.9/99.9

Therefore, the relations in Eqs. (5.6) and (5.7) can be derived

$$T_{N,\mathrm{HP}} > T_{j,\mathrm{HP}} > T_{i,\mathrm{LP}} > T_{1,\mathrm{LP}} \quad i \in 2,\ldots,f-1,\ \ j \in f+1,\ldots,N-1 \qquad (5.6)$$

$$P_{N,\mathrm{HP}} > P_{j,\mathrm{HP}} > P_{i,\mathrm{LP}} > P_{1,\mathrm{LP}} \quad i \in 2,\ldots,f-1,\ \ j \in f+1,\ldots,N-1 \qquad (5.7)$$

In addition to the feasible combinations for heat integration, the total work duty can be distributed in two or more compressors. This alternative is called in this chapter multistage mechanical vapor recompression. Figure 5.9 shows the possibilities to set two compressors in parallel (Fig. 5.9a) and in series (Fig. 5.9b).

Heat-integrated stages result in changes in condenser and reboiler heat duty reduction (Sect. 5.1.2.2) and the column temperature profile (Sect. 5.1.2.3); therefore, the best designs for MVR and MVR with heat-integrated stages are different. Table 5.1 shows the simulation conditions for the separation of an n-heptane/benzene mixture.

Simulations were done for this case study in Aspen Plus V8.0 by using the block RadFrac. Sensitivity analysis was done by varying the total number of stages (*N*), feed stage (*FS*) and heat-integrated stage locations (*j*) for MVR and MVR with heat-integrated stages. The simulation results were compared for the best design in terms of energy requirement (ER) and total annual cost (TAC) according to Eqs. (5.8) and (5.9)

Table 5.2 Additional parameters to calculate the TAC

Parameter	Value
Cooling water cost ($/MWh)	0.86
Steam cost ($/MWh)	45.4
Electricity cost ($/MWh)	60.0
Cooling water temperature inlet/outlet (°C)	20/40
Steam temperature (°C)	147.6
Overall heat transfer coefficient condenser/reboiler/exchanger (kW/m^{2}K)	0.7/1.0/0.7
Compressor efficiency (–)	0.7
$\Delta T_{\min}$ (°C)	10.0

$$\mathrm{ER} = Q^{\mathrm{tr}} + \eta \sum_{k \in \mathrm{COMP}} W_k \tag{5.8}$$

$$\mathrm{TAC} = \frac{\mathrm{EC}}{\theta} + \varphi \mathrm{OC} \tag{5.9}$$

where η is the primary energy equivalent of electricity generation, θ is the payback time in years, and φ is the annual operation time in hours. W_k is the work duty of a compressor k, and COMP is the set of all compressors. EC is the equipment cost that comprises the column, trays, heat exchangers, and compressors cost and OC is the operation cost that comprises cooling water, steam, and electricity. The TAC was calculated according to the Guthrie method [10]. Note that η is a parameter that converts second energy sources (i.e., electricity generation) into primary energy sources (i.e., steam generation). The International Energy Agency estimates the primary energy equivalent from the electricity generation by assuming an efficiency of 33 % ($\eta = 1/0.33 = 3.03$), which is the average of nuclear power plants in Europe [11]. According to the Japanese Ministry of Economy, Trade, and Industry [12], the electricity generation efficiency in Japan is around 41 %, and the world average is 35 % ($\eta = 2.44$, and $\eta = 2.86$), respectively. Table 5.2 shows additional parameters to calculate EC and OC in Eq. (5.9).

Figure 5.10 shows the energy requirements for the simulation conditions in Table 5.1. The results show that MVR with heat-integrated stages require less energy than conventional MVR at conditions close to the minimum reflux ratio ($N = 100$), which agree with a previous work [13]. Furthermore, similar energy savings can be obtained at minimum reflux conditions regarding the stage subject to heat integration.

As the total number of stages decreases (higher reflux operation), the energy requirement for MVR with heat-integrated stages increases at a rate higher than that in conventional MVR up to the point that the latter is the best option ($N = 40$). In addition, as the stage subject to heat integration is set further from the reboiler, the increase rate of ER becomes higher ($i = N - 10$).

Figure 5.11 shows the simulation results when TAC is minimized for each given value of N. It shows that MVR with heat-integrated stages ($i = N - 2$) is economically better than conventional MVR for columns over 70 total stages ($N > 70$). This

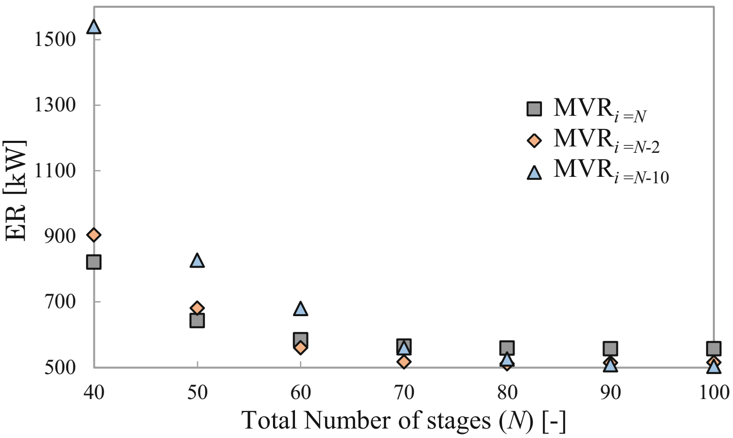


Fig. 5.10 Energy minimization for MVR and MVR with heat-integrated stages for the n-heptane/benzene separation

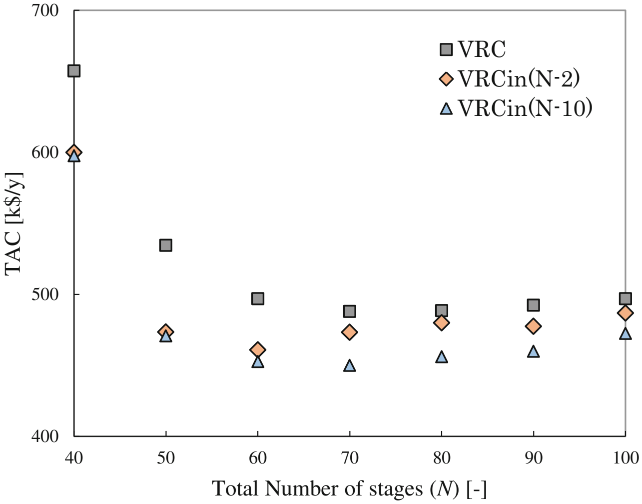


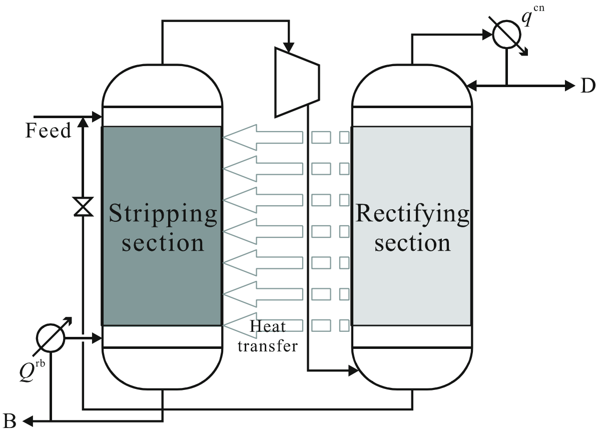
Fig. 5.11 TAC minimization for MVR and MVR with heat-integrated stages for the n-heptane/benzene separation

cost reduction resulted from the reduction of electricity requirements and compressor size.

The comparison between MVR and MVR with heat-integrated stages for the presented separation of an n-heptane/benzene mixture showed that the latter can attain ER reduction around 10 % when the column operates near the minimum reflux ratio, but the ER reduction is less in columns at higher reflux ratio conditions.

For the results in Figs. 5.10 and 5.11, the optimization variable is the top vapor flow rate that enters the compressor. The relation between vapor flow rate and

Fig. 5.12 Conceptual HIDiC representation



pressure change is very important to obtain the best heat exchange between the upgraded heat of the vapor leaving the condenser and a stage subject to heat integration.

5.3.2 Heat-Integrated Distillation Column

The HIDiC is an intensified distillation column that involves internal heat integration between the whole rectifying and the whole stripping sections, and it is also another kind of heat-pump distillation column. Although the idea that actually included internal heat integration between part of the rectifying and the stripping sections was conceived in the late 1970s [14], it was not until 1990s that the importance of internal heat integration gained interest, and it was demonstrated that it plays an important role in energy efficiency for a given separation. Therefore, the idea of internal heat integration was extended to realize heat integration in the whole rectifying and the whole stripping sections. Because HIDiC offers several attractive features, its industrialization in chemical and petrochemical process industries has been encouraged. These features include mainly [15]:

1. Energy efficiency higher than that in conventional distillation columns.
2. In the ideal case, zero external reflux and reboil flows.

Figure 5.12 shows the conceptual representation of a HIDiC, which has been used to find the heat loads at all stages in the column. In addition, the design, simulation, and optimization results of HIDiC show that it can attain energy savings more than 50 %, economic savings, and reduction in the entropy production for the separation of binary mixtures and ternary mixtures [16–31].

Although Fig. 5.12 has been used as conceptual representation for simulation and optimization purposes, the construction can be either done by using two concentric tubes arrangement with different tube circumferences (Fig. 5.13) or

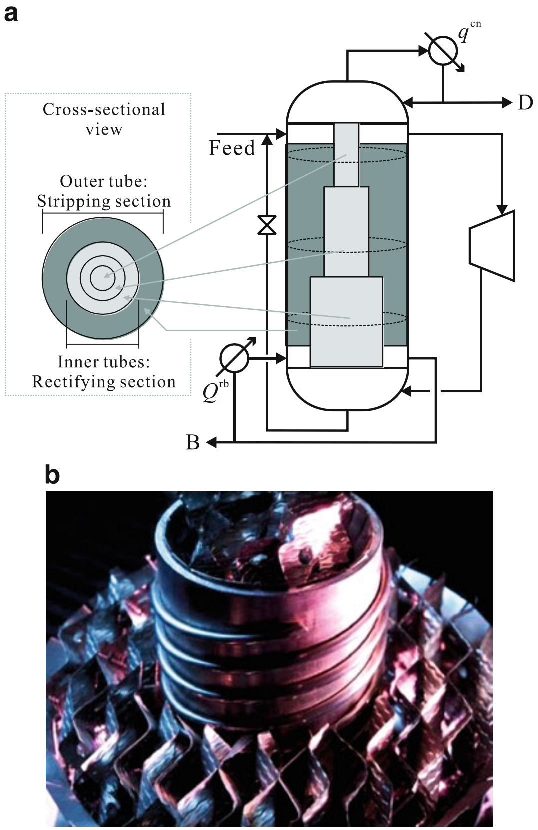


Fig. 5.13 HIDiC design with inner tubes of different diameter. (**a**) conceptual representation. (**b**) practical implementation (*Source*: Kimura Chemical Plants Co., Ltd. in website of New Energy and Industrial Technology Development Organization (NEDO). http://www.nedo.go.jp/hyoukabu/articles/201214kcpc/index.html Accessed 24 Feb 2015)

multiple tubes arrangement in which the rectifying section is in the inner tubes while the stripping section is in the outer tubes (Fig. 5.14).

In Fig. 5.13a, the inner tubes make the rectifying section (lighter solid area) while the outer tubes make the stripping section (darker solid area). It also can be seeing that the cross-sectional area decreases towards the bottom in the stripping section and towards the top in the rectifying section. The diameter of the rectifying section gradually decreases for the ideal case [18] and segmentally for a more practical case [19, 20]. Figure 5.13b shows the actual equipment of a concentric HIDiC. The inner part is the rectifying section and the outer part is the stripping section.

The HIDiC configuration in Fig. 5.14 has multiple concentric cylinders. Similarly, the inner tubes make the rectifying section (lighter solid area) while the outer tubes make the stripping section (darker solid area). Also the cross-sectional area

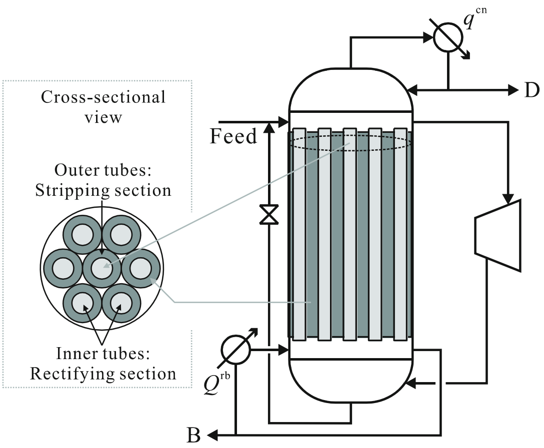


Fig. 5.14 HIDiC design with multiple concentric tubes

decreases towards the bottom in the stripping section and towards the top in the rectifying section, but the changes in diameter are small. This configuration has been implemented at a pilot plant scale [22].

The selection of the best configuration is case specific because for the separation of some mixtures, the constant heat distribution with variable heat transfer area is better than the constant heat transfer area with variable heat load [18].

5.3.3 *HIDiC with Fewer Heat-Integrated Stages*

Typically in HIDiC, heat integration takes place along the whole rectifying and stripping sections, which can raise maintenance issues due to blockage in the column internals (trays or packing) because of deposition of solid particles in mixtures containing suspended solids (e.g., pigments, catalysts, ashes), monomers which can undergo polymerization or solidification reactions, and salts (e.g., calcium sulfate) which can produce crystals that can also deposit in the heat transfer surface [24].

In addition, the operability and controllability of HIDiC are other important issues. The complex heat integration structure of HIDiC might make its operation more difficult than conventional distillation columns because HIDiC can require more complex PID control configurations [25], it can be more sensitive to the system disturbances [26], and it can have multiple steady states depending on the heat load distribution changes along the column during operation [27].

Because of the aforementioned issues in typical HIDiC, its implementation in chemical and petrochemical plants has not been realized. However, the reduction of the number of heat-integrated stages can alleviate maintenance and operability issues while attaining high energy savings. The configurations with less heat-integrated stages have been proven to be better than fully integrated

Table 5.3 Effect of the number of side heat exchangers for the benzene/toluene mixture [29]

Feed molar flow benzene/toluene (kmol/h)	50/50		
Liquid molar fraction in the feed (%)	50		
Product purity benzene/toluene (mol%)	99.9/99.9		
Stages in the rectifying section (M) (–)	15		
Stages in the stripping section (N) (–)	18		
Rectifying section pressure (kPa)	101.3		
Number of side heat exchangers	3	4	5
Total amount of heat exchanged (kW)	1412	1586	1570
Total heat transfer area (m^2)	393	350	399
Rectifying section pressure (kPa)	225	212	213
Combinations of side heat exchanges (i,j) (–) $i \in 1, \ldots, M$ $j \in 1, \ldots, N$	1,3	1,1	1,1
	12,17	8,4	6,4
	15,18	14,17	13,11
		15,18	14,17
			15,18

HIDiC through the solution of optimization techniques and numerical analysis [3, 17, 28, 29].

The optimal heat distribution at stages in HIDiC is crucial for developing a column with a simpler structure. The heat distribution at each column section can be determined by the temperature difference profile between the rectifying section and the stripping section. In addition, the effect of internal heat integration on the reduction of reboiler heat load depends strongly on the location of heat exchange stages [28]. Table 5.3 shows the simulation conditions to design a HIDiC with few heat-integrated stages for the separation of a benzene/toluene mixture. The total heat transfer area of side heat exchangers becomes minimum when the number of side heat exchangers is four as shown in Fig. 5.15. The optimal number of heat integrations is case specific, and it largely depends on the shape of the reversible distillation curve for the given mixture.

5.3.3.1 Comparison Between MVR and HIDiC

Although several works have compared MVR and HIDiC schemes in terms of energy and economic savings, the results are not conclusive to consider one over the other. In fact, the selection of each technology is case specific. As confirmed in many research works [5–8, 13–22, 30, 31], MVR and HIDiC result in lower energy requirements and operation cost; however, they usually have higher equipment cost. Therefore, in some cases, the increase in equipment cost can overtake the reduction in operation cost [23]. Finally, the comparison between MVR, VC, and HIDiC has not considered heat pump systems with heat-integrated stages

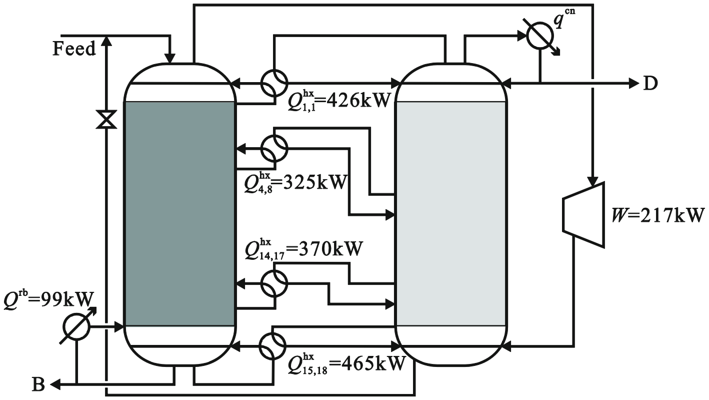


Fig. 5.15 HIDiC design with shifted rectifying and stripping sections [29]

(Sect. 5.3.1) or HIDiC with fewer heat-integrated stages (Sect. 5.3.3). These comparisons remain as open questions that must be assessed from the conceptual level to the final implementation.

5.4 Heat Integration Through Side Heat Exchangers

In addition to heat pump systems, there are other intensified distillation processes that avoid using a compressor. As seen in the previous section, a compressor is used to upgrade the heat of vapor streams; however, another way is by using the heat of vapor streams from other columns or processes to realize heat integration at stages. External heat integration (also known as multiple effect distillation, or multi-effect distillation) has been widely used as energy conservation method in which the condenser of a high-pressure column supplies heat to the reboiler of a low-pressure column. In this section, the concept of multi-effect distillation is extended to consider heat-integrated stages as an option for intensification of distillation columns.

5.4.1 Compressor-Free HIDiC

Although the potential high energy saving of HIDiC has been recognized, there are not commercial-scale HIDiC implementations. One reason is because petrochemical companies have plenty of steam from the direct cracking process which releases high cascade heat [24]. Another problem is that a big compressor with large discharge rate has to be installed. Finally, HIDiC is not suitable for the separation of mixtures with solid suspended particles (see Sect. 5.3.3).

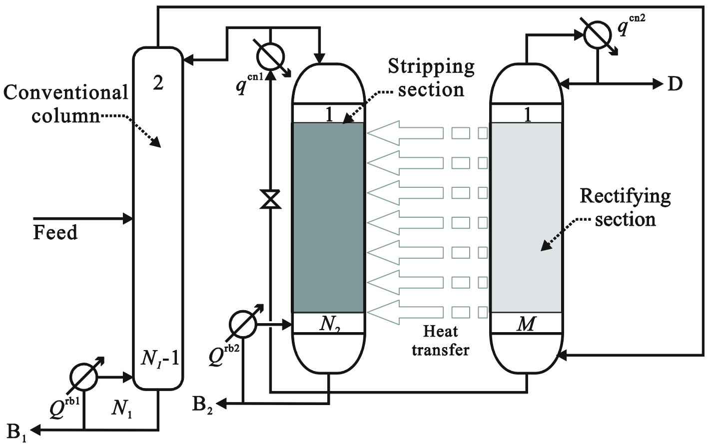


Fig. 5.16 Conceptual representation of a compressor-free HIDiC

To avoid the use of a compressor, a compressor-free HIDiC (CF-HIDiC) has been proposed [24, 32–34]. It has been studied to enrich bioethanol from diluted mixture [30], to recover solvents in wastewater streams [33], and to separate a benzene/toluene mixture [34]. Figure 5.16 shows a conceptual representation of a CF-HIDiC. The feed is supplied to a conventional column at high pressure, and its top vapor stream is fed to the rectifying section of the HIDiC column, then the liquid leaving the rectifying section enters the top of the stripping section of the HIDiC column. It can be seen that the compressor is replaced by an additional column that supplies vapor streams at high pressure. In the case of ethanol enriching, the operation at high pressure results in serious fouling because the deposition of solid components, therefore vacuum conditions in the stripping section can be enforced to avoid fouling. Thus, the conventional column and the rectifying section can operate at atmospheric pressure.

5.4.2 Externally and Internally Heat-Integrated Distillation

Heat-integrated stages by means of side heat exchangers have been proposed to separate binary mixtures of close boiling points [35], the separation of ternary [1, 2, 36, 37], and multicomponent mixtures [38]. However, as the number of components in the mixtures increases, the number of possible distillation sequences increases and the heat integration possibilities for all sequences enormously increase. Therefore, most of the simulation, optimization, and design approaches have been limited to two distillation columns.

Table 5.4 shows the simulation conditions for the separation of two ternary mixtures, in which the conventional, externally heat-integrated sequence (multi-effect distillation), and internally heat-integrated sequence are compared.

Table 5.4 Simulation conditions for ternary mixtures

Mixture	Case 1 Cyclopentane (A)/benzene (B)/toluene (C)	Case 2 Methanol (A)/ethanol (B)/propanol (C)
Feed molar flow (kmol/h)	100	100
Feed composition (A/B/C) (mol%)	40/30/30	25/50/25
Product purity (A/B/C) (mol%)	98/98/98	99/99/99
Feed condition	Saturated liquid	Saturated liquid
Low-pressure column (LPC) (kPa)	100	100
High-pressure column (HPC) (kPa)	Variable	Variable

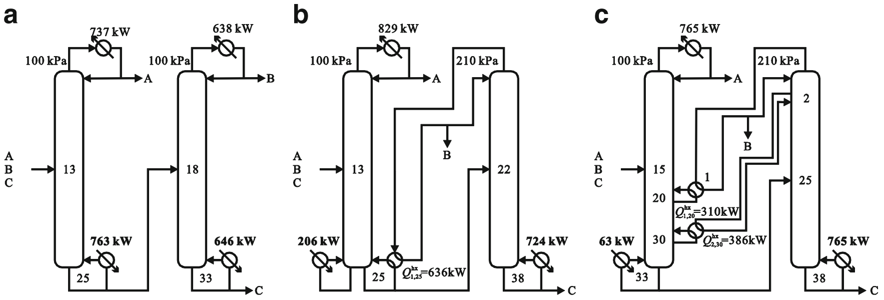


Fig. 5.17 Solutions for case 1. (**a**) Conventional. (**b**) Multi-effect. (**c**) Heat-integrated stages

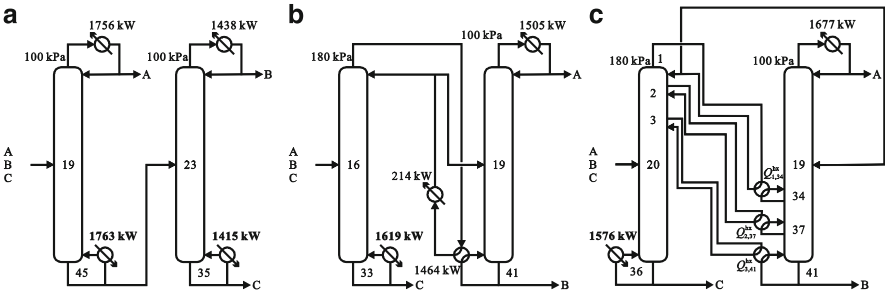


Fig. 5.18 Solutions for case 2. (**a**) Conventional. (**b**) Multi-effect. (**c**) Heat-integrated stages

Figures 5.17 and 5.18 show the results for the mixtures in Table 5.4. For the separation in case 1, the best option is the direct distillation sequence in all cases while for the separation in case 2, the best option is the indirect distillation sequence in all cases. The energy saving for heat-integrated stages is higher than the typical multi-effect distillation for both cases.

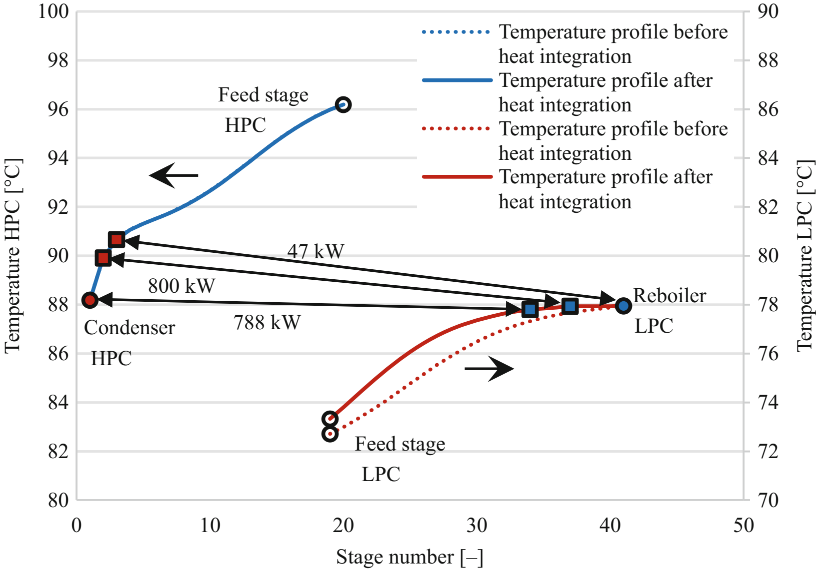


Fig. 5.19 Changes in the temperature profile for case 2 with heat-integrated stages

Each alternative is optimized individually in Figs. 5.17 and 5.18. The trim reboiler heat duty in Fig. 5.17b can be reduced by increasing the heat exchange between columns. Although the total amount of heat exchanged in Fig. 5.17c (696 kW) is higher than that in Fig. 5.17b (636 kW), the temperature difference in the former is also higher than that in the latter; therefore, the total heat transfer area and the exchangers cost will not largely change between Fig. 5.17b, c.

In Fig. 5.18, heat integration between stages can be used to eliminate the trim condenser by supplying heat from stage 1 in the HPC to stage 34 in the LPC. The total amount of heat exchanged in Fig. 5.18c (1635 kW) is higher than that in Fig. 5.18b (1464 kW); however, the temperature difference in the former is also higher than that in the latter; therefore, the total heat transfer area and the exchangers cost will not largely change between Fig. 5.18b, c.

Figure 5.19 shows the changes in the temperature profile in the rectifying section of the HPC and the stripping section of the LPC for case 2 in Table 5.4. When heat integration is done at stages close to the condenser, there are almost no changes in its temperature profile. Contrarily, when heat integration is done at stages far from the reboiler, there are changes in its temperature profile. These changes in the temperature profile, amount of heat exchanged, and heat transfer area must be considered and solved simultaneously at the simulation and optimization of intensified heat-integrated distillation.

5.5 Heat-Integrated Distillation Involving Reactive Systems

By combining two important operations (reaction and separation) into a single vessel, reactive distillation has demonstrated its potential for capital productivity improvements, selectivity improvements, reduced energy use, and the reduction or elimination of solvents in the process. Some reviews about reactive distillation have been done and a total of 562 publications of reactive distillation for the period of 1971–1999 [39], 1105 publications and 814 US patents between 1971 and 2007 [40], and over one hundred industrially or potentially important reactions for reactive distillation applications [41] have been studied. This shows the rapid progress of this technology in recent years, and its importance in industrial applications.

For exothermic reaction systems utilizing reactive distillation, the operating energy can be reduced by making use of this heat of reactions to partially supply vapor traffic inside the column. However, many endothermic reaction systems can still benefit from the reactive distillation technology for conversion and selectivity improvements. For these endothermic reaction systems, operating the reactive distillation column at higher pressure (which means the system is operated at higher temperature condition) would benefit from the shifting of the reaction to the product side. Moreover, heat integration methods via pressurized operation in the open literature can be utilized to further save energy of these reactive distillation systems.

In the following subsections, reactive thermally coupled and reactive multi-effect will be addressed for the hydrolysis of methyl acetate and esterification of isopropyl alcohol.

5.5.1 *Hydrolysis of Methyl Acetate Reactive Distillation Process*

In a polyvinyl alcohol (PVA) plant shown in Fig. 5.20, reaction stoichiometry indicates that equal moles of methyl acetate are generated for every mole of PVA produced. One way to convert methyl acetate back to acetic acid (the raw material of PVA plant) is via methyl acetate hydrolysis. The best design of a reactive

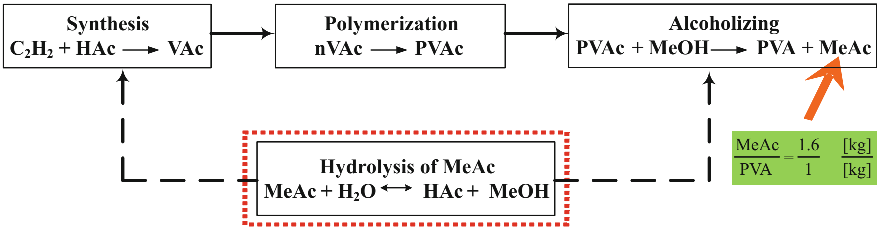


Fig. 5.20 Polyvinyl alcohol production process block diagram

distillation process has been proposed by Lin and his coworkers [42, 43]. The design of this process for exploring the reactive HIDiC and reactive multi-effect of heat-integration in a reactive distillation system with methyl acetate hydrolysis reaction was studied by Lee et al. [44]. From their work, reactive multi-effect is a better configuration than the arrangement of reactive HIDiC. For understanding the reactive multi-effect, the design of this arrangement will be introduced in the following subsections. Moreover, the thermally coupled configuration of this process will be studied to demonstrate the result of energy saving for these two kinds of heat-integrated methods.

5.5.1.1 Reaction Kinetics and Phase Equilibrium

There are four components in the methyl acetate hydrolysis process including two reactants: methyl acetate (MeAc) and water (H_2O); and two products: acetic acid (HAc) and methanol (MeOH). The endothermic reversible reaction of this process is shown below:

$$H_2O + CH_3COOCH_3 \rightleftarrows CH_3COOH + CH_3OH \tag{5.10}$$

Two kinetic model forms (pseudo-homogeneous and adsorption based) were used to fit the experimental data, and the used heterogeneous catalyst was Amberlyst® 15 [45, 46]. It was found that the adsorption-based model fits the experimental data better. Table 5.5 shows the kinetic model based on activity. M_i [kg/kmol] is the molecular weight of component i and R (8.314 kJ/kmol/K) is the gas constant. Notice that the unit of the reaction constants is in kmol/kg_{cat}/s which will be converted to kmol/m^3/s in the simulation study with the assumption of catalyst density at 770 kg/m^3 and catalyst occupied half of the liquid holdup in the reactive tray.

The equilibrium constants ($K_{\text{eq}} = k_f/k_r$) calculated at two different temperatures are also listed in Table 5.5. Since the value of the equilibrium constant is small, excess water design has been conducted in order to drive methyl acetate to near

Table 5.5 Kinetic model and parameters for the studied system

Kinetic model (catalyst)	k_f	K_{eq}
Adsorption-based model (Amberlyst® 15)	At $T = 333$ K $k_f = 1.01 \times 10^{-6}$ [kmol/kg_{cat}/s]	At $T = 333$ K $K_{\text{eq}} = 0.039$
$r = m_{\text{cat}} \cdot \frac{k_f a_{\text{MeAc}} a_{\text{H}_2\text{O}} - k_r a_{\text{HAc}} a_{\text{MeOH}}}{\left(a'_{\text{MeAc}} + a'_{\text{H}_2\text{O}} + a'_{\text{HAc}} + a'_{\text{MeOH}}\right)^2}$ $a'_i = \frac{K_i a_i}{M_i}, K_{\text{MeAc}} = 4.15,\ K_{\text{H}_2\text{O}} = 5.24,\ K_{\text{HAc}} = 3.15,$ $K_{\text{MeOH}} = 5.64$		
$k_f = 1.000 \times 10^4 \exp\left(\frac{-63,730}{RT}\right)$ $k_r = 7.862 \times 10^4 \exp\left(\frac{-60,470}{RT}\right)$ $\Delta H = 3260$ (kJ/kmol)	At $T = 393$ K k_f $= 3.38 \times 10^{-5}$ (kmol/kg_{cat}/s)	At $T = 393$ K $K_{\text{eq}} = 0.046$

complete conversion [42, 43]. Because the reaction is endothermic, the calculated equilibrium constant is more favorable at higher operating temperature ($K_{eq} = 0.046$ at 393 K against $K_{eq} = 0.039$ at 333 K). However, there is an upper limit on the operating temperature for Amberlyst® 15 at 120 °C. This information was used later to set the pressure upper limit in order to achieve heat-integration in the process.

The UNIQUAC model was used to calculate the liquid activity coefficient and Hayden and O'Connell (HOC) model was used to account for association in the vapor phase [47]. The parameters for the UNIQUAC model are listed in Table 5.6.

5.5.1.2 Base Design Flowsheet of the Overall Process

There are two azeotropes in the studied system. The boiling point ranking of the four components, as well as the two azeotropes, is shown in Table 5.7. It is found that although one product (HAc) is the heaviest boiling point component, the other product (MeOH) is in the second lightest boiling point component. Thus, it is more difficult to come up with the overall design flowsheet in Fig. 5.21 [43].

In Fig. 5.21, the flowsheet includes a reactive distillation column and two other columns. The two fresh feed streams enter into the reflux drum of the reactive distillation column, which is under total reflux operation and the reaction section is

Table 5.6 UNIQUAC model parameters for the methyl acetate hydrolysis

(i,j)	a_{ij} (K)	a_{ji} (K)	b_{ij} (K)	b_{ji} (K)	c_{ij} (K^{-1})	c_{ji} (K^{-1})
(1,2)	−0.9704	2.0346	−390.26	−65.245	0.003061	−0.003157
(1,3)	0.4364	−1.1162	62.19	−81.848	−0.0002724	0.001331
(1,4)	0.05101	0.2936	−422.38	98.120	0.0002402	0.00007674
(2,3)	0.7101	−0.7248	−62.97	−326.20	−0.001167	0.002355
(2,4)	−3.1453	2.0585	575.68	−219.04	0.006071	−0.007015
(3,4)	−0.01014	−0.9630	−593.70	265.83	0.002161	−0.0002013

1: HAc; 2: MeOH; 3: MeAc; 4: H_2O

Table 5.7 Boiling point ranking at 1 and 4.6 atm

Components boiling point ranking (from low to high)	1 atm	4.6 atm
MeAc/MeOH	53.65 °C (0.653/0.347)	101.73 °C (0.51/0.49)
MeAc/H_2O	56.43 °C (0.89/0.11)	106.16 °C (0.78/0.22)
MeAc	57.05 °C	109.00 °C
MeOH	64.53 °C	109.14 °C
H_2O	100.02 °C	149.29 °C
HAc	118.01 °C	175.92 °C

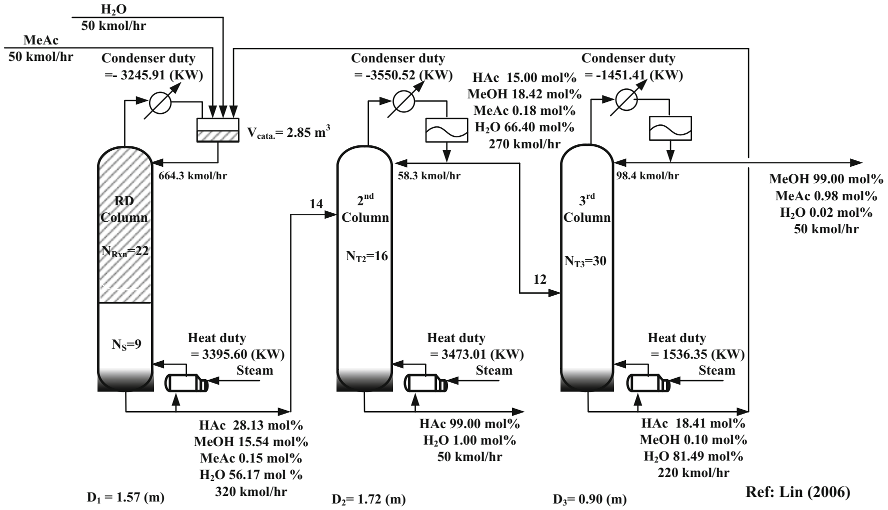


Fig. 5.21 Base design for the methyl acetate hydrolysis process using reactive distillation [43]

at the upper part of the column. All products and unreacted components are withdrawn from the bottom of the column and fed downstream to the separation system consisting of two columns. Since there is negligible methyl acetate in this feed stream to the downstream system, the separation should be easy because there is not an azeotrope in the ternary system of acetic acid, water, and methanol. The first column in the separation system separates acetic acid (heavy product) at the bottom, and the second column separates methanol (light product) at the top. The bottom of the second column is designed to avoid tangent pinch at the pure water end; thus, it contains mostly water with some acetic acid. The water-rich stream is recycled back to the reactive distillation column. The overall design shown in Fig. 5.21 corresponds to the minimum TAC. An extended design flowsheet with a mixed feed of MeAc and MeOH instead of pure MeAc feed has been also proposed, which used a similar design concept [42].

In Fig. 5.21, the indirect sequence (heaviest out first) was used for the design of the separation system. Heat integration of this separation system is possible by using a pre-fractionator column and a main column with side draw, a Petlyuk column, or a column with dividing wall.

5.5.2 *Isopropyl Acetate Reactive Distillation Process*

Another case is the esterification of isopropyl alcohol to produce isopropyl acetate (IPAc). Different process flowsheets for the esterification of acetic acid with C1-C5 alcohols have been developed [48]. These flowsheets show that high-purity ester products can be produced using reactive distillation technology. Furthermore, it was demonstrated that industrial quality ethyl acetate product can be obtained in a pilot plant test [49] by using the flowsheet [48].

Lee et al. [50] had proposed an interesting flowsheet for the heat integration through a thermally coupled arrangement. Unlike the conventional heat-integrated process, the combination of a reactive distillation and a decanter to split the organic and aqueous phases can be intensified by using a thermally coupled arrangement (see Sect. 5.5.3.2). Furthermore, reactive multi-effect distillation for this process will be also studied (see Sect. 5.5.4.2).

5.5.2.1 Reaction Kinetics and Phase Equilibrium

By reacting isopropanol (IPOH) with acetic acid (HAc), the esterification reaction will produce isopropyl acetate (IPAc) and water (H_2O). The reactions are reversible and the stoichiometric balance equation is shown below:

$$CH_3COOH + C_3H_7OH \rightleftarrows CH_3COOC_3H_7 + H_2O. \tag{5.11}$$

The used solid catalyst is the acidic ion-exchange resin of Amberlyst® 15. Table 5.8 displays the reaction rates expressed in the Langmuir-Hinshelwood model form. Notice that the kinetic model is represented in terms of activity and the reaction is catalyst-weight (m_{cat}) based. The catalyst-weight is computed by assuming that the solid catalyst occupies 50 % of the tray holdup and a catalyst density of 770 kg/m^3 is used to convert the volume into catalyst-weight. A FORTRAN subroutine is written in Aspen Plus to compute the extent of reaction at each reactive tray.

The isopropyl acetate process exhibits nonideal phase behavior and has four azeotropes. In order to accurately represent the phase equilibria of the process, it is essential to select a reliable thermodynamic model. To account for the nonideal vapor–liquid equilibrium (VLE) and vapor–liquid–liquid equilibrium (VLLE) for the quaternary system, the NRTL (non-random two-liquid) activity coefficient

Table 5.8 Kinetic equations for IPAc processes

Kinetic model (catalyst)	k_1 ($T = 363$ K)	K_{eq} ($T = 363$ K)
Langmuir-Hinshelwood/Hougen-Watson model (Amberlyst 15 by Gadewar et al. [51])	2.26×10^{-4} (kmol/(kg$_{cat}$ s))	8.7
$r = m_{cat} \frac{k_1 (a_{HAc} a_{IPOH} - a_{IPAc} a_{H_2O} / K_{eq})}{(1 + K_{HAc} a_{HAc} + K_{IPOH} a_{IPOH} + K_{IPAc} a_{IPAc} + K_{H_2O} a_{H_2O})^2}$		
$k_1 = 7.667 \times 10^{-5} \exp\left(23.81 - \frac{68,620.43}{RT}\right)$		
$K_{eq} = 8.7$, $K_{HAc} = 0.1976$, $K_{IPOH} = 0.2396$, $K_{IPAc} = 0.147$, $K_{H_2O} = 0.5079$		
Assumption: mol H$^+$/kg$_{cat}$ = 4.6×10^{-3}		

$R = 8.314$ (kJ/k mol/K), T (K), r (k mol/s), m_{cat} (kg$_{cat}$), x_i (mole fraction)

Table 5.9 The NRTL model coefficients for IPAc process

Comp. *i*	HAc	HAc	HAc	IPOH	IPOH	IPAc
Comp. *j*	IPOH	IPAc	H_2O	IPAc	H_2O	H_2O
b_{ij} (K)	−141.644	70.965	−110.580	191.086	20.057	415.478
b_{ji} (K)	40.962	77.900	424.060	157.103	833.042	1373.462
c_{ij}	0.305	0.301	0.299	0.3	0.325	0.3

Table 5.10 The compositions and temperatures of the azeotropes for IPAc process

Comp. *i*	Experimental components	Experimental Temp. (°C)	Computed components	Computed Temp. (°C)
IPOH-IPAc	(0.6508,0.3492)	80.1	(0.5984,0.4016)	78.54
IPOH-H_2O	(0.6875,0.3125)	82.5	(0.6691,0.3309)	80.06
IPAc-H_2O	**(0.5982,0.4018)**	**76.6**	**(0.5981,0.4019)**	**76.57**
IPOH-IPAc-H_2O	**(0.1377,0.4938,0.3885)**	**75.5**	**(0.2377,0.4092,0.3531)**	**74.22**

Heterogeneous azeotropes are in boldface. Experimental data from Horsley [56]

model is adopted in Aspen Plus. The NRTL model parameter sets shown in Table 5.9 are taken from Tang et al. [48]. The vapor phase non-ideality such as the dimerization of acetic acid is also considered. The second virial coefficients of Hayden-O'Connell [47] are used to account for vapor phase association of acetic acid. The Aspen Plus built-in association parameters are used to compute the fugacity coefficients.

The thermodynamic model predicts three binary minimum boiling azeotropes and one ternary minimum boiling azeotrope [48]. Table 5.10 shows that the model prediction results of the azeotropes temperatures and compositions are in good agreement with the experimental data. Notice that the lowest temperature of the system is at the ternary minimum boiling azeotrope. This ternary azeotrope is shown in the residue curve map (RCM) in Fig. 5.22.

5.5.3 Thermally Coupled Configurations with Reactive Systems

The hydrolysis of methyl acetate and esterification of isopropyl alcohol are taken up as case studies to demonstrate the feasibility of thermally coupled configurations with reactive systems.

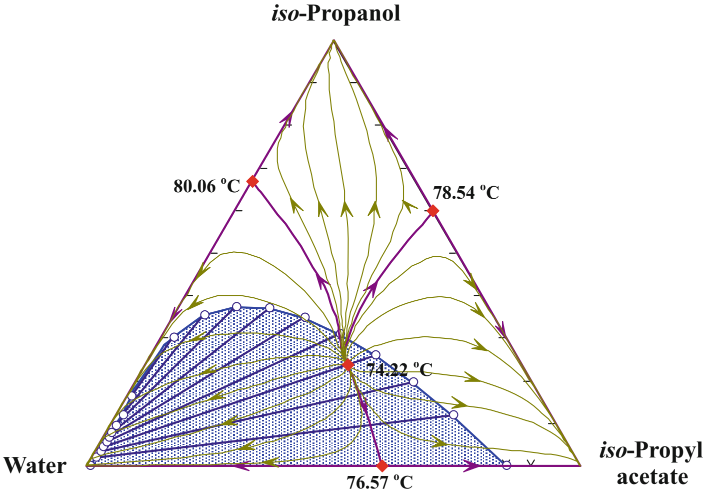
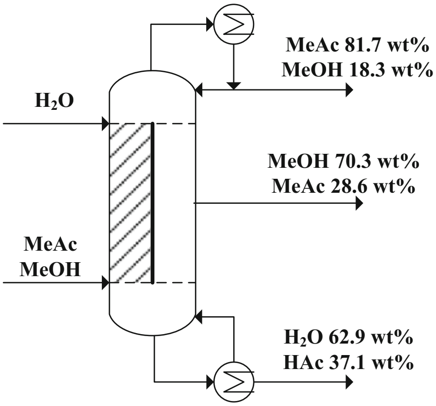


Fig. 5.22 Ternary RCMs and LLEs of IPAc process

Fig. 5.23 The first study of an RDWC for the hydrolysis of methyl acetate [52]



5.5.3.1 Thermally Coupled Process for the Hydrolysis of Methyl Acetate

For the hydrolysis of methyl acetate, Sander et al. [52] had established that the operation of a reactive divided wall column (which called RDWC) is possible; however, the results in Fig. 5.23 show that the purity of products and the desired methyl acetate conversion are not good [52].

To achieve the industrial product specifications, an RD column with a reactive reflux drum and two separation columns have been proposed in Lin's work [42, 43]. The advantages of DWC are combined with the hydrolysis of methyl acetate RD and propose a better thermally coupled configuration (see Sect. 5.5.1.1

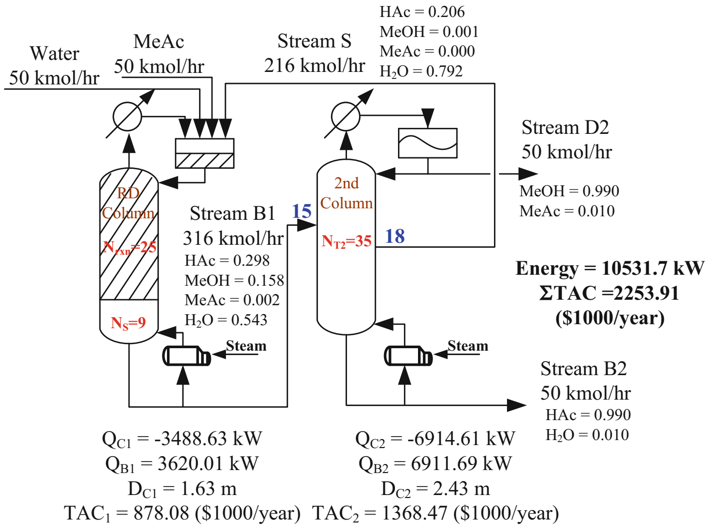


Fig. 5.24 RD with a sidedraw column

for the thermodynamic and kinetic data). The objective function is to minimize TAC, see Eq. (5.9), with a payback of 3 years ($\theta = 3$). The equipment cost comprises the costs of the column, trays, and heat exchangers and they are calculated according to Douglas's textbook [53].

The prototype of thermally coupled configuration comes from the RD with a side draw column, which is shown in Fig. 5.24. This configuration has one RD column and one additional column to separate MeOH and HAc at the top and bottom, respectively. The sidedraw stream which is rich in water recycles back to the RD column reflux drum. The optimal design of RD with a sidedraw column in Fig. 5.24 has a TAC of 2253.91 ($1000/year) and overall energy consumption of 10,531.7 kW.

The composition profiles of RD column are displayed in Fig. 5.25. Because of the small equilibrium constant, a large amount of water-rich stream is fed back to the RD reflux drum to attain complete conversion of the limiting reactant MeAc. The water-rich stream recycle causes the reactant's concentrations to improve the reaction rate of this second-order reaction near the reactive zone. Thus, HAc, MeOH, and water are the major obtained components at the RD column bottom. Although the MeOH reaches 0.40 composition at stage 30, it drops to 0.155 at the column bottom (i.e., stage 34). This phenomenon is the so-called remixing effect.

This configuration can meet the product specifications. Nevertheless, the TAC and energy consumption increased up to 25.3 and 23.5 % in comparison with the base design configuration. For the RD column, TAC and energy consumption increased 8.6 and 6.6 %. For the separation column, TAC and energy consumption increased 34.7 and 38 %. The previous results imply that the TAC and energy consumption in the separation column dominate the overall process TAC and

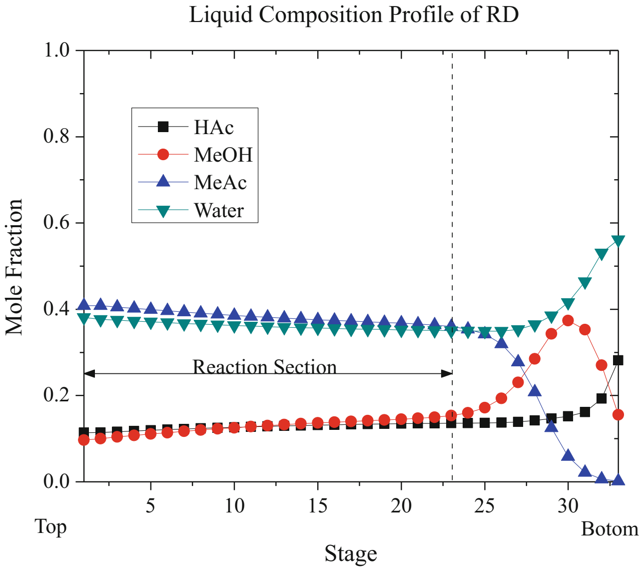


Fig. 5.25 Composition profiles of RD with a side draw column

energy consumption. According to the heuristics proposed by Tedder and Rudd [54] for ternary mixtures, the RD bottom compositions are unfavorable to be separated by a side draw column. This is why the energy consumption in the separation column is high.

Figure 5.26 shows a thermally coupled reactive distillation for the hydrolysis of methyl acetate, which is an alternative that can replace the design of RD with a sidedraw column. Because the liquid and vapor need to interact between RD and sidedraw column, the RD reboiler is removed and replaced by a sidedraw vapor stream from the second column. As a result, the sidedraw vapor stream location and its flow rate are additional design variables.

After the sequential iteration (see Sect. 5.2.2), Fig. 5.26 corresponds to the optimal thermally coupled reactive distillation result. The TAC is 1622.04 ($1000/year) and its overall energy consumption is 5750 kW. Thermally coupled design of RD with a sidedraw column has a great improvement of 31.6 % energy savings and 11.1 % reduction of TAC (see Table 5.11). It can save 45.4 % energy consumption and 28 % TAC compared to RD with a sidedraw column. The use of thermal coupling demonstrates that intensification of RD processes leads to very significant savings in energy consumption, operating cost, and capital cost with a smaller column.

Figure 5.27 shows the RD composition profiles for the thermally coupled solution in Fig. 5.26. MeOH has the highest composition and MeAc has the lowest composition at the RD bottom of the thermally coupled RD configuration. The lightest product MeOH composition steadily increases up to 0.473 mol fraction in

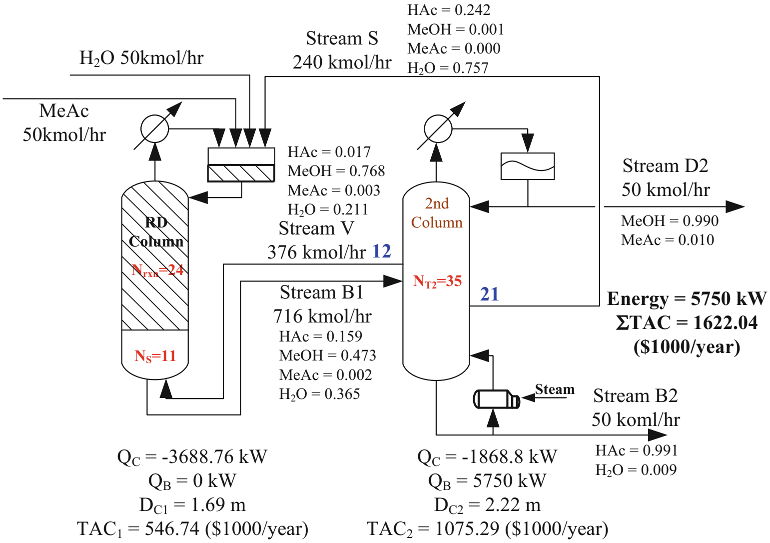


Fig. 5.26 Thermally coupled design of RD with a sidedraw column

Table 5.11 TAC results and energy consumption comparison with conventional and thermally coupled configurations

	Energy (kW)	TAC ($1000/ year)	Energy saving (%)	TAC saving (%)
Base design [43]	8403.1	1824.48	–	–
RD with a sidedraw column	10531.7	2253.91	−25.33	−23.54
RD with thermally coupled configuration	5750.0	1622.04	31.57	11.10

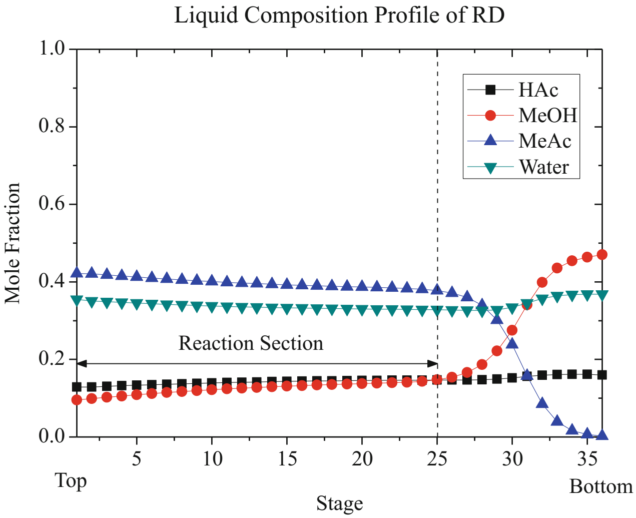


Fig. 5.27 RD composition profiles of the thermally coupled configuration

the RD bottom. In addition, the remixing effect (i.e., poor thermodynamic efficiency phenomenon) of the MeOH product composition disappears in the thermally coupled RD configuration. Thus, larger liquid flow rate with higher MeOH composition feeds the column with side draw. As a result, the MeOH composition is much higher, which would be helpful to attain energy savings.

5.5.3.2 Thermally Coupled Process for the Esterification of Isopropyl Alcohol

In this section, the advantages of reactive distillation with thermally coupled configuration for the esterification of isopropyl alcohol will be introduced based on the work of Lee et al. [50].

Based on the azeotrope and boiling point ranking, the heaviest component is the reactant HAc so that no bottom outlet stream of the RD column is designed. The top composition of the RD column is quite close to the minimum temperature azeotrope of IPOH-IPAc-H_2O. It is found in Fig. 5.22 that the liquid–liquid envelope (LLE) is quite large, and the ternary minimum boiling azeotrope lies well inside the envelope. It can also be seen that all the tie lines point towards the pure water end and, consequently, relatively pure water can be recovered from the aqueous phase in a decanter designed to be located at the top of the RD column. The tie lines can also pass across the distillation boundary so that high-purity IPAc can be obtained by further purification of the organic phase outlet stream in a stripper. Part of the organic phase material is also refluxed back to the RD column in order to withdraw water from the system. Due to economic reasons, the thermally coupled IPAc process configuration uses feed streams from industrial compositions of reactants instead of pure feed streams.

Figure 5.28 shows the optimal result of the conventional IPAc RD process [49]. The IPOH feed is assumed to be close to the azeotrope compositions. The HAc feed composition is set to be 95 mol% and that of IPOH is set to be 64.91 mol %, respectively. The product specifications include IPAc production with 99 mol% while keeping HAc purity below 0.01 mol%. The numbers of stages in the rectifying, reactive, and stripping sections are the same as in the study carried by Lai et al. [49].

Figure 5.29 shows the composition profiles of the IPAc process. The IPAc composition reaches its highest value at stage 3; then, it decreases towards the top of the RD column. This phenomenon is termed “remixing effect,” which hints that there is potential for energy saving by using thermally coupled configuration. Another observation is that the top compositions of the RD column and the stripper are quite close in Fig. 5.28, and these compositions are located into the LLE aqueous phase.

Figure 5.30 shows the thermally coupled RD configuration. Based on the solution in Fig. 5.28, the feed to the stripper is from the organic outlet stream of the decanter; therefore, it has been decided to place the decanter on the stripper. A liquid stream is needed to flow down to the RD column and to act as entrainer so as

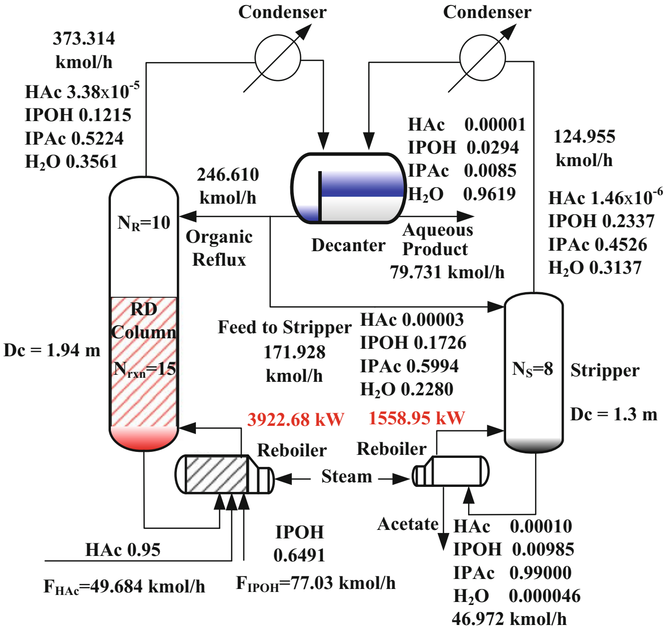


Fig. 5.28 Conventional RD configuration for IPAc process [49]

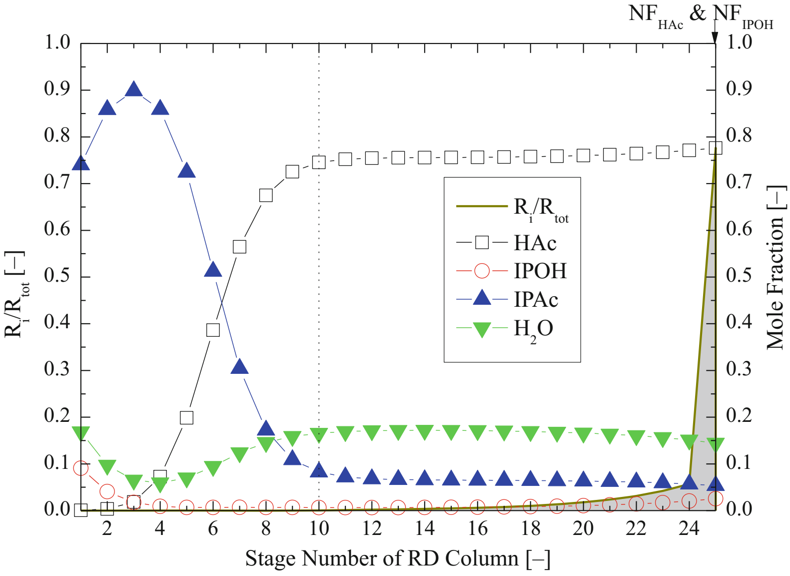
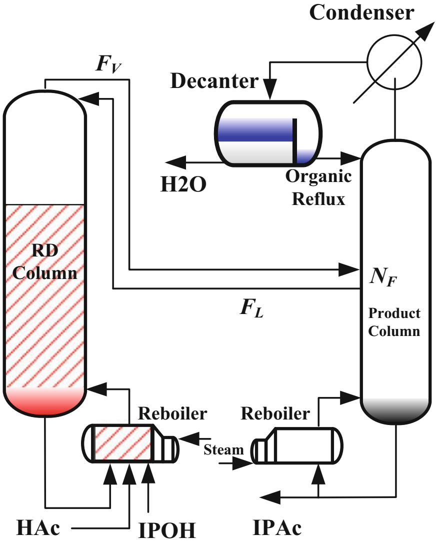


Fig. 5.29 Composition profiles of RD column for conventional IPAc RD configuration [49]

Fig. 5.30 Thermally coupled configuration for IPAc process



to carry more water towards the top of the column; thus, a liquid side draw from the product column is designed. To complete the thermally coupled configuration, the condenser in the RD column is removed and the vapor stream from the overhead is input to the same side draw location at the product column.

In Fig. 5.30, the reboiler duty of the right side product column is an operating variable used to meet the purity of IPAc, and the liquid side draw flow rate is used to maintain the HAc impurity in the product stream. The only design variable is the “vapor–liquid exchange location” (NF) in order to minimize the energy requirement.

The optimization procedure is shown as follows:

1. Initialize the NF.
2. Adjust the FL and reboiler duty of the right side column until the product specifications are met.
3. Go back to step 1 and change NF until the reboiler duty of overall process is minimized.

By following the optimization procedure, the best vapor–liquid exchange locations are at stage 5. Although the RD column reboiler duty remained about the same when the vapor–liquid exchange location varies, the separation column reboiler duty is minimum at the fifth tray when the vapor–liquid exchange location was varied.

The detailed results of the IPAc process with thermally coupled RD are shown in Fig. 5.31. The RD column reboiler duty is 3947.42 kW which is almost the same as in Fig. 5.28. However, the product column reboiler duty is only 265.67 kW, which is significantly lower than the stripper reboiler duty (1558.95 kW) of the conventional RD configuration. The optimal total reboiler duty of the thermally coupled

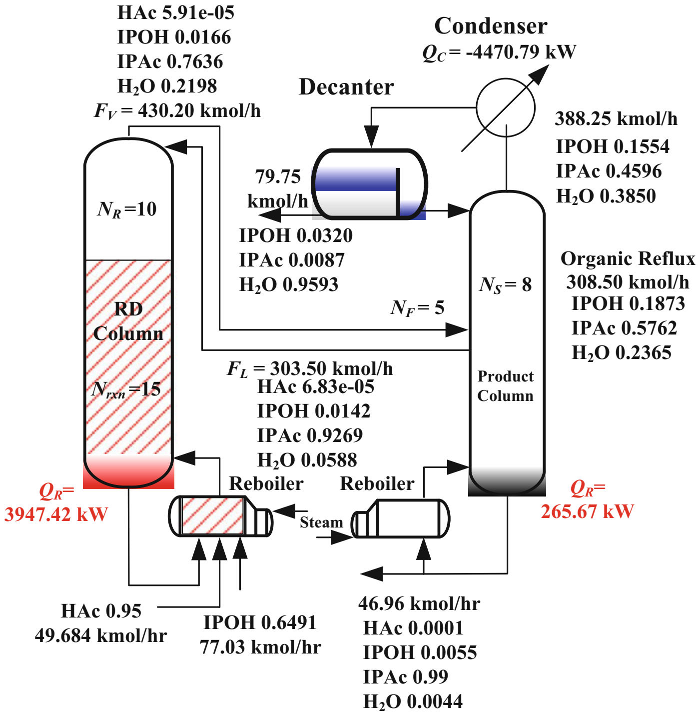


Fig. 5.31 Optimal results of the thermally coupled RD for IPAc process

RD is 23.14 % less than the conventional RD system. The liquid composition profile of the thermally coupled RD for this process is shown in Fig. 5.32. Comparing the composition of IPAc in the upper section of the RD column in the thermally coupled RD with that of the conventional RD configurations, the remixing effect is clearly eliminated because the IPAc composition increases steadily towards the top in the thermally coupled RD column. Another interesting observation in the composition profile can be made from the projection of the tetrahedron three-dimensional space to a two-dimensional space by using the composition variable transformation method [39]. The distillation path of the tray liquid and vapor compositions in the coordinate of composition variable transformation space is shown in Fig. 5.33 and has been demonstrated by Lee et al. [50].

Figure 5.33 also shows the tie lines and the compositions of the organic and aqueous phases. The curves with triangular symbols denote the composition trajectory of the RD column composition profile, and the curves with circles denote the composition trajectory of the product column. In Fig. 5.33a, the vapor and liquid composition trajectories in the conventional RD column show an evident turn in the two composition profiles. In Fig. 5.33b, the turn in the composition trajectories for the thermally coupled RD is eliminated. Additionally, the composition trajectories of the vapor and liquid for the product column with thermally coupled configuration

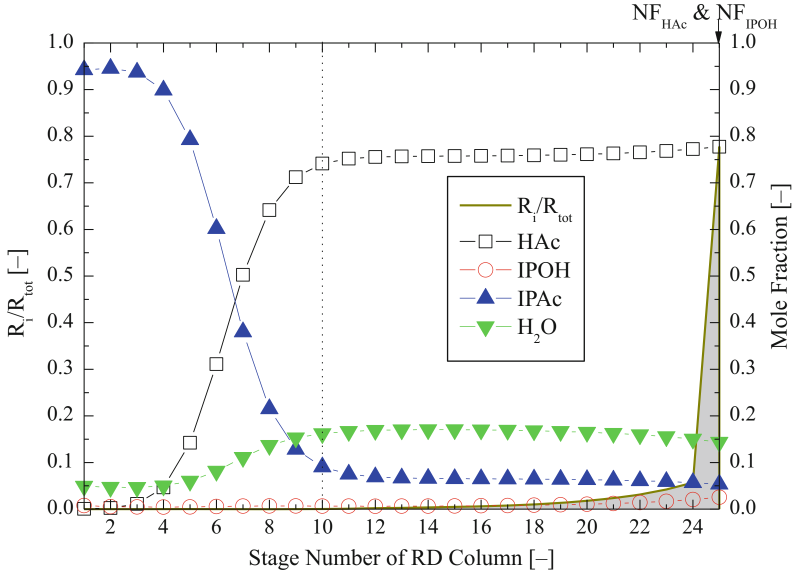


Fig. 5.32 Composition profiles of RD column for thermally coupled IPAc RD configuration

all show a more linear behavior than the stripper in the conventional RD system. This more linear behavior of the composition trajectory in this transformation coordinate hints at the energy saving in the product column.

In this section, the potential energy savings of the thermally coupled RD is introduced for IPAc system. The thermally coupled configuration includes moving the location of the decanter to the stripper side, totally refluxing the organic phase outlet stream, and adding a side draw liquid stream from the stripper to the RD column. The simulation result shows that 23.14 % energy savings can be realized by using the thermally coupled configuration.

5.5.4 *Heat-Integrated Reactive Systems with Multiple Effect*

For the multi-effect distillations, heat integration utilizes the heat of top distillate vapor in one column to supply the heat to the reboiler of next column. In order to provide the necessary temperature difference, the columns are operated under different pressures. In this section, the hydrolysis of Methyl Acetate and esterification of Isopropyl Acetate are chosen to illustrate the use of multi-effect distillation in reactive processes.

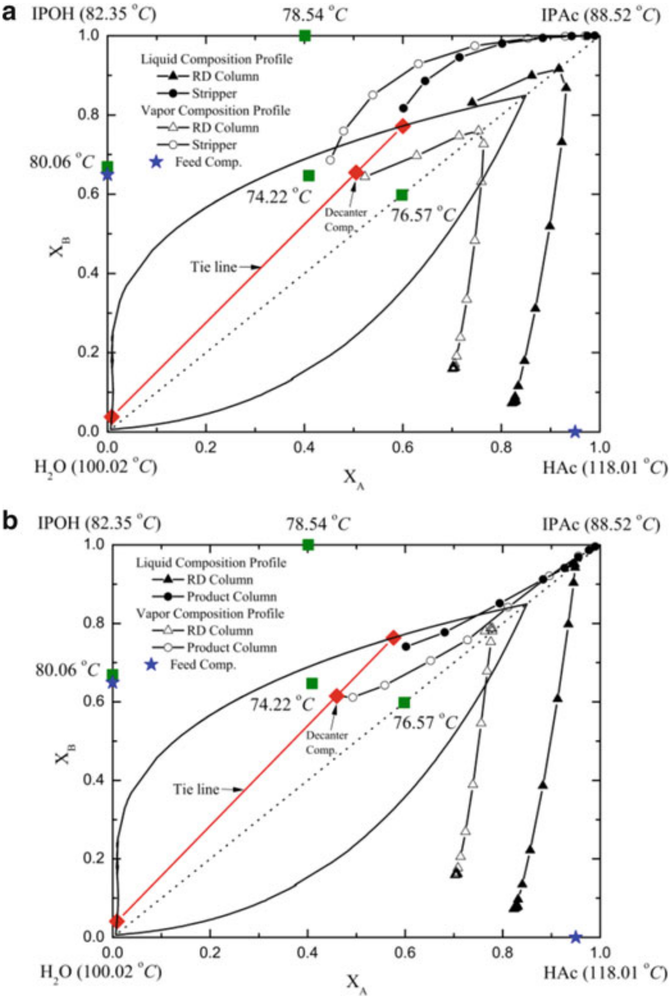


Fig. 5.33 Composition trajectories of IPAc process: transformed liquid and vapor composition in the quaternary system ($X_A = X_{HAc} + X_{IPAc}$, $X_B = X_{IPOH} + X_{IPAc}$) for (**a**) conventional RD configuration, (**b**) thermally coupled RD configuration [50]

5.5.4.1 Multiple Effect Process for the Hydrolysis of Methyl Acetate

The concept of the multi-effect distillation column entails splitting the feed stream into two smaller reactive distillation columns operated at different pressures. The operating pressure of the high-pressure column is determined so that the heat removal at the condenser of the high-pressure column can be matched to the heat input at the reboiler of the low-pressure column, thus, energy savings can be achieved by means of heat integration. It is worthy to mention that the boiling

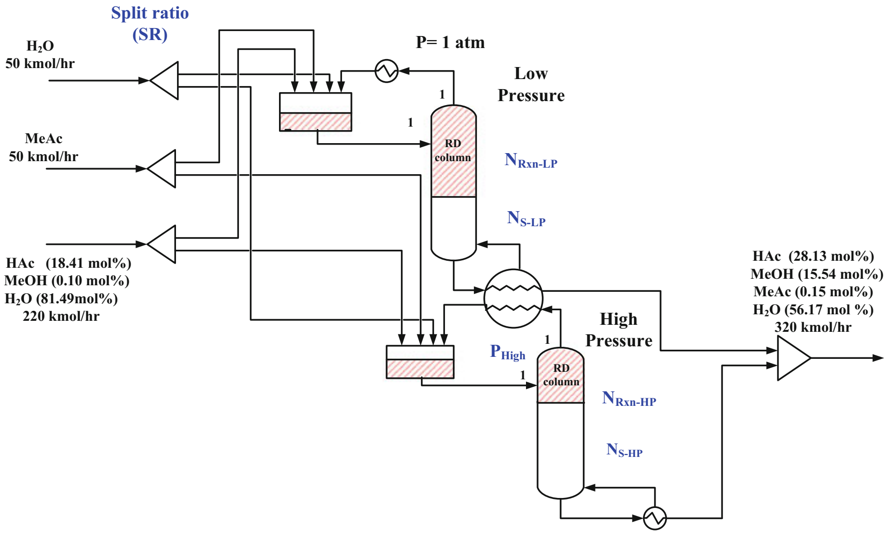


Fig. 5.34 Conceptual design of the multi-effect reactive distillation system [44]

point ranking of this RD system should not change due to the pressure increase in RD column (see Table 5.7).

Figure 5.34 shows the conceptual flowsheet of the reactive multi-effect configuration. The low-pressure column is assumed to operate at atmospheric pressure. The design variables include operating pressure at high-pressure column (P_{High}), stripping stages in the high-pressure column ($N_{\text{S-HP}}$), reactive stages in the high-pressure column ($N_{\text{Rxn-HP}}$), stripping stages in the low-pressure column ($N_{\text{S-Low P}}$), reactive stages in the low-pressure column ($N_{\text{Rxn-LP}}$), and the feed-splitting ratio (SR). The methyl acetate composition at the combined columns bottom is specified at 0.15 mol% by varying the reboiler duty of the high-pressure column.

The upper limit for the operation pressure of the reactive distillation is 8 atm to avoid a side reaction that generates dimethyl ether. The operating temperature in the reaction section has to be lower than 120 °C to meet the catalyst (Amberlyst® 15) operation conditions. The minimum temperature difference for feasible heat exchange between the condenser of the high-pressure and the reboiler of the low-pressure column is 10 °C.

For determining the optimal values of the six design variables, an iterative sequential optimization search procedure was adopted. The objective function is to minimize the TAC. The steam prices of high-pressure column and low-pressure column are 3.04 ($/1000 lb) and 2.28 ($/1000 lb), respectively. The catalyst cost is assumed to be $3.5/lb and to be replaced every 3 months. The payback of 3 years ($\theta = 3$) is assumed. The equipment cost was calculated according to Douglas's textbook [52].

The optimal values for the six design variables are: high-pressure column operated at 4.6 atm, 17 total stages of the high-pressure column, 2 reactive stages

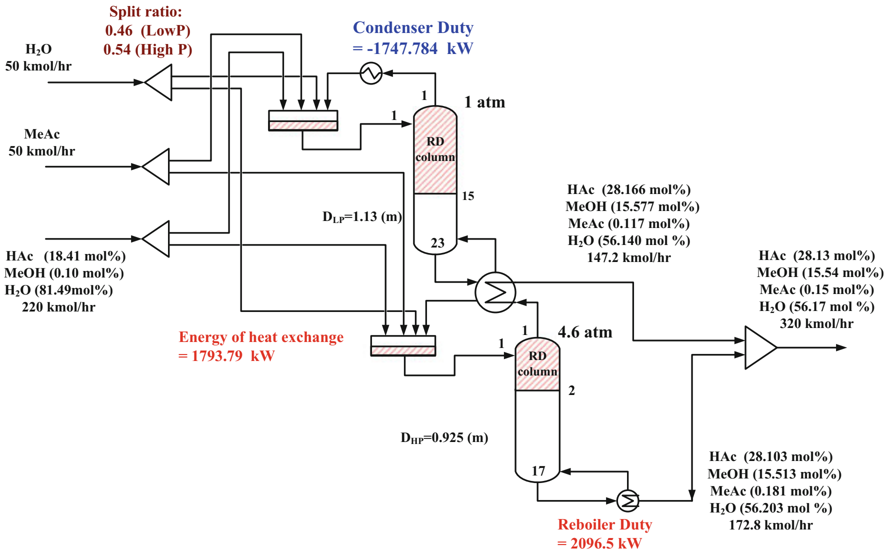


Fig. 5.35 Optimal flowsheet of the reactive multi-effect design for RD column

of the high-pressure column, 23 total stages of the low-pressure column, 15 reactive stages of the low-pressure column, and the feed-splitting ratio at 0.54.

Figure 5.35 shows the resulting optimal flowsheet for this feed-splitting heat integration configuration (reactive multi-effect). The detailed comparison of this reactive multi-effect configuration to the original configuration without heat integration shows that the energy saving and the operating cost saving of this heat integration configuration are at 38.26 % and 15.19 %, respectively. The cost of this reactive multi-effect configuration only increases slightly and the TAC is still lower than the original configuration without heat integration by 6.42 %.

Figure 5.36 shows the composition and reaction profiles of the two RD columns shown in Fig. 5.35. For each column, most of the reaction takes place at the reflux drum. The MeAc composition diminishes at each column bottom as it was specified. Notice that under the optimal condition, the shaded area in Fig. 5.36 displays that over 90 % of the reaction takes place in the high-pressure reflux drum; however, only about 70 % of the reaction takes place in the low-pressure reflux drum.

5.5.4.2 Multiple Effect Process for the Esterification of Isopropyl Alcohol

The base case of isopropyl alcohol reactive distillation configuration was taken from Lai et al. [49]. Thermodynamic and kinetic models are shown in previous sections. The original design of Isopropyl acetate reactive distillation configuration

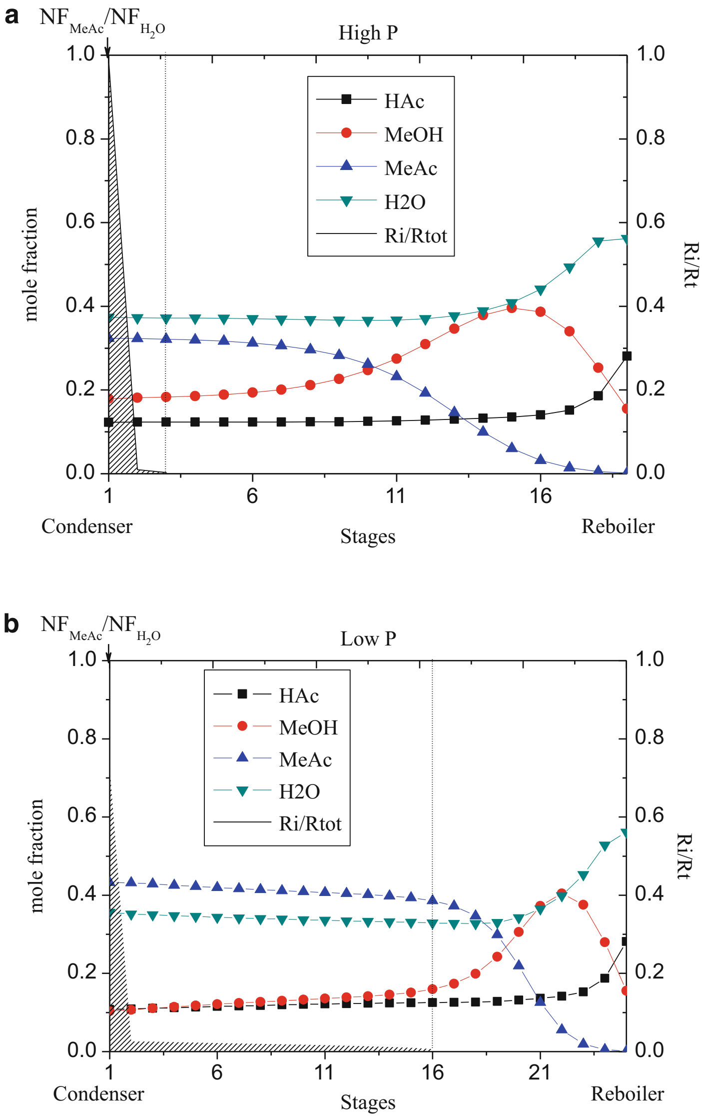


Fig. 5.36 Composition profile. (**a**) High-pressure RD. (**b**) Low-pressure RD [44]

contains a reactive column with a decanter and a stripping column. The lower part of the reactive column is the reaction section and the upper part of the reactive column is the rectifying section, with both pressures at 1.2 atm. Acetate and isopropanol are fed to the bottom. Acetic acid has the highest boiling point in this case. In order to avoid materials loss, there is no product coming out from the bottom. In the original reactive distillation configuration, the removed energy from the condenser at the top is greater than the energy supplied to the reboiler at the bottom. However, the temperature in the top is lower than the temperature in the bottom. Therefore, heat transfer is infeasible.

In order to transfer heat from condenser to reboiler in the reactive distillation column, it is necessary to increase the pressure in the reactive distillation column. The pressure increase will affect the performance in the reaction and separation sections. High-pressure distillation column will result in higher operating temperatures, which speed up the reaction rate and the reaction system moves towards the equilibrium faster. Therefore, the overall effect resulted from increasing the pressure is beneficial.

When the top pressure of the reaction column is higher than 2.7 atm, the temperature difference between top and bottom in the reactive distillation column is higher than the minimum heat transfer temperature difference ($\Delta T_{\min} = 10\ °C$), which implies that heat can effectively be transferred. Figure 5.37 shows the design results for the multi-effect configuration. The energy consumption of multi-effect was reduced from 5481.63 kW to 3766.5 kW, which results in 31.3 % energy savings.

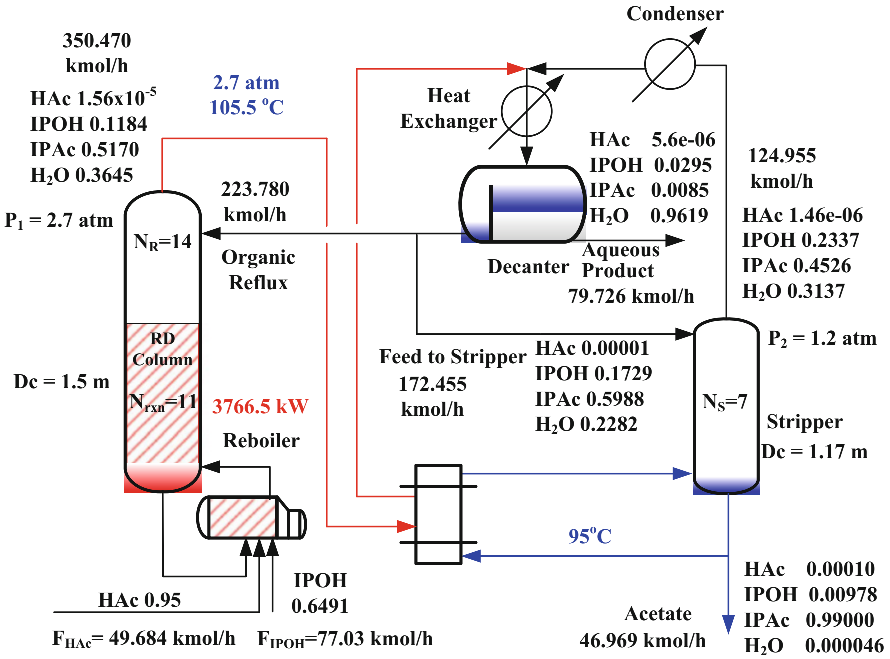


Fig. 5.37 Isopropyl acetate RD process for multi-effect configuration

5.5.5 Energy Saving and Cost Comparisons of Whole Two Configurations

5.5.5.1 Process Comparison for the Hydrolysis of Methyl Acetate

Table 5.12 is a comprehensive table that summarizes the energy consumption and TAC for the original RD configuration, multi-effect configuration and thermally coupled configuration. Compared with the original RD configuration, the reactive multi-effect configuration can save energy and this type of heat integration is very common in the industry. However, the main drawback is that the multi-effect reactive distillation needs to use high-pressure steam to supply energy at the reboiler. As a result, it only saves 2.84 % of the TAC for the overall process including two separation columns. The thermally coupled configuration saves 31.57 % energy compared with the original RD configuration. The reason is because the thermally coupled configuration can eliminate the remix effect in the columns bottom. The heat integration of thermally coupled configuration can also save energy. Overall, the TAC of thermally coupled configuration can still save 11.10 % energy consumption compared with the original RD configuration.

5.5.5.2 Process Comparison for the Esterification of Isopropyl Alcohol

Table 5.13 is a comparison table that summarizes the energy consumption of isopropyl alcohol for the original reactive distillation configuration, multi-effect configuration and thermally coupled configuration. For the original reactive distillation configuration, the thermally coupled of reactive distillation configuration can save 23.14 % of the energy consumption in the overall energy use. The reason is the

Table 5.12 Hydrolysis of methyl acetate's energy consumption and TAC comparison of RD versus multi-effect and thermally coupled

Framework	Energy consumption (kW)	TAC ($1000/year)	Energy saving (%)	TAC saving (%)
RD	8403.07	1824.48	–	–
Multi-effect	7104.11	1772.63	15.46	2.84
Thermally coupled	5750	1622.04	31.57	11.10

Table 5.13 Esterification of isopropyl alcohol's energy consumption comparison of RD versus multi-effect and thermally coupled

Framework	Energy consumption (kW)	Energy saving (%)
RD	5481.63	–
Thermally coupled	4213.09	23.14
Multi-effect	3766.5	31.28

thermally coupled configuration can eliminate the remixing effect in the bottom. The multi-effect via reactive distillation configuration can save 31.28 % more energy than the original reactive distillation configuration. However, operation at higher pressure is required. Caution must be taken to apply this arrangement because it may result in catalyst deactivation or decomposition due to higher temperature and pressure conditions.

5.6 Future Directions in Heat-Integrated Intensified Distillation Processes

The advantages of heat-integrated distillation at stages over typical condenser–reboiler heat integration in terms of energy consumption and TAC have been shown in this chapter. As the complexity of intensified distillation increases, the development of efficient and reliable optimization approaches is necessary. The combination of simulations, which handle nonlinear and non-convex equations such as thermodynamics and mass balances, and optimization, which is a strong tool to find optimal locations and heat load in heat-integrated distillation, can be superior to approaches based on only simulations or optimization. In addition, MIP, MINLP, or stochastic optimization methods can be interchanged according to the users' skills and preferences.

Figure 5.38 shows a qualitative comparison of several approaches to find heat-integrated intensified distillation. Although simulation driven approaches can handle a large number of components, the simulation time and the lack of robustness to find a global optimum solution are the two main drawbacks. For optimization driven approaches, so far they have been used for the separation of binary mixtures or separations done in one column. Simulation/optimization approaches for the separation of multicomponent mixtures is one topic that needs further research.

The presented cases were optimized at steady state; however, dynamic optimization and the controllability assessment of heat-integrated intensified distillation is also an open field that needs further study.

It easy to envision that the process dynamic response of heat-integrated configurations will be more oscillatory than conventional distillation due to the compactness in process flowsheet and/or less control degree of freedom.

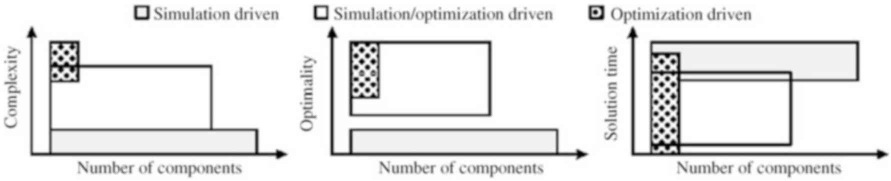


Fig. 5.38 Simulation and optimization approaches for heat-integrated intensified distillation

Regarding thermally coupled configuration, the control of the sidedraw flows is an important issue especially when the sidedraw is withdrawn as vapor. Luyben [55] proposed a concept of "pressure-compensated temperature" to adjust the temperature control loop as a function of the top pressure of a column. Straightforward PID control might not be enough to control the process; therefore, pressure-compensated control, cascade control, and nonlinear control techniques might be necessary.

Regarding thermally coupled configuration, the control of the sidedraw flows is an important issue especially when the sidedraw is withdrawn as vapor. Unlike liquid sidedraws, vapor sidedraws are not easy to control due to the pressure fluctuation of the column.

The effect of heat-integrated intensified distillation in arising multiple steady-states has not been evaluated. This also shows an open area to further research the presented ideas. The implementation of lab scale or bench scale to validate the theoretical foundations of heat-integrated distillation is another area that needs to be explored.

5.7 Concluding Remarks

The presented ideas related to the further intensification of complex distillation by means of heat integration can be useful for engineers and researchers in the field of process systems engineering.

Heat integration is preferred for clean services, for geographical regions where fuel and electricity prices are expensive, or for processes at atmospheric or subatmospheric pressure to prevent the deposition of solid particles.

Although the energy consumption can be reduced, the implementation of heat-integrated intensified distillation processes can be limited because two main reasons:

1. The use of expensive utilities (i.e., high-pressure steam) can reduce the economic savings. This was demonstrated in this chapter. The intensification of reactive distillation results in higher operating costs.
2. The use of complex control configurations due to high process interaction between the vapor and liquid streams involved in heat integration.

The first reason is related with the steady-state design and optimization while the second reason is related with the dynamic state operation and selection of controlled and manipulated variables. One way to deal with the aforementioned limitations is to simultaneously optimize the design and control in intensified distillation. Therefore, new approaches handling this issue are urged in order to bust the implementation of intensified processes.

The presented ideas can be extended to multicomponent mixtures and reactive systems involving more reactions without lack of generality.

References

1. Alcántara-Avila JR, Hasebe S, Kano M (2013) New synthesis procedure to find the optimal distillation sequence with internal and external heat integrations. Ind Eng Chem Res 52 (13):4851–4862. doi:10.1021/ie302863p
2. Alcántara-Avila JR (2012) Process intensification in distillation sequences. Dissertation, Kyoto University
3. Harwardt A, Marquardt W (2012) Heat-integrated distillation columns: vapor recompression or internal heat integration? AIChE J 58(12):3740–3750. doi:10.1002/aic.13775
4. Wang Y, Huang K, Wang S (2010) A simplified scheme of externally heat-integrated double distillation columns (EHIDDiC) with three external heat exchangers. Ind Eng Chem Res 49 (7):3349–3364. doi:10.1021/ie901534q
5. Kiss AA, Flores Landaeta SJ, Infante Ferreira CA (2012) Towards energy efficient distillation technologies–making the right choice. Energy 47:531–542. doi:10.1016/j.energy.2012.09.038
6. Fonyo Z, Benkö N (1998) Comparison of various heat pump assisted distillation configurations. Chem Eng Res Des 76(3):348–360. doi:10.1205/026387698524776
7. McCabe DL, Vivona MA (1999) Treating process wastewater employing vacuum distillation using mechanical vapor recompression. Environ Prog 18(1):30–33
8. Schmal JP, Van der Kooi HJ, De Rijke A et al (2006) Internal versus external heat integration operational and economic analysis. Chem Eng Res Des 84(A5):374–380. doi:10.1205/cherd05041
9. Alcántara-Avila JR, Gómez-Castro FI, Segovia-Hernández JG et al (2014) Optimal design of cryogenic distillation columns with side heat pumps for the propylene/propane separation. Chem Eng Process 82:112–122. doi:10.1016/j.cep.2014.06.006
10. Seider WD, Seader JD, Lewin DR, Widagdo S (2010) Product and process design principles: synthesis, analysis, and evaluation. Wiley, Asia
11. IEA (2012) Energy balances of non-OECD countries 2012. OECD, Paris, http://dx.doi.org/10.1787/energy_bal_non-oecd-2012-en
12. Ministry of Economy, Trade and Industry (2014) Nihon no enerugi 2014 (The energy in Japan 2014). http://www.enecho.meti.go.jp/about/pamphlet/pdf/energy_in_japan2014.pdf. Accessed 24 Feb 2015
13. Shenvi AA, Herron DM, Agrawal R (2011) Energy efficiency limitations of the conventional heat integrated distillation column (HIDiC) configuration for binary distillation. Ind Eng Chem Res 50(1):119–130. doi:10.1021/ie101698f
14. Mah RSH, Nicholas JJ, Wodnik RB (1977) Distillation with secondary Reflux and vaporization: a comparative evaluation. AIChE J 23:651–657
15. Nakaiwa M, Huang K, Endo A et al (2003) Internally heat-integrated distillation columns: a review. Chem Eng Res Des 81(1):162–177. doi:10.1205/026387603321158320
16. Ho TJ, Huang CT, Lee LS et al (2010) Extended Ponchon-Savarit method for graphically analyzing and designing internally heat-integrated distillation columns. Ind Eng Chem Res 49 (1):350–358. doi:10.1021/ie9005468
17. Shahandeh H, Ivakpour J, Kasiri N (2014) Internal and external HIDiCs (heat-integrated distillation columns) optimization by genetic algorithm. Energy 64(1):875–886. doi:10.1016/j.energy.2013.10.042
18. Suphanit B (2010) Design of internally heat-integrated distillation column (HIDiC): uniform heat transfer area versus uniform heat distribution. Energy 35(3):1505–1514. doi:10.1016/j.energy.2009.12.008
19. Olujic Z, Fakhri F, de Rijke A et al (2003) Internal heat integration—the key to an energy-conserving distillation column. J Chem Technol Biotechnol 78(2–3):241–248. doi:10.1002/jctb.761
20. Olujic Z, Sun L, de Rijke A et al (2006) Conceptual design of an internally heat integrated propylene-propane splitter. Energy 31(15):3083–3096. doi:10.1016/j.energy.2006.03.030

21. Olujic Z, Sun L, Gadalla A et al (2008) Enhancing thermodynamic efficiency of energy intensive distillation columns via internal heat integration. Chem Biochem Eng Q 22 (4):383–392
22. Horiuchi K, Yanagimoto K, Kataoka K (2008) Energy saving characteristics of the internally heat integrated distillation column (HIDiC) pilot plant for multicomponent petroleum distillation. J Chem Eng Jpn 41(8):771–778
23. Cabrera-Ruiz J, Jiménez-Gutiérrez A, Segovia-Hernández JG (2011) Assessment of the implementation of heat-integrated distillation columns for the separation of ternary mixtures. Ind Eng Chem Res 50(4):2176–2181. doi:10.1021/ie101939e
24. Kataoka K, Noda H (2014) Naibu netsukokan Shiki jyoryuto (HIDiC) no gijutsu Kaihatsu (technological development of internal heat-integrated distillation column (HIDiC)). Synthesiology 7(3):163–178
25. Ho TJ, Huang CT, Lin JM et al (2009) Dynamic simulation for internally heat-integrated distillation columns (HIDiC) for propylene–propane system. Comput Chem Eng 33:1187–1201. doi:10.1016/j.compchemeng.2009.01.004
26. Huang K, Shan L, Zhu Q et al (2007) Design and control of an ideal heat-integrated distillation column (ideal HIDiC) system separating a close-boiling ternary mixture. Energy 32 (11):2148–2156. doi:10.1016/j.energy.2007.04.007
27. Kano M, Fukushima T, Makita H et al (2007) Multiple steady-states in a heat integrated distillation column (HIDiC). J Chem Eng Jpn 40(10):824–831. doi:10.1252/jcej.06WE278
28. Wakabayashi T, Hasebe S (2011) Naibu netsukokan gata jyoryuto (HIDiC) ni okeru naibu netsukokan ryobunpu no shoenerugi Seino ni ataeru ekyo (effect of internal heat exchange rate distribution on energy saving in heat integrated distillation column (HIDiC)). Kagaku Kogaku Ronbunshu 37(6):499–505
29. Wakabayashi T, Hasebe S (2013) Design of heat integrated distillation column by using H-xy and T-xy diagrams. Comput Chem Eng 56:174–183. doi:10.1016/j.compchemeng.2013.05.020
30. Mane A, Jana AK (2010) A new intensified heat integration in distillation column. Ind Eng Chem Res 49(19):9534–9541. doi:10.1021/ie100942p
31. Kiran B, Jana AK, Samanta AN (2012) A novel intensified heat integration in multicomponent distillation. Energy 41(1):443–453. doi:10.1016/j.energy.2012.02.055
32. Taseibunkei naibu-netsukokanshiki joryu-sochi (Internal heat integrated distillation system for multi-component distillation). Patent No. 4819756
33. Kataoka K, Noda H, Yamaji H et al (2009) A compressor-free HIDIC system for recovery of waste solvent mixtures. Paper presented at 8th World Congress of chemical engineering, Montreal, Canada, 23–27 August 2009
34. Kataoka K, Noda H, Yamaji H et al (2009) Heat transfer and flow characteristics of a double-tube HIDiC trayed column. Paper presented at 8th World Congress of chemical engineering, Montreal, Canada, 23–27 August 2009
35. Zhang X, Huang K, Chen H et al (2011) Comparing three configurations of the externally heat-integrated double distillation columns (EHIDDiCs). Comput Chem Eng 35(10):2017–2033. doi:10.1016/j.compchemeng.2010.11.008
36. Miyazaki A, Alcántara-Avila JR, Sotowa KI, Horikawa T (2014) Trade-off assessment between controllability and energy savings in internally and externally heat integrated distillation structures. Paper presented at the 5th international symposium on advanced control of industrial processes, Hiroshima, Japan, 28–30 May 2014
37. Alcántara-Avila JR, Sotowa KI, Horikawa T (2014) Iterative procedure for updating the temperature profile in distillation columns with heat-integrated stages. Paper presented at 10th international conference on separation science and technology (ICSST14), Nara, Japan, 30 October–1 November 2014
38. Alcántara-Avila JR, Hasebe S (2013) Hierarchical synthesis procedure of optimal distillation sequences with internal and external heat integrations. Paper presented at 9th World Congress of chemical engineering, Seoul, South Korea, 18–23 August 2014

39. Malone MF, Doherty MF (2000) Reactive distillation. Ind Eng Chem Res 39:3953–3957
40. Luyben WL, Yu CC (2008) Reactive distillation design and control. Wiley, Hoboken
41. Sundmacher K, Kienle A (eds) (2003) Reactive distillation: status and future directions. Wiley-VCH Verlag CmbH & Co. KgaA, Weiheim, Germany
42. Lin YD, Chen JH, Cheng JK et al (2008) Process alternatives for methyl acetate conversion using reactive distillation. 1. Hydrolysis. Chem Eng Sci 63(6):1668–1682. doi:10.1016/j.ces.2007.11.009
43. Lin YD (2012) Design and control of a reactive distillation process for methyl acetate hydrolysis. Dissertation, Master thesis, National Taiwan University
44. Lee HY, Lee YC, Chien IL, Huang HP (2010) Design and control of a heat integrated reactive distillation system for the hydrolysis of methyl acetate. Ind Eng Chem Res 49:7398–7411. doi:10.1021/ie9016754
45. Pöpken T, Götze L, Gmehling J (2000) Reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis. Ind Eng Chem Res 39(7):2601–2611. doi:10.1021/ie000063q
46. Pöpken T, Steinigeweg S, Gmehling J (2001) Synthesis and hydrolysis of methyl acetate by reactive distillation using structured catalytic packings: experiments and simulation. Ind Eng Chem Res 40(6):1566–1574. doi:10.1021/ie0007419
47. Hayden JG, O'Connell JP (1975) A generalized method for predicting second virial coefficients. Ind Eng Chem Process Des Dev 14(3):209–216. doi:10.1021/i260055a003
48. Tang YT, Chen YW, Huang HP et al (2005) Design of reactive distillations for acetic acid esterification with different alcohols. AIChE J 51(6):1683–1699. doi:10.1002/aic.10519
49. Lai IK, Liu YC, Yu CC et al (2008) Production of high-purity ethyl acetate using reactive distillation: experimental and start-up procedure. Chem Eng Process 47(9–10):1831–1843. doi:10.1016/j.cep.2007.10.008
50. Lee HY, Lai IK, Huang HP, Chien IL (2012) Design and control of thermally coupled reactive distillation for the production of isopropyl acetate. Ind Eng Chem Res 51:11753–11763. doi:10.1021/ie300647h
51. Gadewar SB, Malone MF, Doherty MF (2002) Feasible region for a countercurrent cascade of vapor-liquid CSTRS. AIChE J 48(4):800–814. doi:10.1002/aic.690480414
52. Sander S, Flisch C, Geissler E, Schoenmakers H et al (2007) Methyl acetate hydrolysis in a reactive divided wall column. Chem Eng Res Des 85(1):149–154. doi:10.1205/cherd06106
53. Douglas JM (1998) Conceptual design of chemical processes. McGraw-Hill, New York
54. Tedder DW, Rudd DF (1978) Parametric studies in industrial distillation: part 1 design comparisons. AIChE J 24:303–315. doi:10.1002/aic.690240220
55. Luyben WL (2008) Design and control of a fully heat-integrated pressure-swing azeotropic distillation system. Ind Eng Chem Res 47(8):2681–2695. doi:10.1021/ie071366o
56. Horsley LH (1973) Azeotropic data—III, Advances in chemistry series no.116. American Chemical Society, Washington, DC

Chapter 6
Process Intensification by Reactive Distillation

Alvaro Orjuela, Miguel A. Santaella, and Paola A. Molano

Abstract Reactive distillation stands out as a successful example of a process intensification technology for enhanced chemical manufacture. After almost a century of development, it has achieved a high degree of maturity in terms of design capabilities, the availability of commercial suppliers of hardware and software, and a large variety of processes effectively implemented at the industrial scale. Based upon an extensive review of the classical and recent literature on reactive distillation, this chapter briefly describes the context in which the technology was developed, its current status, and the expected areas for progress in the near future. In addition, the intensification principles behind the operation, its fundamentals, constrains, design methodologies, the optimization approaches, and the control strategies are discussed with fair detail. Finally, a case study on the ethyl acetate production via esterification of acetic acid with ethanol by reactive distillation is presented. It this example, a complete process synthesis procedure is described, from the conceptual design all the way to the process optimization.

6.1 Past, Present, and Future of Reactive Distillation

Since the advent of systematic methods for the synthesis of chemical processes based upon the economic performance [1, 2], to the current ones involving additional considerations (e.g., environmental indicators, health and safety, uncertainties, controllability, etc.) [3–7], the reaction steps have been always considered the core of the process flowsheet. The reaction characteristics (thermochemistry, reacting phases, catalysts, selectivity, safety, etc.), and the change in physicochemical properties from reactants to products, as well as their mutual interactions, are key factors that shape the overall architecture of the process. The separation and purification of raw materials and products, the recycle structure of

---

A. Orjuela (✉) • M.A. Santaella • P.A. Molano
Department of Chemical and Environmental Engineering, Universidad Nacional de Colombia,
Sede Bogotá, Cra. 30 # 45-03, Ed. 412, Of. 201, Bogotá, Colombia
e-mail: aorjuelal@unal.edu.co

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_6

the flowsheet, the mass and heat integration, the utilities consumption, and the treatment and disposal of effluents; all of them are heavily influenced by the performance of the reaction system.

In this sense, the efforts on developing process improvements, preferentially in the reaction steps, have major potential to generate smaller, cleaner, more energy efficient, environmentally friendly, and consequently, cost-effective technologies. Among the different scales, methods, and apparatus to carry out intensified processes, reactive distillation (RD) technology stands out as a successful example of multifunctional reactors for enhanced chemical manufacture at the industrial scale [8–13].

Essentially, a RD column is a functional integration of a reactor within a distillation system. In this device, reactants are transformed into products which are simultaneously and selectively separated from the reacting media by distillation. This operating policy is especially useful when applied to reactive systems where conversion is limited by chemical equilibrium, so product removal enhances yield following Le Chatellier's principle.

Because of the above, RD has gained attention from different academic and industrial researchers in recent decades. As observed in Fig. 6.1, according to abstracts and citations databases, a large number of articles and patents have been published on the development of RD processes, equipment, and catalytic internals; mainly in China, USA, and Germany.

Even though the interest on RD seems recent, the fundamental idea of the operation was already established by the end of the industrial revolution. By the 1860s, the classic Solvay soda ash process had already implemented a RD application for ammonia recovery [14]. In that same decade, and several years before Le Chatellier's publications [15], the principles of chemical equilibrium were described from studies on esterification reactions [16–18]. Since those days, the continuous removal of water by distillation during semi-batch esterification processes became a common practice. However, a generalized industrial exploitation of these principles only came years later.

After the First World War, large quantities of nitrocellulose with little or no peace-time use were available. With a production infrastructure already built, the nitrocellulose lacquers were developed as a substitute product mainly for the emerging market of the automotive industry. Consequently, the need for lacquer solvents and also for fuel additives pushed the chemical companies to develop technologies for the synthesis of such materials, using continuous processing [19].

In that historical context, early in the 1920s, Arthur Backhaus, process engineer at US Industrial Alcohol Co. in Baltimore (Historically related to current Lyondell Basell), obtained the first patents describing the production of pure and mixed esters by semi-batch and continuous RD using homogeneous catalysts (sulfuric acid) and a bubble cap tray column [20–30], see Fig. 6.2.

Some RD reports were published in the following years, primarily in esterification reactions using homogeneous catalysis [32–36], but most developments were maintained confidential even after the end of the Second World War. A publication

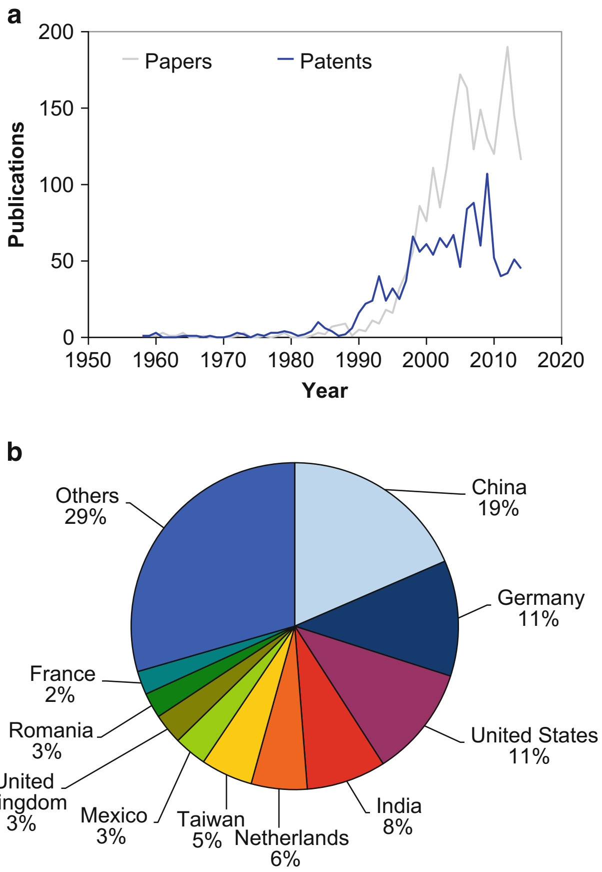


Fig. 6.1 Number of publications and patents on reactive distillation in last decades (**a**), and major contributions by country (**b**). Searching terms: reactive or catalytic distillation, reactive or reacting column, reactive or catalytic packing. (Source: Scopus. February 2015)

by Harmsen indicates that in the 1940s, Shell implemented one of the first continuous RD units at the industrial scale [8].

Half a century after Backhaus patents, and once a certain degree of maturity in heterogeneous catalysis was achieved [37, 38], solid catalysts were used within RD columns in the so-called catalytic distillation (CD) process. In the 1970s, Sennewald reported the use of side catalytic reactors in a distillation column [39]. At the same time, researchers at Chevron disclosed some of the first applications of CD in the separation of olefins by etherification [31, 40, 41], see Fig. 6.2. In this case, the etherification was carried out by placing a heterogeneous catalyst in the downcomers of the top trays of the distillation column. Based upon these technical developments, and because leaded gasoline was phased out at that time, Methyl tertbutyl Ether (MTBE) started to be used as tetraethyl lead substitute, becoming one of the first chemicals to be produced in large quantities via RD. With the Clean Air Act

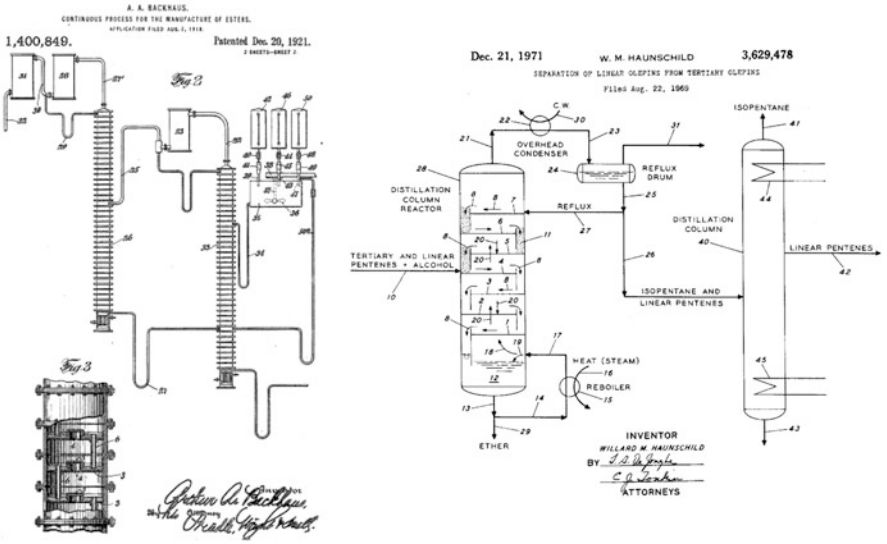


Fig. 6.2 First reported claims on homogeneous (*left*) and heterogeneous (*right*) reactive distillation processes. Taken and adapted from [20, 31].

amendments requiring the use of oxygenated compounds in reformulated gasolines, MTBE came into widespread use, boosting also RD investigation. Later in the middle 2000s, MTBE was banned in most US states due to soil and ground water contamination [42], and RD applications moved toward other ethers (e.g., ETBE: Ethyl tertbutyl ether, TAME: tertamyl methyl ether).

Another iconic event that brought attention into RD research was the implementation of the methyl acetate process at Eastman Chemical Co. in the 1980s [43, 44]. One reactor followed by nine separation columns in the traditional process was substituted by a single RD column, reducing by one-fifth the operating and capital costs [45]. As observed in Fig. 6.3, the conventional process involved:

- Equilibrium reaction (Task 1)
- Light and heavy components pre-fractionation accompanied by extractive distillation to recover methyl acetate with removal of methanol and water (Task 2)
- Methanol recovery and recycle (Task 3)
- Acetic acid dehydration by liquid–liquid extraction and azeotropic distillation (Task 4)
- Acetic acid purification and recycle to reactor (Task 5), and waste catalyst removal.

In comparison, the RD system accomplished most of those tasks in the different sections of one single column. Even an extractive distillation section was included within the RD configuration (Fig. 6.3). A photograph of the industrial RD column implemented at Eastman facilities in Kingsport, Tennessee (USA) is presented in Fig. 6.4.

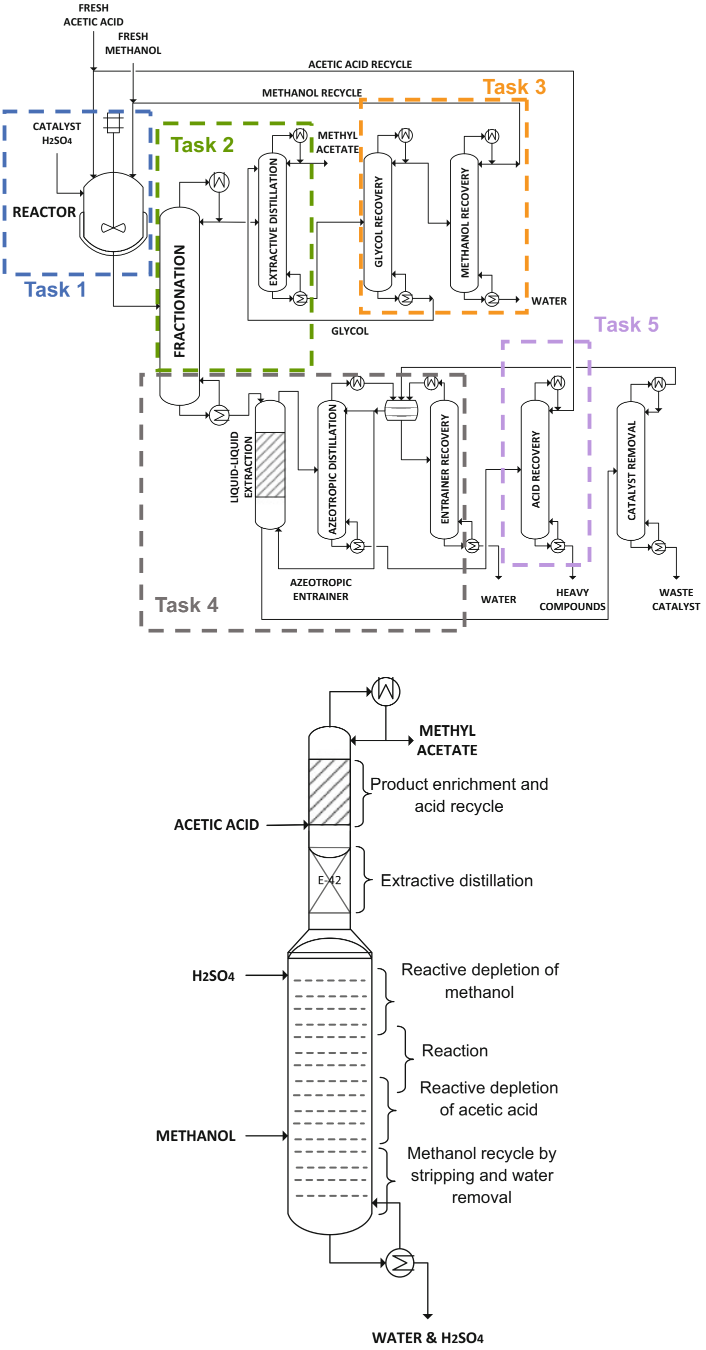


Fig. 6.3 Methyl acetate process at Eastman Chemical Co. Adapted from [45, 46]

Fig. 6.4 High-purity methyl acetate RD column at Eastman Chemical Co.—Tennessee. 180,000 ton/year (Courtesy by Jeff Siirola)

By the end of last century a large number of RD processes were implemented at the industrial scale [47–53], most design methodologies for RD columns were established, and research focused on their experimental validation. Different group leaders helped moving the field forward up to current status, and their contributions -some of them mentioned here- are now classical in the RD open literature. Interested readers can deepen in the different topics of RD by reviewing contributions of: Andrzej Stankiewicz (TU Delf), Andrzej Gorak and Hartmut Schoenmakers (TU Dortmund, BASF), James Fair (University of Texas at Austin), Johann Stichlmair (TU Munchen), Kai Sundmacher and Achim Kienle (Max Planck Institute, Magdeburg, Germany), Leonid Serafimov and Yuri Pisarenko (Moscow State University of Fine Chemical Technology), Michael Doherty (UCSB), Michael Malone (UMASS), Rajamani Krishna (Van 't Hoff Institute, Netherlands), Steiner Hauan (former at Carnegie Mellon), Thomas Frey (University of Applied Sciences Nuremberg), Ulrich Hoffmann (TU Clausthal), and many other researchers that only the limited space (and the lack of memory) does not allow their proper acknowledgement.

Despite current RD maturity, the field is still under active investigation. Recent studies have been focused on evaluating the feasibility of implementation in a variety of reactive systems (including multi-reaction RD). Also, enhanced column internals design and the scale-up of the operation are still topics of interest. Novel research trends also involve process development with higher degree of intensification by using pressure swing, heat integration, dividing wall columns, cyclic distillation, centrifugal distillation, membrane separations, etc. (Table 6.1).

Table 6.1 Main research groups working on RD during last decade (2004–2015) (according to the number of records reported in Scopus®)

Leading researchers	Institution	Areas
Sanjay M. Mahajani	Indian Institute of Technology, Mumbai, India	Design, simulation, and operation of lab scale RD
Andrzej Gorak	TU Dortmund. Dortmund, Germany	Design, simulation, and operation of lab and pilot scale RD (including Hybrid RD). Internals
Hsiao-ping Huang, and I-Lung Chien	National Taiwan University, Taipei, Taiwan	RD modeling and control
Anton A. Kiss	AkzoNobel RD&I Process Technology SRG, Netherlands	Design, simulation, and operation of lab, pilot and industrial scale RD. Dividing wall and cyclic RD
Kai Sundmacher and Achim Kienle	Max Planck Institute for Dynamics of Complex Technical Systems—Otto-von-Guericke-University Magdeburg, Magdeburg, Germany	Design, operation, control, lab scale, and pilot scale RD. Internals
Dennis J. Miller, and Carl T. Lira	Michigan State University, East Lansing, MI, United States	Design, operation, lab scale, and pilot scale RD (high pressure RD). Biobased molecules by RD
Juan Gabriel Segovia-Hernández	Universidad de Guanajuato, Guanajuato, Mexico	Design and optimization of RD and dividing wall RD. Pilot scale dividing wall RD
Nitin Kaistha	Indian Institute of Technology, Kanpur, India	RD modeling and control
Kejin Huang	Beijing University of Chemical Technology, Beijing, China	Design and simulation of traditional and integrated RD
William L. Luyben	Lehigh University, Bethlehem, PA, United States	Design and control of RD
Evgeny Kenig	University of Paderborn, Paderborn, Germany	Advanced modeling of RD units using different column internals

In spite of the long history, RD innovations continue blooming at the industrial scale. In 2014, the European Institution of Chemical Engineers (IChemE) conferred to Johnson Matthey Davy Technologies, the sustainable technology award for the development of a biodiesel production process from waste cooking oils using a RD process [54].Together with Davy, some of the major current suppliers of RD technologies at the industrial scale are listed in Table 6.2.

As research on RD topics, the written literature on the field has been prolific in the last years. In addition to the large amount of papers, patents, conference contributions; several reviews, book chapters, and entire books covering the RD field have been published [55–75]. The following sections will provide a comprehensive summary of such materials, and will include a description of the principles behind RD processes, some design methodologies, as well as some discussions on the optimization and control of the operation. Details on the theoretical and experimental validations are also provided.

Table 6.2 Commercial suppliers of RD technologies [49, 51, 140]

Institute/Company	Country
Maleta cyclic distillation	Estonia
BASF	Germany
Bayer Technical Services	Germany
Degussa	Germany
Uhde (Thyssen Krupp)	Germany
Enichem Technologie	Italy
Toyo Engineering Co.	Japan
Sulzer Chemtech	Switzerland
AkzoNobel	The Netherlands
DSM	The Netherlands
Shell Global Solutions	The Netherlands
Chemoxy	United Kingdom
Davy Process Technology	United Kingdom
ABB Lummus (CDTECH)	USA
Koch-Glitch	USA

6.2 Intensification Behind Reactive Distillation

Because of the synergic effect of combining reaction with separation, RD can be utilized in different ways to improve chemical processing [14, 50, 52, 58]. As mentioned before, this synergy may lead to overcome chemical equilibrium limitations, increasing productivity, reducing environmental foot prints, and consequently reducing costs. The selective removal of products and the depletion of reactants within a RD column simplify downstream separations and reduce recycling. This has been widely exploited in several applications such as esterifications (acetates, acrylates, fatty-acid esters, etc.), etherifications/acetalization (MTBE, ETBE, TAME, methylal, etc.), and hydrolysis (methyl acetate).

An additional advantage of the selective removal of products, when carrying out equilibrium reactions, is the reduction of the excess of reactants compared with the traditional processes. As a consequence, the required catalyst loading is also reduced for the same degree of conversion. Furthermore, when heterogeneous catalyst are used and raw materials are fed below the catalytic stages of a RD column, such feed location helps protecting the catalyst from suffering deactivation caused by nonvolatile impurities (which might occur in a traditionally packed reactor).

In some other cases, selectivity enhancement is the key factor for implementing an RD process such as in the case of butene alkylation.

$$\text{Isobutane} + \text{1-Butene} \rightarrow \text{Isooctane} + \text{1-Butene} \rightarrow C_{12}H_{24} \qquad (6.1)$$

In this process, continuous removal of isooctane keeps it away from further alkylation avoiding formation of undesirable long-chain hydrocarbons.

For the butyl acrylate production, the continuous removal of water helps reacting acrylic acid away, limiting its polymerization. At the same time, butyl acrylate removal from the reactive media also reduces the chances of addition polymerization within the RD column.

$$n\text{-Butanol} + \text{Acrylic acid} \leftrightarrow n\text{-butyl acrylate} + \text{H}_2\text{O} \tag{6.2}$$

$$\text{Acrylic acid} \rightarrow \text{polyacrylic acid} \tag{6.3}$$

$$n \text{ butyl acrylate} \rightarrow \text{polybutyl acrylate} \tag{6.4}$$

An interesting application that makes use of selectivity enhancement is the innovative utilization of biodiesel-derived glycerol to produce cyclic glycerol acetals (GA) or ketals via reaction with aldehydes or ketones. In this case, a mixture cyclic GA in chemical equilibrium is produced, and interconversion of GA isomers into the desired one (with low volatility) is facilitated by combination of reaction and distillation [76].

From the downstream standpoint, RD has several advantages too. For instance another synergic benefit in RD systems is related with the heat utilization, as in the case of ethylene glycol and cumene production [77, 78]. Ethylene glycol can be produced by hydration of ethylene oxide in a highly exothermic reaction, with the polymerization to polyethylene glycol (PEGn) as side reaction, (6.5) and (6.6). In the case of cumene, the side production of diisopropyl benzene (DIPB) and tripropylbenzene (TIPB) also occur at high temperatures, see (6.7)–(6.9).

$$\text{Ethylene Oxide} + \text{H}_2\text{O} \rightarrow \text{Ethylene glycol } \Delta HR = -84\text{kJ/mol} \tag{6.5}$$

$$\text{Ethylene glycol} + n \text{ Ethylene Oxide} \rightarrow \text{PEG } n \tag{6.6}$$

$$\text{Propylene} + \text{Benzene} \rightarrow \text{Cumene } \Delta HR = -113\text{kJ/mol} \tag{6.7}$$

$$\text{Propylene} + \text{Cumene} \rightarrow \text{DIPB} \tag{6.8}$$

$$\text{Propylene} + \text{DIPB} \rightarrow \text{TIPB} \tag{6.9}$$

The heat evolved during this type of reactions can be used for distillation, saving energy required in the reboiler. In the mentioned cases, and in some other applications, by-products formation increases with temperature. This phenomenon can be controlled by the evaporative heat removal in the RD column, which operates at the bubble point of the reactive mixture, avoiding hotspots, product decomposition, and catalyst damage.

Difficult separations can also be accomplished by RD methods. A classic example is the isolation of isobutylene from catalytic cracking C4s streams [50], where relative volatility of isobutylene with respect to other C4 components is very close to the unity, making distillation unfeasible. Nonetheless separation is accomplished by selective etherification with C3–C4 alcohols.

$$\text{Isobutylene} + \text{Butanol} + \text{C4s} \rightarrow \text{Isobutyl ether} + \text{C4s} \tag{6.10}$$

$$\text{Isobutyl ether} \rightarrow \text{Isobutylene} + \text{Butanol} \tag{6.11}$$

Isobutylene ether is removed as heavy product in a RD column, and then cleaved to recover the pure isobutylene required for alkylates production. The use of reactive entrainers in RD columns can also be found in other difficult separations such as *m*-xylene/*p*-xylene and cyclohexane/cyclohexene.

Additionally, RD processes fit well when high-purity separations are needed, as in the case of hexamethylene diamine recovery in Nylon 6,6 production [79]. In this case a concentration of hexamethylene diamine lower than 300 ppm is required in the vented vapors (i.e., water concentrations must be greater than 99.9997 %). Thus, adipic acid is used as reactive entrainer in the RD column to recover the diamine from the mentioned stream.

Another benefit of using RD processes is the avoidance of azeotropes by reacting them away. The methyl acetate production is an outstanding example, since the existence of different azeotropes is responsible for the complexity of the traditional process. When using RD, acetic acid acts as an extracting entrainer pulling water to bottoms, and also by consuming alcohol, breaking methanol–methyl acetate azeotrope in the upper part of the RD column.

The quantification of the above-mentioned synergic effects is difficult and anyhow subjective. However, some authors have come to characterization approaches by using quantitative parameters as the dimensionless numbers such as the heat utilization factor (ξ) [80]. This factor is calculated as the ratio of reaction and vaporization enthalpies, and it might provide a good insight of the potential exploitation of the reaction heat during distillation. If a new chemistry is planned to be carried out by RD, an analysis of the operating window in the space of the heat utilization factor and the driving force (chemical equilibrium constant) might give an idea of the implementation feasibility of this technology and its benefits. The results of such analysis for several industrially applied RD processes are presented in Fig. 6.5 [80]. As it can be seen, RD schemes have been implemented for highly exothermic reactions (molar heat of reaction around four times the heat of vaporization) taking advantage of the temperature control effect together with the product vaporization. In the case of thermoneutral reactions ($\xi \rightarrow 0$, e.g., transesterifications) the benefits of RD are mainly related to the ability of driving reaction to completion by affecting chemical equilibrium through product removal.

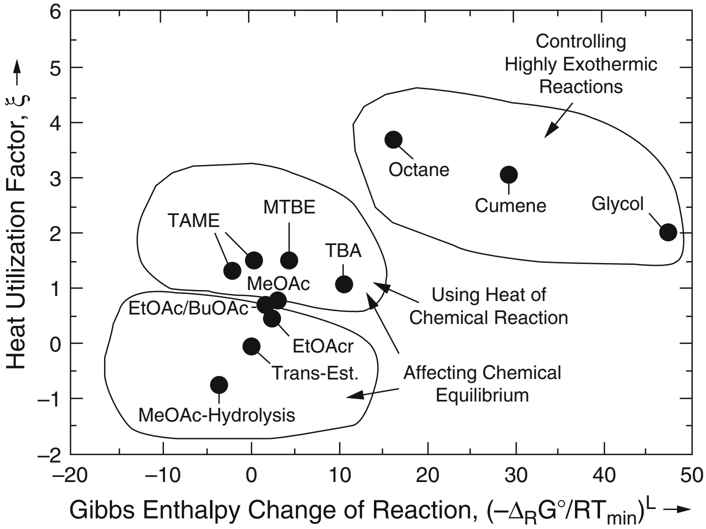


Fig. 6.5 Intensification benefits regarding the reaction driving force (chemical equilibrium) and heat utilization factor (heat of reaction over heat of vaporization of the mixture) in different industrially applied RD processes (from [80], reprinted with permission from the publisher, Taylor & Francis Ltd.)

6.3 Limitations and Constrains During Reactive Distillation Implementation

Recently, RD has been criticized in the industrial community because it has not consolidated the widely claimed potentials of the technology; RD has been considered as a "hammer looking for the right nail" [81]. These opinions are mainly a consequence of the drawbacks during technology implementation.

To carry out a chemical reaction in a RD system, it must be feasible at the bubble point range of the reacting mixture (matching the operating pressure and temperature ranges for both reaction and separation). This is not always the case in chemical systems where reactive separations might improve performance. In general, there is a narrow operating window for a RD system when compared with the reactor-separator arrangement. Temperature and pressure ranges currently used in some industrial RD applications are presented in Fig. 6.6. As indicated, one additional and important factor to establish feasibility is the catalyst thermal stability under RD processing conditions. For instance, in the case of most ion exchange resins commonly used as industrial catalysts, the maximum operating temperature is around 130–150 °C. This limits the capacity of using this type of catalysts for RD applications when operating at high pressures (higher temperatures).

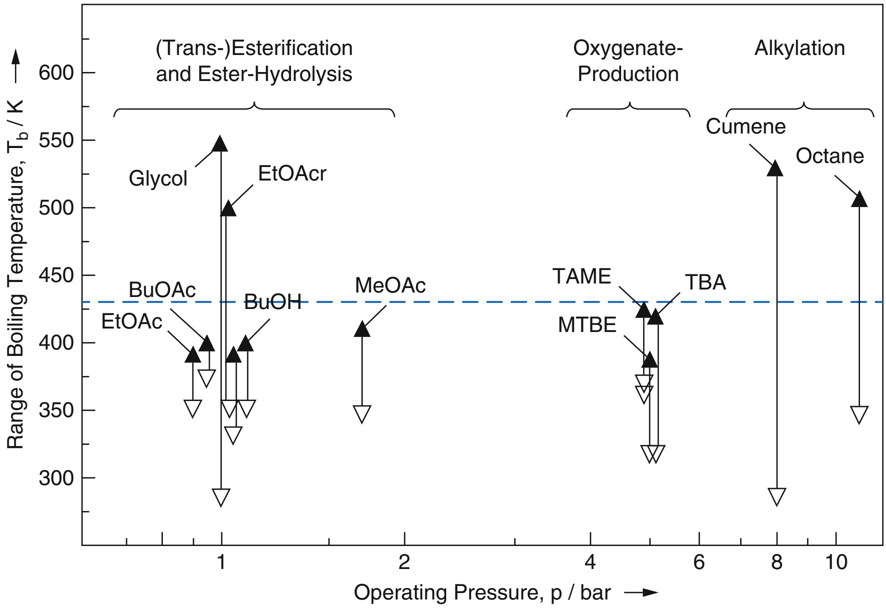


Fig. 6.6 Boiling temperature range versus operating pressure for industrially applied RD processes. *Dashed line* represents the maximum operating temperature for most commonly used ion exchange resin catalysts in RD (from [80], reprinted with permission from the publisher, Taylor & Francis Ltd.)

The industrial implementation of a RD process requires the correct combination of different attributes of the reactive system, some of which are conflicting among each other, for instance: relative volatilities, reaction driving force (equilibrium constant), heat of reaction, mass and heat transfer resistances, thermal sensitivity of the main and side reactions, catalyst stability, etc.

Thus, in order to benefit from product removal in a RD column, reactive mixture must have suitable relative volatilities to maintain reagents in and products out of the reactive stages. This means that the RD process is more easily implemented if products are the heaviest and/or the lightest components of the mixture. For instance, consider production of diethyl succinate by RD [82],

$$\text{Ethanol} + \text{Succinic acid} \leftrightarrow \text{Monoethyl succinate} + H_2O \tag{6.12}$$

$$\text{Ethanol} + \text{Monoethyl succinate} \leftrightarrow \text{Diethyl succinate} + H_2O \tag{6.13}$$

In this system, reagent succinic acid and the intermediate monoethyl succinate remain in the bottom product because they are heavier than the diester. Then, high temperature (i.e., high column pressure) and ethanol excess are required to achieve complete conversion, and to obtain high-purity diethyl succinate product. Similarly, ethanol is lighter than the produced water, and both form an azeotrope, so it is necessary to remove alcohol to pull water out of the system. If no further purification of the top stream is undertaken, the reflux might bring some water back into the column affecting reaction performance.

An additional requirement for a feasible implementation of a RD process is the long-life of the catalyst when using heterogeneous catalysis. Generally, the costs of catalyst replacement and regeneration are prohibitive when using commercially structured packings. To overcome these problems, specifically in the case of ion exchange resin catalysts, hypersulfonation, and chlorination have been used to enhance stability (e.g., Amberlyst 70® is stable up to 190 °C) [83]. However, the resulting lower active sites content would require a higher catalyst hold-up within the column.

Another requirement for RD application is a fast kinetics at the operating conditions of the reactive stages. Fast reactions mean that chemical equilibrium is nearly reached within the typical residence time of the liquid in a stage. Slow rates of reaction will require high-residence times and large catalyst loadings forcing to use high-liquid hold-ups, with the consequent hydraulic inconveniences and higher capital costs. For slow reactions, it might be better to use the traditional reactor-distillation column scheme, or even distillation columns with side reactors. This is the major inconvenience in the synthesis of triethyl citrate (TEC) [84]

$$\text{Ethanol} + \text{Citric acid} \leftrightarrow \text{Monoethyl citrate} + H_2O \tag{6.14}$$

$$\text{Ethanol} + \text{Monoethyl citrate} \leftrightarrow \text{Diethyl citrate} + H_2O \tag{6.15}$$

$$\text{Ethanol} + \text{Diethyl citrate} \leftrightarrow \text{Triethyl citrate} + H_2O \tag{6.16}$$

In this case, the thermal instability of citric acid avoids increasing reaction rate by increasing temperature above a certain level (~140 °C). The last substitution of the three consecutive steps in the reaction pathway is very slow, and a prohibitive large number of stages with large hold-ups would be required for complete conversion if using a traditional RD scheme. Here, a prereactor–separator arrangement or a RD column with side reactors fits better for the operation [85].

The above examples indicate that different RD configurations can be chosen depending on the different combinations of reaction velocity and separation easiness. Figure 6.7 shows some typical configurations that can be implemented according to the limiting conditions of reaction velocity and relative volatility. As observed, two main operating conditions can occur. In the “distillation-controlled RD” reaction rates are fast, and the process efficiency is controlled by the separation task. On the other hand, if reaction kinetics is slow, the system is “kinetics-controlled”, and overall conversion is primarily influenced by the residence time within the RD system. As observed in Fig. 6.7, the understanding of these conditions might help during conceptual design of RD operations. For instance, when working with mixtures characterized by a high relative volatility between products and reactants, reactive flashes can be used. In the opposite case, a low volatility

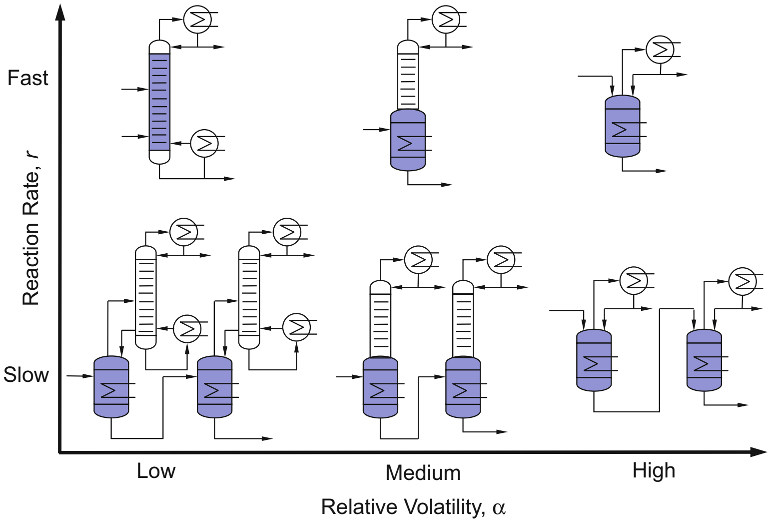


Fig. 6.7 RD configurations according to reaction rate and relative volatility between products and reactants. *Shadowed areas* indicate reactive stages. Adapted from [86]

would indicate the need for a high number of separating stages in a traditional RD column, or a distillation column coupled with side reactors.

An additional drawback of the RD operations is the complexity of the phenomena involved when up-scaling the process, mainly when using heterogeneous catalysts. This task is very difficult considering the variability of column hydrodynamics, and the mass and heat transfer behavior in the different reactive packing geometries at different scales. This is aggravated by the incomplete catalyst wetting caused by liquid maldistribution, and the concentration and temperature gradients within the catalyst particles [48, 87]. As a matter of example, Fig. 6.8 presents some geometric characteristics of two similar commercial catalytic packings (MULTIPAK®). Type I has layers of corrugated wire gauze with an inclination of 60°, while type II corrugated sheets have an inclination of 45°. As observed, there is a substantial change in the catalyst content, the void fraction for vapor flow, and the surface area for vapor–liquid contact between the two packings, and also when up-scaling from laboratory and bench columns (0.05 m > diameter > 0.1 m) up to industrial ones (diameter > 1 m). This indicates that hydrodynamics, mass and heat transfer, and also the reaction performance might substantially change when using different catalytic internals and when up-scaling the operation.

Because of the highly complex effects occurring within a RD system, it is not expected for a process to be up-scaled without prior pilot scale experimental validations. This makes RD an expensive and time-consuming technology to implement at the industrial scale. Additionally, sometimes a process complication arises when combining reaction and separation in RD systems. In some specific cases, and under certain operating conditions, for each component in the mixture, the rate of vaporization and the rate of formation (or consumption) are equal.

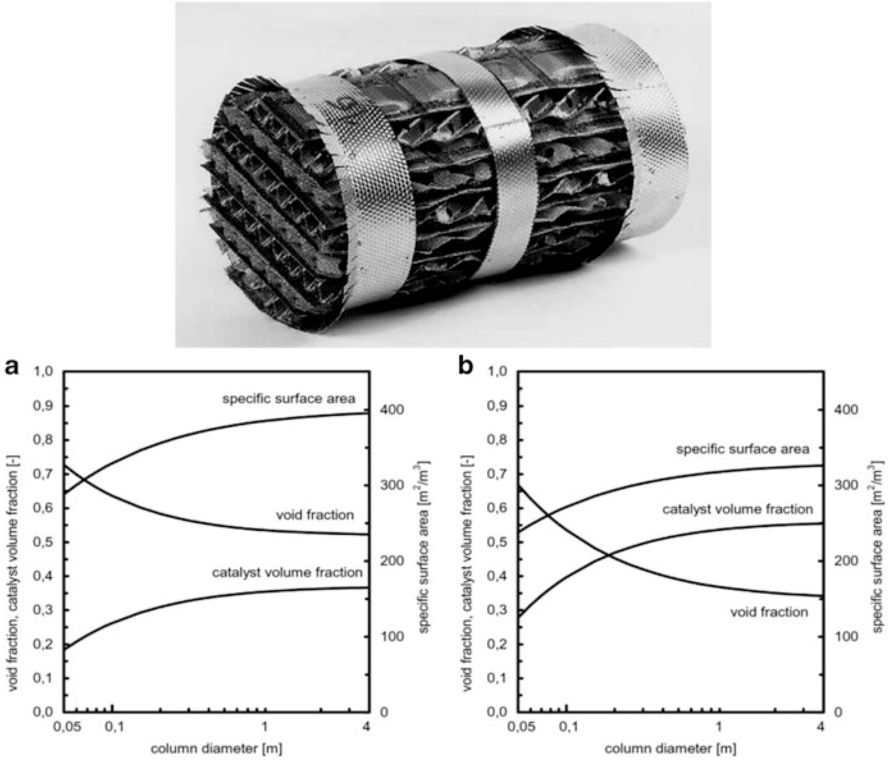


Fig. 6.8 Dependence of the geometric characteristics of commercial catalytic packings (MULTIPAK®) with the column diameter (from [87], reprinted with permission from the publisher, Elsevier). (**a**) MULTIPAK®-I, (**b**) MULTIPAK®-II

When this rarity happens, the net composition change of both liquid and vapor phases is zero, and a reactive azeotrope appears. Despite it was theoretically predicted, experimental verification of reactive azeotropy was only confirmed when studying the isopropyl acetate system [88]. As in the case of traditional azeotropes, the reactive ones might create separation difficulties, but they can be overcome, for example, by changing operating conditions for reaction (i.e., catalyst nature and concentration, pressure).

6.4 RD Fundamentals

In principle, RD is the functional combination of distillation and reaction. This creates a synergic effect that can be exploited in equilibrium reactions. For example, in an equilibrium reaction of the type: $A + B \leftrightarrow C + D$; and with relative

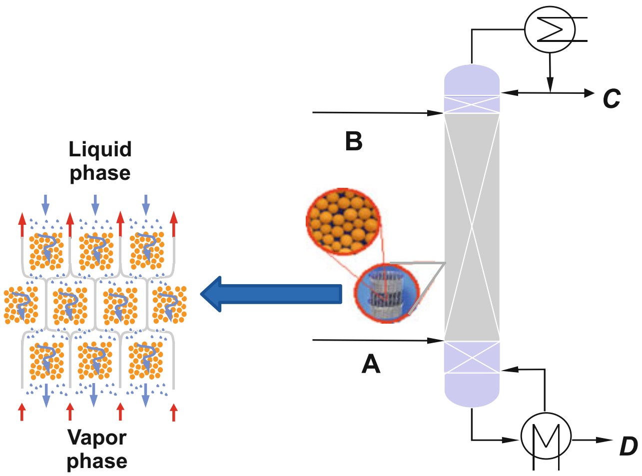


Fig. 6.9 Catalytic distillation scheme applied to the equilibrium reaction A + B ↔ C + D, with product being the most and less volatile components

volatilities $\alpha_C > \alpha_A > \alpha_B > \alpha_D$; RD can be implemented in such a way that separated pure products can be obtained in a single apparatus. As observed in the catalytic distillation scheme of Fig. 6.9, vapor rich in component A rises from below the reactive stages encountering component B that flows downward. Because the reaction stages contain catalyst (in a suitable catalytic packing or in the trays), the reaction proceeds to produce C and D. As the more volatile component, C flows to the top, while D as the heaviest product is pushed to the bottoms. Though in principle the process seems straightforward, establishing the best technical and economical operating conditions of a particular chemical system is a major design challenge.

Similar to the design of conventional distillation columns and reactors, knowledge of phase and chemical equilibrium, chemical kinetics, and transport phenomena are also essential for the design of RD operations. Both, the equilibrium-stage-based model and the rate-based model used in traditional distillation, are the most common tools to describe and study the performance of RD columns (either considering the reaction through chemical equilibrium or reaction kinetics). The simplest RD models require only a good knowledge of phase and chemical equilibria, while the more complexes require a complete set of reaction kinetics, together with mass and heat transfer and also hydraulic correlations. Because the reliability of such models depends strongly on how good the model parameters describe the physicochemical phenomena, experimental measurement or verification of thermodynamics, transport properties and kinetics is mandatory.

6.4.1 Thermodynamics of RD Processes

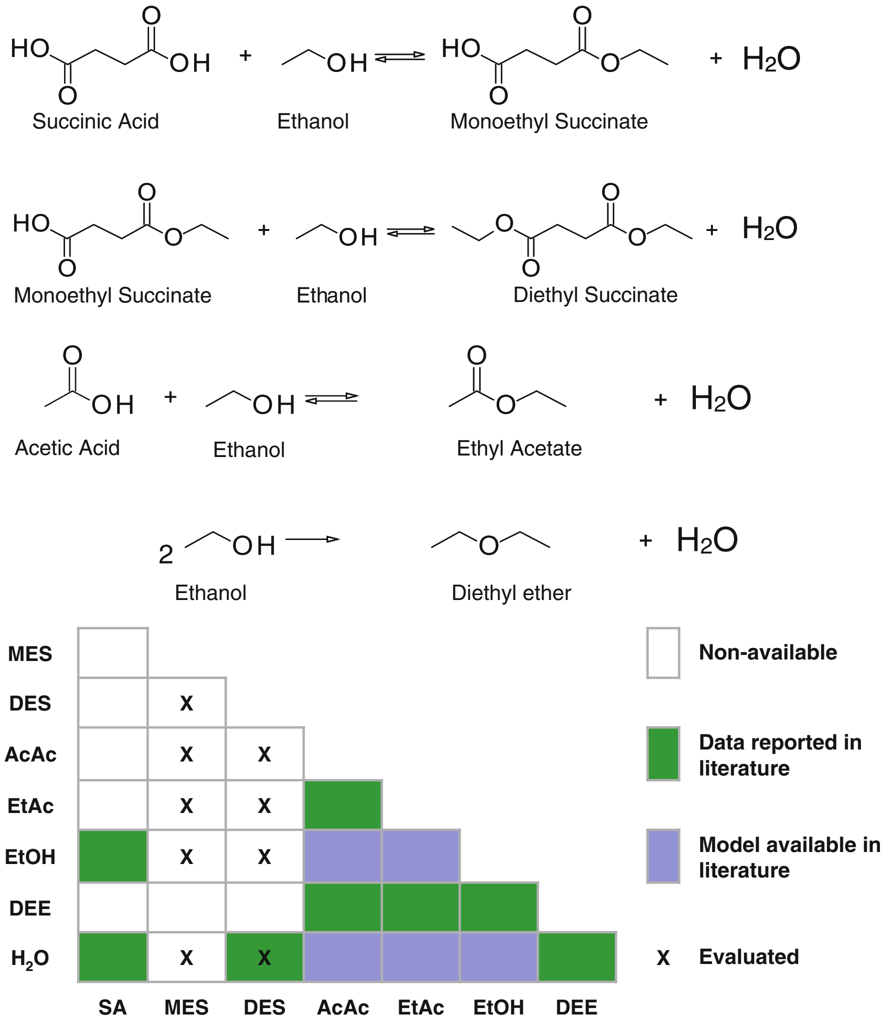
Multicomponent phase equilibria in RD systems have been the focus of attention for a long time [89–95]. Physicochemical interactions among reacting compounds can be complex, and the concurrence of phase equilibria and chemical reaction may lead to unexpected phenomena such as the appearance of reactive azeotropes or the disappearance of the traditional ones.

Despite the crucial importance of a basic understanding of applied thermodynamics for RD modeling, not all technology developers are trained in the fundamentals. The value of "good thermodynamics" in RD applications is tangible when doing flash calculations; making the wrong assumptions or selecting the wrong thermodynamic model may lead to erroneous to disastrous results. Nevertheless, and because of the lack of experimental data or the expertise required to validate thermodynamic models, process engineers working on RD simulation mostly rely on estimation techniques such as group-contribution methods (e.g., UNIFAC). These models are not only based upon incomplete experimental datasets, but also tend to fail when predicting the behavior of highly functionalized molecules, electrolytes, isomers, or when estimating simultaneous vapor–liquid–liquid equilibrium [96].

As there is no universal model to fit all chemical systems, phase equilibria calculations in RD simulations have been carried out with a set of proven methods and models, each for a specific type of chemicals [96–99]. Among the variety of methods used for vapor–liquid equilibrium calculations for RD we can identify: ideal vapor—non-ideal liquid, non-ideal vapor—ideal liquid, or extremely non-ideal phases (fugacity–fugacity or activity–fugacity methods) [80]. For the vapor phase fugacity calculation, equations of state models are mostly used (e.g., Peng Robinson, Soave–Redlich–Kwong, etc.) even including corrections accounting for molecular association (e.g., Hayden O'Connell, Northnagel). For activity coefficient calculation, local composition models are preferred (e.g., NRTL, UNIQUAC); however, they do not always extrapolate well from binary to multicomponent systems, especially for liquid–liquid equilibrium.

Yet, because the importance of the binary interactions between all components in a reacting mixture is not the same, and binary parameters are not always available, predictions by group-contribution methods might be used as well. Nonetheless, sometimes an experimental evaluation of some specific binary interaction parameters is necessary to improve the multicomponent phase equilibrium calculation. The identification of those key interaction parameters to be measured in the lab can be done, for example, by evaluating the impact of the uncertainty of a given parameter in the process performance [14]. A smart balance is important in those cases, considering that even if the resources are available, the task of evaluating every single interaction parameter in a reactive mixture can be sometimes overwhelming, and not worth it for preliminary calculations.

As a matter of example, in Fig. 6.10, it is described that the reaction path for a mixed-acids esterification system is carried out in a RD system [100]. The complete



	SA	MES	DES	AcAc	EtAc	EtOH	DEE
MES	☐						
DES	☐	☐ X					
AcAc	☐	☐ X	☐ X				
EtAc	☐	☐ X	☐ X	🟩			
EtOH	🟩	☐ X	☐ X	🟪	🟪		
DEE	☐	☐	☐	🟩	🟩	🟩	
H_2O	🟩	☐ X	🟩 X	🟪	🟪	🟪	🟩

☐ **Non-available**

🟩 **Data reported in literature**

🟪 **Model available in literature**

X **Evaluated**

Fig. 6.10 Reactions path in a mixed succinic-acetic acids esterification with ethanol, and binary interactions required to describe phase equilibria for RD design. *SA* succinic acid, *MES* monoethyl succinate, *DES* diethyl succinate, *AcAc* acetic acid, *EtAc* ethyl acetate, *EtOH* ethanol, *DEE* diethyl ether, and H_2O water [100]

set of binary interactions occurring in the reactive mixture totals 28 (including a side reaction—ethanol dehydration to diethyl ether). In this case not only vapor–liquid, but also liquid–liquid and solid–liquid equilibria are required for a complete modeling of the process, as solid precipitation and liquid–liquid phase splitting might occur within the RD column [100–104]. Additionally, in extreme cases like this, the lack of commercial reagents makes necessary the synthesis, purification, and isolation of a specific component before performing phase equilibrium experiments [103]. If phase equilibrium of ternary or multicomponent mixtures is also required during parameter estimation, the amount of experimental work may increase exponentially, and the costs can become prohibitive. In cases like this, predictive methods are useful.

Regardless of the method and models used for thermodynamics calculations, consistency is the key factor. For instance, if an activity-based method is used for phase equilibrium calculation, the equilibrium constant K_{EQ} (and desirably the kinetics) has to be calculated in a consistent way:

$$K_{\mathrm{EQ}} = \prod_{i=1}^{NC} (x_i \gamma_i)_{\mathrm{EQ}}^{v_i} \tag{6.17}$$

Here the constant is computed from the activities (mole fraction multiplied by the activity coefficient, $x_i \gamma_i$). In this case, the use of a molar-basis value of the equilibrium constant might generate inconsistent results. As an illustration, when computing residue curve maps (RCM) of a non-ideal reactive system, phase equilibrium must be represented with non-ideal models. However, if a molar-basis value of the equilibrium constant is used to account for reaction, it may happen that an azeotrope no longer coincides with an extremum in the temperature. This is inconsistent according to Gibbs–Konovalov theorem applied to reactive mixtures, and it has been observed when constructing RCM for ethyl acetate production by RD [14]. A broader discussion on the importance of thermodynamics consistency for RD modeling can be found in the open literature [14, 91].

Other important element when performing process design (not only in RD), is the knowledge of reference state properties and thermal properties of the reactive mixture, such as phase change enthalpies, heat of mixing, and heat capacities. All this information is used, for example when calculating temperature dependence of the equilibrium constant. As indicated in (6.18), for a good estimation of the equilibrium constant in absence of experimental data, enthalpy (ΔH_{R}) and entropy (ΔS_{R}) of reaction are required.

$$\ln K_{\mathrm{EQ}} = \frac{-\Delta G_{\mathrm{R}}}{\mathrm{RT}} = \frac{-\Delta H_{\mathrm{R}}}{\mathrm{RT}} + \frac{\Delta S_{\mathrm{R}}}{R} \tag{6.18}$$

Additional thermal data are also used when performing energy balances that account for the impact of the heat of reaction in the distillation process. When a reaction is exothermic, the heat from the reaction will create additional vapor flow in the column. As the separation efficiency in the column is dependent on the ratio of vapor flow to liquid flow, if the process simulator wrongly predicts heat of reaction, a poor column design will be obtained. Because heats of reaction can be comparable or larger than heats of vaporization, the error can be considerable. The occurrence of this wrong modeling is probable considering that process simulators typically base heat of reaction calculations on heats of formation for ideal gas

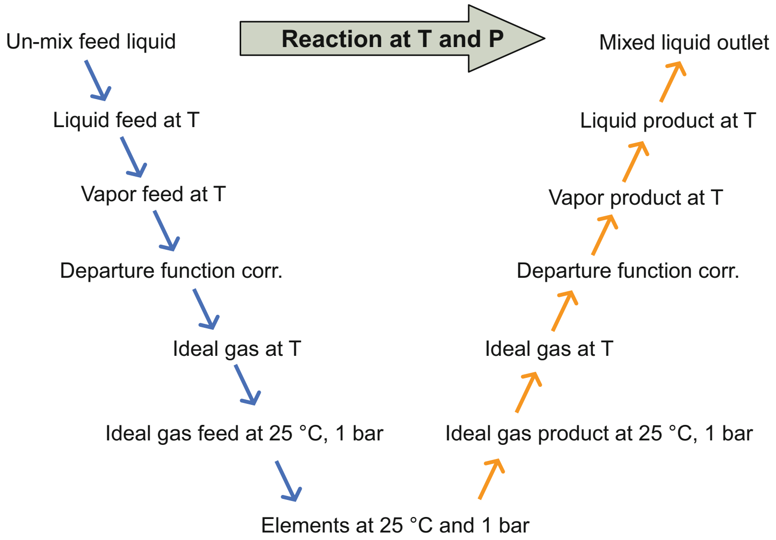


Fig. 6.11 Aspen plus® default pathway to calculate state functions for a liquid phase reaction

species, even when the reaction occurs in the liquid phase. Then, the heat of reaction is commonly tuned to match experimental information.

As a matter of example, in (6.19) the energy balance over a liquid phase reactor (similar to a reactive stage within an RD column) is described:

$$H^{\text{in}}\,\dot{n}^{\text{in}} - H^{\text{out}}\,\dot{n}^{\text{out}} + \dot{Q} + \dot{W}_{\text{s}} = 0 \tag{6.19}$$

Superscripts indicate inlet (in) and outlet (out) streams, H is the molar enthalpy, and n is the molar flow. For simplicity, assume an adiabatic system ($Q = 0$) and negligible shaft work ($W_S = 0$), so the overall energy change can be computed from the difference of enthalpy flows.

Now, during calculation of state properties, a specific route is used. A route is a combination of a pathway (e.g., Hess's law), methods (e.g., activities, enthalpies from heat of formation), and a model (e.g., NRTL). In general these routes are prepackaged in commercial process design software. For example, a pathway for the enthalpy change-calculation of (6.19) using the heat of formation method is described in Fig. 6.11. Equations (6.20) and (6.21) represent the corresponding inlet and outlet enthalpy flows.

$$H^{\text{in}}\,\dot{n}^{\text{in}} = \sum_{\text{NC}} \dot{n}_i^{\text{in}} \left(\Delta H_{fi}^{0} + \int_{Tr}^{T^{\text{in}}} CpdT \right) + \Delta H_{\text{vap}} + \Delta H_{\text{mix}} \tag{6.20}$$

$$H^{\text{out}}\dot{n}^{\text{out}} = \sum_{\text{NC}} \dot{n}_i^{\text{out}} \left(\Delta H_{fi}^0 + \int_{Tr}^{T^{\text{out}}} CpdT \right) + \Delta H_{\text{vap}} + \Delta H_{\text{mix}} \tag{6.21}$$

As noticed in the previous equations, our ability to estimate the heat evolved during a reaction, and its potential impact on the coexisting distillation phenomena in a RD column, is entirely dependent on our knowledge of the required thermal data (and their temperature, pressure, and composition dependence). A recent work describing a cyclohexene acetylation process via RD to produce cyclohexyl acetate, emphasizes on the importance of a good heat of reaction prediction (or measurement) to match pilot scale experiments with simulations [105]. The same can be expected in other highly exothermic or endothermic reactive systems.

6.4.2 Kinetic Models for RD Applications

Likewise in the reactor design, kinetic models are a necessary tool for the design of RD processes. Taking into account the higher molar density and hold-up, chemical reaction is considered to occur only in the liquid phase within a RD column.

Unlike phase equilibrium thermodynamics, reaction kinetics cannot be predicted; it is specific for each chemical system and needs to be experimentally evaluated. Kinetic expressions are generally obtained from batch or continuous reaction experiments, using either the integral or the differential analysis approach.

In general, liquid phase kinetics can be expressed as function of temperature, concentrations, and catalyst loading. For highly non-ideal systems, activity-based kinetics are preferred over molar concentrations or molar fraction-based models. Regardless of the kinetic model responding to a specific reaction mechanism, or if it is just the product of a parametric adjustment, the model has to describe the intrinsic kinetics. The mass and heat transfer effects have to be ruled out during experimental determinations; otherwise the obtained model would not work well during up-scaling.

Assuring an intrinsic kinetic model is sometimes difficult, in particular when using heterogeneous catalysts. Figure 6.12 is a schematic representation of the mass transfer resistances using heterogeneous catalysts within a reactive media. During experiments only the concentration in the bulk phase ($C_{\text{A, bulk}}$) is measurable, so the observable rate of reaction (r') might be calculated with respect to it. However, intrinsic kinetics must depend on the concentration within the catalyst particles. Thus the observable kinetics has to be correlated with the intrinsic one for example by using the following expression:

$$r' = \eta_{\text{ext.}} \times \eta_{\text{int.}} \times [\text{intrinsic}] \tag{6.22}$$

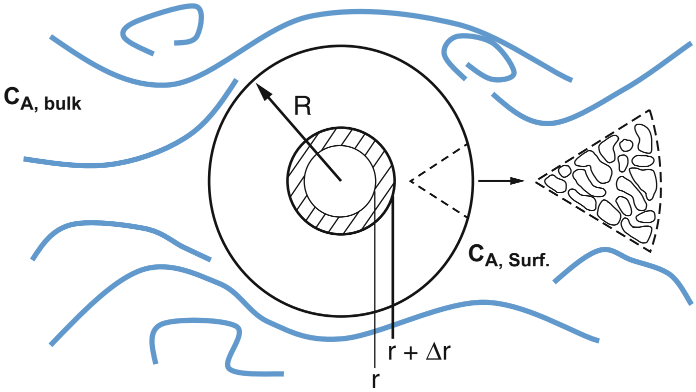


Fig. 6.12 Mass transfer limitations in a catalytic particle submerged in a reactive media

Here, the external ($\eta_{\text{ext.}}$) and the internal ($\eta_{\text{int.}}$) effectiveness factors account for mass transfer limitations between the bulk and the catalyst surface, and diffusion inside the particle, respectively. If the Damköhler number (*Da*) represents the ratio of the observed rate of reaction to the bulk mass transfer rate, and the Thiele modulus (Φ) corresponds to the ratio of chemical reaction rate to intraparticle diffusion rate; both internal and external effectiveness factors can be calculated as function of them for a given kinetic model [106]. Figure 6.13 represents the dependence of external and internal effectiveness factors with the corresponding *D*a and Φ values.

According to (6.22), the intrinsic kinetics is obtained when both effectiveness factors are close to unity (reaction rate limited regime). Figure 6.13 indicates that this would occur if both external and intraparticle mass transfer coefficients are high (turbulent flow and small particle diameter), and also when reaction rate is slow enough compared with mass transfer (i.e., at low temperature). This implies that experimental measurements to obtain kinetic expressions have to be performed in well mixed reactors, with small size catalytic particles, and in the lower level of the operating temperature range. While external mass transfer can be avoided by fluid mixing, the intraparticle mass transfer rates depend strongly on the solid properties (e.g., particle geometry and size, porosity distribution, tortuosity, surface area, effective diffusion of liquids within the pores, etc.). To quantify if intraparticle mass transfer limitations are happening in such complex systems, the observable Weisz–Prater parameter ($\Phi W = \eta_{\text{int.}}\Phi 2$) can be used as criterion. The absence of intraparticle mass transfer effects can be assured if the observable Weisz–Prater criterion is close to zero [107].

The usage of heterogeneous catalysis can lead to complex kinetic models such as the one described in (6.23) for the reaction A + B ↔ C + D. In this case an activity-based LHHW-type model is presented [106].

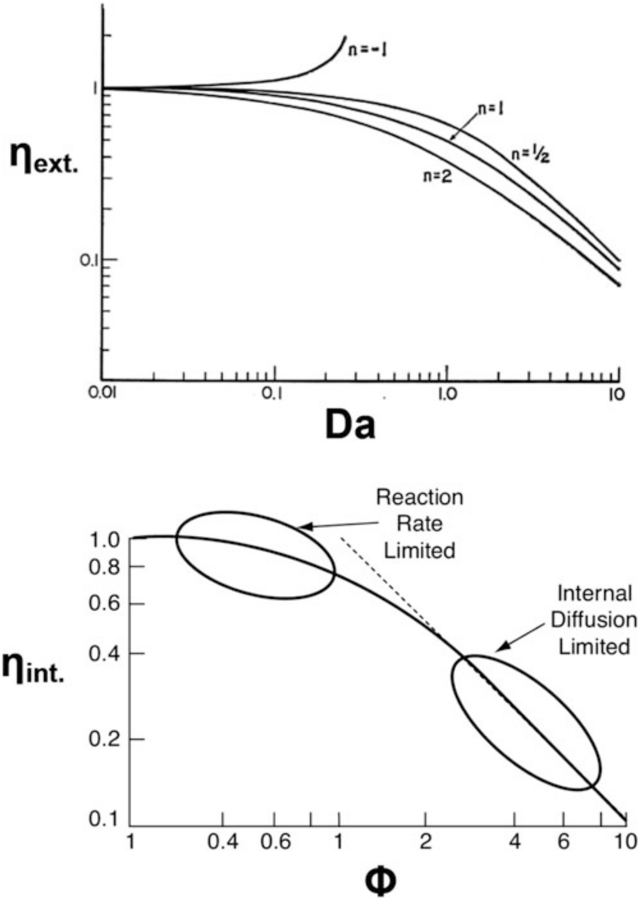


Fig. 6.13 External (*up*) and internal (*down*) isothermal effectiveness factors for a catalytic particle as function of Damköhler number (*Da*) and Thiele modulus (*Φ*), and different orders of reaction (*n*). Adapted from [106]

$$r' = \frac{\eta_{\text{Global}} w_{\text{cat}} [k_0 \exp(-E_{\text{a}}/\text{RT})] \left[(x\gamma)_A (x\gamma)_B - (x\gamma)_C (x\gamma)_D / K_{\text{EQ}} \right]}{\left[1 + k_A (x\gamma)_A + k_B (x\gamma)_B + k_C (x\gamma)_C + k_D (x\gamma)_D \right]^2} \tag{6.23}$$

Each term in the kinetic model represents the following effects:

$$r' = \frac{(\text{Global effectiveness factor})(\text{cat. loading})[\text{kinetic term}][\text{net driving force}]}{[\text{adsorption terms}]} \tag{6.24}$$

This kind of models require not only a reliable thermodynamic model to calculate non-idealities of the mixture, but also physi-sorption constants (k_i), the chemical equilibrium constant (K_{EQ}), the energy of activation (E_a), the pre-exponential factor (k_0), and the correction factor (η_{Global}). In general, all these parameters are independently obtained by chemical equilibrium experiments (or estimation), absorption isotherms, and kinetics assays. When the intrinsic kinetic is obtained, process up-scaling is possible. In the case of RD operations, incomplete wetting, dead volumes, and different residence time distributions along the catalytic packing or the column internals can happen leading to a reduced global effectiveness factor that has to be accounted for during simulations. The problem can be even more complex when simultaneous reactions occur within a RD column.

6.4.3 Design of Reactive Distillation Processes

Despite the promise of achieving process intensification by implementing RD, the industrial community still hesitates of adopting this new technology. One of the reasons for this reluctance is that there is not such a thing like a universal methodology for the design of reactive distillation operations. Most industrial RD systems currently under operation were implemented over the shoulders of experienced process engineers, more than on the basis of systematic design methodologies. This is understandable because of the complexity of combining reaction and separation phenomena [108, 109].

Most traditional approaches for process design involve the use of a preliminary feasibility analysis, followed by the synthesis of the process, and then the final design is achieved based upon computer simulations. Researchers working on the design of RD processes have followed the same pathway. Because the design methodologies for traditional distillation have been well established for several years, they were mostly incorporated and adapted to the case of RD operations design.

As in the case of traditional distillation operations design, the RD feasibility analysis can be carried out through graphical methods such as the residue curve maps (RCM). In this case the reaction effects have to be considered, so the set of curves produce the so-called reactive residue curve maps (RRCM). These graphic representations can be constructed by assuming chemical equilibrium condition in every reactive stage, or by taking into account the reaction kinetics. Interpretation of these maps can be difficult, mainly when more than three components are considered in the reactive system (including inerts). In consequence, this methodology, even when valuable for simple reactive systems, is still quite limited for implementing real RD operations (most raw materials contain inerts, side reactions are more the rule than the exception, chemical equilibrium condition is not achieved, etc.).

As a matter of example, and by using a molar fraction basis, consider the following reaction at the chemical equilibrium condition,

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C + \nu_D D \tag{6.25}$$

Here, v_i are the stoichiometric coefficients. At chemical equilibrium

$$K_{\mathrm{EQ}} = \frac{\left(x_C^{\mathrm{EQ}}\right)^{\nu_C}\left(x_D^{\mathrm{EQ}}\right)^{\nu_D}}{\left(x_A^{\mathrm{EQ}}\right)^{\nu_A}\left(x_B^{\mathrm{EQ}}\right)^{\nu_B}} = \prod_{i=1}^{\mathrm{NC}}\left(x_i^{\mathrm{EQ}}\right)^{\nu_i} \tag{6.26}$$

At the beginning of the reaction there are n_0 total moles while at the end n_{T} moles remain. For simplicity, the superscript indicating equilibrium condition at the end (EQ) is dropped. By doing a mole balance for each component at the beginning and at the equilibrium condition.

$$n_i = n_{i0} + \nu_i \xi \tag{6.27}$$

$$x_i n_{\mathrm{T}} = x_{i0} n_{i0} + \nu_i \xi \tag{6.28}$$

$$x_i = \frac{x_{i0} n_{i0} + \nu_i \xi}{n_{\mathrm{T}}} \tag{6.29}$$

where ξ is the extent of reaction. Also by computing the total number of moles of all the components from (6.27)

$$n_{\mathrm{T}} = n_0 + \nu_T \xi \tag{6.30}$$

Here v_T is the sum of all stoichiometric coefficients over all components participating in the reaction (NC), which indicates the net change of moles

$$v_T = \sum_{i=1}^{\mathrm{NC}} v_i \tag{6.31}$$

By substituting every component concentration in the equilibrium constant, (6.26), we have

$$K_{\mathrm{EQ}} = \prod_{i=1}^{\mathrm{NC}}\left(x_i^{\mathrm{EQ}}\right)^{v_i} = \prod_{i=1}^{\mathrm{NC}}\left(\frac{x_{i0} n_0 + v_i \xi}{n_{\mathrm{T}}}\right)^{v_i} = \frac{\prod_{i=1}^{\mathrm{NC}}\left(x_{i0} n_0 + v_i \xi\right)^{v_i}}{\left(n_{\mathrm{T}}\right)^{v_T}} \tag{6.32}$$

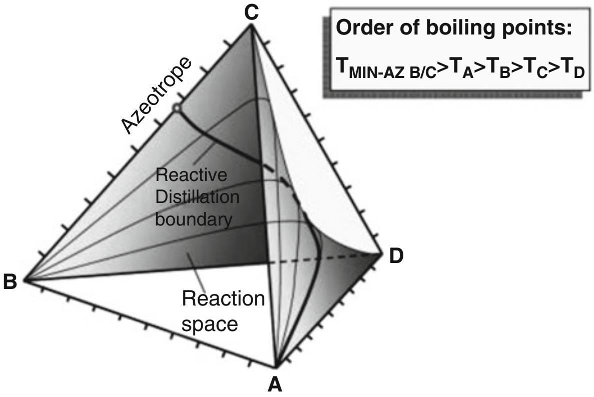


Fig. 6.14 Mole fraction reaction space for a A + B ↔ C + D reaction. From [66] reprinted with permission from the publisher Springer

$$K_{\mathrm{EQ}} = \frac{\prod_{i=1}^{\mathrm{NC}} (x_{i0} n_0 + v_i \xi)^{v_i}}{(n_0 + v_T \xi)^{v_T}} \tag{6.33}$$

Then, provided a set of initial conditions, the stoichiometry coefficients, and obtaining the value of the equilibrium constant at a given temperature using (6.18) (e.g. bubble point), it will be possible to calculate the extent of reaction at equilibrium by solving (6.33).

A plot of every equilibrium condition obtained from any initial composition of the quaternary mixture, depicts the chemical equilibrium surface (or reaction space in Fig. 6.14). Assuming that the reaction occurs very fast (i.e., at chemical equilibrium), the composition of all feasible liquids at any reactive stage within the RD column must lie on the chemical equilibrium surface. Also the distillation boundaries and the distillation regions of the reactive system are located within this surface.

Now, the path followed by reaction from the initial conditions to the chemical equilibrium state is represented by the so-called stoichiometric lines [57]. These set of lines are obtained with respect to a reference component k (e.g., limiting reactant).

From (6.27), and summing over all components:

$$\xi = \frac{\Delta n_i}{v_i} = \frac{\Delta n_k}{v_k} = \frac{\Delta n}{v_T} \tag{6.34}$$

By substituting n_{T} from (6.30) in (6.28), and rearranging

$$\frac{n_0}{\xi} = \frac{v_i - v_T x_i}{x_i - x_{i0}} \tag{6.35}$$

This relationship is also valid for the reference component *k*

$$\frac{n_0}{\xi} = \frac{\nu_k - \nu_T x_k}{x_k - x_{k0}} \tag{6.36}$$

Then, clearing x_i from (6.35) and (6.36)

$$x_i = \frac{x_{i0}(\nu_k - \nu_T x_k) + \nu_i(x_k - x_{k0})}{\nu_k - \nu_T x_{k0}} \tag{6.37}$$

Equation (6.37) is called the stoichiometric line, which corresponds to the pathway followed by each component from the initial composition up to the chemical equilibrium condition located on the reaction space (Fig. 6.14).

Now that the space of achievable liquid compositions within the column caused by the chemical equilibrium was obtained, feasible separations might be established by observing the RCM. In general, residue curves represent the liquid concentration profile of a continuous distillation column operating at total reflux with infinite number of stages. In this case, reaction is occurring, so the analysis has to be done on the RRCM. These curves can be constructed from the model that describes the time-changing composition of the residual liquid remaining in a simple distillation device [58] as presented in Fig. 6.15.

Assuming that in a given time *t*, the composition in the vapor (*y*) is in phase equilibrium with the corresponding liquid (*x*), the mole change with time for component *i* in the vessel is described as:

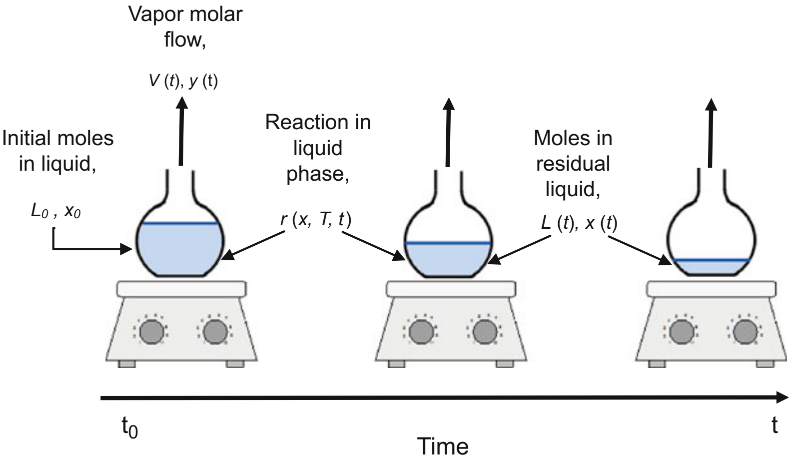


Fig. 6.15 Scheme of a simple distillation accompanied by reaction

$$\frac{d(L_i)}{dt} = \frac{d(x_iL)}{dt} = -Vy_i + \sum_{j=1}^{\mathrm{NR}} v_{i,j} r_j L \tag{6.38}$$

$$x_i \frac{dL}{dt} + L\frac{dx_i}{dt} = -Vy_i + \sum_{j=1}^{\mathrm{NR}} v_{i,j} r_j L \tag{6.39}$$

where L is the total number of moles in the liquid phase, V is the instantaneous vapor molar flow, $v_{i,j}$ correspond to the stoichiometric coefficient of component i in reaction j, NC is the total number of components in liquid phase, and NR is total number of reactions occurring in the vessel. The overall mole balance is then

$$\frac{d(L)}{dt} = -V + \sum_{j=1}^{\mathrm{NR}} v_{T,j} r_j L \tag{6.40}$$

Substituting the total change of moles of the vessel from (6.40) into (6.39) and simplifying

$$\frac{dx_i}{dt} = -\frac{V}{L} y + \sum_{j=1}^{\mathrm{NR}} v_{i,j} r_j + \frac{V}{L} x_i - x_i \sum_{j=1}^{\mathrm{NR}} v_{T,j} r_j \tag{6.41}$$

If we use a heating policy such as there is a constant evaporation ratio

$$\frac{V_0}{L_0} = \frac{V(t)}{L(t)} = \text{constant} \tag{6.42}$$

A dimensionless variable can be defined as

$$d\xi = \frac{V_0}{L_0} dt \tag{6.43}$$

By combining (6.41)–(6.43), and rearranging we obtain the reactive residue curve equation

$$\frac{dx_i}{d\xi} = (x_i - y_i) + \frac{L}{V} \sum_{j=1}^{\mathrm{NR}} \left[r_j \left(v_{i,j} - x_i v_{T,j} \right) \right] \tag{6.44}$$

In order to solve (6.44), and so obtaining the path followed by the concentration of component i in the vessel, a value for L/V must be provided. For large values of this ratio (L/V $\rightarrow \infty$) evaporation is very slow or liquid hold-up is very large, and there is enough residence time to achieve chemical equilibrium in the liquid phase. Eventually the liquid composition moves towards a stable node resulting in a chemical equilibrium residue curve (located on the reaction space of Fig. 6.14). On the other hand, for small values of L/V (tending to zero) the curve trajectory would be identical to that of a nonreactive residue curve, as there is not enough residence time or liquid hold-up for reaction to occur.

Now, if a reference state rate of reaction (r^0), and the dimensionless Damköhler number (Da) are used

$$R_j(x,T)=\frac{r(x,T)}{r^0} \tag{6.45}$$

$$Da=\frac{L/V}{1/r^0} \tag{6.46}$$

Equation (6.44) can be written as

$$\frac{dx_i}{d\xi}=(x_i-y_i)+\sum_{j=1}^{\mathrm{NR}}\left[DaR_j\left(\nu_{i,j}-x_i\nu_{T,j}\right)\right] \tag{6.47}$$

Here, Da is ideally used to describe the relative effects of the reaction rate versus the vaporization rate, reason why Da behavior is equivalent to the L/V ratio.

The same procedure described in (6.38)–(6.47), can be done using a new set of transformed compositions that have similar properties to those of mole fractions in nonreactive mixtures [110, 111].

$$X_i=\frac{x_i-\frac{\nu_i}{\nu_k}x_k}{1-\frac{\nu_T}{\nu_k}x_k} \tag{6.48}$$

$$Y_i=\frac{y_i-\frac{\nu_i}{\nu_k}y_k}{1-\frac{\nu_T}{\nu_k}y_k} \tag{6.49}$$

The evaporation rate and the liquid hold-up can be then redefined with respect to the reference component k as

$$\overline{V}=V\left(1+\frac{\nu_T}{\nu_k}y_k\right) \tag{6.50}$$

$$\overline{L}=L\left(1+\frac{\nu_T}{\nu_k}x_k\right) \tag{6.51}$$

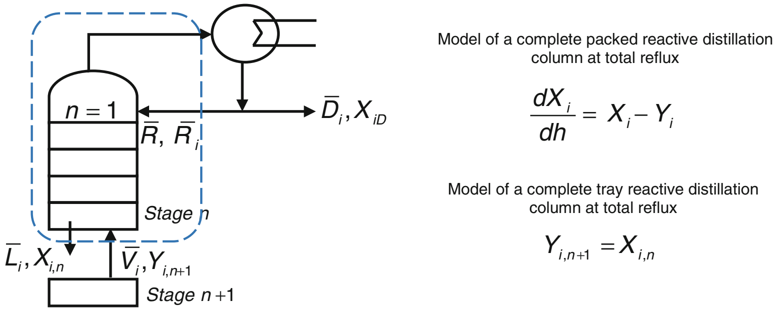


Fig. 6.16 Scheme of a complete reactive distillation column using transformed variables. Adapted from [14, 111]

$$\bar{L}_i = L_i + Hx_k \frac{v_T}{v_k} = L_i X_i \tag{6.52}$$

With these new variables, the model that describes a reactive simple distillation is formally identical to the nonreactive residue curve

$$\frac{dX_i}{d\xi} = X_i - Y_i \tag{6.53}$$

Now, a complete RD column can be described through the transformed compositions and flows as presented in Fig. 6.16. Doing the mole balance over the column, over a single reactive stage within it, combining and presenting the results in transformed variables as described by Barbosa [111], it can be shown that similar equations to those of a nonreactive distillation column are obtained. If the operation occurs at total reflux and with an infinite number of stages, a model identical to the reactive residue curve described in (6.53) is obtained. If the analysis is done over a tray column, the model would be identical to the reactive distillation line.

The above indicates that, by using the reactive distillation lines or RRCM in the transformed coordinates, a graphical analysis on the feasibility of the RD operation can be performed. Nonreactive and reactive azeotropes as well as the pure components will be the singular points (nodes) of the concentration space. Reactive distillation regions and boundaries can be also identified.

For instance, in Fig. 6.17 there is a representation of the quaternary system described in Fig. 6.14, but using transformed concentrations. Feasible product areas can be determined in the two-dimensional space similarly to the bow–tie regions in nonreactive curve maps. The total mole balance over the RD column is still represented as a straight line that connects feed, bottom, and distillate compositions. Similarly, for a feasible separation, distillate and bottom concentrations must lie in the same residue curve, within the same distillation region.

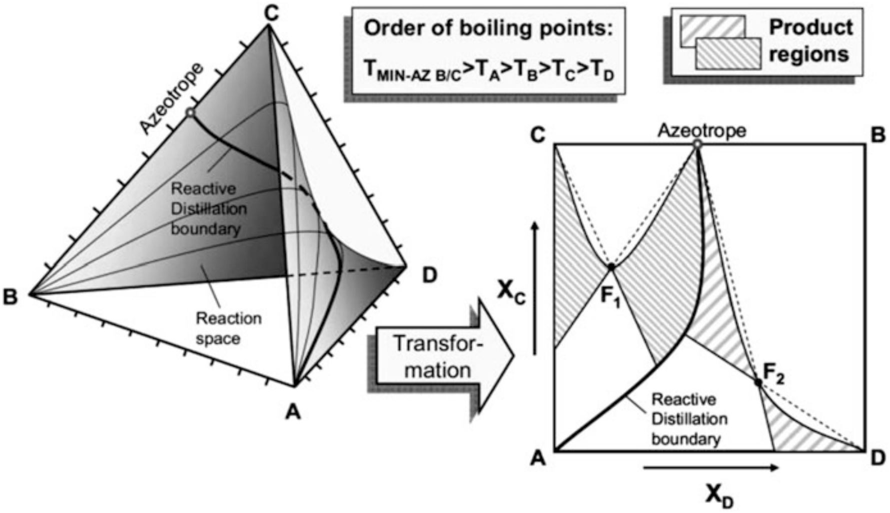


Fig. 6.17 Transformation of a mole fraction reaction space (*left*) to transformed coordinates (*right*). From [66] reprinted with permission from the publisher, Springer

While the RRCM can help defining feasibility of the operation, the complete design of the operation is still required. Different approaches have been used for the design of RD columns, each one with its own limitations and/or advantages. As a schematic diagram, Fig. 6.18 summarizes the different design methodologies reported in the literature, from the feasibility study to the optimization of the RD operation [109].

The above diagram illustrates the various routes a designer may select depending on the number of components, the available kinetic information, the number of reactions, etc. It is also intended to guide through the different design stages rather than to limit the designer's flexibility. Other methodologies not described in Fig. 6.18, and new ones to come, may also be used together or independently from the ones suggested here.

As observed in Fig. 6.18, for a limited number of RD systems (three to four components including inerts), the construction of equilibrium residue curve maps (ERCM), simple distillation RCM, and kinetically controlled RRCM can be used as a key tool for the feasibility analysis. An alternative solution if kinetic models are not known when constructing RRCM, is to assume specific values for *Da* number, but only in reactive systems where only one reaction occurs. If the process is feasible, it would be an incentive to investigate further, and to obtain an experimentally based kinetic model. Nevertheless, the RRCM approach does not apply for hybrid columns (those having nonreactive sections). For that reason, other approaches have to be used when the desired components are not stable nodes in the RRCM.

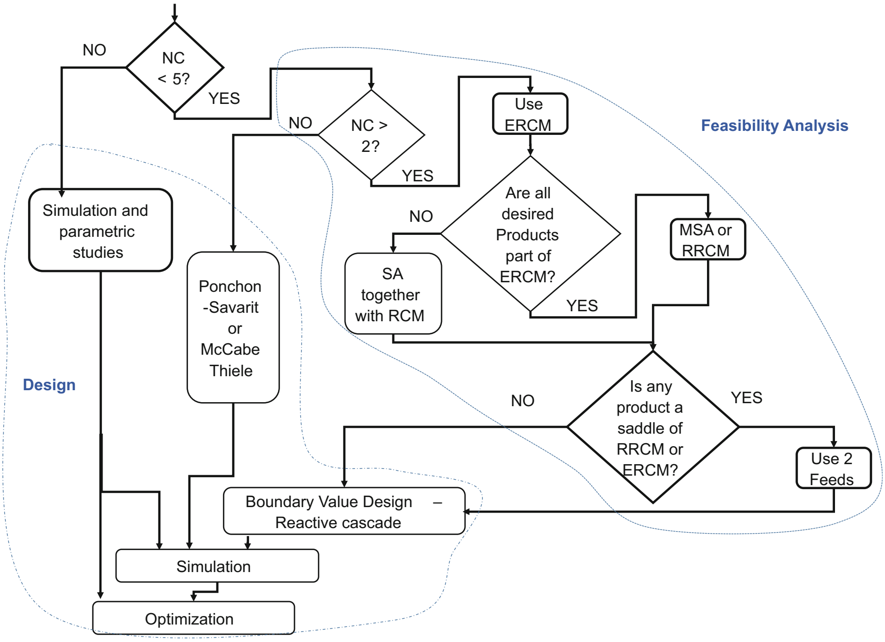


Fig. 6.18 Schematic approach for the design of a RD process from feasibility to optimization. *NC* number of components (including inerts), *SA* static analysis, *MSA* modified static analysis, *ERCM* equilibrium residue curve maps, *RCM* nonreactive residue curve maps, *RRCM* reactive residue curve maps with kinetics

For systems with less than five components, there are a set of graphical analyses that may be used. For systems containing two components, extensions of McCabe–Thiele and Ponchon–Savarit [112, 113] are possible. For mixtures with three components RCM may be plotted in a ternary diagram. For mixtures with four components a quaternary diagram with molar compositions or a rectangular diagram in the transformed composition may be used. Therefore, the boundary value method (BVM) may be used for systems with three to four components to define design variables such as reflux ratio, boil-up ratio, number of plates, etc.

Systems with 5 of more components are the most common in the industrial applications. There, solvents and inert entrainers are used, secondary reactions occur, feeds contain impurities, etc. In these cases, the graphical methods begin to hide too many of the insights from the system and therefore it should be analyzed very carefully. Bearing into account that computational power has increased vastly over the last decades, the computational resolution of the MESH equations (mass and energy balance, phase equilibrium, summation of mole fractions) that describe the system, may also be used for the conceptual design of multicomponent mixtures. With nowadays computers and convergence methods, the solutions for very complex problems can be achieved within a few seconds. Besides, both the equilibrium and non-equilibrium stage models for RD columns have been implemented with success in commercial process design software [114, 115].

A sensitivity analysis from the design variables may be performed easily using a commercial simulator or otherwise using adhoc programmed models for a given RD unit. Results from a sensitivity analysis when two or three variables are being analyzed simultaneously, may be plotted in a 2D or 3D diagram respectively. If more variables are being investigated, two to three variable subsets need to be selected to express the results graphically. Simulation may also be used for previously conceptually designed operations resulting from the BVM, static analysis, and the modified static analysis. In this case complete simulations have the advantage that energy consumption in the reboiler and in the condenser can be calculated, something that was not possible from the previous conceptual design stage.

Another advantage of using the complete simulation as design tool is that equipment costs may be readily calculated and included in optimization functions. Even though reflux and boil-up ratios are a good indicator of the variable costs and should therefore be used in the preliminary design stages, the total annual costs (TAC) is a better indicator of a process economic feasibility.

As mentioned before, the primary tools for RD modeling are the equilibrium and non-equilibrium stage approaches. Both are well known in traditional distillation design, but some specific remarks have to be mentioned when applied to RD. Depending on whether the reactive separation process is distillation-controlled or reaction-controlled, different models may fit better for the operation. This characterization can be done according to the dimensionless Hatta number (ratio of reaction to diffusion rates at the liquid film) [66].

As observed in Fig. 6.19, when reaction rate is fast (Hatta number higher than 3), there might be enough time in every stage to achieve phase equilibria, so the equilibrium-stage model would work. Contrary, if the reaction rate is slow (Hatta numbers less than 1) it occurs in the liquid bulk, and it can be modeled with the reaction kinetics. However, if reaction rate is intermediate as well as the mass transfer, they would affect each other. In this case, rate-based approaches are better including their mutual interaction (enhancement factor) [46, 116].

Another aspect to consider in the RD modeling is related with the column hydrodynamics during operation. As observed in Fig. 6.20, different types of internals can be used in RD columns. When operating with homogeneous catalysts, traditional trays, random packing and structured packing can be used. In the case of heterogeneous catalysts, the internals are mainly catalytically active random packings, catalytic-coated structures, or immobilized catalytic particles loaded within structured packings, catalytic bales or internal/external packed beds.

Because of the different types of internals that can be installed within the columns, and the corresponding hydrodynamic regime and flow patterns at different scales, reaction and separation residence times do not necessarily coincide. In some cases, reaction efficiency is higher than separation efficiency, so the non-idealities of the flow behavior have to be accounted for.

The simplest method used, in both equilibrium and non-equilibrium stage models, is the consideration of complete mixing in each phase. Of course there is a composition profile at the interphase when working with non-equilibrium model (negligible volume compared with the total hold-up) but the bulk is assumed well

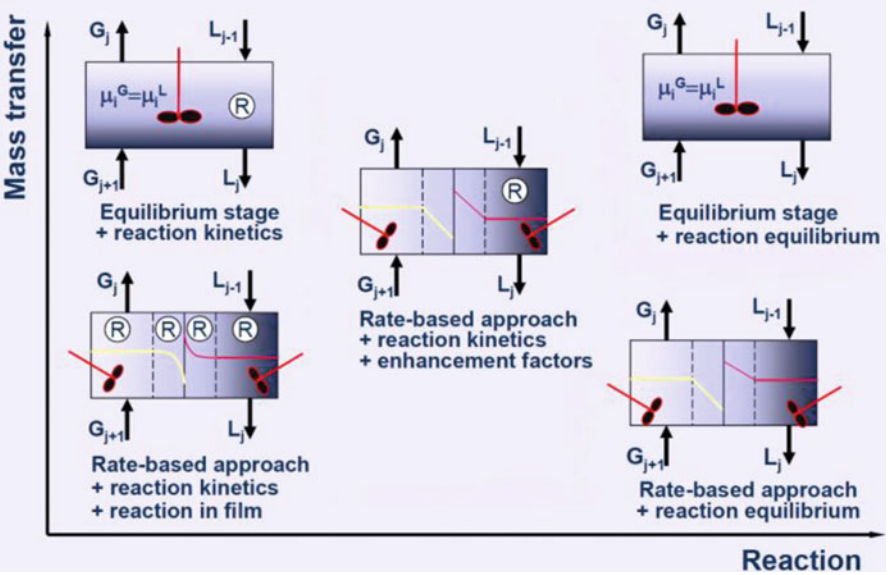


Fig. 6.19 Recommended modeling approaches according to the different combinations of distillation-limited or reaction-limited regimes in RD columns. *G* gas flow, *L* liquid flow, ® stands for the location where reaction kinetics needs to be accounted for. Adapted from [116]

mixed. An improvement of this representation can be done by discretizing the equilibrium stages, creating multiple CSTR reactors in series, mimicking the plug flow reactor residence time distribution within every stage. In Fig. 6.21, the composition profiles obtained with a non-equilibrium discretized stage model, in the esterification of acrylic acid with butanol are presented. As observed, experimental values fit differently with different number of discrete elements per stage. This also indicates that there must be an optimal number of discrete elements that allows adjusting the model to the back-mixing effects.

More refined models that take into consideration non-ideal flow behavior (e.g., back-mixing) such as the cell model [116], or the use of hydrodynamic analogies [119] can further improve hydrodynamic modeling, and help recognizing the effects of flow patterns in RD performance.

6.5 Optimization of Reactive Distillation Operations

As in any other process engineering case, optimization is a fundamental step in the conception of a RD process, highlighting modifications in plant design and in the operating procedures for the achievement of design goals, which include not only profitability and product specifications, but also environment-related constraints.

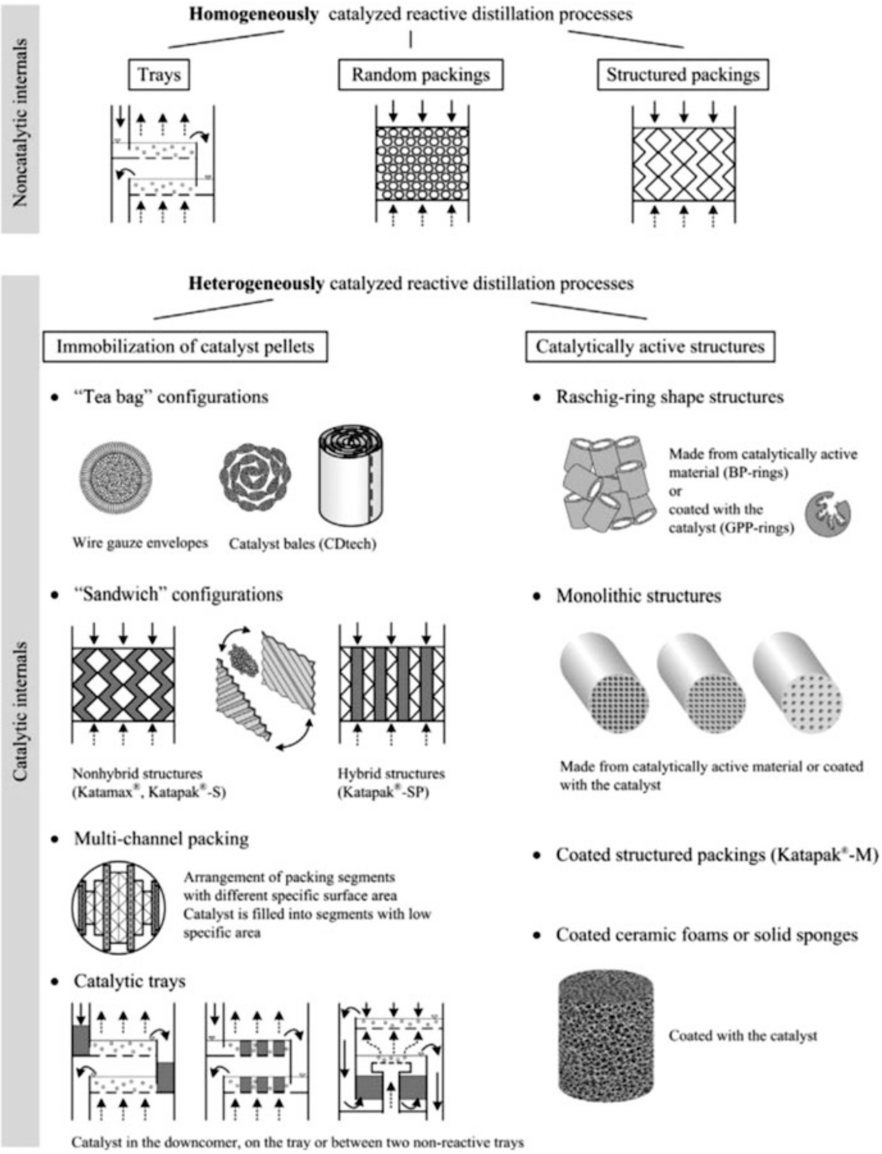


Fig. 6.20 Some common internals used for reactive distillation columns. From [46] reprinted with permission from the publisher, Elsevier books

Although there are different design methodologies for any type of process (including heuristics and graphical/topological approaches), optimization is the most widespread and reliable, since it is based on mathematical models that describe the system and that incorporate both physical (thermodynamics, kinetics,

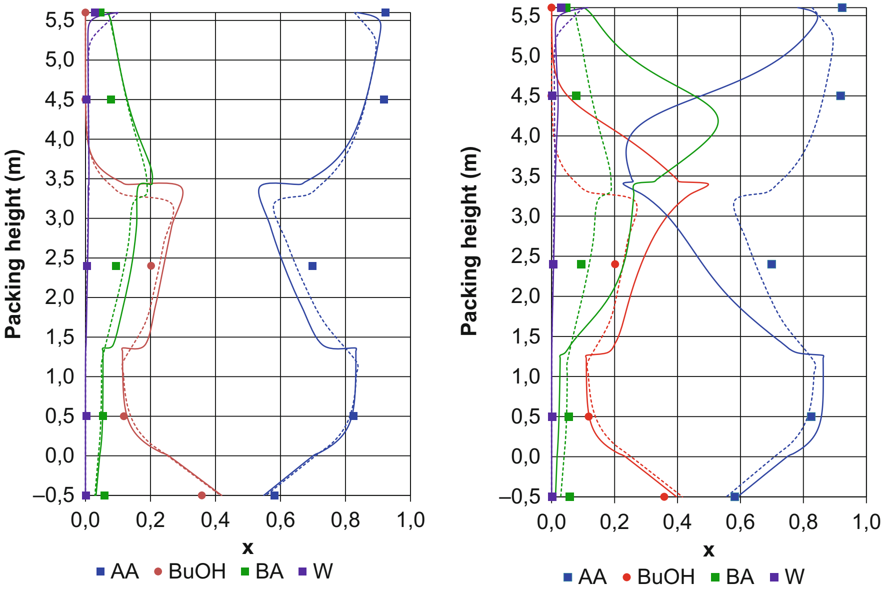


Fig. 6.21 Concentration profiles along a RD column during esterification of acrylic acid (AA) with butanol (BuOH) to produce butyl acrylate (BA) and water (W). Twenty discretes per stage in nonreactive sections, and no discretization in reactive zone (*left*) or four discretes per stage in reactive zone (*right*). *Continuous lines* represent profiles with discretization and *dashed lines* without it. Taken from [117], with experimental data from [118]

mass and energy balances) and economic information (operating cost and capital investment) [120]. Heuristic rules, on the other hand, are very easy to use and can be helpful for the estimation of parameters such as column pressure, reactive zone location, mass of catalyst and reactant feed locations, among others [121]. Nonetheless, the modeling of a chemical process (as in the case of RD) usually leads to mixed-integer nonlinear problems (MINLP) [46], meaning that a strong interdependence exists among the variables and, thus, their optimization should not be considered independently. In consequence, available heuristic rules do not offer an optimal design solution; yet, they can be used for the definition of the initial guesses of an optimization problem.

In comparison to the conventional distillation case, optimization of RD systems has a higher degree of difficulty. The main reason for this, it is that some assumptions valid in nonreactive distillation (as a constant molar flow rate in each column section or the introduction of the feed in a single tray) are only valid in very limited cases when a RD column is used (e.g. negligible heat of reaction and constant number of moles) [122].

The optimization algorithms can be classified into deterministic and stochastic. Whether one algorithm or the other should be used depends on the case of study. For the deterministic algorithms, an exact knowledge of the behavior of the objective function is required, as they are based on gradient information [121].

This implies that the optimal point can be found in a reproducible way and that, considering the gradient criteria, the found point is actually an optimum. Nonetheless, when local minima exist (as for RD problems), the usage of this type of algorithms must be careful to ensure that the found optimal point is a global and not a local one.

Conversely, the stochastic methods find values randomly, is the reason why this method is based on multiple function evaluations rather than in a precise awareness of how the objective function behaves [123]. Using domain sampling and adaptation as searching criteria, stochastic algorithms are not as sensible to local optimal as the deterministic algorithms, and they require an elevated number of function evaluations to provide good results [121].

Several studies on RD using both stochastic and deterministic methods can be found in the literature. Some authors [124–126] have used hybrid approaches in order to reduce the computational effort while increasing the robustness of the algorithm.

In general, total annual cost (TAC) is the most common objective function in optimization procedures. However, the controllability of the process is not normally included in the early stage design. Therefore, the optimum TAC for RD processes may result in an optimization design variable vector that has low controllability. To strictly evaluate the process controllability, the dynamic response with step, pulse, and sinusoidal perturbations should all be calculated [127]. Approaches which require less computational power include the integral error from Set Point (SP), step perturbations of dynamic models, and the controllability number assessment from perturbations of steady-state models [128]. As example, a Pareto front obtained during the optimization of a RD process for the production of TEC by esterification of citric acid with ethanol is presented in Fig. 6.22. As observed, there is a clear competition between controllability objective function (higher is less controllable) and annual costs function, reason why a trade-off must be considered when selecting the optimal operating condition [129].

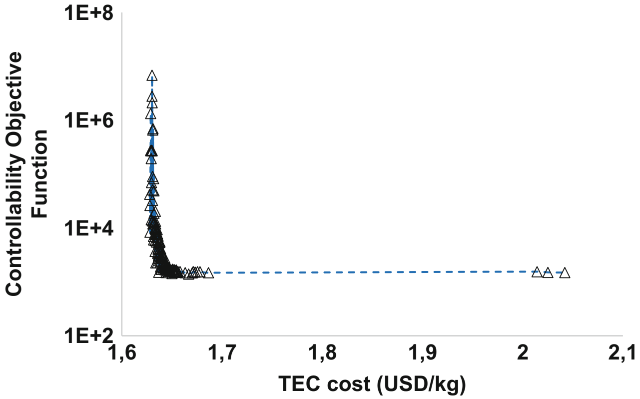


Fig. 6.22 Pareto front for a RD column for the production of triethyl citrate (TEC). Competition of controllability and costs [129]

6.5.1 Control of Reactive Distillation Operations

The definition of an appropriate control structure adds up to the tasks to be performed for the design of a reactive distillation system. The general concepts of process controlling are extendible to RD, but in some cases the influence of some parameters over the dynamic behavior of the column is not evident and sometimes rather counterintuitive or exclusive of reactive distillation [65].

The general guideline for the control of a RD column is the fact that, in principle, an exact feed ratio of reagents (neat operation) would be required in order to obtain the most conversion possible and to guarantee the product purity. Nonetheless the low precision of the control element (valve) avoids the fulfilling of such a condition, reason why an excess of reactant is preferable and a feed-ratio control strategy is not feasible. In consequence, a temperature-based strategy is preferred [65].

From the "control structure" point of view, the potential input variables in a reactive distillation system are reflux rate, reflux ratio, reboiler duty, reboiler ratio, distillate rate, bottoms rate, and the fresh feeds; while as output variables, stream/tray temperatures and compositions are preferred as they are easy to measure [130]. How the control structure is built depends on the case of study and, as deeply analyzed by Luyben [65], on the type of reactions occurring in the column: when two or more products are generated in the column, or when only one product is produced but excess of reactant is desirable, temperature can be used as control variable. If not, a composition analyzer may be required [130] (Table 6.3).

Additionally to the conception of the control structure, the selection of the control tray is an important task. The main feature of the control tray is that it should have a direct action. Nonetheless there are already available methods for the control tray selection, as by means of the usage of steady-state gains, where the singular value decomposition method (SVD) allows the identification of the sensitive trays to be controlled [65].

In terms of control methodologies for RD, it is possible to find several studies in the literature about this topic, and going from a simple proportional-integral (PI) controller to advanced model predictive controllers (MPC), such as dynamic matrix control (DMC), quadratic dynamic matrix control (QDMC), robust multivariable predictive control technology (RMPCT), generalized predictive control (GPC), and other advanced control techniques [130].

As a closing remark, it is worth it to emphasize on the importance of taking care of both design-optimization and controlling in order to get feasible results.

Table 6.3 Measured and manipulated variables in a reactive distillation [131]

Measured variable	Manipulated variable
Tray temperature	Reflux (ratio)
Bottoms product concentration	Reboiler ratio
Top product concentration	Feed-stream
Internal concentration	Top and bottoms streams
Column pressure	Cooling water stream

This comes to the fact that in some cases, the process dynamics of an economic optimum are so poor that the operation in the designed steady-state is unprovable. As an example, in some cases, an excess reactant system (requiring a recovery and a recycle system that increases the capital and operation costs) is preferred over a nearly-neat operating one (with lower costs), just because the exact adjust of the feed-streams, as mentioned before, makes the controllability of the process not viable [65].

Furthermore, the design of optimal controllers offering optimal performance is becoming a major topic for industry and academia. Methodologies as sequential or simultaneous design and control optimization are, thus, of increasing interest. Despite the complexity of adding an accurate enough dynamic representation to the design model, this perception of the process as a whole is showing promising results on the improvement of controllability without abandoning the economic perception [132].

6.5.2 Case Study: Ethyl Acetate Production

In order to apply the major concepts discussed in this chapter, and to briefly depict a design methodology, the production of ethyl acetate by RD distillation in a 100,000 tons per year plant is presented. In this case, the chemical route is the esterification of ethanol and acetic acid using sulfuric acid as catalyst.

$$\text{Ethanol (EtOH)} + \text{Acetic acid (HAC)} \leftrightarrow \text{Ethyl acetate (EtAc)} + \text{Water } (\mathrm{H_2O}) \tag{6.54}$$

The phase equilibria of this reactive system has been studied and validated by using an NRTL-HOC model [133], and it was successfully implemented by different researchers [134–137]. Parameters of thermodynamic models and singular points of the reactive system are presented in Tables 6.4, 6.5, 6.6, and 6.7.

Ethyl acetate esterification kinetics have been widely investigated using different acid catalysts, and a recent work presents a compilation of some kinetic models that can be implemented for the RD design [137]. According to that work, a kinetic model using sulfuric acid as catalyst [138] fit well the experimental observations and is suitable for process simulations. The self-catalytic reaction also plays an important role and it is accounted for using the corresponding kinetic model [139]. A complete description of these models is presented in the following equations. Here, the catalytic kinetic model corresponds to:

$$r_{\mathrm{EtAc}} = \frac{dC_{\mathrm{EtAc}}}{dt} = k_1 C_{\mathrm{HAc}}^{n} C_{\mathrm{EtOH}}^{m} - k_2 C_{\mathrm{EtAc}}^{p} C_{\mathrm{H_2O}}^{q} \tag{6.55}$$

Table 6.4 NRTL interaction parameters for the liquid phase

	Components					
	H_2O	H_2O	H_2O	EtOH	EtOH	HAC
Parameters	EtOH	HAC	EtAc	HAC	EtAc	EtAc
a_{ij}	0.5143	3.3293	3.8538	0	1.8173	0
a_{ji}	0.8065	−1.9763	−2.3456	0	−4.4129	0
b_{ij}	444.89	−723.89	−4.43	225.48	−421.29	−235.28
b_{ji}	−266.53	609.89	1290.46	−252.48	1614.29	515.82
c_{ij}	0.4	0.3	0.3643	0.3	0.1	0.3

Table 6.5 Hayden O'Connell interaction parameters for the vapor phase

Components	H_2O	EtOH	HAC	EtAc
H_2O	1.7	1.55	2.5	1.3
ETOH	1.55	1.4	2.5	1.3
HAC	2.5	2.5	4.5	2
ETAC	1.3	1.3	2	0.53

Table 6.6 Extended Antoine equation[a] coefficients

	Components				
Parameter	H_2O	EtOH	HAC	EtAc	DEE
A	61.0371	61.7911	41.7571	55.3111	125.3871
B	−7206.7	−7122.3	−6304.5	−6227.6	−6954.3
C	−7.1385	−7.1424	−4.2985	−6.41	−19.254
D	4.05E−06	2.89E−06	8.89E−18	1.79E−17	0.024508
E	2	2	6	6	1
Min temp (°C)	0.01	−114.1	16.66	−83.55	−116.3
Max temp (°C)	374.14	240.85	318.8	250.15	193.55

[a] $\ln P\ (\mathrm{bar}) = A + B/T(°\mathrm{C}) + C\ln(T) + DT^E$

$$k_1 = 4.86 \times 10^{-4} + 0.496\exp(-310/T(°\mathrm{C})) + 0.205w^{0.85} \tag{6.56}$$

$$k_2 = 3.715 \times 10^{-4} + 0.01572\exp(-220/T(°\mathrm{C})) + 0.09785w^{0.85} \tag{6.57}$$

$$n = m = 0.5; \quad p = q = 1 \tag{6.58}$$

where C_i is the molar concentration of components (kmol/m^3), w is the concentration of sulfuric acid as catalyst (weight fraction), and r_{EtAc} the volumetric rate of reaction (kmol/min m^3). For simplification, the catalyst loading was assumed constant (0.5 wt%) along the reactive stages within the columns. On the other hand, the self-catalytic reaction kinetic model corresponds to

Table 6.7 Predicted azeotropes from NRTL–HOC model at 1013 bar and experimental data obtained from [133]

Components	Exp. temp (°C)	Calc. temp (°C)	Type and classification	Exp. mole fraction			Calc. mole fraction		
				x_{H_2O}	x_{EtOH}	x_{EtAc}	x_{H_2O}	x_{EtOH}	x_{EtAc}
EtOH–EtAc	71.81	71.81	Homogeneous	0	0.462	0.538	0	0.4572	0.5428
			Saddle						
EtOH–EtAc–H_2O	70.23	70.09	Homogeneous	0.3085	0.1126	0.5789	0.2858	0.1069	0.6073
			Unstable node						
EtOH–H_2O	78.17	78.18	Homogeneous	0.0963	0.9037	0	0.0984	0.9016	0
			Saddle						
EtAc–H_2O	70.38	70.37	Heterogeneous	0.3115	0	0.6885	0.3131	0	0.6869
			Saddle						

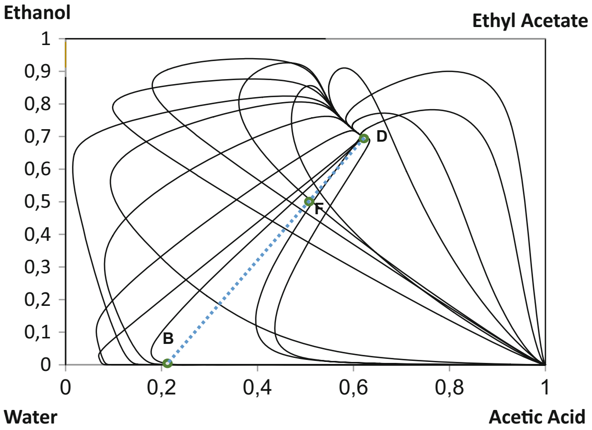


Fig. 6.23 Reactive residue curve map in the transformed concentration for the production of EtAc using $Da = 0.1$ and sulfuric acid as catalysts. *Dots* represent composition of feed (F), distillate (D), and Bottoms (B) of a feasible RD scheme. *Dashed line* represents the overall mass balance in the RD column

$$r_{\mathrm{EtAc}} = \frac{dC_{\mathrm{EtAc}}}{dt} = \hat{k}_1 C_{\mathrm{HAc}} C_{\mathrm{EtOH}} - \hat{k}_2 C_{\mathrm{EtAc}} C_{\mathrm{H_2O}} \tag{6.59}$$

$$\hat{k}_1 = 0.123\exp(-58{,}994/\mathrm{RT}(^\circ\mathrm{K})) \tag{6.60}$$

$$\hat{k}_2 = 0.485\exp(-59{,}774/\mathrm{RT}(^\circ\mathrm{K})) \tag{6.61}$$

In this self-catalytic kinetics C_i is given in mol/m^3, and the volumetric rate of reaction (r_{EtAc}) in mol/s m^3. Regarding the methods to be used for the preliminary conceptual design as described in Fig. 6.18, the number of components (NC) in ethyl acetate systems is 4. Then a reactive residual curve map (RRCM) in transformed compositions as the one shown in Fig. 6.23, can be used for conceptual design. Ethyl acetate was used as the reference *k*-component in (6.48)–(6.53) for RRCM construction and analysis. Assuming an acid–alcohol equimolar feed (middle point of a line joining the ethanol and acid corners), and according with the map topology, pure EtAc is not a feasible product of a RD column (it is not a node). In consequence, the distillate (D in Fig. 6.23) was selected as the ternary azeotrope (EtAc–EtOH–H_2O), and the bottoms (B in Fig. 6.23) were located near an acid–water rich mixture. Because the bottoms are near a saddle (water corner), a two-feed column was selected this time.

Concerning the modelling approach, a reaction-limited regime (Fig. 6.19) considering chemical kinetics and equilibrium-stage model is used for preliminary calculations. A further evaluation of the Hatta numbers from the results obtained in

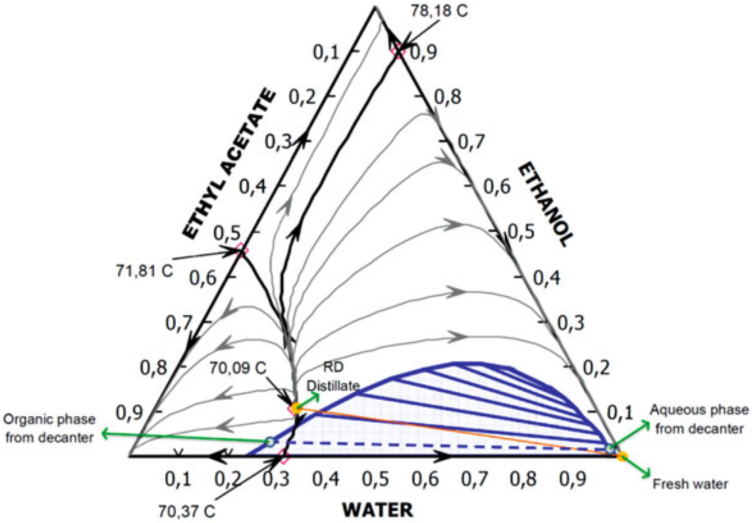


Fig. 6.24 Ternary diagram for the system EtOH–H_2O–EtAC at 1013 bar. Liquid–liquid envelope at 30 °C

the reactive stages can help deciding if the use of a more rigorous approach (non-equilibrium-stage model) would be necessary. For simplicity of the example, only the equilibrium-stage model was evaluated. Taking into account that a homogeneous catalyst is used, the characteristics of a bubble cap tray RD column are considered for simulation (Fig. 6.20).

With the preliminary information and assumptions discussed above, the case was simulated using Aspen Plus® (v.8.6). From the base case results, it was verified that the distillate was nearly the ternary azeotrope, very close to the immiscibility region (Fig. 6.24). According to the ternary diagram, and the liquid–liquid envelope, a fresh water stream can be added to trigger phase splitting in the distillate. In order to remove water and driving reaction to completion, a decanter was installed after the condenser as presented in Fig. 6.25. The aqueous phase from decanter was discarded, and the organic phase was partially refluxed. To obtain pure EtAc, the distillate which now is part of a different nonreactive distillation region, was introduced into a recovery column (RC). The whole process was simulated and the TAC was calculated based upon 2010 raw material and energy prices. The design specifications and variables range studied during simulation are presented in Table 6.8.

The simulation was optimized using a mixed deterministic and stochastic approach. This process took a computing time of around 24 h in a 2 GHz processor and 4 GB DDR computer. From the optimization results it was observed that the bottoms of the column had high-purity unreacted AcAc, reason why the design was

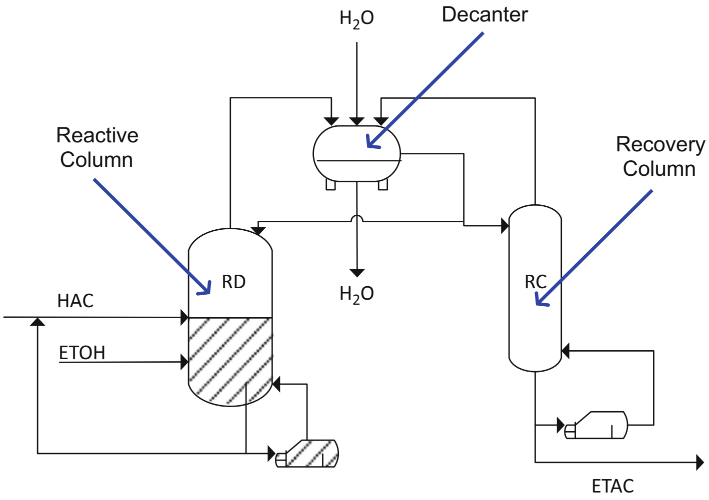


Fig. 6.25 Scheme for ethyl acetate (EtAc) production using a RD column and a recovery column to achieve 99 mol% purity

Table 6.8 Design specifications and variable ranges for studying a RD configuration

Design specification (intervals[a])	Column RD	 RC
Reflux ratio	0.001–10[b]	
Material	Stainless steel	Carbon steel
Pressure (bar)	1013	1013
Tray type	Bubble cap	Bubble cap
Number stages	28–30	8–10
Feed stage for reactive mixture	9–11	1
Feed stage for ethanol stream	26–28	
Approx. residence time (min)	2	2
Distillate/feed	0.9–1	0.6–0.7
Fresh water to decanter (kg/h)	0–2000	

[a] Some design specifications are not fixed because are subjected to optimization
[b] Reflux ratio from the organic phase leaving the decanter

modified to mix this stream with the fresh AcAc and recycle it back to the RD column (together with the sulfuric acid catalyst). The process was once again optimized and the final design variable values for a production of pure EtAc (99 mol%) are presented in Table 6.9, while the main results of the final configuration are presented in Fig. 6.26.

Table 6.9 Optimized results of a RD process for the production of ethyl acetate

Design variable	Value
Reflux ratio from the organic phase leaving the decanter	5.13
Reflux ratio recovery column	1.87
Ethanol feed plate	26
Acetic acid feed plate	11
Number of plates—RD column (including decanter)	29
Number of plates—recovery column	9
Fresh water to decanter molar flow	69.3 kmol/h
Bottoms molar flow rate (EtAc 99 mol%)	28.8 kmol/h
Acetic acid conversion (%)	100
Heat duty (kW-h)	29,213
Cooling duty (kW-h)	29,704
Diameter RD column (m)	7.4
Diameter recovery column (m)	3.1
Raw material costs (Million USD/year)	97.3
Energy costs (Million USD/year)	7.1
Capital costs (Million USD/year)	0.8
TAC (Million USD/year)	105.2

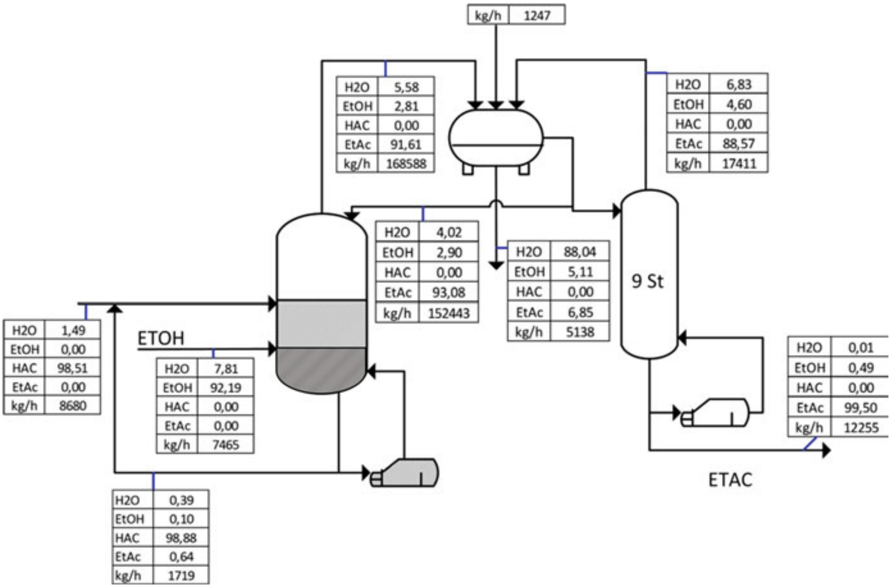


Fig. 6.26 Operating conditions for an optimized RD configuration for ethyl acetate (EtAc) production

References

1. Rudd DF, Watson CC (1968) Strategy of process engineering. Wiley, New York
2. Douglas JM (1988) Conceptual design of chemical processes. McGraw-Hill, Singapore
3. Yuan Z, Chen B (2012) Process synthesis for addressing the sustainable energy systems and environmental issues. AIChE J 58(11):3370–3389
4. Yuan Z, Chen B, Gani R (2013) Applications of process synthesis: moving from conventional chemical processes towards biorefinery processes. Comput Chem Eng 49:217–229
5. Shonnard D, Askicherer A, Saling P (2003) Industrial applications using BASF eco-efficiency analysis: perspectives on green engineering principles. Environ Sci Technol 37(23):5340–5348
6. Cremaschi S (2014) A perspective on process synthesis: challenges and prospects. In: Eden MR, Siirola JD, Towler GP (eds) Proceedings of the 8th international conference on foundations of computer-aided process design—FOCAPD 2014, July 13–17 2014, Washington, DC
7. Li X, Kraslawski A (2004) Conceptual process synthesis: past and current trends. Chem Eng Process 43:589–600
8. Harmsen GJ, Chewter LA (1999) Industrial applications of multifunctional, multi-phase reactors. Chem Eng Sci 54:1541–1545
9. Stankiewicz AI, Moulijn JA (2000) Process intensification: transforming chemical engineering. Chem Eng Prog 96(1):22–34
10. Stankiewicz AJ (2002) Process intensification. Ind Eng Chem Res 41:1920–1924
11. Stankiewicz A (2003) Reactive separations for process intensification: an industrial perspective. Chem Eng Process 42:137–144
12. Gerven TV, Stankiewicz A (2009) Structure, energy, synergy, time—the fundamentals of process intensification. Ind Eng Chem Res 48(5):2465–2474
13. Lutze P, Gani R, Woodley JM (2010) Process intensification: a perspective on process synthesis. Chem Eng Process 49:547–558
14. Sundmacher K, Kienle A (eds) (2003) Reactive distillation—status and future directions. Wiley–VCH, New York
15. Le Chatelier H (1888) Recherches Experimentales et Theoriques sur les Equilibres Chimiques (Experimental and Theoretical Research on Chemical Equilibria). Annales des Mines, Hutieme Serie, Memiories, XIII. Dunod, Paris
16. Berthelot M, Pean de St. Gilles L (1862) Recherches sur les afinites de la formation et de la descomposition des ethers (Research on the affinities of formation and decomposition of esters). Ann Chim Phys 3(65):385–422
17. Berthelot M, Pean de St. Gilles L (1862) Recherches sur les afinites de la formation et de la descomposition des ethers—II (Research on the affinities of formation and decomposition of esters—part II). Ann Chim Phys 3(66):5–109
18. Berthelot M, Pean de St. Gilles L (1863) Recherches sur les afinites de la formation et de la descomposition des ethers—III–IV (Research on the affinities of formation and decomposition of esters—part III and IV). Ann Chim Phys 3(68):225–359
19. Keyes DB (1932) Esterification processes and equipment. Ind Eng Chem 24(10):1096–1103
20. Backhaus A (1921) Continuous process for the manufacture of esters. US Patent 1400849
21. Backhaus A (1921) Apparatus for the manufacture of esters. US Patent 1400850
22. Backhaus A (1921) Apparatus for the production of esters. US Patent 1400851
23. Backhaus A (1921) Method for the production of esters. US Patent 1400852
24. Backhaus A (1922) Apparatus for producing high-grade esters. US Patent 1403224
25. Backhaus A (1922) Process of esterification. US Patent 1403225
26. Backhaus A (1922) Apparatus for the manufacture of esters. US Patent 1425624
27. Backhaus A (1923) Process for the manufacture of esters. US Patent 1425625
28. Backhaus A (1923) Method for the production of ester-condensation products. US Patent 1425626

29. Backhaus A (1923) Process of producing high-grade esters. US Patent 1454462
30. Backhaus A (1923) Process of esterification. US 1454463
31. Haunschild WM (1971) Separation of linear olefins from ternary olefins. US Patent 3629478
32. Steffens JA (1922) Process of obtaining complete alcoholysis. US Patent 1433308
33. Leyes CE, Othmer DF (1945) Continuous esterification of butanol and acetic acid, kinetic and distillation considerations. Trans Am Inst Chem Eng 41:157–196
34. Berman S, Isbenjian H, Sedoff A, Othmer D (1948) Continuous production of dibutyl phthalate in a distillation column. Ind Eng Chem 40(11):2139–2148
35. Vodonik J (1958) Continuous ester interchange process. US Patent 2829153 A
36. Hurt D, Pieper H (1959) Production of bis(2-hydroxyethyl) terephthalate through ester interchange. US Patent 2905707 A
37. Tanabe K, Hölderich WF (1999) Industrial application of solid acid-base catalysts. Appl Catal Gen 181:399–434
38. Marcilly C (2003) Present status and future trends in catalysis for refining and petrochemicals. J Catal 216:47–62
39. Sennewald K, Gehrmann K, Schafer S (1971) Column for carrying out organic chemical reactions in contact with fine particulate catalyst. US patent 3579309
40. Haunschild WM (1972) Separation of chemicals using fractionation and heterogeneous catalysis. US Patent 3634534
41. Haunschild WM (1972) Separation and catalysis. US Patent 3634535
42. McCarthy JE, Tiemann M (2006) MTBE in gasoline: clean air and drinking water issues. Congressional Research Service Reports. Paper 26
43. Agreda VH, Partin LR (1984). Reactive distillation process for the production of methyl acetate. US Patent 4435595
44. Agreda VH, Partin LR, Heise WH (1990) High-purity methyl acetate via reactive distillation. Chem Eng Prog 86(2):40–46
45. Siirola JJ (1996) Industrial applications of chemical process synthesis. Adv Chem Eng 23:1–62
46. Keller T (2014) Reactive distillation. In: Górak A, Olujić Z (eds) Distillation: equipment and processes. Academic, London, Chapter 8
47. Tuchlenski A, Beckmann A, Reusch D, Düssel R, Weidlich U, Janowsky R (2001) Reactive distillation—industrial applications, process design & scale-up. Chem Eng Sci 56:387–394
48. Beckmann A, Nierlich F, Popken T, Reusch D, von Scala C, Tuchlenski A (2002) Industrial experience in the scale-up of reactive distillation with examples from C4-chemistry. Chem Eng Sci 57:1525–1530
49. Schoenmakers H, Bessling B (2003) Reactive and catalytic distillation from an industrial perspective. Chem Eng Process 42:145–155
50. Hiwale R, Bhate N, Mahajan Y, Mahajani S (2004) Industrial applications of reactive distillation: recent trends. Int J Chem Eng 2(R1):1–52
51. Harmsen GJ (2007) Reactive distillation: the front-runner of industrial process intensification—a full review of commercial applications, research, scale-up, design and operation. Chem Eng Process 46:774–780
52. Lutze P, Dada E, Gani R, Woodley J (2010) Heterogeneous catalytic distillation—a patent review. Recent Pat Chem Eng 3:208–229
53. Siirola JJ (2012) Goal-oriented process synthesis augmented with constraint oriented process synthesis. https://www.sintef.no/globalassets/project/trondheim_gts/seminar-series/jeff-siirola---process-synthesis.pdf. Accessed 22 Feb 2015
54. Matthey (2014) New biodiesel technology wins prestigious IChemE Sustainable Technology Award. http://www.matthey.com/media_and_news/news/2014/biodiesel-icheme-sustainable-technology-award. Accessed 22 Feb 2015
55. Alper E (ed) (1983) Mass transfer with chemical reaction in multiphase systems. Springer, Dordrecht, pp 391–414

56. McKetta J (ed) (1993) Encyclopedia of chemical processing and design, vol 46. CRC, New York, pp 230–243
57. Stichlmair J, Fair J (1998) Distillation, principles and practice. Wiley–VCH, New York, pp 252–283
58. Doherty M, Malone M (2001) Conceptual design of distillation systems. McGraw–Hill, New York, Chapter 10
59. Wilson ID, Edlard TR, Poole CA, Cooke M (eds) (2001) Encyclopedia of separation science. Academic, London, pp 4075–4082
60. Horvath I (Editor-in-Chief) (2002) Encyclopedia of catalysis, vol 2. Wiley, New York, pp 477–505
61. Kulprathipanja S (ed) (2002) Reactive separation processes. Taylor & Francis, New York, pp 18–40, Chapter 2
62. Mujtaba I (2004) Batch distillation: design and operation. Imperial College Press, London, pp 270–301, Chapter 9
63. Lei Z, Chen B, Ding C (2005) Special distillation processes. Elsevier, Amsterdam, pp 178–218, Chapter 4
64. Afonso C (2005) Green separation processes. Wiley-VCH, Weinheim, pp 127–154, Chapter 3.2
65. Luyben W (2006) Distillation design and control using AspenTM simulation. Wiley, Hoboken, pp 232–250, Chapter 9
66. Schmidt-Traub H, Górak A (eds) (2006) Integrated reaction and separation operations—modelling and experimental validation. Springer, New York
67. Keil F (ed) (2007) Modeling of process intensification. WILEY-VCH, Weinheim, pp 323–363, Chapter 10
68. Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) (2008) Handbook of heterogeneous catalysis. Wiley-VCH, Weinheim, Part 10:10.6, pp 2188–2198
69. Luyben W, Yu C (2008) Reactive distillation design and control. Wiley, Hoboken
70. Sakuth M, Reusch D, Janowsky R (2008) Ullmann's encyclopedia of industrial chemistry, vol 31. Wiley-VCH, Weinheim, pp 263–276
71. Rangaiah G, Kariwala V (eds) (2012) Plantwide control: recent developments and applications. Wiley, Taipei, pp 319–338, Chapter 15
72. Boodhoo K, Harvey A (2013) Process intensification for green chemistry: engineering solutions for sustainable chemical processing. Wiley, Hoboken, pp 251–274, Chapter 9
73. Kiss A (2013) Advanced distillation technologies: design, control and applications. Wiley, Hoboken, pp 353–391, Chapter 10
74. Ramaswamy S, Huang H, Ramarao B (eds) (2013) Separation and purification technologies in biorefineries. Wiley, Chichester, Chapter 16
75. Górak A, Olujić Z (eds) (2014) Distillation: equipment and processes. Academic, London, pp 261–294, Chapter 8
76. Hong X, McGiveron O, Lira C, Orjuela A, Peereboom L, Miller D (2012) A reactive distillation process to produce 5-hydroxy-2-methyl-1,3-dioxane from mixed glycerol acetal isomers. Org Process Res Dev 16:1141–1145
77. Okasinski M, Doherty M (1998) Design method for kinetically controlled, staged reactive distillation columns. Ind Eng Chem Res 37(7):2821–2834
78. Dimian A, Bildea C (2008) Chemical process design: computer-aided case studies. Wiley-VCH, Weinheim
79. Doherty M (1993) Design and synthesis of reactive separation systems. http://www.osti.gov/scitech/servlets/purl/10129139. Accessed 22 Feb 2015
80. Sundmacher K, Rihko L, Hoffmann U (1994) Classification of reactive distillation processes by dimensionless numbers. Chem Eng Commun 127:151–167
81. Ottewell S (2014) Reactive distillation: will a sea change occur? Chemical processing. http://www.chemicalprocessing.com/articles/2014/reactive-distillation-edges-forward/. Accessed 22 Feb 2015

82. Orjuela A, Kolah A, Hong X, Miller D, Lira C (2012) Diethyl succinate synthesis by reactive distillation. Sep Purif Technol 88:151–162
83. Dow (2011) AMBERLYST™ polymeric catalysts. http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_07c8/0901b803807c82cb.pdf?filepath=liquidseps/pdfs/noreg/177-02436.pdf&fromPage=GetDoc. Accessed 22 Feb 2015
84. Kolah A, Asthana N, Vu D, Lira C, Miller D (2008) Triethyl citrate synthesis by reactive distillation. Ind Eng Chem Res 47(4):1017–1025
85. Kolah K, Lira C, Miller D, Doctor R, Prindle J, Panchal C (2014) Heat integrated reactive distillation using external side reactors for synthesis of tri-ethyl citrate. AIChE Spring Meeting, March 30–April 3, New Orleans
86. Rihko-Struckmann L (2006) Integrated catalytic processes. Modern methods in heterogeneous catalysis research. Fritz Haber Institute, Berlin. http://www.fhiberlin.mpg.de/acnew/department/pages/teaching/pages/teaching__wintersemester__2006_2007/rihkostruckmann_integratedcatalyticprocesses_241106.pdf. Accessed 22 Feb 2015
87. Hoffmann A, Noeres C, Górak A (2004) Scale-up of reactive distillation columns with catalytic packings. Chem Eng Process 43:383–395
88. Song W, Huss R, Doherty M, Malone M (1997) Discovery of a reactive azeotrope. Nature 338:561–563
89. Barbosa D, Doherty M (1988) The influence of equilibrium chemical reactions on vapor-liquid phase diagrams. Chem Eng Sci 43:529–540
90. Barbosa D, Doherty M (1998) The simple distillation of homogeneous reactive mixtures. Chem Eng Sci 43(3):541–550
91. Okasinski M, Doherty M (1997) Thermodynamic behavior of reactive azeotropes. AIChE J 43(9):2227–2238
92. Arlt W, Spuhl O, Klamt A (2004) Challenges in thermodynamics. Chem Eng Process 43:221–238
93. Frey T, Stichlmair J (1999) Thermodynamic fundamentals of reactive distillation. Chem Eng Technol 22(1):11–18
94. Gorovits B, Toikka A, Pisarenko Y, Serafimov L (2006) Thermodynamics of heterogeneous systems with chemical interaction. Theor Found Chem Eng 40(3):239–244
95. Sundmacher K, Kienle A, Seidel-Morgenstern A (2005) Integrated chemical processes. WILEY-VCH, Weinheim
96. Prausnitz J, Tavares F (2004) Thermodynamics of fluid-phase equilibria for standard chemical engineering operations. AIChE J 50(4):739–761
97. Carlson E (1996) Don't gamble with physical properties for simulation. Chem Eng Prog 92:35–46
98. Chen C, Mathias P (2002) Applied thermodynamics for process modeling. AIChE J 48 (2):194–200
99. Hill D, Justice F (2011) Understand thermodynamics to improve process simulation. CEP Dec 20–25
100. Orjuela A, Kolah A, Lira C, Miller D (2011) Mixed succinic acid/acetic acid esterification with ethanol by reactive distillation. Ind Eng Chem Res 50:9209–9220
101. Orjuela A, Yanez A, Vu D, Bernard-Brunel D, Miller DJ, Lira CT (2010) Phase equilibria for reactive distillation of diethyl succinate: part I. System diethyl succinate + ethanol + water. Fluid Phase Equilib 290(1–2):63–67
102. Orjuela A, Yanez A, Rossman P, Vu D, Bernard-Brunel D, Miller DJ, Lira CT (2010) Phase equilibria for reactive distillation of diethyl succinate. Part II: systems diethyl succinate + ethyl acetate + water and diethyl succinate + acetic acid + water. Fluid Phase Equilib 290(1–2):68–74
103. Orjuela A, Yanez A, Evans J, Miller DJ, Lira CT (2011) Phase equilibria in binary mixtures with monoethyl succinate. Fluid Phase Equilib 309:121–127
104. Orjuela A (2010) Separation of succinic acid from fermentation broths and esterification by a reactive distillation method. Dissertation, Michigan State University

105. Pappu V (2012) Process intensification in the synthesis of organic esters: kinetics, simulations and pilot plant experiments. Dissertation, Michigan State University
106. Carberry J (2001) Chemical and catalytic reaction engineering. Dover, New York
107. Weisz P, Prater C (1954) Interpretation of measurements in experimental catalysis. Adv Catal 6:143–196
108. Kaibel G, Schoenmakers H (2002) Process synthesis and design in industrial practice. Comput Aided Chem Eng 10:9–22
109. Thery R, Meyer XM, Joulia X, Meyer M (2005) Preliminary design of reactive distillation columns. Chem Eng Res Des 83(A4):379–400
110. Ung S, Doherty MF (1995) Vapor-liquid equilibrium in systems with multiple chemical reactions. Chem Eng Sci 50(1):23–48
111. Barbosa D (1987) Distillation of reactive mixtures. Doctoral Dissertation, University of Massachusetts
112. Lee JW, Hauan S, Lien KM, Westerberg AW (2000) A graphical method for designing reactive distillation columns. I. The Ponchon-Savarit method. Proc R Soc A Math Phys Eng Sci 456:1953–1964
113. Lee JW, Hauan S, Lien KM, Westerberg AW (2000) A graphical method for designing reactive distillation columns. II. The McCabe-Thiele method. Proc R Soc A Math Phys Eng Sci 456:1965–1978
114. Venkataraman S, Chan W, Boston J (1990) Reactive distillation using ASPEN PLUS. Chem Eng Prog 86(8):45–54
115. Taylor R, Krishna R (2000) Modelling reactive distillation. Chem Eng Sci 55:5183–5229
116. Kenig E (2012) Non-equilibrium modeling for reactive separations. International seminar on advanced separation operations. Universidad Nacional de Colombia, Bogotá
117. Molano P (2013) Process analysis of a reactive distillation column for the synthesis of n-Butyl acrylate—impact of the reactive section and the use of biological feedstock. Undergraduate dissertation, Universidad Nacional de Colombia
118. Fuhrmeister R (2011) Experimentelle und theoretische Untersuchung der Synthese von n-Butylacrylat in einer Vakuum-Reaktivrektikationskolonne. Master's dissertation, TU Dortmund University
119. Kenig E (2008) Complementary modelling of fluid separation processes. Chem Eng Res Des 86:1059–1072
120. Almeida-Rivera CP, Grievink J (2004) Feasibility of equilibrium-controlled reactive distillation process: application of residue curve mapping. Comput Chem Eng 28:17–25
121. Domingues L, Pinheiro C, Oliveira N (2014) Optimal design of reactive distillation systems: application to the production of ethyl tert-butyl ether (ETBE). Comput Chem Eng 64:81–94
122. Cardoso MF, Salcedo RL, Feyo de Azevedo S, Barbosa D (2000) Optimization of reactive distillation processes with simulated annealing. Chem Eng Sci 55:5059–5078
123. Edgar TF, Himmelblau DM, Lasdon LS (2001) Optimization of chemical processes. McGraw-Hill, New York
124. Kiss AA, Segovia-Hernández JG, Bildea CS, Miranda-Galindo EY, Hernández S (2012) Reactive DWC leading the way to FAME and fortune. Fuel 95:352–359
125. Urselmann M, Barkmann S, Sand G, Engell S (2011) Optimization-based design of reactive distillation columns using a memetic algorithm. Comput Chem Eng 35:787–805
126. Miranda-Galindo E, Segovia-Hernández J, Hernández S, Gutiérrez-Antonio C, Briones-Ramírez A (2011) Reactive thermally coupled distillation sequences: pareto front. Ind Eng Chem Res 50(2):926–938
127. Coughanowr DR (1981) Process systems analysis and control, 2nd edn. McGraw-Hill, New York
128. Cabrera-Ruiz J, Segovia-Hernandez JG, Alcantara-Avila, JR, Hernandez S (2012) Optimal dynamic controllability in compressor-aided distillation schemes using stochastic algorithms. In: Proceedings of the 22nd European symposium on computer aided process engineering, June 17–20, 2012, London

129. Santaella M, Rodriguez G, Segovia-Hernandez JG, Orjuela A (2014) Design of a thermally coupled reactive distillation sequence for triethyl citrate production. AIChE annual meeting, Atlanta, Nov 2014
130. Shatma N, Singh K (2010) Control of reactive distillation column: a review. Int J Chem React Eng 8(1), 1542–6580
131. Goedecke R (2011) Fluidverfahrenstechnik: Grundlagen, Methodik, Technik. Wiley, Praxis
132. Georgiadis MC, Schenk M, Pistikopoulos E, Gani R (2002) The interactions of design, control and operability in reactive distillation systems. Comput Chem Eng 26:735–746
133. Tang Y, Huang H, Chien I (2003) Design of a complete ethyl acetate reactive distillation system. J Chem Eng Japan 36(11):1352–1363
134. Huang H, Chien I, Lee H (2012) Plantwide control of a reactive distillation process. In: Kariwala V, Rangaiah GP (eds) Plantwide control: recent developments and applications. Wiley, Taipei, pp 319–338
135. Tian H, Zheng H, Huang Z, Qiu T, Wu Y (2012) Novel procedure for coproduction of ethyl acetate and n-butyl acetate by reactive distillation. Ind Eng Chem Res 51:5535–5541
136. Lai I, Liu Y, Yu C, Lee M, Huang H (2008) Production of high-purity ethyl acetate using reactive distillation: experimental and start-up procedure. Chem Eng Process: Process Intensif 47:1831–1843
137. Santaella M, Orjuela A, Narváez P (2015) Comparison of different reactive distillation schemes for ethyl acetate production using sustainability indicators. Chem Eng Process: Process Intensif 96:1–13
138. Atalay F (1994) Kinetics of the esterification reaction between ethanol and acetic acid. Dev Chem Eng Miner Process 2:181–184
139. Alejski K, Duprat F (1996) Dynamic simulation of the multicomponent reactive distillation. Chem Eng Sci 51:4237–4252
140. Schoenmakers H (2010) European roadmap of process intensification—technology report—reactive distillation. Creatieve Energie. EUROPIN

Chapter 7
Process Intensification in Biotechnology Applications

Oscar Andrés Prado-Rubio, Ricardo Morales-Rodríguez, Paloma Andrade-Santacoloma, and Héctor Hernández-Escoto

Abstract This chapter presents an overview on how process intensification has influenced biotechnology applications from a multidisciplinary perspective. Initially, the process intensification philosophy is contextualized into biotechnology due to the particular challenges of these processes. This leads to a conceptual map analyzing the disciplines' interaction to achieve bioprocesses intensification. Subsequently, intensification is explored mainly from transforming biomass into chemicals point of view as an integrated solution addressed within the biorefinery concept. The chapter focuses into revising and presenting representative examples from process engineering perspective. First, how to enhance raw materials utilization in fermentations and enzymatic systems is presented. Secondly, advances on in situ product removal/recovery in order to enhance the reaction environment are presented, emphasizing on membrane bioreactor technologies. Finally, some current and future challenges are assessed to achieve bioprocess intensification. We strongly believe that developing bioprocess intensification philosophy will bring new perspectives to increase the cost-effectiveness of industrial applications towards a more sustainable future.

O.A. Prado-Rubio
Department of Chemical Engineering, Universidad Nacional de Colombia - Manizales, Manizales, Colombia
e-mail: oaprador@unal.edu.co

R. Morales-Rodríguez • H. Hernández-Escoto (✉)
Department of Chemical Engineering, Universidad de Guanajuato, Noria Alta s/n, Col. Noria Alta, Guanajuato, 36050 Guanajuato, Mexico
e-mail: hhee@ugto.mx

P. Andrade-Santacoloma
Technical University of Denmark, Lyngby, Denmark

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_7

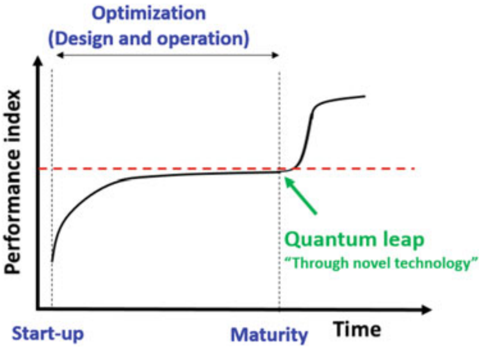
7.1 Introduction

It is evident how the growing world population stresses world climate, natural resources, and the environment. A trend to mitigate the adverse influence of humans is by developing an economy based on bioproducts from renewable resources, which can be transformed into food/feed, chemicals, materials or energy. As any other, bioprocesses are subject to continuous structural changes in order to achieve sustainable use of energy and resources. These structural changes can be accomplished through optimization of the design and operational conditions. However, it is expected that these processes achieve the top of their performance indexes as they reach maturity; then, a further improvement through an approach of intensification is appealing (as shown in Fig. 7.1).

Process intensification (PI) philosophy is essential to cope with sustainability challenges in the forthcoming years due to the expected radical innovation achieved by a design paradigm shift. Only by 'quantum leaps' in performance resulting from novel technologies, it would be possible to have the ability to deliver the grail of sustainability required for processes. Intensified processes can contribute significantly to the competitiveness of process industries worldwide by making them faster, more efficient and less adverse environmentally. From the chemical process intensification perspective, the quantum leaps are achieved by increasing several times performance indexes [1]. However, in bioprocesses is not always possible to see such changes in performance through technology innovations. Bioprocesses impose relevant challenges (i.e., lack of process understanding, complex dynamics, composition variability in renewable raw materials, microorganisms/enzyme sensibility, and monitoring difficulties, among other) that limit potential technological breakthroughs.

Bioprocess intensification represents one of the research focuses especially because approximately 50 % of the elements we use to decrease our dependency on fossil feedstock can be obtained from renewable sources. Then, there is a tremendous need to develop bioprocesses that further optimize biomass harnessing through reaction and advanced separation techniques relying on sustainable ideologies [2]. Additionally, bioprocesses face relevant challenges to be overcome in

Fig. 7.1 Evolution on bioprocess improvement towards intensification



order to provide a sustainable future. Amongst the milestones identified within the international project Delft Skyline Debates for Process Intensification, the ones related to bioprocesses are [2]:

- Low-cost small-scale processing technologies for production applications in varying environments.
- Recycling of composite materials: design, engineering, and intensified production technologies.
- Towards perfect reactors: gaining full control of chemical transformations at the molecular level.
- Elemental sustainability: the total recovery of scarce elements.
- Production systems for personalized medicine.
- Bio-hybrid organs and tissues for patient therapy.
- Chemicals from biomass—integrated solution for chemistry and processing.

It is foreseen that achieving those milestones through bioprocess intensification, new breakthrough technologies will address not only processing issues but crucial societal problems, such as human health, the availability of water and food, energy and material resources, transport, and living standards.

Bioprocesses intensification cannot be seen as a single area, because this has been developed from different perspectives considering multidisciplinary and multiscale aspects, allowing improvements in production, purification and in the overall performance. Figure 7.2 illustrates an interpretation of how bioprocesses have been intensified in different areas (e.g., genetic engineering, biology,

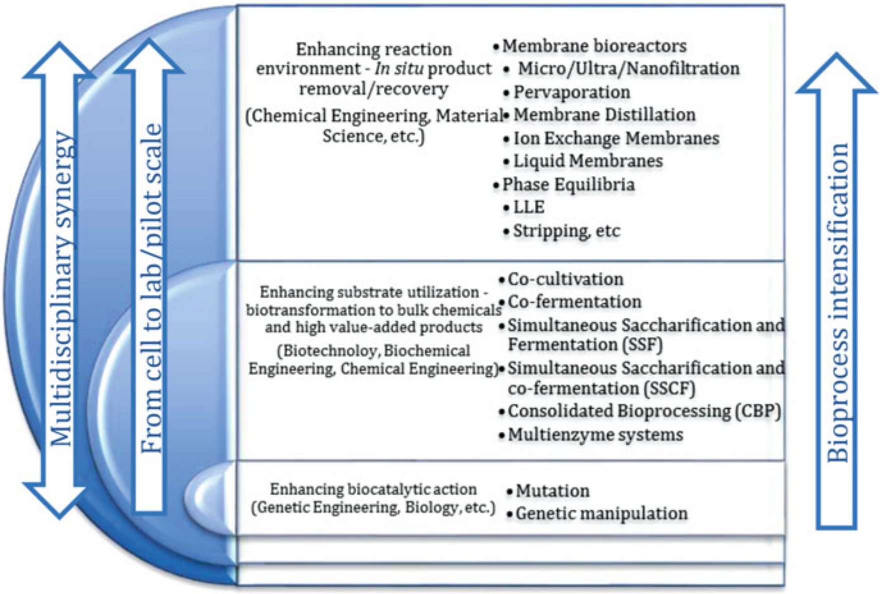


Fig. 7.2 Multidisciplinary interaction for achieving bioprocess intensification

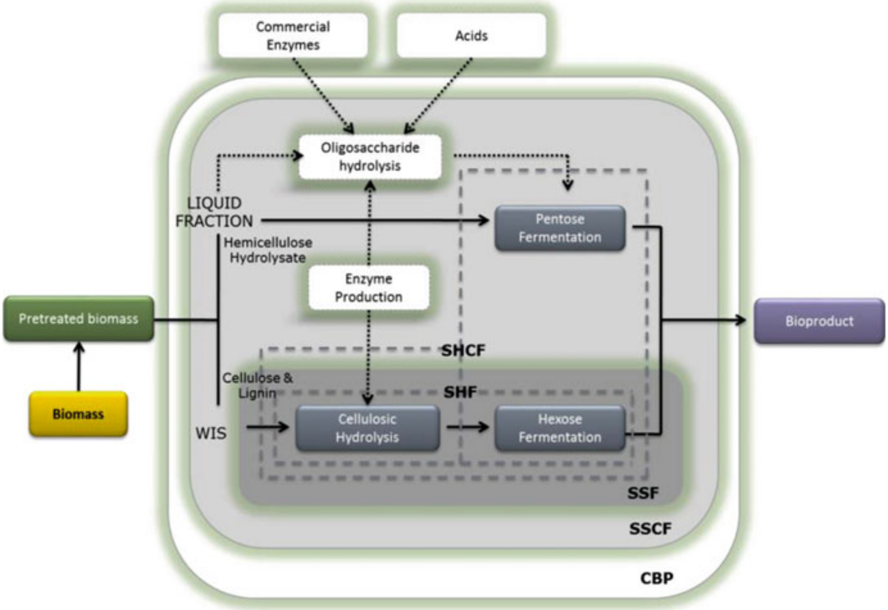


Fig. 7.3 Enhancing the water-insoluble solids (WIS) substrate utilization in one unit operation: simultaneous saccharification and fermentation (SSF) rather than separate hydrolysis and fermentation (SFC); simultaneous saccharification and co-fermentation (SSCF) instead of separate hydrolysis and co-fermentation (SHCF); consolidated bioprocessing (CBP). Adapted from Gírio et al. [3]

biotechnology, chemical engineering, material science), the synergy among them, and the analysis at different levels of abstraction by a multiscale approach (from a cell manipulation up to lab/pilot plant scale). In order to accomplish a bioprocess intensification, the different areas have to interact and also have a feedback for further improvements. For instance, the product yield in a biological system have been enhanced by increasing biocatalytic action (performed by genetic engineers and biologists), resulting in better substrate utilization (executed in the biotechnology and biochemical area) and have also been intensified by improving the reaction environment technologies (especially by chemical engineers).

Starting from the core, there is a trend in bioprocess intensification for metabolizing multiple carbon sources to enhance substrate utilization (such as sugars, alcohols, etc.) by the same microorganism. This issue has originated the exploration of new manners to boost the performance of the biological entity by internal manipulation (i.e., microorganism mutation and genetic manipulation to adapt part of the metabolic route from a different microorganism). Enhancing the biocatalytic action has also allowed getting more robust microorganisms towards inhibitors and reaction conditions, letting to intensify product yield and productivity.

The developments in the microorganism's level have allowed improving the substrate utilization at the lab and reactor level. Figure 7.3 illustrates the different strategies for intensifying the reactor performance. This includes fermentation of one or more carbon sources with multiple microorganisms in the same bioreactor (the so-called co-cultivation), and the fermentation of two or more carbon sources by one microorganism (the so-called co-fermentation) instead of individual reactors for pentose and hexose in an ethanolic fermentation, for instance. The simultaneous saccharification and fermentation (SSF) has been another intensification approach for substrate conversion where the enzymatic hydrolysis and fermentation of one of the liberated carbon sources from the water-insoluble solids (WIS) is carried out simultaneously, instead of separate hydrolysis and fermentation (SHF). Another approach is the simultaneous saccharification and co-fermentation (SSCF) with the synchronized enzymatic hydrolysis and fermentation of two or more liberated carbon sources in the same unit, rather than separate hydrolysis and co-fermentation (SHCF). There is another manner to intensify the process known as consolidated bioprocessing (CBP) where the microorganism produce the necessary enzymes to liberate the carbon sources which are fermented by the same microorganism in the desired bioproduct [3].

Even though the previous bioprocesses intensification has been achieved specifically from the reaction point of view, there is a top layer approach that includes the modification of the reaction environment. This layer refers to the in situ removal of the products obtained in the biochemical reaction. For certain bioprocesses, some of the products can impair the microorganism(s), thus, decreasing the productivity and product yield. In situ product removal/recovery (ISPR) investigates how to adapt external or internal devices to bioprocesses that permits to in situ remove inhibitors from the reacting vessel (i.e., main or secondary products). There is a special interest on how to integrate bioreactors with membrane separation processes such as micro/ultra/nanofiltration, pervaporation, membrane distillation, ion exchange membranes, and liquid membranes. Beyond those, other approaches have also been considered as the use of the removal/separation based on phase equilibria, such as liquid–liquid equilibria, stripping removal, etc.

In this chapter, bioprocess intensification is explored mainly from the perspective of transforming biomass into chemicals as an integrated solution for bioprocessing. Then, bioprocess intensification is addressed within the biorefinery context. Examples are analyzed at the processing levels depicted as the multidisciplinary interaction of Fig. 7.2.

7.2 Biorefinery: Biomass to Chemicals

Considering that the chief component of oil is carbon, and that many products that currently drive our daily life proceed from crude oil, the interest on biomass harnessing, to begin substituting oil-based products, woke up in a natural way since plants are the most abundant source of renewable carbon.

Following a similar concept on the refining of crude oil, the chain or network of processing steps for obtaining several products from a certain biomass is called

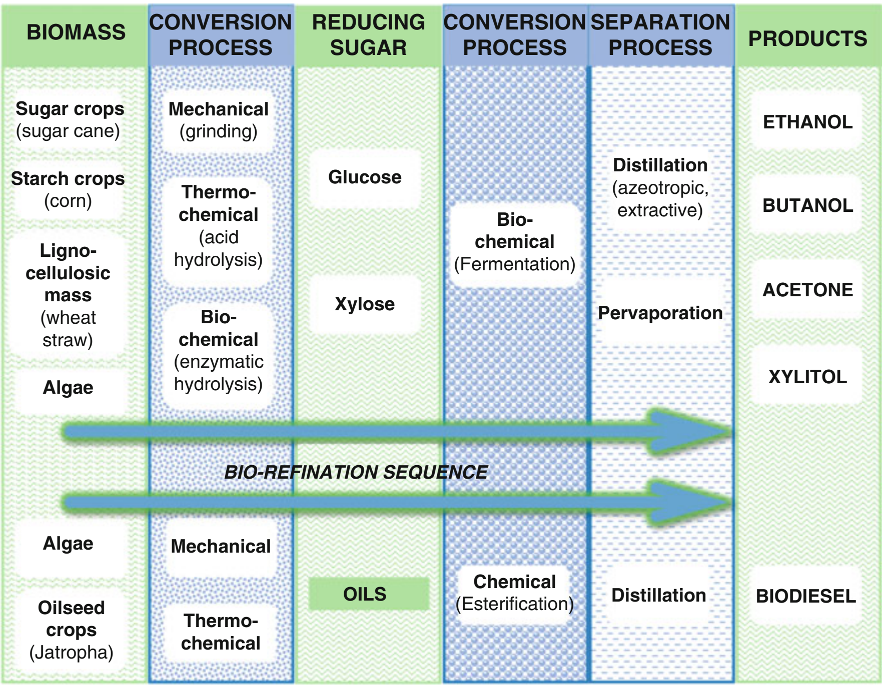


Fig. 7.4 Basic sequence on biomass refination

“biorefinery”. The diverse forms of biomass are classified in three main groups: (1G) plants rich in either sugar, starch, or oil (e.g., sugarcane, corn, and soybean); (2G) lignocellulosic material with high content of cellulose but also of lignin and hemicellulose, coming from either agroindustrial waste or forest residues (e.g., wheat straw, grass, wood); and (3G) algae, rich in both oil and cellulose, which can be farmed at large scale. This biomaterial diversity lays a diversity of processing steps that, in turn, comes from the variety of reagents either chemical or biological that can be used, and from the diversity of equipment and process conditions that are implied (see Fig. 7.4). Diverse biorefineries arise depending on the raw biomaterial to be profited and the kind of conversion processes to be implemented (either chemical, biological, or thermochemical), and they are typically classified just according to the type of biomaterial in terms of “generations”. First generation biorefinery uses biomaterial of the 1G group, second generation biorefinery harnesses 2G biomass and the third generation biorefinery processes algae. Moreover, it can be devised as different classifications of biorefineries; for example, one that distinguishes biorefineries based on converting reducing sugars from those based on vegetable oils transformation; or another that distinguishes biorefineries with a major part of pure biological conversion steps from those majorly based on chemical and thermochemical processes. In this sense, for example biodiesel is considered as a product of biological nature just because the raw material, but the corresponding processes are chemical and thermochemical.

Going upstream on the flowsheet of any biorefinery that mainly encloses biological processes for converting reducing sugars (see Fig. 7.4), two common steps appear: fermentation and purification. In general terms, through the growth of either yeast, fungi, or bacteria during fermentation, reducing sugars are converted into different products such as ethanol, butanol, acetone, xylitol, lactic acid, succinic acid, etc. [4]. Reducing sugars can also be used as carbon source to grow cells that secrete certain metabolites capable of, for example, working as reducing agents of metals in water treatment [5]. In any cell family, different metabolic pathways can be driven depending on the process conditions, yielding in turn, different products. For example, the growing of the *Saccharomyces cerevisiae*, the most famous of yeasts, must be carried out at anaerobic and warm conditions (~30 °C and pH in-between 4 and 7) to produce ethanol. But, if the process is carried out in aerobic conditions, the pathway to produce more yeast is favored. It is worthwhile to recall that *Saccharomyces cerevisiae*, by itself, has always gotten (and will have) a prominent place in the baking and beverage industry. Fermentation processes inherently imply diluted broths in such a way that purification processes are generally necessary. Typical separation systems are based on distillation but other alternatives as the use of membranes are also drawn on (as will be exposed in a following section); as in the case of bioethanol where either of mentioned processes can be applied. The purification processes become so important because they could account for more than 50 % of the transformation costs in a biorefinery [6].

As it can be noticed, the chief raw material for growing biomass and obtaining products corresponds to reducing sugars, and its source type provides the biorefinery type. Continuing upstream, in a 1G biorefinery of sugarcane, the feedstock is grinded up and passed by hot water or vapor to obtain syrups of reducing sugars of six carbons (fructose); meanwhile, in 1G-of-grains and 3G biorefineries, enzymatic hydrolysis processes to unfold starch up to glucose are involved, and even in 3G biorefineries an additional enzymatic hydrolysis could be included to depolymerize the cellulose contained in the algae wall. Through a more complex kinetics mechanism, in a 2G biorefinery, syrups of reducing sugars of six- and five-carbon sugars (e.g., glucose and xylose) are obtained through a process of enzymatic hydrolysis of cellulose and hemicellulose contained in corresponding pretreated feedstock. Since the complexity provided by the condition in which the starch, or cellulose and hemicellulose are available, the enzymatic reagent typically consists of a blend of specific enzymes. In the case of starch, the enzyme family of amylases is applied in such a way the starch passes through steps of gelatinization, liquefaction, and saccharification at temperatures around 100 and 60 °C. On the other hand, in the hydrolysis of pretreated lignocellulosic mass, the enzyme family of cellulases are applied at temperatures around 50 °C to unfold cellulose and hemicellulose in molecules of lower size up to glucose and five-carbon sugars, respectively.

In 1G-of-grains and 3G biorefineries, the pretreatment of feedstock consists on mechanical and thermal operations to soften the starch content and allow the working of enzymes. Meanwhile, lignocellulosic feedstock in 2G biorefineries must be pretreated more severely to break or eliminate the lignin wall that wraps the cellulose and hemicellulose content in such a way that enzymes can work. There are many different ways to carry out a pretreatment in 2G biorefineries, whose variety comes from the different chemicals (and even biological reagents) that can be used [7]. For example, applying diluted sulfuric acid at high temperature (around 120 °C) is attractive because is cheaper than any other thermochemical pretreatment. In addition to the breaking or reduction of lignin wall, hemicellulose is hydrolyzed yielding five-carbon sugars. Another example is the thermal pretreatment called "autohydrolysis", that has become attractive because implies minimum amount of chemicals with a similar performance than sulfuric acid application.

Summarizing, the processes of pretreatment, enzymatic hydrolysis, fermentation, and purification are identified as the basic ones to conform a biorefinery. Each of them can be carried out in different ways (considering the diversity on chemicals or biochemicals, equipment, and process conditions) that in turn yield different products. Therefore, many different configurations of biorefination can arise. The above description relates a conventional form of biomass harnessing. However, as it will be discussed in the next sections, each process step by itself is susceptible of performance enhancement, and even the bundling of two of them in just one process equipment aims to a major productivity; say, the Process Intensification on a framework of biorefination for biomass processing is discussed in the following sections.

7.3 Relevance of Process Intensification Within Biotransformations: Bulk Chemicals, Biofuels, and High Value-Added Products

7.3.1 Enzyme-Assisted Transformations: Fine Chemicals Application

The use of enzyme-assisted transformation, also known as biocatalysis, has grown enormously over the last decade and recently it has been extended to a wide range of applications at industrial level due to the exceptional selectivity of enzymatic reactions, combined with transformation under mild reaction conditions. Such characteristics drive the desired reactions to achieve cost-effective processes with the additional advantage of working under a friendly environment. While the current majority of biocatalytic reactions are implemented in the pharmaceutical industry, they are increasingly finding value at various points in the value chain.

In biorefinery, enzymes can be used in the early stages of the process in order to transform the low cost feedstock into a high cost feedstock (see Figs. 7.4 and 7.5). For example, the enzymes can be used for the saccharification of biomass in which a cocktail of different enzymes breaks down big carbohydrate molecules such as starch, hemicellulose, and cellulose into fermentable sugars. Likewise in the

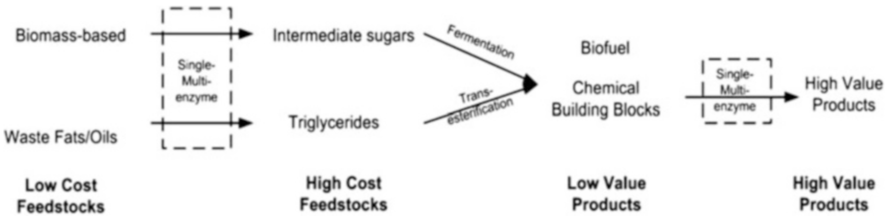


Fig. 7.5 Single or multienzyme steps applied in biorefinery

production of biodiesel, lipases enable unpurified triglycerides to be used as a starting point for the transesterification and thus the production of biodiesel and glycerol (as a co-product). The utilization of a low-cost feedstock drives to a lower costs for the process. Nevertheless, a real process sustainability can only be achieved when the production of biofuels is integrated in an efficient way with the production of other value-added products such as chemicals, fine chemicals, materials, food, feed, and pharmaceuticals. During the biorefinery steps, important building blocks are produced such as 1,4-Diacids, 2,5-Furan dicarboxylic acid, glycerol, sorbitol among others, and those are the main intermediates for the production of high-value products such as solvents, fibers, polymers, pharmaceuticals, food, and personal care. In these cases, another set of enzymatic reactions must be added to the chain in order to reach the desired product in an efficient manner [8].

Although enzymatic transformations can be found in many industrial sectors (e.g., food, fine chemicals, and pharmaceuticals), it remains the case that the vast majority of these processes use merely a single enzymatic step. Frequently the mild conditions of the enzyme reaction are in contrast to the other reactions preceding and following the enzymatic step. Hence, some changes to the process conditions may be required in order to adapt the optimal enzymatic operation within an existing process. However, this impact can be minimized when using two or more adjacent enzymatic steps in the process, since most enzymes operate under similar conditions. In the following section, such multienzymatic processes will be discussed as a superb example of PI in biotechnology.

7.3.2 Multienzyme Processes

A multienzyme process is characterized by the combination of two or more adjacent enzymes that react in a specific pathway to a given product of interest, via a cascade, parallel or network scheme (see Fig. 7.6). In nature, such pathways are characteristic of cells and are essential for the control of energy and redox inside microorganisms. For industrial application, the use of such pathways outside the cell is more useful since perfect control of each enzyme activity can be assured. Hence in vitro enzyme pathways studies help providing useful and controllable schemes to obtain certain products of interest.

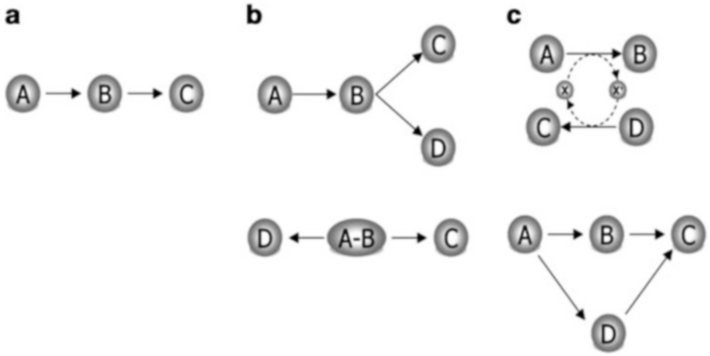


Fig. 7.6 Basic multienzyme reactions: (**a**) cascade, (**b**) parallel, and (**c**) network. Adapted from [9]

In the cell, such schemes are the way nature achieves process intensification and by analogy therefore in vitro applications also provide opportunities to develop PI technologies. Unfortunately, bioprocesses, via microorganisms or enzymatic, can experience physical, chemical, and/or thermodynamic limitations which can be caused by substrate/product inhibitions, unfavorable equilibrium constants, multiple phases, and co-factor dependency. The first most common way of overcoming these limitations is by applying controlled feeding processes, in situ product removal technologies, or/and protein engineering. Such process control strategies and biocatalyst modifications can give significant improvements to the processes in terms of higher yield, product concentration, and space–time yield at lower catalyst usage. The second way can be achieved via integration of two or more reaction steps into a single reaction unit. In this case, a PI is generated since the separation of intermediate products is no longer required. This combination of enzymes in a one-post reactor is perhaps the most common definition of a multienzyme process, but in all cases it represents an example of process intensification. Depending on the multienzyme arrangements, the reaction can be classified as cascade, parallel or network (see Fig. 7.6), and the spatial and temporal integration or separation can be envisaged depending upon the constraints in process integration. Two pharmaceutical applications are illustrated later in this section i.e., production of lactobionic acid and synthesis of iminosugar D-fagomine.

7.3.3 Implementation of Multienzyme-Based PI

The utilization of several enzymes gives the opportunity to use different reactor configurations. This depends on the characteristic of each individual enzyme and the most feasible and economical format (e.g., isolated, immobilized, or contained in a cell) in order to reach the required cost-effective process. Bioreactor can be designed applying the enzymes as crude or purified versions as well as soluble and

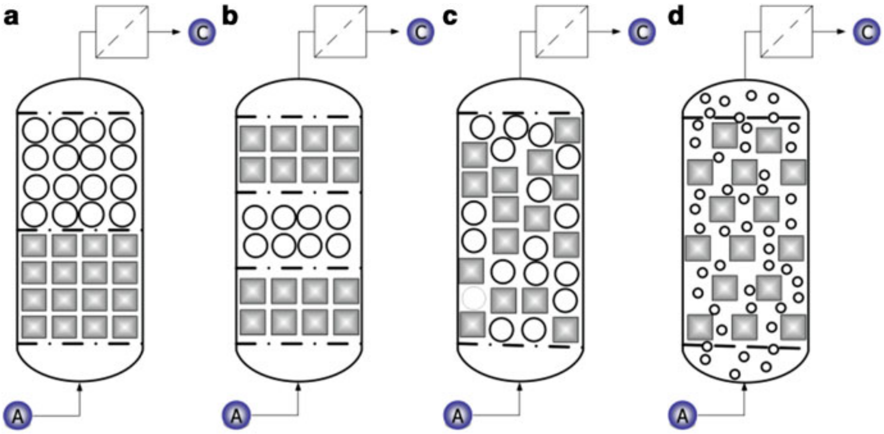


Fig. 7.7 Multienzyme process implementations using immobilized enzyme in a packed bed reactor. (**a**) Two sequential beds, (**b**) alternate beds, (**c**) mixed enzyme bed, and (**d**) one enzyme bed with a soluble enzyme. Adapted from [9]

immobilized (see Fig. 7.7). The use of immobilized enzymes can allow separation and compartmentalization, both of which can be useful concepts to exploit with multienzyme processes. Immobilization can also allow recycle of enzymes, hence improving biocatalyst yield (product obtained per amount of enzyme added). Where enzymes have matching stability, immobilization of multiple enzymes on a single support can also be achieved [10]. Aside from immobilization on particles (hydrophobic or hydrophilic), immobilization on membranes can also be used, where enzymes can be impregnated in the membrane or adsorbed on the surface.

The application of multienzyme processes has been mostly achieved in the production of higher value products such as pharmaceuticals and fine chemicals, where the specificity and region-selectivity of a chiral structure may play an important role in the final application. For example, an interesting case occurs during the synthesis of functionalized sugars from glycerol (a biodiesel co-product) that can be used as a raw material for the production of phosphate esters. These products are used as valuable intermediates in the synthesis of iminosugars which are monosaccharide-analogues capable of a specific inhibition of glycosidases, and are currently used therapeutically in several human disorders [11]. The synthesis of the iminosugar D-fagomine, from glycerol and a variety of aldehydes, has been proven by using a four-enzyme one-pot cascade reaction in which an acid phosphatase, glycerol-3-phosphate oxidase, catalase, and aldolase have been combined in a simple packed bed reactor configuration [12]. This work highlights the potential value of using enzymes in cascade reactions to selectively form complex products that by previous traditional organic chemistry could only be obtained via repeated isolation and purification of intermediates. Another multienzyme process that can be applied in biorefinery is the production of lactobionic acid

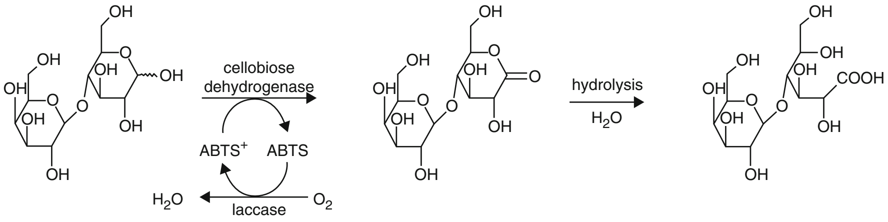


Fig. 7.8 Bi-enzymatic production of lactobionic acid from lactose

which is obtained by the enzymatic oxidation of lactose (see Fig. 7.8). Lactobionic acid is used as high-value product in pharmaceutical and food technology applications. The production of lactobionic acid has been achieved by the combination of two enzymes in one-pot in which cellobiose dehydrogenase (CDH) and laccase, in the presence of a redox mediator, has produced a successful multienzyme application [13].

7.4 Co-cultivation of Carbon Sources

The synthesis of bioproducts via single fermentation processes consists of the conversion of one or more renewable carbon sources into specific products by the action of one microorganism. The search for improving the production of biobased chemicals have opened new opportunities such as the co-cultivation, where two or more different microorganisms as a consortia are employed during fermentation. The intensification by the co-culture fermentation occurs by the synergistic exploitation of the metabolic pathways of the involved strains. Here the cell growth of a given strain may be enhanced or inhibited by the activities of other microorganisms present in the medium. Enhanced growth rate can also be observed when the enzymatic activity of one strain in the co-culture supplies the substrate required by another strain. Another positive interaction is the reduction of the available oxygen by aerobic microbes, creating an anaerobic environment that promotes the growth of anaerobic strains. Similar phenomena appear with the formation of primary and secondary metabolites [14].

7.4.1 Use of Co-cultivation for Different Products

The co-cultivation have been applied in different areas, for example, pharmaceutical products manufacture [15], biofuels, food additives, enzymes production, bulk chemical, fine chemicals, microbial fuel cells, among others. In the following, the most famous applications are described.

7.4.1.1 Ethanol Production

The production of bioethanol from lignocellulosic material involves various steps where the implementation of co-cultivation could enhance the process performance. He et al. [16] proposed a co-cultivation employing a *Clostridium thermocellum* and *Thermoanaerobacter* spp. and found an improvement by 194–440 % in the production by combining different microorganisms rather than using only a *C. thermocellum*. The combination of co-cultivation and enhanced operating policies has also shown larger improvements in the production of ethanol by at least two orders of magnitude in the concentration. The advantage of using different microorganisms from the frequently used (e.g., *Saccharomyces cerevisiae*, *Zymomonas mobilis*, etc.) for ethanol production is that more extreme conditions can be used. For example, higher temperatures at the fermentation process, which facilitates in situ product removal and recovery, reduction in cooling costs and least chance of contamination [17]. A recent study has evaluated the combination of as *S. cerevisiae* and *Z. mobilis* ATCC31825 [18] varying the ratio of microorganisms concentration in order to metabolize pentose and hexose molecules from pretreated sweet sorghum bagasse; the *Z. mobilis* to *C. cerevisiae* ratio of 5:10 g/L allowed to reach a yield of 0.5 g-ethanol/g-reducing sugars. Ethanol production has also been carried out by using *S. cerevisiae* ITV-01 and *Scheffersomyces stipitis* NRRL Y-7124 strains, by fermenting hydrolyzed bagasse residues and sugarcane molasses from cane sugar production process [19]; the yield in the co-cultivation reach up to 0.41 g-ethanol/g-sugars, compared to 0.38 and 0.37 g-ethanol/g-sugars when only using *S. stipitis* NRRR Y-7124 and *S. cerevisiae* ITV-01 strains, respectively.

7.4.1.2 Acetone–Butanol–Ethanol Production

The ABE process (acetone, butanol, and ethanol production) have once again become important, capturing attention from the research community due to the variety of products obtained in one single fermentation pot; specially for the butanol production which has several advantages as a biofuel [20, 21]. The aims for improving the yields, conversion of intermediate products, and selectivity for specific products have also made possible to explore the co-culture fermentation for ABE process. The *Clostridium* strains are the most employed microorganisms to produce acetone, butanol, and ethanol, and the combination with different strains to improve sugars conversion has also been evaluated. The co-culture fermentation employing *Clostridium beijerinckii* and *Clostridium cellulovorans* was tested using alkali-extracted deshelled corn cobs as substrate. It was possible to determine the mechanism of cooperation and competition between the two strains to increase the ABE production, thereby opening a pathway to optimize the artificial symbiosis between the strains [22]. Li et al. [23] proposed the butanol production employing *C. beijirinckii* and *Clostridium tyrobutyricum* in a free cell and immobilized cell reactors, observing that the co-culture fermentation enhanced significantly the butanol production over the fermentation in a single culture. Yao and Nokes [24] presented the co-cultivation and strategy for intermittent flushing of the fermentation media for the cellulolytic and/or solventogenic phases using *Clostridium thermocellum* and *C. beijerinckii*; from the operating point of view, this study has tested five operating strategies where it was observed that cycling through the cellulolytic phase with or without the re-inoculation of *C. thermocellum* improved glucose availability for the following solventogenic phase, increasing the solvent accumulation.

7.4.1.3 Hydrogen Production

Hydrogen has become another promising biofuel. Biobased hydrogen is naturally produced through a dark fermentation, which is a series of biochemical reaction employing a microorganism consortia in the absence of light. Thereby co-culture fermentation is the most common way to carry out the hydrogen production. This process comprises the hydrolysis of the polysaccharides, acidogenesis to break down the molecules into acetic acid, hydrogen and carbon dioxide, and finally the acetogenesis which also produces hydrogen and carbon dioxide. One of the main challenges during hydrogen production is avoiding methane production, thus the use of a suitable co-culture media during the fermentation has a paramount importance. Anaerobic microbes employed in the several steps during hydrogen production are diverse including *Clostridium*, *Enterobacter,* and *Escherichia* [14]. The combination of such microorganisms has been tested for example by the use of *Clostridium butyricum* and *Escherichia coli*, showing a more efficient utilization of glucose than with each single microorganism [25]. Another approach using *Clostridium thermocellum* and *Clostridium themosaccharolyticum* was evaluated by Li and Lui [26]. The authors tried different operating scenarios by changing the culture feeding policy, operating under continuous or batch conditions, and comparing fermentation performance when using each single culture against the co-culture. Under the best condition co-culture fermentation showed 94 % higher hydrogen production. Other authors have evaluated the interaction of various strains. For instance Masset et al. [27] used four different *Clostridium* cultures and three different co-culture systems in order to determine the best conditions for hydrogen production. The system with *C. butyricum* CWBI1009 and *Clostridium pasteurianum* DSM525 showed the highest hydrogen production among the three synergies.

Another interesting raw material for hydrogen production is the glycerol obtained from biodiesel production. In an interesting review, Sarma et al. [28] mentioned several studies employing different co-culture systems to produce hydrogen from glycerol via fermentation process.

7.4.1.4 Other Important Products in the Market

There are other bioproducts with relevant importance as a bulk or fine chemicals. The lactic acid is one of those important compounds, which has been produced using co-culture fermentation. Some studies have employed the sugars derived from lignocellulosic raw material, finding the advantage of using the intensified fermentation by the use of two cultures rather than a single one [29]. Even that one of the obstacles is the carbon catabolite repression existing using renewable resources as raw material [30], the results have shown in general an intensification in the lactic acid yield using co-cultivation. Enzymes production has also been accomplished via co-cultivation, in order to increase the productivity and performance in certain biological systems. For instance, the β-glucosidase is an important enzyme in the production chain of lignocellulosic derivatives, and the co-culture have been also applied to this end [31]. Xylanases and laccases enzymes are other enzymes with high importance in the industry, for example, in the paper production and potentially in the biofuels industry since are useful for lignin and xylan degradation; those enzymes have similarly been produced using co-culture fermentation in order to improve the production [32]. Citric acid from lignocellulosic residues have likewise been also produced using co-cultures (Y*arrowia lipolytica* SWJ-1b and Immobilized *Trichoderma reesei* Mycelium), and this has resulted in an increased production of product by 91 % [33].

The scope of the co-culture implementation is wide and it is still necessary to analyse the combination of other microorganisms, relying on the previous analysis of the metabolic pathways and possible drawbacks by the present of certain inhibitors of cultures. This could be achieved with the creation of one multidisciplinary team including specialist from the biotechnology, genetic and engineering areas.

7.5 Co-fermentation of Renewable Carbon Sources

The main objective of fermentation and one of the core sections in a bioprocessing system, is the transformation of a carbon source into a specific product (such as alcohols, organic acids, gases, etc.) by the use of a microorganism. The well-known process of metabolizing glucose to produce ethanol and carbon dioxide by using baker's yeast *Saccharomyces cerevisiae* is an example of such approach. However, some microorganisms (including the mentioned *S. cerevisiae*) are not able to ferment other types of sugars (e.g., xylose), reducing the opportunity of increasing ethanol productivity when combining different types of sugars in the same unit. This bottleneck was identified many years ago and since the beginning of the 80s, scientists have been working on manipulating and developing a genetically engineered *Saccharomyces* yeast capable of metabolizing xylose. In 1993 some researchers achieved the development of genetically engineered *Saccharomyces* yeasts, which can ferment both glucose and xylose to ethanol [34]. This was carefully accomplished by redesigning the yeast metabolic pathway, cloning three xylose-metabolizing genes pathways for fermenting xylose to ethanol. Thereby, it was possible obtaining a microorganism capable of metabolizing a compound that was impossible to transform before. During the genetic manipulation techniques, the metabolic flux is altered by blocking undesirable pathways, typically via homologous recombination-mediated “gene knockout” and/or by the overexpression of genes associated with desirable pathways [35]. The co-fermentation of glucose and xylose by the same microorganisms was a breakthrough from the biotechnology point of view, which permitted the intensification of the ethanol production.

Figure 7.9 shows details of the two different pathways available in nature for the conversion of pentose: (1) oxidoreductase-based pathways (type I pathways) found in most fungi, and (2) isomerase-based pathways (the type II pathway) found in most bacteria. In major enzymes, the genes encoding the pentose pyrophosphate pathway are XR (xylose reductase), XDH (NAD+-dependent xylitol dehydrogenase), and XK (xylulose kinase). However, these genes are expressed at such a low level that the xylose utilization by *S. cerevisiae* is not allowed, while XK is the rate-limiting step of the pentose phosphate pathway. By using DNA technologies, the genes linked to the pentose metabolism from bacteria and other fungi have been inserted into the genome of *S. cerevisiae* for the utilization of sugars from hemicellulose hydrolysates [36].

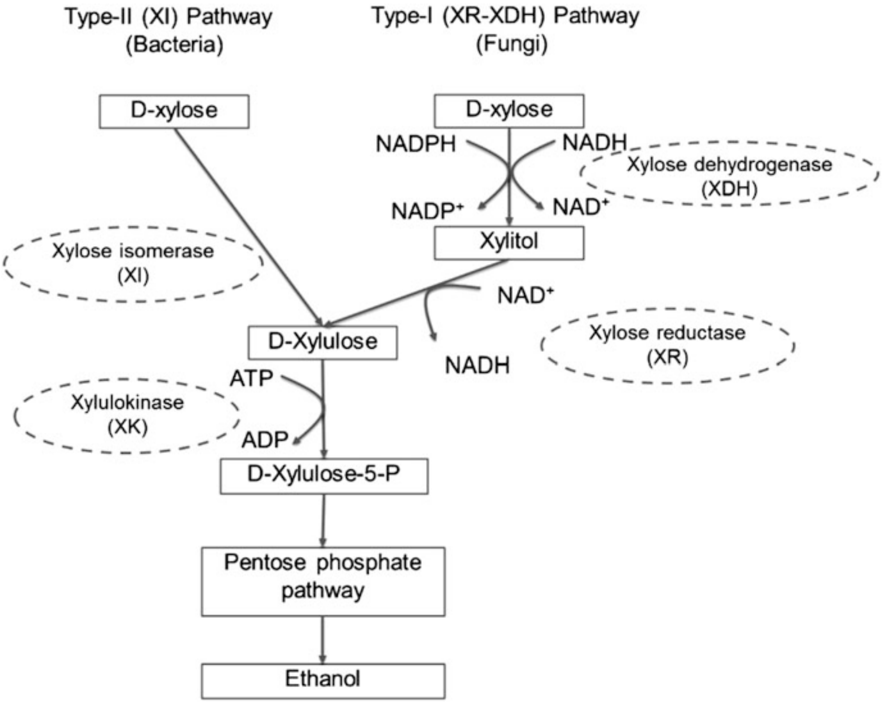


Fig. 7.9 Outline of the xylose metabolism pathway in fungi and bacteria as previously reported. Adapted from Laluce et al. [36]

The demand of some specific products, such as biofuels or other high value-added products has triggered out the search of new manners to produce the same product using different raw materials simultaneously in the same pot. The second generation bioprocesses employing lignocellulosic residues release a list of several compounds at the pretreatment section, for example, arabinose, xylose, galactose, lignin, among others; the mixture of available sugars exhibits a huge opportunity for improving in the most "simple manner", the production of certain compound metabolizing two (or more) different sugars by a genetically engineered microorganism under an intensified process scheme in a co-fermentation.

7.5.1 Co-fermentation Applied for Ethanol Production

The production of ethanol in a biobased process has captured the attention of researchers in the intensification area. Many *Saccharomyces* strains have been subject to genetic manipulation techniques, essentially for the simultaneous glucose and xylose fermentation, working with hypothetical mixtures and also with different lignocellulosic residues. The identification of glucose and xylose as raw materials relies on the high concentration of these sugars after the pretreatment or enzymatic hydrolysis. The glucose and xylose compounds could theoretically reach in average up to 650 g/kg before entering to the fermenter, rather than only glucose concentration (up to 415 g/kg) for a simple fermentation. Thus, the amount of carbon source is 1.6 times higher thereby ethanol production as well. The last permits to visualize the potential improvement using a co-fermentation technology.

The cellobiose molecule is an intermediate bioproduct at the pretreatment and enzymatic hydrolysis stage [37]. Cellobiose is converted into glucose by the β-glucosidase enzyme but due to the variety of factors during the enzymatic hydrolysis reaction (e.g., enzyme adsorption, product inhibition, etc.), cellobiose is not completely converted. The efforts to overcome this issue have also promoted the genetically engineered modification of certain microorganisms. For example some strains of *Escherichia coli* have been modified to metabolize glucose and cellobiose [38]. Also *S. cerevisiae* strains were genetically modified to convert xylose and cellobiose into ethanol in an intensified process [39].

7.5.2 Co-fermentation for Other Biofuels and High Value-Added Products

Besides ethanol, there are several products that are also produced by using co-fermentation such as hydrogen, lactic acid, lipids, food preservatives, basic biochemical products, etc.

The production of hydrogen through a biobased process relies on a dark fermentation, where the most common substrates are sugars that could also be obtained from lignocellulosic residue, carbon sources from livestock waste, and organic fraction of municipal waste. Even though the research for enhancing biohydrogen production relies mostly on the bioreactor operation, the search for the appropriate combination of carbon sources and the use of diverse microorganisms individually or as a consortia have been studied [40]. Different pure cultures that have been intensively investigated include strict anaerobic genera (*Clostridia*, metanogenic bacteria, archaea), facultative anaerobic genera (*E. coli*, *Enterobacter*, *Citrobacter*), and also aerobic genera (*Alcaligenes*, *Bacillus*) [41]. Biohydrogen production intensification has also included the combination of several of these cultures, aiming to transform combined substrates or sugars in a co-fermentation.

Lipids production from sugars by using microorganism has become important, since triglycerides can be subsequently used as raw material for biofuels production. Unfortunately, most of the microorganisms are not naturally able to convert pentose and hexose simultaneously, thus, the search for improving the performance of microorganisms has been directed towards their bioengineering manipulation [42]. Glucose and xylose are the most used carbon sources to produce lipids when employing genetically engineered microorganisms, such as, *E. coli* [43], *S. cerevisiae* [44], *Rhodococcus opacus* [42], among others.

Other bioproducts with high relevance in the market are starting to be produced employing intensified processes with genetically modified microorganisms. Lactic acid, which is used for biobased polymers production, is usually obtained by glucose fermentation; however recent investigations have focused on the fermentation of different sugars such as xylose [45]. The new studies, also including modified microorganisms, aim to carry out co-fermentation of different feedstocks containing hexoses and pentoses [46]. Other bioproducts obtained by co-fermentation process that have been recently studied include propionic acid from glucose and glycerol [47], butanodiol from glucose and xylose [48], and ε-poly-L-lysine from glucose and glycerol [49].

7.5.3 Glucose, Xylose, and Arabinose as Raw Material in Co-fermentation

Due to the low concentration of other liberated sugars such as mannose, galactose, etc. during hydrolysis of polysaccharides, few studies on the exploitation of such sugars with modified microorganisms have been reported. The simultaneous fermentation of xylose and glucose has been carried out with arabinose that could be considered as the third sugar with the higher concentration after the pretreatment. The intensified conversion of arabinose + glucose + xylose into ethanol has been achieved by modification of *Zymomonas mobilis* [50], and *P. stipitis* [51]. Hydrogen production has been accomplished by simultaneous conversion of arabinose and glucose using a thermophilic anaerobic mixed culture [52], and by conversion of glucose, xylose, and arabinose using a consortium of *E. coli* strains [53].

Beside the advantage of co-fermentation, the intensification in the performance of the microorganisms should not only cover the modification of the metabolic pathways to ferment new compounds. The inhibition effect is another bottleneck that should be tackled in order to improve the performance of a microorganism. The robustness of the microorganism to support higher temperatures, resistance to toxic compounds concentrations that inhibit and reduce the capability of the microorganism to work properly.

7.6 Simultaneous Saccharification and Co-fermentation

The SSCF consists of one unit operation where the liberation of carbon sources such as hexose and pentose sugars is performed by the action of specific enzymes, and the subsequent sugars fermentation is carried out at the same time by microorganisms. Figure 7.10 represents a SSCF unit where the process is performed in one reactor rather than two, reducing the reacting volume and the operating costs, and also improving the yield of desired products.

The SSCF have been mostly analyzed for the ethanol production from glucose and xylose employing mainly genetically engineered microorganisms able to perform a co-fermentation process. The modified microorganisms to produce ethanol have allowed to use diverse lignocellulosic sources such as hardwoods [55], sugarcane bagasse [56], Kraft mill sludge [57], corn stover [58], wheat straw [59], among others. A validated mathematical model to describe the SSCF process was already presented by Morales-Rodriguez et al. [54], which allowed to perform a process design, operation, and control [60, 61].

The SSCF have also been implemented to produce lactic acid mostly employing modified microorganisms of *Bacillus*, *Aspergillus*, and *Lactobacillus* [62–

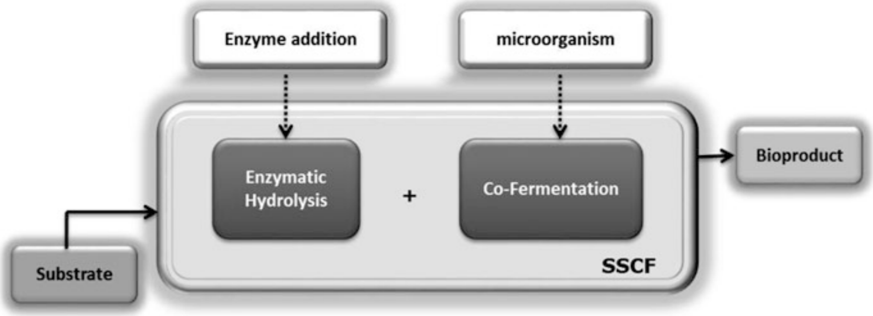


Fig. 7.10 Simultaneous saccharification and co-fermentation process. Adapted from Morales-Rodriguez et al. [54]

64]. The production of lactic acid via SSCF is still on development, thus, it is necessary to try implementing the SSCF for other feedstock, process conditions, other manipulated strains, etc.

The application of SSCF has not achieved maturity for other systems as it has been the case for SSF or bioethanol production. There are still potential processes that can be subject of intensification by performing saccharification and fermentation in the same unit, for example, in the production of acetone–butanol–ethanol, xylitol, citric acid, etc. It is important to highlight that the use of SSCF requires microorganisms capable of metabolizing the two or more carbon sources released by the enzymes.

7.7 Consolidated Bioprocessing

The CBP has been applied specially in biofuels production from lignocellulosic biomass. The CBP have been conceived as the unit operation, where the microorganism(s) is able to produce, in situ, the required enzymes for the lignocellulose hydrolysis, in which, the sugars are obtained and fermented by the same microorganism(s). These are all the required steps to get a bioproduct performed in one pot (Fig. 7.11). By avoiding enzyme addition, utility consumptions are reduced (water and cooling water) allowing reduction in the operating cost. Most likely this is the ultimate configuration for low-cost hydrolysis and fermentation of lignocellulosic biomass [65].

Olson et al. [66] argued that CBP-enabling microbes must be able to both solubilize a practical biomass substrate, and produce desired products at high yield under industrial conditions. Unfortunately, microorganisms with those characteristics have not been found in nature and it is necessary to employ genetic engineering. For example, the Trichoderma reesei Rut-C30 strain is able to produce xylanases and cellulases simultaneously from plasma pretreated wheat straw, which could liberate xylose and cellulose from the xylan and cellulose of the lignocellulosic material, but the fungi would not be able to convert those sugars into a specific bioproduct [67].

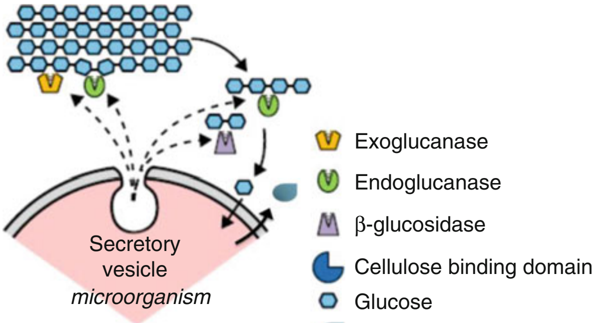


Fig. 7.11 CBP by production of secreted enzymes that allow random free access to insoluble cellulosic material. Adapted from [68]

den Haan et al. [68] have classified the approaches to achieve CBP in two categories relying on the capability of the microorganism: (1) cellulases production by naturally fermentative microorganisms (e.g., yeasts and bacteria), and (2) engineering cellulases producers to produce ethanol or other desirable products (e.g., fungi). Regarding the first category, the genetic modification for constructing *Saccharomyces cerevisiae* strains include three strategies related with the mechanisms in the CPB: (a) production of secreted enzymes that allow random free access to insoluble cellulosic material (see Fig. 7.11), (b) binding of cellulases to the cell wall and (c) tethering of cellulases to the cell wall in mini-cellulosomes; the final end of the genetic modification includes increasing the production of the necessary total enzymes by the host microorganism improving both total expression and specific activity of the enzyme system. The genetic engineering application has not been exclusive of *S. cerevisiae*, because some non-cellulolytic bacteria (such as, *Clostridium thermocellum*, *Clostridium cellulolyticum*, *Zymomonas mobilis*, *Escherichia coli*, and *Bacillus subtilis*) have also been modified in order to include cellulases production. Regarding the second category, there have been some assessments using modified fungi to achieve a CBP approach, for example, the use of *Fusarium oxysporum* [69], *Aspergillus*, *Trichoderma*, and *Rhizopus strains* [70].

The use of CBP has been employed for ethanol production, and also there are some studies that have focused on butanol production employing model substrates (for example, avicel, filter paper, cellulose MN 301, etc.) as well as lignocellulosic biomass (such as, hardwood, grass, rice straw, corn stover, etc.) [66].

The current state of the art illustrates some reached goals, but in order to succeed at industrial scale employing CBP, there are still challenges to overcome. First of all, from the microorganism's point of view, it is however necessary to improve the tailor-made genetic modification of the organisms, for instance, it is still required to improve the proportional enzyme production and carbon source consumption by the microorganism aiming to obtain higher product yield and titer, promote the fermentation of more than one substrate, enhance the behavior of the microorganisms for recombinant fermentation, among others. Another opportunity for process intensification that has not been yet considered is the inclusion of simultaneous removal/recovery of the substances during the fermentation, in order to accomplish a better environment for the microorganism and increasing yield of the desired products.

7.8 Simultaneous Reaction and Purification processes: In Situ Product Removal/Recovery

It has been recognized that downstream processing is both technical and economically challenging, especially in bioprocesses (e.g., complex mixtures, dilute solutions, sensible microorganisms and enzymes, time variant systems, among others). In order to improve the bioprocesses cost-effectiveness especially in batch operation, process intensification framework proposes to integrate the reaction and separation stages in the same processing unit [71]. This technological trend has been called ISPR. There is a small difference between product removal and product recovery. Product removal is usually referred to any product that is removed from the reactor (i.e., main or secondary components that can have negative effect such as inhibition, degradation, or transformation into unwanted substances). On the other hand, product recovery is used when the main product is removed.

ISPR has been extensively investigated since early 1990s, and several hundreds of publications have been referenced in relevant reviews [71–74]. The processes have been classified from the technology and, more recently, from the product point of view. The ISPR technologies include a diverse gamma of hybrid reactive processes with extraction, adsorption, ion-exchange, high-gradient magnetic field fishing, membrane-based, among other units. Recently, there is an increasing interest in hybrid membrane bioreactors mainly for biofuels and organic acids production; therefore, recent advances on those topics are analyzed.

7.8.1 Hybrid Membrane Bioreactors

Membrane separation processes are not new technologies, they have been under development since XVII century. Nevertheless, it took many years to scale-up from laboratory to industrial level due to high capital and operating costs, limited selectivity, low productivity, and the poor reliability of the membranes. It was only until 1960s when real commercial applications drove substantial improvements in membrane technology, mainly with pressure and electrically driven separation processes [75]. Relevant breakthroughs in membranes manufacture, process design, and system operation have boosted the application of other membrane-based technologies at industrial level, and lately within the process intensification framework. Taking into account the membrane technology development trend, it can be said that these separation processes are still evolving where others have reached their technological limits.

An overview of the membrane technology applications in biotechnology has been summarized in Fig. 7.12. It can be seen that pressure driven membrane separation processes are applied in broad spectra of industrial biotransformations at different stages. Notice that specific applications have not been included such as dialysis, membrane chromatography, gas separation, liquid membranes, and electrophoresis.

In most of the revised membrane technology applications, they have shown formidable performance at laboratory and pilot plant scale in terms of some of the following indexes: selectivity, products purity, increasing productivity, minimizing/eliminating chemical usage, working at more friendly conditions for microorganism, reducing plant and carbon footprint, enabling continuous operation, reducing energy consumption, favoring process safety, among others [76–78].

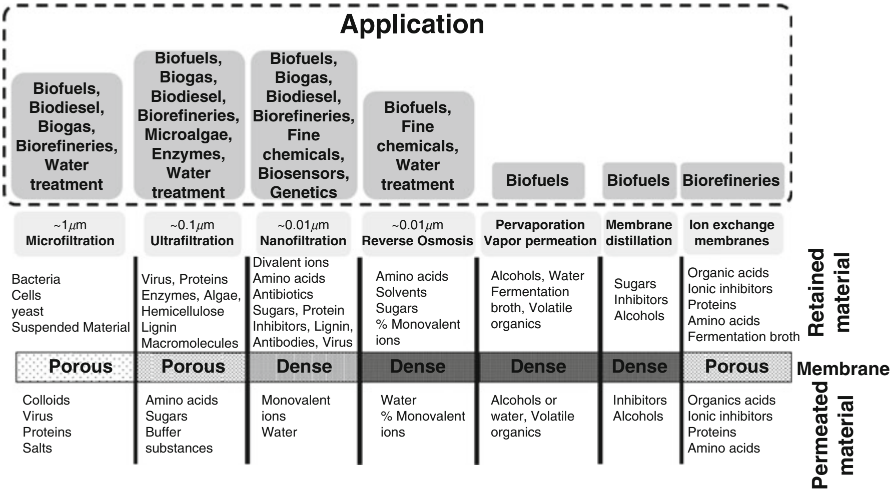


Fig. 7.12 Overview of membrane-based separation technology applications in bioprocesses

However, not all the applications stated in Fig. 7.12 can be considered as intensified processes. The most relevant applications of membrane-based process intensification lie within the so-called hybrid membrane bioreactors. Hybrid technologies can combine membrane-based in situ product removal and cultures/enzymes retention, if required, in order to: increase productivities, improve product yield, ensure sterility, enable continuous operation at higher dilution rates, favors the control of the cultivation parameters, decrease the energy requirements, enhance the product separation, and ease scalability [79].

Two different configurations for membrane bioreactors are reported in literature: submerged membranes and external loop systems. Those have been nicely reviewed recently [74]. Representation of both configurations is shown in Fig. 7.13. Submerged membranes are advantageous since they minimize the induced shear stress, reduce energy consumption, facilitate sterilization, and reduce the risk of contamination. On the other hand, external membranes provide a better fouling control at the expense of extra equipment volume and energy requirements, and they are also easy to replace. When using recirculation loops, cells as subject to extra shear stress that might inhibit metabolite production and cell viability, which is particularly critical in animal cells. However, it has been pointed out that membrane bioreactors provide such as protective environment for cell growth that compensates the induced stress [80].

Several efforts had been made in order to reduce the adverse influence of the membrane fouling, especially in submerged membranes. Mechanisms have been proposed as backflushing, backshoking, agitation, aeration, membrane vibration, cross-flow operation, rotating membranes, turbulence enhancers, and ultrasonic waves. Depending on the application, submerged or external loop membranes are appropriate. Submerged membranes have great potential be used for high-value

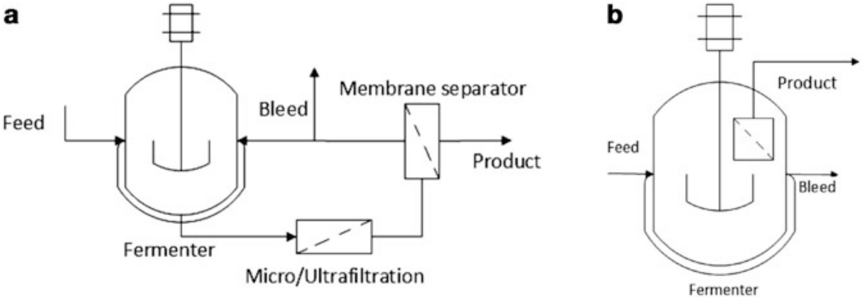


Fig. 7.13 Scheme of external loop and submerged membrane configuration for hybrid membrane bioreactors. (**a**) External loop, (**b**) submerged membrane

products such as antibodies or enzyme production. On the other hand, external loop membranes are advantageous for commodities production due to the large membrane area required. Specific applications impose challenges to overcome in order to allow hybrid membrane bioreactors to be used extensively in the future. Some relevant challenges are discussed in the following sections.

7.8.2 Hybrid Membrane Bioreactor for Cell/Enzyme Retention and Proteins/Enzymes Separation

Micro/Ultrafiltration membranes have been used within hybrid membrane bioreactors for different purposes. Filtration membranes have the ability to retain components depending on their size, affinity with the membrane material, and operational conditions. Microfiltration (MF) membranes have been used to retain microorganisms such as cells, bacteria, and yeast in the bioreactor and/or to clarify the fermentation broth before another separation stage (see Fig. 7.13a). Clarification of the fermentation broth considerably reduces the fouling potential of a subsequent membrane module. Simultaneously, cell retention allows operation at higher cell densities, which promotes a better substrate utilization. Cell retention is particularly interesting during continuous operation since it allows operating at dilution rates higher than the specific growth rate. However, cell retention using membranes does not necessarily imply an improved culture viability. For aerobic cultivations, it is more difficult to achieve high cell-density operation since the oxygen transport rate might become the limiting growth factor. If that is the case, the bioreactor design must account for the limitation and enhance oxygen transport rate, for instance, through jet diffusors and static mixers [81, 82]. Additionally, a purge or bleeding must be done in order to avoid accumulation of unviable cells in the reactor. This task is not necessarily straightforward from the monitoring and control point of view [83]. Despite those limitations, most of the reviewed contributions show an improved performance compared to conventional fermentation [74].

For cell retention in bioreactors, ceramic, polymeric, glass and metallic membranes have been studied. Among the investigated materials, ceramic membranes are attractive due to its superior performance, thermal/mechanical/chemical stability and well distributed pore sizes (i.e., compared to polymeric membranes). However, ceramic membranes are still expensive compared to polymeric. Membrane fluxes up to 1–70 LMH ($L/m^2/h$) have been achieved with microfiltration submerged membranes for *Saccharomyces* retention. An external loop had achieved up to 30–80 LMH in comparable systems and concentrations [74].

Ultrafiltration (UF) membranes can retain suspended material and colloids. This ability makes them interesting to apply for enzyme and protein retention in bioreactors. UF membranes are used to retain free enzymes or, more conveniently, be the support for the enzyme immobilization [10]. When membranes are utilized to retain free enzymes, those tend to adsorb on the membrane surface due to affinity with the material. As a consequence, the adsorption can lead to the enzyme activity reduction. The operational conditions need to be carefully selected in order to minimize membrane fouling and enzyme activity decay [84].

Due to this limitation, enzyme immobilization has been recently investigated. The available commercial membranes require modifications to make them suitable for enzyme immobilization [85]. Results have shown the benefits of using ultrafiltration membranes as support, including total retention of the enzymes and a trade-off between activity lost and system stability after the immobilization process [86–88]. This compromise suggests that more research is required to find the appropriate immobilization mechanisms in order to improve the biocatalytic performance before this technology can be scaled up.

From the modelling perspective, efforts have been focused on membrane bioreactors for wastewater treatment using semi-empirical fouling models within resistance in series approach. Due to the models nature, they have reduced predictive power and their application is limited [89]. Therefore, pilot plant experiments are mandatory in order to scale-up the processes [16].

7.8.3 Hybrid Membrane Bioreactors for Biofuels Production

Besides the fermentation challenges during the biofuels production, another big limitation is the separation stage to recover and purify the key component from the dilute mixture, since it is one of the most energy consuming stages. Conventional bioethanol production using fermentation and distillation is energetically deficient because 5.99 kJ are invested to produce 4.19 kJ contained in the alcohol [78]. The high temperatures required to separate ethanol from the fermentation broth using distillation enable a deeper integration between reaction and separation processes. Therefore, the untransformed substrates are not reused. The product inhibition and the separation of the biofuel issues are addressed from a process intensification perspective within the in situ product removal framework. Integrated bioreactors with alternative separation processes can selectively remove in situ, the components that impair the microorganisms, i.e., alcohols, phenols (flavors), butanol, and acetone, among others. Besides, it has been shown that lower product concentrations reduce the fermentation broth osmotic pressure, then the undesired glycerol production during the fermentation decreases and there is an increase in the number and viability of cells. Combining these factors, there is a substantial improvement of the bioprocess productivity using hybrid technologies [90, 91]. Two similar systems have been investigated:

7.8.3.1 Hybrid Fermentation–Pervaporation System

For few decades, pervaporation (PV) has been considered as the most promising process for azeotropic mixtures separation due to its effectiveness, reduced energy demand and it is environmental friendly. As result, for 2006 there were more than 100 pervaporation plants worldwide operating for alcohols dehydration [92]. More recently, the hybrid fermentation and pervaporation process have been investigated in order to intensify the biofuels production, mainly bioethanol and the ABE process (Acetone, Butanol, and Ethanol).

Pervaporation is a chemical potential-driven membrane separation process, where the transport mechanism is solution-diffusion. The driven force is induced by a pressure difference across the membrane generated by a vacuum pump, rapid condensation, or a sweeping gas (N_2). In pervaporation, dense inorganic, polymeric or composite membranes are used. These materials can be hydrophilic or hydrophobic depending on the key component to separate, i.e., water or organics (VOC), respectively [75, 93].

A conventional integrated pervaporation bioreactor system uses hydrophobic membranes in order to have continuous separate inhibitors from the fermentation broth [78, 94]. Two configurations have been investigated, submerged membranes (SM) or external loop membranes (EL) [74]. In external loop membrane configurations, there are possibilities to control fouling issues at the expense of induced cells stress and potential fermentation fluctuations. This can be done by using an intermediate micro/ultrafiltration stage. On the other hand, submerged membranes do not stress biomass but are subject to substantial membrane fouling, as previously discussed.

The most used material as selective layer to remove ethanol and butanol is Polydimethylsiloxane (PDMS). This material is stable at the fermentation conditions showing high transport rates (up to, 8000 $g/m^2/h$ for ethanol and 300 $g/m^2/h$ for butanol) [94, 95]. Hybrid pervaporation and fermentation systems have shown an improved performance compared to conventional bioethanol cultivations increasing productivity up to three times [78]. Still, research is required to improve selectivity, performance, and stability and reducing the membranes cost, especially for the biobutanol case.

7.8.3.2 Hybrid Fermentation–Membrane Distillation System

Membrane distillation (MD) has been proposed for desalination as a cost-effective alternative of reverse osmosis (RO) [96]. It is also an alternative separation process to remove ethanol and another inhibitory component from fermentation broths [97]. MD is a thermally driven separation process, similar to pervaporation. In this process, a microporous hydrophobic membrane separates vapor molecules. The driving force is generated by vapor pressure difference induced by the temperature gradient between both sides of the membrane. The separation is determined by the vapor–liquid equilibrium of the feed solution, which can lead to high rejection factors. In MD, the transport mechanisms are Knudsen diffusion, Poiseuille flow (viscous flow) and molecular diffusion, where the thermal boundary layer is considered to be the mass transfer-limiting factor. MD is economically competitive due to the high selectivity ethanol/water, high transport rate, high thermal efficiency, and reduced energy consumption [98].

Several results on integrated membrane bioreactors for bioethanol production have been reported. Volatile components (i.e., ethanol and other inhibitors) were removed from the fermentation broth increasing productivity and conversion rate. During batch fermentation, the ethanol yield was increased over 10 % and productivity was enhanced up to three times using an external loop bioreactor and membrane distillation system [99]. When using the intensified process, besides the transport limitations imposed by the thermal and concentration polarization, the yeast presence in the fermentation broth impaired severely the ethanol transport. Besides, it has been evidenced that the carbon dioxide in the mixture favors the transport of volatile components due to an increased turbulence [100]. Membrane fouling by biomass issue has been addressed including an intermediate microfiltration stage. Despite the advantages, it has been stated that membrane distillation is more difficult to apply on industrial scale due to limitations in the module design as well as heat loss during the process, which may lead to uncertain economic costs [101].

7.8.4 Hybrid Membrane Bioreactors for Organic Acid Bioproduction

Organic acids have already a place as chemical feedstock in chemical, food, cosmetic, and pharmaceutical industries. Among the organic acids obtained by fermentation, lactic acid has gained an increasing interest since it is the precursor for a sustainable production of Polylactic acid (PLA). PLA has been promoted due to its environmentally friendly characteristics such as: energy savings during production compared with traditional polymers, biodegradability, and suitability for PLA waste composting. Besides, lactic acid fermentation is relevant for the production of biomass as probiotic culture or starter culture for food industry [102]. Then, it is expected that industrial applications of lactic acid overpass other organic acids in the future (e.g., citric, acetic) [103]. The bottleneck of most organic acid fermentations is that the microorganisms are normally impaired by product inhibition at a certain concentration level of the main metabolic product or one of the bi-products by disruption of cellular replication, disruption of sugar metabolism, or disruption of membrane integrity [104].

The inhibitory effect generated by the presence of organic anions can be potentially diminished by their continuous removal from the fermenter, resulting in a higher productivity and product yield. Additionally, continuous recycle of biomass will allow obtaining higher cell densities that minimizes the risk of a cell wash-out [83]. However, in situ separation of organic acids is challenging and costly. It has been estimated that the cost of recovery and concentration of lactate from the cultivation broth can be up to 80 % of the total production cost, and then the research has been focused on developing alternatives for downstream processing [105]. Processes such as solvent extraction, adsorption, direct distillation, and membrane separation processes have been extensively investigated. Among these processes, membrane-based separations are attractive since they can selectively remove lactate, are capable of operating aseptically, there are no by-products generation, and they allow biomass/substrates confinement.

7.8.4.1 Hybrid Fermentation–Solid Membrane Systems

The application of hybrid fermentation and solid membrane is well documented in literature; there in, pioneer developments are cited. Hybrid processes have used dialysis for lactic acid removal [106], Donnan dialysis carboxylic acid removal [107], electrodialysis for lactate removal [108, 109], electrodialysis with bipolar membranes for lactic acid recovery and concentration [110], ultrafiltration for cell-recycle [111, 112], nanofiltration, and reverse osmosis for lactic acid separation [113] and their combination to separate and concentrate the lactic acid [114–117]. Recent studies have been focused on electrically driven membrane separations such as electrodialysis, reverse electrodialysis, and reverse electro-enhanced electrodialysis - REED [118–121]. In electrically driven membrane separation processes, ion exchange membranes are used to selectively separate ions from dilute solutions. The main driving force is an electrical potential gradient across the membranes stack. However, concentration gradients play an important role in the transport mechanism [120]. The biggest obstacle using ion exchange membranes integrated to bioreactors is the membrane fouling. Fouling can be generated by bacterial attachment, extracellular protein adsorption, or colloidal particle deposition on the membrane surface. This process occurs because biomass, proteins, and colloids have local charged groups that are attracted by the ion exchange membranes. Additionally, certain multivalent ions such as calcium and magnesium contained in the feed solution are allowed to pass through cation exchange membranes, precipitating over the surface. These problems are minimized using REED technology since only anion exchange membranes are used and the periodic inversion of the potential gradient [119]. The use of hybrid membrane bioreactors for lactic acid production has shown how productivity can be increased several times (four to ten times), achieving a better substrate utilization while reducing the operation time (for batch operation cases). However, the energy consumption to generate the external electrical potential gradient is still a concern.

Despite the promising results for lactic acid in situ recovery using membrane bioreactors, several design, and operability problems have been encountered. The main limitations are lack of system understanding, the dynamic nature of the processes (i.e., fermentation, membrane separation, or both), low predictive power of models if available (especially for the membrane) and the sequential strategy for process design and control [83]. Those issues might be the main constraints for scale-up of membrane bioreactors to industrial level. It is expected that further research within process intensification framework can supply the fundamental to address the mentioned limitations.

7.8.4.2 Hybrid Fermentation–Liquid Membrane Systems

A liquid membrane or carrier facilitated transport membrane is defined as an immiscible liquid barrier (membrane) between two liquid phases (donor and acceptor phases) that allows a selective transport of substances between them [75]. The liquid membrane systems have been referred to as perstraction. In order to have selective transport, the solute must be soluble in the membrane phase. The transport mechanisms are: passive diffusion due to a concentration gradient, facilitated transport generated by a chemical reaction between the carrier and the transported substance, and coupled transport that is the facilitated mechanism involving two counter transported species. The liquid membranes can be used as bulk liquid membranes, supported membranes or emulsified membranes. These membranes have been used to purify effluents and for separation of organic acids, polysaccharides, metals, and hydrocarbons [122]. Liquid membranes are interesting since they offer transport rates several orders of magnitude higher than solid membranes, since diffusion is faster in liquids than in solids [123]. The high permeation rate results in designs that are more compact, lower energy intensive, and with higher selectivity. However, liquid membranes hybrid systems are still under development since emulsion membranes need chemical additives to keep a stable emulsion. Besides, in supported systems there is a continuous membrane lost.

It has been shown through the previous sections the potential that hybrid membrane bioreactors have to be considered as process intensification within biotransformation industry. Most of the results analyzed here were obtained in laboratory or pilot plant scale. Still this technology faces relevant challenges to be overcome before can reach industrial scale.

7.9 Perspectives

There is no doubt that an increasing number of biocatalytic applications are found in industry, where the excellent selectivity and environmental profile of new or replacement processes offer a great potential for their further implementation. As expertise has been developed, the trend in research and development is from enhancing biocatalytic action to reaction/separation environment, representing an important development in biotechnology. Most interestingly, in the context of this chapter, the motivating driving force is process intensification achieved through removal of inherent constraints or alternatively through various degrees of integration in phenomena, space, and time. Many more of such examples will be reached in the near future, both, in the context of higher value products such as pharmaceuticals as well as lower value products such as biofuels and bulk chemical building blocks in biorefineries.

The biocatalytic improvements by using mutation or genetic manipulation of microorganisms have allowed increasing substrate utilization, by using diverse bioprocessing configurations, such as, co-cultivation, co-fermentation, SSF, SSCF, and CBP. Most of these studies have been performed employing a pragmatic point of view, which have permitted to visualize the opportunities on intensifying the production of bioproducts. In contrast, few works have developed and employed mathematical models in order to analyze and improve the performance of these intensified bioprocesses. Thus, there is an opportunity to improve bioprocessing production by employing mathematical modelling. This approach could be used to provide a screening tool to evaluate the performance of different intensified processes, which afterwards could potentially be experimentally implemented.

It is relevant to mention that the activities looking for the intensification of bioprocesses are not individual tasks, since include diverse expertise areas. Therefore, it is important to emphasize the conformation of multidisciplinary teams in order to improve the production of bioproducts using intensified technologies, that is, specialists on areas such as genetic engineering, biotechnology, process engineering, and purification processes.

Novel membrane bioreactors proposed within process intensification framework have a great potential to become a common technology at industrial level in the future, due to their versatility and performance. Membrane technology includes a broad gamma of possibilities for separation that have not reached their maximum capabilities. Continuous efforts are made to minimize the loss of the hybrid process performance due to fouling and thermal/concentration polarization. This can be achieved from design and operation perspectives as discussed previously. We believe there is still room for improvements in order to consolidate hybrid technologies. From the membranes manufacturing point of view, it is desired to produce more permeable and selective materials at lower cost. This is especially critical for the commodity chemicals production (biofuels and volatile organic components), since it is necessary that the membranes to be used are cost-effective. From operation perspective, research is focused on how to find the appropriate set of conditions that enhance the process performance in a more systematic way. Then, there are opportunities in this field if more model-based approaches are used. Modelling is a powerful tool useful for system understanding, process design, process control, and optimization. However, it is understandable that model-based approaches are not popular due to the complexity of the hybrid biological-membrane systems. In several systems, process modelling is still based on semi-empirical approaches that provide little system understanding and have low predictive power. Then, the hybrid process design, optimization, operation, and scale-up require considerable experimental work.

We believe that hybrid technologies must be investigated as much as biotechnological processes in order to have a sustainable development. The promising results obtained at pilot scale constitute the driving force to scale-up hybrid technologies.

References

1. Gerven TV, Stankiewicz AJ (2009) Structure, energy, synergy, time—the fundamentals of process intensification. Ind Eng Chem Res 48:2465–2474
2. Górak A, Stankiewicz A (2011) Research agenda for process intensification—towards a sustainable world of 2050. Institute for Sustainable Process Technology, Amersfoort
3. Gírio F, Fonseca C, Carvalheiro F, Duarte L, Marques S, Bogel-Łukasik R (2010) Hemicelluloses for fuel ethanol: a review. Bioresour Technol 101:4775–4800
4. Parajuli R, Dalgaard T, Jørgensen U, Adamsen APS, Knudsen MT, Birkved M, Gylling M, Schjørring JK (2015) Biorefining in the prevailing energy and materials crisis: a review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies. Renew Sustain Energy Rev 43:244–263
5. Coreño-Alonso A, Solé A, Diestra E, Esteve I, Gutiérrez-Corona JF, Reyna-López GE, Fernández FJ, Tomasini A (2014) Mechanisms of interaction of chromium with Aspergillus niger var tubingensis strain Ed8. Bioresour Technol 158:188–192
6. Collura MA, Luyben WL (1988) Energy-saving distillation designs in ethanol production. Ind Eng Chem Res 27:1686–1696
7. Toquero C, Bolado S (2014) Effect of four pretreatments on enzymatic hydrolysis and ethanol fermentation of wheat straw. Influence of inhibitors and washing. Bioresour Technol 157:68–76
8. Pollard DJ, Woodley JM (2007) Biocatalysis for pharmaceutical intermediates: the future is now. Trends Biotechnol 25:66–73
9. Santacoloma PA (2012) Multi-enzyme process modeling. PhD thesis, Technical University of Denmark
10. Santacoloma P, Woodley J (2014) Perspectives on multienzyme process technology. In: Riva S, Fessner W-D (eds) Cascade biocatalysis: integrating stereoselective and environmentally friendly reactions. Wiley, New York, pp 231–247
11. Padró M, Castillo JA, Gómez L, Joglar J, Clapés P, de Bolós C (2010) Cytotoxicity and enzymatic activity inhibition in cell lines treated with novel iminosugar derivatives. Glycoconj J 27:277–285
12. Babich L, Peralta JLVM, Hartog AF, Wever R (2013) Phosphorylation by alkaline phosphatase: immobilization and synthetic potential. Int J Chem 5:87–98

13. Van Hecke W, Ludwig R, Dewulf J, Auly M, Messiaen T, Haltrich D, Van Langenhove H (2009) Bubble-free oxygenation of a bi-enzymatic system: effect on biocatalyst stability. Biotechnol Bioeng 102:122–131
14. Bader J, Mast-Gerlach E, Popovic MK, Bajpai R, Stahl U (2010) Relevance of microbial coculture fermentations in biotechnology. J Appl Microbiol 109:371–387
15. Marmann A, Aly AH, Lin W, Wang B, Proksch P (2014) Co-cultivation—a powerful emerging tool for enhancing the chemical diversity of microorganisms. Mar Drugs 12:1043–1065
16. He Q, Hemme CL, Jiang H, He Z, Zhou J (2011) Mechanisms of enhanced cellulosic bioethanol fermentation by co-cultivation of Clostridium and Thermoanaerobacter spp. Bioresour Technol 102:9586–9592
17. Jiang H-L, He Q, He Z, Hemme CL, Wu L, Zhou J (2013) Continuous cellulosic bioethanol fermentation by cyclic fed-batch cocultivation. Appl Environ Microbiol 79:1580–1589
18. Ndaba B, Chiyanzu I, Marx S, Obiero G (2014) Effect of Saccharomyces cerevisiae and Zymomonas mobilis on the co-fermentation of sweet sorghum bagasse hydrolysates pretreated under varying conditions. Biomass Bioenergy 71:350–356
19. Gutiérrez-Rivera B, Ortiz-Muñiz B, Gómez-Rodríguez J, Cárdenas-Cágal A, González JM, Aguilar-Uscanga MG (2014) Bioethanol production from hydrolyzed sugarcane bagasse supplemented with molasses "B" in a mixed yeast culture. Renew Energy 74:399–405
20. Morales-Rodriguez R, Rodriguez-Gomez D, Sales-Cruz M, de los Reyes-Heredia J, Pérez-Cisneros E (2014) Model-based analysis for acetone-butanol-ethanol production process through a dynamic simulation. Comput Aided Chem Eng 33:133–138
21. Mayank R, Ranjan A, Moholkar VS (2013) Mathematical models of ABE fermentation: review and analysis. Crit Rev Biotechnol 33:419–447
22. Wen Z, Wu M, Lin Y, Yang L, Lin J, Cen P (2014) Artificial symbiosis for acetone-butanol-ethanol (ABE) fermentation from alkali extracted deshelled corn cobs by co-culture of Clostridium beijerinckii and Clostridium cellulovorans. Microb Cell Fact 13:1–11
23. Li L, Ai H, Zhang S, Li S, Liang Z, Wu Z-Q, Yang S-T (2013) Enhanced butanol production by coculture of Clostridium beijerinckii and Clostridium tyrobutyricum. Bioresour Technol 143:397–404
24. Yao W, Nokes S (2014) First proof of concept of sustainable metabolite production from high solids fermentation of lignocellulosic biomass using a bacterial co-culture and cycling flush system. Bioresour Technol 173:216–223
25. Seppälä JJ, Puhakka JA, Yli-Harja O, Karp MT, Santala V (2011) Fermentative hydrogen production by Clostridium butyricum and Escherichia coli in pure and cocultures. Int J Hydrogen Energy 36:10701–10708
26. Li Q, Lui C-Z (2012) Co-culture of Clostridium thermocellum and Clostridium thermosaccharolyticum for enhancing hydrogen production via thermophilic fermentation of cornstalk waste. Int J Hydrogen Energy 37:10648–10654
27. Masset J, Calusinska M, Hamilton C, Hiligsmann S, Joris B, Wilmotte A, Thonart P (2012) Fermentative hydrogen production from glucose and starch using pure strains and artificial co-cultures of Clostridium spp. Biotechnol Biofuels 5:1–15
28. Sarma SJ, Brar SK, Sydney EB, Le Bihan Y, Buelna G, Soccol CR (2012) Microbial hydrogen production by bioconversion of crude glycerol: a review. Int J Hydrogen Energy 37:6473–6490
29. Zhang Y, Vadlani PV (2015) Lactic acid production from biomass-derived sugars via co-fermentation of Lactobacillus brevis and Lactobacillus plantarum. J Biosci Bioeng 119:694–699
30. Wang Y, Tashiro Y, Sonomoto K (2015) Fermentative production of lactic acid from renewable materials: recent achievements, prospects, and limits. J Biosci Bioeng 119:10–18
31. Juhász T, Kozma K, Szengyel Z, Réczey K (2003) Production of beta-glucosidase in mixed culture of Aspergillus niger BKMF 1305 and Trichoderma reesei RUT C30. Food Technol Biotechnol 41:49–53

32. Dwivedi P, Vivekanand V, Pareek N, Sharma A, Singh RP (2010) Bleach enhancement of mixed wood pulp by xylanase–laccase concoction derived through co-culture strategy. Appl Biochem Biotechnol 160:255–268
33. Liu X, Lv J, Zhang T, Deng Y (2014) Direct conversion of pretreated straw cellulose into citric acid by co-cultures of Yarrowia lipolytica SWJ-1b and immobilized Trichoderma reesei Mycelium. Appl Biochem Biotechnol 173:501–509
34. Ho NW, Chen Z, Brainard AP, Sedlak S (1999) Successful design and development of genetically engineered saccharomyces yeasts for effective cofermentation of glucose and xylose from cellulosic biomass to fuel ethanol. In: Tsao GT (ed) Recent progress in bioconversion of lignocellulosics. Springer, Heidelberg, pp 163–192
35. Kumar R, Singh S, Singh OV (2008) Bioconversion of lignocellulosic biomass: biochemical and molecular perspectives. J Ind Microbiol Biotechnol 35:377–391
36. Laluce C, Schenberg AC, Gallardo JC, Coradello L, Pombeiro-Sponchiado SR (2012) Advances and developments in strategies to improve strains of saccharomyces cerevisiae and processes to obtain the lignocellulosic ethanol—a review. Appl Biochem Biotechnol 166:1908–1926
37. Tsai C-T, Morales-Rodriguez R, Sin G, Meyer AS (2014) A dynamic model for cellulosic biomass hydrolysis: a comprehensive analysis and validation of hydrolysis and product inhibition mechanisms. Appl Biochem Biotechnol 172:2815–2837
38. Luo Z, Zhang Y, Bao J (2014) Extracellular secretion of β-glucosidase in ethanologenic E. coli enhances ethanol fermentation of cellobiose. Appl Biochem Biotechnol 174:772–783
39. Nakamura N, Yamada R, Katahira S, Tanaka T, Fukuda H, Kondo A (2008) Effective xylose/cellobiose co-fermentation and ethanol production by xylose-assimilating S. cerevisiae via expression of glucosidase on its cell surface. Enzyme Microb Technol 43:233–236
40. Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PN, Esposito G (2015) A review on dark fermentative biohydrogen production from organic biomass: process parameters and use of by-products. Appl Energy 144:73–95
41. Guo XM, Trably E, Latrille E, Carrère H, Steyer J-P (2010) Hydrogen production from agricultural waste by dark fermentation: a review. Int J Hydrogen Energy 35:10660–10673
42. Fei Q, Wewetzer SJ, Kurosawa K, Rha C, Sinskey AJ (2015) High-cell-density cultivation of an engineered Rhodococcus opacusstrain for lipid production via co-fermentation of glucose and xylose. Process Biochem 50:500–506
43. Yan Y, Liao JC (2009) Engineering metabolic systems for production of advanced fuels. J Ind Microbiol Biotechnol 36:471–479
44. Peralta-Yahya PP, Keasling JD (2010) Advanced biofuel production in microbes. Biotechnol J 5:147–162
45. Eiteman MA, Lee SA, Altman R, Altman E (2009) A substrate-selective co-fermentation strategy with escherichia coli produces lactate by simultaneously consuming xylose and glucose. Biotechnol Bioeng 102(3):822–827
46. Yang M, Kuittinen S, Zhang J, Vepsäläinen J, Keinänen M, Pappinen A (2015) Co-fermentation of hemicellulose and starch from barley straw and grain for efficient pentoses utilization in acetone–butanol–ethanol production. Bioresour Technol 179:128–135
47. Wang Z, Yang S-T (2013) Propionic acid production in glycerol/glucose co-fermentation by Propionibacterium freudenreichii subsp. shermanii. Bioresour Technol 137:116–123
48. Ji X-J, Huang H, Du J, Zhu J-G, Ren L-J, Li S, Nie Z-K (2009) Development of an industrial medium for economical 2,3-butanediol production through co-fermentation of glucose and xylose by Klebsiella oxytoca. Bioresour Technol 100:5214–5218
49. Zeng X, Chen X-S, Ren X-D, Liu Q-R, Wang L, Sun Q-X, Tang L, Mao Z-G (2014) Insights into the role of glucose and glycerol as a mixed carbon source in the improvement of ε-poly-L-lysine productivity. Appl Biochem Biotechnol 173:2211–2224
50. Mohagheghi A, Evans K, Chou Y-C, Zhang M (2002) Cofermentation of glucose, xylose, and arabinose by genomic DNA-integrated xylose/arabinose fermenting strain of Zymomonas mobilis AX101. Appl Biochem Biotechnol 98–100:885–898

51. Delgenes JP, Moletta R (1989) Fermentation of o-xylose, 0-glucose, r-arabinose mixture by Pichia stipitis: effect of the oxygen transfer rate on fermentation performance. Biotechnol Bioeng 34:398–402
52. Abreu AA, Karakashev D, Angelidaki I, Sousa DZ, Alves M (2012) Biohydrogen production from arabinose and glucose using extreme thermophilic anaerobic mixed cultures. Biotechnol Biofuels 5(6):1–12
53. Xia T, Eiteman MA, Altman E (2012) Simultaneous utilization of glucose, xylose and arabinose in the presence of acetate by a consortium of Escherichia coli strains. Microb Cell Fact 11(77):1–9
54. Morales-Rodriguez R, Gernaey KV, Meyer AS, Sin G (2011) A mathematical model for simultaneous saccharification and co-fermentation (SSCF) of C6 and C5 Sugars. Chinese J Chem Eng 19:185–191
55. Wang R, Koppram R, Olsson L, Franzén CJ (2014) Kinetic modeling of multi-feed simultaneous saccharification and co-fermentation of pretreated birch to ethanol. Bioresour Technol 172:303–311
56. Patel MA, Ou MS, Ingram LO, Shanmugam KT (2005) Simultaneous saccharification and co-fermentation of crystalline cellulose and sugarcane bagasse hemicellulose hydrolysate to lactate by a thermotolerant acidophilic Bacillus sp. Biotechnol Prog 21(5):1453–1460
57. Kang L, Wang W, Lee Y (2010) Bioconversion of kraft paper mill sludges to ethanol by SSF and SSCF. Appl Biochem Biotechnol 161:53–66
58. Zhu J-Q, Qin L, Li B-Z, Yuan Y-J (2014) Simultaneous saccharification and co-fermentation of aqueous ammonia pretreated corn stover with an engineered Saccharomyces cerevisiae SyBE005. Bioresour Technol 169:9–18
59. Olofsson K, Palmqvist B, Lidén G (2012) Improving simultaneous saccharification and co-fermentation of pretreated wheat straw using both enzyme and substrate feeding. Biotechnol Biofuels 3:17
60. Hernandez-Escoto H, Rodriguez-Gomez D, Morales-Rodriguez R (2013) Regulatory control for the operation of a simultaneous saccharification and co-fermentation reactor for bioethanol production. Comput Aided Chem Eng 32:43–48
61. Morales-Rodriguez R, Meyer AS, Gernaey KV, Sin G (2011) Dynamic model-based evaluation of process configurations for integrated operation of hydrolysis and co-fermentation for bioethanol production from lignocellulose. Bioresour Technol 102:1174–1184
62. Budhavaram NK, Fan Z (2009) Production of lactic acid from paper sludge using acid-tolerant, thermophilic Bacillus coagulan strains. Bioresour Technol 100:5966–5972
63. Wakai S, Yoshie T, Asai-Nakashima N, Yamada R, Ogino C, Tsutsumi H, Hata Y, Kondo A (2014) L-lactic acid production from starch by simultaneous saccharification and fermentation in a genetically engineered Aspergillus oryzae pure culture. Bioresour Technol 173:376–383
64. Zhu Y, Lee YY, Elander RT (2007) Conversion of aqueous ammonia-treated corn stover to lactic acid by simultaneous saccharification and cofermentation. Appl Biochem Biotechnol 136–140:721–738
65. Lynd LR, van Zyl WH, McBride JE, Laser M (2005) Consolidated bioprocessing of cellulosic biomass: an update. Curr Opin Biotechnol 16:577–583
66. Olson DG, McBride JE, Shaw AJ, Lynd LR (2012) Recent progress in consolidated bioprocessing. Curr Opin Biotechnol 23:396–405
67. Rodriguez-Gomez D, Lehmann L, Schultz-Jensen N, Bjerre AB, Hobley TJ (2012) Examining the potential of plasma-assisted pretreated wheat straw for enzyme production by Trichoderma reesei. Appl Biochem Biotechnol 166:2051–2063
68. den Haan R, van Rensburg E, Rose SH, Görgens JF, van Zyl WH (2015) Progress and challenges in the engineering of non-cellulolytic microorganisms for consolidated bioprocessing. Curr Opin Biotechnol 33:32–38
69. Panagiotou G, Topakas E, Moukouli M, Christakopoulos P, Olsson L (2011) Studying the ability of Fusarium oxysporum and recombinant Saccharomyces cerevisiae to efficiently

cooperate in decomposition and ethanolic fermentation of wheat straw. Biomass Bioenergy 35:3727–3732

70. Xu Q, Singh A, Himmel ME (2009) Perspectives and new directions for the production of bioethanol using consolidated bioprocessing of lignocellulose. Curr Opin Biotechnol 20:364–371
71. Freeman A, Woodley J, Lilly M (1993) In-situ product removal as a tool for bioprocessing. Biotechnology 11:1007–1012
72. Schügerl K (2000) Integrated processing of biotechnology products. Biotechnol Adv 18:581–599
73. Stark D, von Stockar U (2003) In situ product removal (ISPR) in whole cell biotechnology during the last twenty years. In: von Stockar U, van der Wielen L (eds) Process integration in biochemical engineering. Springer, Berlin, pp 149–175
74. Carstensen F, Apel A, Wessling M (2012) In situ product recovery: submerged membranes vs. external loop membranes. J Membr Sci 394-395:1–36
75. Baker R (2012) Membrane technology and applications. Wiley, New York
76. Charcosset C (2006) Membrane processes in biotechnology: an overview. Biotechnol Adv 24:482–492
77. Abels C, Carstensen F, Wessling M (2013) Membrane processes in biorefinery applications. J Membr Sci 444:285–317
78. Wei P, Cheng L-H, Zhang L, Xu X-H, Chen H-L, Gao C-J (2014) A review of membrane technology for bioethanol production. Renew Sustain Energy Rev 30:388–400
79. Castilho L, Medronho R (2002) Cell retention devices for suspended-cell perfusion cultures. In: Schügerl K, Zeng A-P (eds) Tools and applications of biochemical engineering science. Springer, Berlin, pp 129–169
80. Chang N, Furusaki S (1991) Membrane bioreactors: present and prospects. Adv Biochem Eng Biotechnol 44:21–64
81. Pedersen L (1996) Modeling of mass transfer in jet loop fermenters. PhD thesis, Technical University of Denmark, Lyngby
82. Prado-Rubio O (2007) Single cell protein production: modeling, control and optimization. MSc thesis, Technical University of Denmark, Lyngby
83. Prado-Rubio O (2010) Integration of bioreactor and membrane separation processes: a model based approach. PhD thesis, Technical University of Denmark, Lyngby
84. Rios G, Belleville M, Paolucci D, Sanchez J (2004) Progress in enzymatic membrane reactors—a review. J Membr Sci 242:189–196
85. Jochems P, Satyawali Y, Dielsab L, Dejonghea W (2011) Enzyme immobilization on/in polymeric membranes: status, challenges and perspectives in biocatalytic membrane reactors (BMRs). Green Chem 13:1609–1623
86. Güleç H (2013) Immobilization of β-galactosidase from Kluyveromyces lactis onto polymeric membrane surfaces: effect of surface characteristics. Colloids Surf B Biointerfaces 104:83–90
87. Luo J, Meyer A, Jonsson G, Pinelo M (2014) Enzyme immobilization by fouling in ultrafiltration membranes: impact of membrane configuration and type on flux behavior and biocatalytic conversion efficacy. Biochem Eng J 83:79–89
88. Tang C, Saquing CD, Sarin PK, Kelly RM, Khan SA (2014) Nanofibrous membranes for single-step immobilization of hyperthermophilic enzymes. J Membr Sci 472:251–260
89. Jonsson G, Prado-Rubio O (2011) Modeling and operation of dynamic membrane processes. In: Key note at ICOM conference 2011, vol 425, Amsterdam, the Netherlands
90. Kaseno, Miyazawa I, Kogugan T (1998) Effect of product removal by a pervaporation on ethanol fermentation. J Ferment Bioeng 86(5):488–493
91. O'Brien DJ, Craig JC (1996) Ethanol production in a continuous fermentation/membrane pervaporation system. Appl Microbiol Biotechnol 44(6):699–704

92. Dong Y, Zhang L, Shen JN, Song MY, Chen HL (2006) Preparation of poly(vinyl alcohol)-sodium alginate hollow-fiber composite membranes and pervaporation dehydration characterization of aqueous alcohol mixtures. Desalination 193:202–210
93. Mulder M (1997) Basic principles of membrane technology. Kluwer Academic, Holland
94. Peng P, Shi BL, Lan YQ (2011) A review of membrane materials for ethanol recovery by pervaporation. Sep Sci Technol 46(2):234–246
95. García V et al (2011) Challenges in biobutanol production: how to improve the efficiency? Renew Sustain Energy Rev 15(2):964–980
96. Alkhudhiria A, Darwishb N, Hilala N (2012) Membrane distillation: a comprehensive review. Desalination 287:2–18
97. Izquierdo-Gil M, Jonsson G (2003) Factors affecting flux and ethanol separation performance in vacuum membrane distillation (VMD). J Membr Sci 214:113–130
98. Lei Z, Chen B, Ding Z (2005) Special distillation processes. Elsevier, Amsterdam
99. Gryta M, Morawski A, Tomaszewska M (2000) Ethanol production in membrane distillation bioreactor. Catal Today 56:159–165
100. Grypta M (2001) The fermentation process integrated with membrane. Sep Purif Technol 24:283–296
101. Lewandowicz G, Białas W, Marczewski B, Szymanowska D (2011) Application of membrane distillation for ethanol recovery during fuel ethanol production. J Membr Sci 375:212–219
102. Ljungh A, Wadström T (2006) Lactic acid bacteria as probiotics. Curr Issues Intest Microbiol 7:73–89
103. SRI-Consulting (2010) SRI-consulting—lactic acid, its salts and esters [Online]. http://www.sriconsulting.com. Accessed June 2010
104. Nielsen J, Villadsen J, Lidén G (2011) Bioreaction engineering principles, 3rd edn. Springer, New York
105. Hulse J (2004) Biotechnologies: past history, present state and future prospects. Trends Food Sci Technol 15:3–18
106. Friedman M, Gaden E (1970) Growth and acid production by lactobacillus delbrueckii in a dialysis culture system. Biotechnol Bioeng 12:961–974
107. Zheleznov A, Windmöller D, Körner S, Böddeker K (1998) Dialytic transport of carboxylic acids through an anion exchange membrane. J Membr Sci 139:137–143
108. Hongo M, Nomura Y, Iwahara M (1986) Novel method of lactic acid production by electrodialysis fermentation. Appl Environ Microbiol 52:314–319
109. Lee E, Moon S, Chang Y, Yoo I, Chang H (1998) Lactic acid recovery using two-stage electrodialysis and its modelling. J Membr Sci 145:53–66
110. Glassner D, Datta R (1990) Process for production and purification of lactic acid. European Patent No. EP0393818A1
111. Ohleyer E, Wilke C, Blanch E (1985) Continuous production of lactic acid from glucose and lactose in a cell-recycle reactor. Appl Biochem Biotechnol 11:457–463
112. Zhang D, Cheryan M (1994) Starch to lactic acid in a continuous membrane bioreactor. Process Biochem 29:145–150
113. Timmer J, Kromkap J, Robbertsen T (1994) Lactic acid separation from fermentation broths by reverse osmosis and nanofiltration. J Membr Sci 92:185–197
114. Boyaval P, Corre C, Terre S (1987) Continuous lactic acid fermentation with concentrated product recovery by ultrafiltration and electrodialysis. Biotechnol Lett 9:207–212
115. Heriban V, Skára J, Sturdík E, Ilavský J (1993) Isolation of free lactic acid using electrodialysis. Biotechnol Techn 7:63–68
116. Hábová V, Melzoch K, Rychtera M (2004) Modern method of lactic acid recovery from fermentation broth. Czech J Food Sci 22:87–94
117. Raucourt A, Girard D, Prigent Y, Boyaval P (1989) Lactose continuous fermentation with cells recycled by ultrafiltration and lactate separation by electrodialysis: modelling and simulation. Appl Microbiol Biotechnol 30:521–527

118. Garde A (2002) Production of lactic acid from renewable resources using electrodialysis for product recovery. PhD thesis, Technical University of Denmark
119. Rype J (2003) Modelling of electrically driven processes. PhD thesis, Technical University of Denmark, Lyngby
120. Strathmann H (2004) Ion-exchange membrane separation processes. Elsevier, Amsterdam
121. Prado-Rubio O, Jørgensen S, Jonsson G (2011) Reverse electro-enhanced dialysis for lactate recovery from a fermentation broth. J Membr Sci 374:20–32
122. Kislik V (2010) Liquid membranes principles & applications in chemical separation & wastewater treatment, 1st edn. Elsevier, Amsterdan
123. Noble R, Stern S (2003) Membrane separations technology: principles and applications, 3rd edn. Elsevier, Amsterdan

Chapter 8

Process Intensification: Industrial Applications

Anton A. Kiss

Abstract The chapter presents process intensification technologies used in industrial applications, for increasing the eco-efficiency of the chemical equipment with the benefit of lower capital costs, substantial energy saving, reduced footprint, and safety by design. The key topics cover compact heat exchangers, static mixers, green chemical reactors (e.g., microreactors), high-gravity (HiGee) technology, cyclic distillation, dividing-wall column, and reactive distillation.

8.1 Introduction

Process Intensification (PI) is defined as a set of innovative principles applied in process and equipment design, which can bring significant benefits in terms of process and chain efficiency, lower capital and operating expenses, higher quality of products, less wastes, and improved process safety. There are several specialized books, reviews, and research papers that address topics related to PI developments and application in the chemical process industry [1–8]. The main principles of process intensification were recently described in the research paper of van Gerven and Stankiewicz [2]:

1. *Maximize the effectiveness of intra- and intermolecular events*. This principle is primarily about changing the kinetics of a process, which is actually the root of low conversions and selectivities, unwanted side products, and other issues.
2. *Give each molecule the same processing experience*. When all molecules undergo the same history, the process delivers ideally uniform products with minimum waste. The meso- and micro-mixing, temperature gradients,

---

A.A. Kiss (✉)
AkzoNobel Research, Development and Innovation, Process Technology Strategic Research Group, Zutphenseweg 10, Deventer 7418 AJ, The Netherlands

Faculty of Science and Technology, Sustainable Process Technology Group, University of Twente, 217, Enschede 7500, AE, The Netherlands
e-mail: tonykiss@gmail.com; Tony.Kiss@akzonobel.com; A.A.Kiss@utwente.nl

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_8

macroscopic residence time distribution, dead zones, or bypassing plays an important role. For example, a plug-flow reactor (PFR) with gradientless, volumetric heating (e.g., by means of microwaves) is clearly much closer to the ideal described by this principle as compared to a continuous stirred-tank reactor (CSTR) with jacket heating.

3. *Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply*. This principle is about the transport rates across interfaces. The resulting effect of the driving forces (e.g., concentration difference) needs to be maximized, and this is done by maximizing the interfacial area, to which that driving force applies. Increased transfer areas (or surface-to-volume ratios) can be obtained by moving from mm to μm scales of channel diameters, e.g., a circular micro-channel of 400 μm in a microreactor delivers a specific area of 15,000 m^2/m^3. While impressive, this figure is lower than what is encountered in natural systems: e.g., capillary veins are 10 μm in diameter, with specific areas of ca. 400,000 m^2/m^3.
4. *Maximize the synergistic effects from partial processes*. Synergistic effects should be required and utilized, whenever possible and at all possible scales. Such utilization occurs in the form of multi-functionality on the macroscale, as for example in reactive separation units, where the reaction equilibrium is shifted by removing the products in situ, from the reaction environment.

These principles are not entirely new to chemical engineering, but in process intensification they are seen as explicit goals aimed to be reached by intensified processes. Moreover, the PI interpretation of these principles often goes beyond the boundaries of the classical chemical engineering approach. A completely intensified process is successful in realizing all these PI principles, by making use of one or more fundamental approaches in four domains [2]: spatial (*structure*), thermodynamic (*energy*), functional (*synergy*), and temporal (*time*). In addition, it is worth noting that most of the process intensification technologies also adhere to the guiding principles for the conceptual design of safe chemical processes, thus providing *inherent safety* or *safety-by-design*:

- *Avoid*: no extra chemicals, no solvent, no strip gas, no extra vessels, no extra pumps.
- *Small*: reduced holdups, low number of equipment units and interconnections.
- *Control*: continuous processing, inherent process control (e.g., boiling systems).

In the context of PI, it is worth noting that on the macroscale of reactor and plant, the classic concept of unit operations (one function per unit) cannot take into account the positive effect of integration. For example, in reactive separation processes the combination of reaction–separation can increase the conversion to 100 % in case of reversible reactions, by taking advantage of the Le Chatelier principle—pulling the equilibrium by the continuous removal of products, instead of the classic push of the equilibrium by using an excess of reactants. Not surprisingly, Freund and Sundmacher [9] claimed that knowledge of the existing apparatuses that perform unit operations immediately narrows our creativity in search for new solutions, and they proposed to shift from unit apparatuses to functions. A function (or a fundamental task) describes *what* should happen, and not *how* it should happen. Some examples of functions include mass movement, chemical reaction, mixing, separation, heat transfer, phase change, temperature change, pressure change, and form change. Within the development of PI technologies, the integration of functions led to two main directions [1, 2, 6]:

1. Process intensification equipment
   - *Equipment for nonreactive systems*: rotating packed bed (RPB), centrifugal absorber, static mixer, and compact heat exchanger (CHE).
   - *Chemical reactors*: spinning disk reactor (SDR), static mixer reactor, microreactor, and monolithic reactor.
2. Process intensification methods
   - *Multifunctional reactors*: heat-integrated reactor, reactive separation processes (reactive distillation/stripping/absorption/extraction/crystallization, as well as membrane reactors), reactive comminution, reactive extrusion, and fuel cells.
   - *Hybrid separations*: dividing-wall column (DWC), membrane distillation, pervaporation, membrane adsorption, and adsorptive distillation.
   - *Alternative energy sources*: solar energy, microwave, ultrasound, electric field, and centrifugal field.
   - *Other methods*: supercritical fluids, plasma technology, periodic operation.

Table 8.1 provides a summary of the domain-based process intensification technologies available at pilot and industrial scales, or still under research at various

Table 8.1 Domain-based process intensification technologies

Domain and focus	Drive and incentives	Examples of PI technologies
Structure Internal geometry	• High mass- and heat-transfer rates • Maximum specific surface areas • Minimum energy expenses	Compact heat exchangers (plate, spiral, multi-stream, mini-channel, shell and tube) Static mixers, micro-mixers Structured internals for mass-transfer monolithic catalysts/reactors Micro-channel reactors/heat exchangers
Energy Energy forms and transfer mechanisms	• Excitation of targeted molecules • New operational windows • Selective local energy supply	Microwave reactors Sonochemical reactors Supersonic gas–liquid reactors Plasma/photochemical reactors Spinning disc reactors Magnetic field-assisted reactors/separators Supercritical separations/fluid processes Ultrasound-enhanced crystallization Acoustic field-enhanced mass transfer Hydrodynamic cavitation reactors Electric field-assisted extraction–dispersion Rotor stator devices/mixers

(continued)

Table 8.1 (continued)

Domain and focus	Drive and incentives	Examples of PI technologies
		Microwave and radio frequency drying Microwave heating and drying Rotating packed beds Centrifugal contactors/extractors Impinging streams reactor
Synergy Integration of functions and steps	• Synergistic effects • Overcome equilibrium limitations • Compact equipment • Increase of overall efficiency	Membrane reactors/crystallization Membrane distillation/absorption Membrane extraction/crystallization Extractive distillation/crystallization Distillation–pervaporation systems Dividing wall column (DWC) technology Heat-integrated distillation column (HIDiC) Reactive distillation (RD) Reactive absorption/extraction/extrusion Membrane-assisted reactive distillation Simulated moving bed reactors Rotating annular chromatographic reactor Gas–solid–solid trickle flow reactors Static mixer reactors and SM heat exchangers
Time Timing of the events, introducing dynamics	• Controlled energy input • Increased energy efficiency • Minimized side reactions	Cyclic distillation Millisecond reactor Pulsing operation of multiphase reactors Pulsed compression reactor Reverse flow reactors Oscillatory baffle reactors Oscillatory flow baffle reactors Pulsed combustion drying

research groups. This work describes hereafter only selected process intensification equipments and technologies, namely the ones that became successful stories at industrial scales. Among them, reactive separation processes are perhaps the most promising, as they can bring substantial process economic benefits. For example, reactive separation processes improve the production efficiency by integrating reaction and separation into a single unit that allows the simultaneous production and removal of products, therefore enhancing the productivity and selectivity, reducing the energy use, eliminating the need for solvents, intensifying the mass and heat transfer, and ultimately leading to high-efficiency systems.

8.2 Compact Heat Exchangers

Heat exchangers are widely used in the chemical process industry for both heating and cooling. A compact heat exchanger (CHE) is a piece of equipment built for efficient heat transfer from one medium to another, being characterized by large heat transfer area-to-volume ratio (minimum 300 m^2/m^3), high heat-transfer coefficients (up to 5000 W/m^2 K), small flow passages, and laminar flow. CHE have dense arrays of finned tubes or plates and are widely used to achieve large heat rates per unit volume, particularly when at least one of the two fluids is a gas [10, 11]. The type and size of CHE can be tailored to suit a particular process depending on the type of fluid, phase, composition, temperature, pressures, density, viscosity, and other physical properties [12]. A large section of compact and non-tubular heat exchanger can be found in the eighth edition of Perry's Chemical Engineers' Handbook. The industrial suppliers of CHE include: Alfa Laval AB, Gea Canzler, Heatric, Marston, Linde, Schmidt Bretten, Vatherus, Kobe Steel, Gooch Thermal Systems, Kurose, Tranter HES, Sulzer, etc. The most common types of CHE are summarized hereafter [13]:

- *Plate heat exchangers* (PHE) use metal plates to transfer heat between two fluids which are exposed to a much larger surface area, being spread out over the plates. The thin, corrugated plates used in PHE are gasketed, welded, or brazed together depending on the application. The plates are compressed together in a rigid frame to form an arrangement of parallel flow channels with alternating hot and cold fluids (Fig. 8.1, top). The increase and reduction of heat-transfer area is made through the addition or removal of plates from the stack.
- *Plate-fin heat exchangers* (PFHE) use plates and finned chambers to transfer the heat between fluids (Fig. 8.1, middle). A PFHE is made of layers of corrugated sheets separated by flat metal plates that create a series of finned chambers. The hot and cold fluid streams flow through alternating layers of the HE and are enclosed by side bars at the edges. The fins also serve to increase the structural integrity of the PFHE, allowing it to withstand high pressures while providing an extended heat-transfer area. PFHE can operate with any combination of gas, liquid, and two-phase fluids. Moreover, it can accommodate the heat transfer between multiple process streams by using a variety of fin heights and types as different entry and exit points for each stream. The main types of fins are: *plain* (simple straight-finned triangular or rectangular), *herringbone* (fins are placed sideways to provide a zig-zag path), *serrated*, and *perforated* (cuts and perforations in the fins to enhance flow distribution and heat transfer). Some disadvantages of PFHE include the prone to fouling and difficult mechanical cleaning.
- *Spiral heat exchangers* (SHE) consists of a pair of flat surfaces that are coiled to form the two channels in a counterflow arrangement, e.g., helical/coiled tube configuration (Fig. 8.1, bottom). SHE is highly efficient in using the space, thus having a small footprint and low capital costs. The most common application is handling slurries. There are three main types of flow patterns in an SHE: (1) spiral–spiral flow used for all heating and cooling service, (2) spiral–cross flow (one fluid is in spiral flow and the other in a cross flow) used for condenser and reboiler purposes, and (3) distributed vapor–spiral flow that can condense and subcool in the same unit.
- *Mini-channel heat exchangers* (MCHE) and *micro-channel heat exchangers* are used in various industrial applications, being produced in large quantities with different geometries and lengths. The use of tubes with external or internal fins, and with reduced wall thicknesses allows higher heat-transfer area per unit

Fig. 8.1 Schematics of a plate and frame heat exchanger, plate finned-tube heat exchanger, and spiral heat exchanger

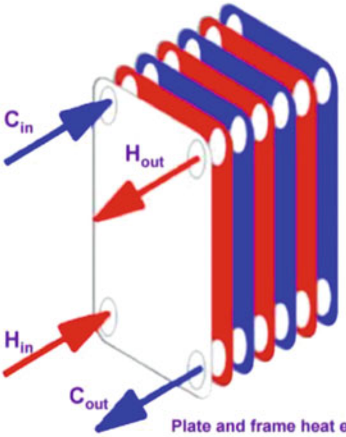


Plate and frame heat exchanger

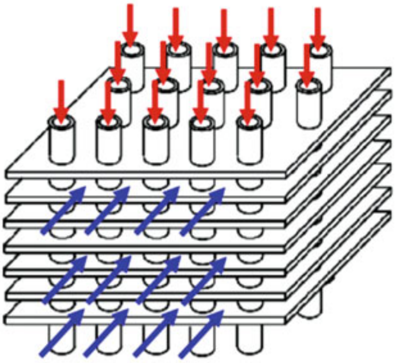
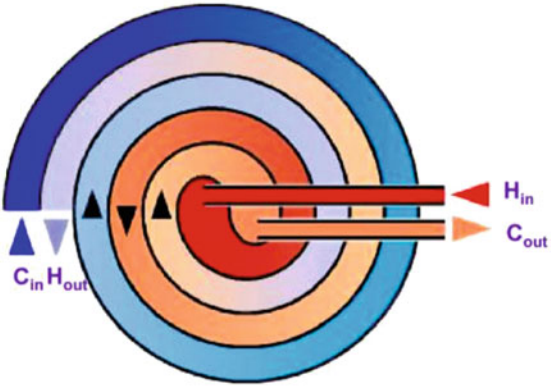


Plate finned-tube heat exchanger



Spiral heat exchanger

volume. Therefore, mini- and micro-channel tubes are ideal for use in compact and light weight heat exchangers (e.g., refrigeration equipment), with high heat-transfer coefficients. Note that channels of diameters higher than 3 mm are conventional, while mini-channels have a diameter of 0.2–3 mm and micro-channels have a diameter of 0.01–0.2 mm.

8.3 Static Mixers

Static mixers (SM) are precision engineered devices for the continuous mixing of fluids without the need of moving parts. SM can be used to mix liquid and gas streams, disperse gas into liquid or blend immiscible liquids. The energy required for the efficient mixing of fluids comes from the pressure drop through the static mixer's elements. Details about design and applications can be found elsewhere [14]. The main benefits of static mixers are: small volumes, low maintenance, simple installation and cleaning, and excellent reliability [13]. Two main types of static mixers are available on the market and largely used at industrial scale:

- *Housed-elements type*, consisting of mixer elements contained in a cylindrical (tube) or squared housing. As the streams move through the mixer, the static elements continuously blend the fluid materials. The degree of mixing depends on several variables: fluids properties, inner diameter of the tube, the number of elements and their design [15]. Helical elements can simultaneously produce patterns of flow division (number of striations produced being 2^N, where N is the number of elements in mixer) and radial mixing to reduce or eliminate radial gradients in temperature, velocity, and material composition (Fig. 8.2, top-left).
- *Plate-type mixer*. In the plate-type design, mixing is accomplished through intense turbulence in the flow. The corrugated plate static mixer is capable of mixing low-viscosity liquids, blending gases, dispersing immiscible liquids and creating gas–liquid dispersions with a very high degree of mixing in a short length. Many geometric configuration variables—such as the number of layers, corrugation angle, spacers between mixing elements—can be used to impact the intensity of mixing created within any given pipe diameter and create mixing solutions that are difficult to achieve with any other technology [13].

Nowadays, static mixers are used for a wide range of applications, such as chemical processing, wastewater treatment, acid–base neutralization, oxidation and bleaching, gaseous reactant blending, blending of multicomponent drugs, fertilizer and pesticide preparation, steam injection, organic-aqueous dispersions, and oil and gas industry [14, 15]. The current suppliers of static mixers include: *Sulzer Chemtech Ltd.* (SMX, SMX Plus, KVM, CompaX), *Komax Systems Inc.* (A&M, Hi-Pass sludge, wafer type, channel mixer), *Chemineer-Kenics* (HEV, KMX, KME, WVM, Thermogenizer, Ultratab), *Statiflo International* (Series 100-850, DesalMixers, S Types), *Verdermix* (VMV, VML, VMS), *Ross Engineering* (ISG, LPD, LLPD), *Koflo Corporation*, *Fluitec*, *ZelenTech*, *Toray*, *Prematechnik*, *Noritake*, *Wymbs Engineering* and *Westfall Manufacturing*.

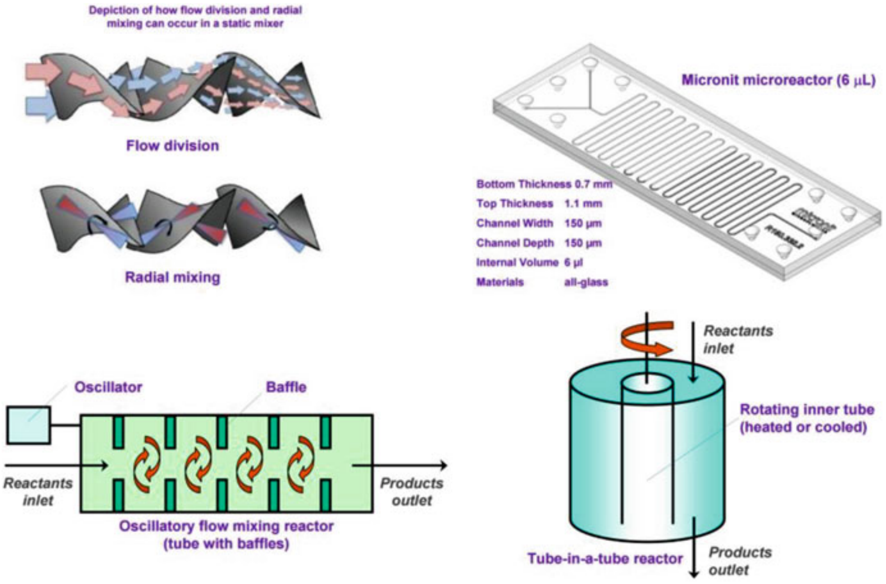


Fig. 8.2 Flow division and radial mixing that occur in a static mixer (*top-left*). Micronit glass microreactor (www.micronit.com)—6 μL, 150 μm channel width and depth (*top-right*). Oscillatory flow mixing reactor (*bottom-left*). Tube-in-a-tube reactor (*bottom-right*)

8.4 "Green" Chemical Reactors

PI technologies have key opportunities related to chemical reactors: smaller units, improved safety, inventory reduction, and moving from batch to continuous processing. Several new reactor designs were proposed as *green* solutions to many industrial problems related to mass-transfer and heat-transfer resistances, decrease of mixing time, convert diffusion-limited reactions to kinetics-controlled reactions, and rapid scale-up [16, 17]. Using new PI reactors, it is possible to carry out extremely unsafe (e.g., highly exothermic) and hazardous reactions, speed up the rate of reaction, eliminate side reactions, reduce waste formation, combine several steps, etc. Table 8.2 provides a brief overview of the most common types of green chemical reactors, along with a pro/con analysis and recommended applications [16]. The next sections provide more details about the key types of such reactors, e.g., microreactors, spinning disk reactors, etc.

8.4.1 Microreactors

Microreactors—also known as micro-structured reactors or micro-channel reactors—are very small devices, with channel dimensions of less than 1 mm, in which chemical reactions take place (Fig. 8.2, top-right). They are used in microprocess engineering,

Table 8.2 Green chemical reactors: types, pro/con analysis, and applications

Reactor type	Benefits (+) and drawbacks (−)	Applicability
Micro-plate or *micro-channel reactor*	+ High surface-area-to-volume ratio + Short residence times + Can be stacked for scale-up − Low velocity (parabolic and laminar) − Mixing through molecular diffusion − Fouling and clogging of solids	• Exothermic reactions • Organometallic reactions • Reactions involving various species: chlorine, bromide, amines, and acid chlorides
Reactor on a chip	+ Compact. Very small quantity of reactants − Solids handling, precipitates, or crystals	• Catalyst/enzyme screening • Drug discovery
Loop reactor	+ High gas dispersion + Precise control of liquid–liquid mixing − Generates high pressure	• Exothermic gas–liquid reactions • Manufacture of polymers: e.g., poly-ethylene and poly-propylene
Oscillatory flow mixing reactor	+ Mixing of heterogeneous phases + Allow mechanically sensitive compounds + Good radial mixing − Back-mixing (reduction in reaction rates)	• Synthesis/handling of mechanically sensitive compounds: biomolecules (enzymes, proteins), and crystals
Plate-type reactor	+ High surface-area-to-volume ratio + Can handle highly exothermic reactions − Solids fouling	• Oxidation reactions
Catalytic endo/exo reactor (*plate or tube*)	+ No hot spots and catalyst deactivation + High intra-catalyst diffusion − Reaction takes place only at the surface	• Exothermic reactions (e.g., Fischer–Tropsch)
Spinning tube-in-a-tube reactor	+ High surface-area-to-volume ratio + High shear forces − Fouling of surfaces	• Reaction between low-viscosity and high-viscosity fluids • Temperature-sensitive reactions
Rotating packed bed (*RPB*)	+ High gas–liquid mass transfer + Short contact time + Low flooding tendency − Liquid flow depends on speed, which can lead to maldistribution on packing	• Reactions with G/L absorption • Reactions leading to precipitation • Oxidation reactions that use ozone
Spinning basket	+ High solid–liquid mass-transfer rate − Catalyst attrition	• Kinetically controlled catalytic chemical reactions

(continued)

Table 8.2 (continued)

Reactor type	Benefits (+) and drawbacks (−)	Applicability
Spinning disc reactor (*SDR*)	+ Thin (micron scale) liquid films + High heat- and solid–liquid mass transfer − Design of rotating system is a challenge − Throughput is generally low	• Food processing • Handling highly viscous fluids • Fast exothermic reactions • Reactions of nanoparticles
Microwave reactor	+ Cost and energy savings + Increased safety − No clear scale-up rules available	• Reactions involving chemicals that are sensitive to microwaves (MW)
Supersonic reactor	+ Cost and energy savings + Increased capacity and safety − No clear scale-up rules available	• Oxygen injection in aerobic fermentation, electric steel furnaces • Very fast oxidation processes
Photochemical reactor	+ High conversion, yield, and selectivity + Low-temperature operation is possible + Free solar energy − Solar energy must be concentrated	• Photochemical reactions (sometimes the only chemical pathway known) • Light-induced polymerization (inks, coatings, packaging, electronics)

along with other devices involving physical processes (e.g., micro-heat exchangers and micro-distillation). Microreactors are devoted mainly to processes at smaller production rate, as encountered in analytical chemistry, production of pharmaceuticals and biochemicals, specialty chemicals and polymers, carrying out hazardous reactions or special organic synthesis. Once the process development is solved for a single device, the scale-up to larger throughput is simply solved by multiplying the number of devices (numbering-up or scale-out). Examples of industrial applications and processes using micro-devices can be found in specialized monographs [18–20].

Microreactors are a valuable tool for chemists and engineers, providing significant benefits:

- Continuous operation (typically) that allows the subsequent processing of unstable intermediates with better selectivity, and avoids batch workup delays and batch-to-batch variations.
- Different concentration profile as compared to batch reactors, due to continuous operation and mixing. Since in a microreactor the reactants are mixed almost instantly, none of them will be exposed to a large excess of the other reactants. Depending on the reaction mechanism, this may be an advantage or disadvantage, so one must be aware of such different concentration profiles.
- Very short reaction times, of order of magnitude of seconds, which offer the possibility of isolating valuable intermediate species in consecutive reactions.

- Because of the very small inventory, the microreactors are particularly adapted for carrying out difficult organic synthesis processes involving hazardous and toxic reactants.
- Microreactors have high heat exchange coefficients, in the range of 1–500 MW/m^3 K, so they can remove heat much more efficiently than classic vessels due to the high area-to-volume ratio. The hot spots and duration of high temperature exposure also decrease significantly. Reaction rates are better controlled as local temperature gradients are much smaller than in classic batch vessels. Heating and cooling is much quicker, allowing a large range of operating temperatures.
- Pressurization of materials is typically easier than in traditional batch reactors; hence, it is possible to perform reactions at higher rates by raising the temperature beyond the boiling point of the solvent and improve the dissolution of gasses within the liquid flow stream.

Nonetheless, microreactors also suffer from several problems associated to their small scale, such as bad toleration of particles leading to clogging, corrosion, shorter residence time, pulsating flow, and scaling up issues, compared to other types of vessels [13]. Microreactors can involve liquid–liquid systems but also solid–liquid systems (e.g., channel walls coated with a solid catalyst), and they are generally applied in combination with photochemistry, electro-synthesis, polymerization, multicomponent reactions, and purification of the product. By suitably coating the microreactor channel walls with catalysts, moderators, promoters, surfactants, or other materials, the unit can be used for manufacturing a wide range of chemicals [16]:

- Ethylene oxide produced via the oxidation of ethylene—which is highly exothermic and complete oxidation cannot be avoided—in a microreactor coated with silver catalyst, which can achieve controlled partial oxidation of ethylene (65 % conversion, at 290 °C and 5 bar).
- Hydrogenation of an array of alkenes and alkynes (Pd-catalyzed) using supercritical CO_2.
- Photoreactions performed in TiO_2-coated microreactors ($500 \times 10 - 500 \times 50$ mm w/d/L).
- Bioprocesses using enzyme catalysts immobilized on the walls of a microreactor.
- Direct synthesis of hydrogen peroxide in microreactors is possible with a special catalyst.
- Phosgene synthesis from chlorine, in a silicon packed-bed microreactor.
- Ciprofloxacin antibiotic produced in a multistep synthesis route in a stainless-steel microreactor (dimensions 100 × 150 × 10 mm, channel width <0.1 mm).
- Methyl isocyanate and hydrogen cyanide synthesis in a silicon wafer stack microreactor

There are many hardware suppliers, offering various microreactors depending on the application:

- *Ready-to-run* (*turnkey*) *systems*: used for new chemical synthesis schemes, for high throughput of 10–100 experiments per day and production scales ranging from 10 mg/exp to 1 kt/y.
- *Modular* (*open*) *systems*: used for continuous process engineering layouts, where a measurable advantage is anticipated. Multiple process layouts can be assembled on a scale ranging from 1 g/exp to 100 kg/day. The engineering findings provide targets capacity of single product plants.
- *Dedicated developments*: in the search of novel synthesis technologies, the manufacturers and scientists set up investigation and supply schemes, model a desired contacting pattern or spatial arrangement of matter, and establish the overall application analytics until the critical initial hypothesis can be validated and further confined [19].

8.4.2 Oscillatory Flow Mixing Reactors

An oscillatory flow mixing (OFM) reactor is a tubular reactor containing baffles located perpendicular to the axis to form several compartments (Fig. 8.2, bottom-left). Using an external oscillator, the fluid is oscillated at a frequency of 0.5–15 Hz and amplitude of 1–100 mm. The oscillating fluid impinges on each baffle to form vortices, such that the resulting fluid motion leads to efficient and uniform mixing in the space between the baffles. At high throughput, the oscillatory motion approaches a steady flow curve as the oscillations get dampened and flow remains constant. An OFM reactor is characterized by plug-flow residence time distribution (RTD), high heat transfer, finely controlled mixing, and short reaction times. The absence of mechanical agitators is clearly an advantage, allowing the OFM reactors to be used for the synthesis and handling of mechanically sensitive compounds, such as biomolecules and crystals, among others [16].

8.4.3 Catalytic Endo/Exo Reactors

Performing endothermic and exothermic catalytic reactions adjacent to each other allows efficient energy use due to the transfer of heat from the exothermic to the endothermic process, while avoiding hot spots, preventing catalyst deactivation, and achieving heat transfer through conduction rather than convection. One design is known as *catalytic plate reactor* (CPR) and consists of metal plates with channels or grooves in a criss-cross pattern. The channels have a height on the order of millimeters, and catalyst thickness on the order of microns. The grooves can be coated with suitable catalyst and arranged such that the exothermic and endothermic reactions take place in alternating channels. The advantages of CPR designs include higher heat-transfer rates, very high intra-catalyst diffusion rates, and minimal resistances. As these reactors are small and have low pressure drops, the savings in capital and operating costs can be significant. Scale-up or rather scale-out of CPR is achieved by adding more plates to the stack, rather than changing the size of the plates.

By combing two reactions in a plate reactor, one can achieve energy savings and desired product distribution, as for example in the case of Fischer–Tropsch exothermic reaction which can be coupled with the endothermic dehydrogenation of ethylbenzene to form styrene [16].

Another reactor design is known as the *hot finger*, and consists of two annular tubes (inner and outer) coated with different catalysts to carry out adjacent endothermic and exothermic reactions. The problem of catalyst deactivation in a CPR is addressed here by providing several easily removable sections that can be dismantled and replaced with sections containing active catalyst.

8.4.4 Tube-in-a-Tube Reactors

Spinning tube-in-a-tube (STT) reactor consists of a tube placed inside another tube with a small gap between them (Fig. 8.2, bottom-right). The inner tube spins within the outer tube that is filled with reactants. Upon entry, the reactants encounter very large shear rates (30,000–70,000 s^{-1}) leading to high surface renewal rates, thus significantly enhancing the mass transfer and mixing. The mixing power requirements for STT reactors are lower than for conventional reactors. Reaction rates are influenced by the molecular-diffusive mixing time and the minimum length of turbulent eddies. Heat-transfer film coefficients as high as 10 kW/m^2 K can be achieved, thus reducing the formation of unwanted by-products due to wall effects. STT is suitable for highly viscous reactants, and processes that develop high viscosity during operation, e.g., bulk polymerization [16].

Summing it up, micro-reaction technology is clearly a valuable PI technique for rapidly optimizing reaction parameters; reducing reaction time, mass-transfer and heat-transfer resistances; generating less waste; efficiently scaling up processes; and developing inherently safer chemical processes. As the design, performance and advantages of these green reactors becomes better understood and appreciated, the industry will accept and use them more in the manufacturing plants [16].

8.5 High-Gravity Technology

The essence of HiGee technology is replacing the gravitational field by a high centrifugal field achieved by rotating a specially shaped rigid bed, typically a disk with an eye in the center. The higher mass-transfer coefficients and flooding limits allow the use of high surface-area packing. In this way, the momentum, heat, and mass transfer can be tremendously intensified [21].

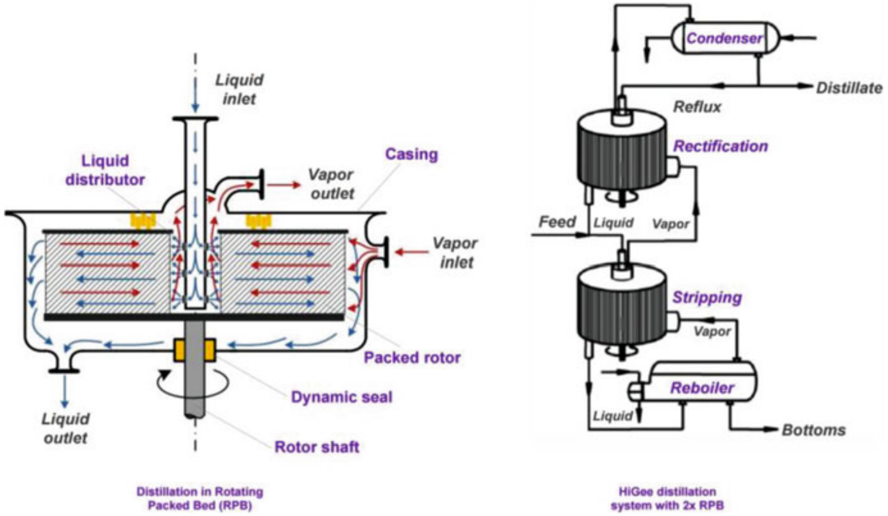


Fig. 8.3 Rotating packed-bed (*left*) and HiGee distillation (*right*)

8.5.1 Rotating Packed-Bed Contactors

RPB technology is enabling PI in absorption, distillation, multiphase reactors (e.g., trickle bed reactors), and the production of micro- and nanoparticles and ultrafine emulsions [22, 23]. In an RPB, the packing rotates at high speed, such that the high acceleration forces the liquid out toward the periphery of the bed, forming thin films over the packing and leading to high gas–liquid mass-transfer rates, generally by two to three orders of magnitude compared to conventional packed towers. The high void fraction (90–95 %) and high specific surface area (2000–5000 m^2/m^3) of the packing material also contribute to the high mass-transfer rates. Both random (glass and acrylic beads) and structured packing (metal foam and wire mesh) were successfully used in practice. RPB can be operated at high gas or liquid flow rates, since the high acceleration forces reduce the tendency toward flooding [16].

Figure 8.3 shows a simplified diagram of a typical RPB with a vertical axis [24], usable in a distillation setup [25]. The rotor of RPB is an annular, cylindrical packed-bed housed in a casing and driven by a motor. The liquid is fed onto the packing at the inner periphery, through a stationary distributor located at the eye of the rotor. The liquid leaves the packing as a shower of droplets, collected by the casing wall and runs downwards along the walls by the action of gravity, leaving the casing. The gas/vapor is tangentially introduced into the casing, entering into the packing at the outer periphery, and is forced to flow radially inward by pressure driving force. The gas/vapor leaves the packing at the eye of the rotor through the outlet pipe. Another variation of RPB design is the *spinning basket reactor*, where a supported or immobilized catalyst or packing is placed in a basket that rotates at high speed in a pool of liquid, creating very high liquid–solid mass transfer, thereby increasing the overall rate of reaction. Less catalyst per unit volume of liquid is needed to achieve the same rate of reaction as observed in conventional catalytic packed-bed reactors [16].

8.5.2 Spinning Disc Reactor

SDR is another technology based on centrifugation, which operates on the principle of thin, wavy film flow generated when a liquid is introduced at the center of a horizontal disc surface rotating at high speeds. The important features of the thin films are: highly sheared films (typical thicknesses of 50–300 μm), very short residence times (few seconds) that are easy to control, intense micro-mixing and plug-flow characteristics. The speed of rotation can reach 4000 rpm creating centrifugal field accelerations of up to 1000 *g* at the edge of a typical disc (10 cm diameter). There is no back-mixing, so surface-to-volume ratios on the disc surface range from 10^3 m^2/m^3 for high-viscosity materials up to 10^5 m^2/m^3 for low-viscosity systems. Heating/cooling is done by a heat-transfer fluid that circulates through a chamber below the rotating disc or through a hollow disc. SDR units are mounted on a rotating axle and can be operated horizontally or vertically. Liquid is fed near the center and flows across the surface of the disc due to centrifugal force, which stretches and spreads the thin liquid films allowing high mass-transfer rates [16]. Heat- and mass-transfer studies have shown that high heat- and mass-transfer coefficients can be achieved in an SDR: convective film heat-transfer coefficients of 20 kW/m^2 K, mass-transfer coefficients up to $k_L = 30 \cdot 10^{-5}$ m/s (liquid side) and $k_G = 12 \cdot 10^{-8}$ m/s (gas side). These enhanced transport rates provides the proper environment in an SDR for fast and highly exothermic reactions, allowing also mass-transfer-limited processes to be carried out in fractions of a second. Since the reactor holdup is very small (<100 mL), very hazardous reactions can be carried out as well.

8.5.3 HiGee Distillation

HiGee distillation is using the RPB concept in a high-gravity field (100–1000 *g*) technology—claiming HETP values as low as 1–2 cm, about three to six times higher throughput and a volume reduction of two to three orders of magnitude lower than that of conventional packed columns [6, 22, 26]. Figure 8.3 (right) shows a HiGee distillation setup [25], where the main component is the rotor, the structure of which determines the characteristics of different devices. There are several types of rotating beds, described elsewhere [6, 22, 26, 27]: waveform disks, helical rotating bed, multistage spraying rotating bed, RPB with blade packing, rotating zig-zag bed, and rotating split packing bed. In case of HiGee distillation, the vapor–liquid countercurrent flow is horizontal and not vertical, as typical for conventional operation. This means that the capacity depends on the height of the rotor, while the separation efficiency is given by the diameter of the rotor—in contrast to classic distillation where the diameter gives the capacity, while the height of the column gives the separation efficiency [32].

Many commercial applications of HiGee are well known in absorption, stripping, and reactive precipitation but only few commercial applications in distillation were reported so far. A key reason is that several problems such as the dynamic seal, middle feed, liquid distributor, and the multi-rotor configuration were not well addressed. In order to successfully solve these problems, a novel kind of HiGee device was recently proposed and developed [25]—the so-called rotating zigzag bed (RZB) that contains a unique rotor. Remarkable, the RZB fills the gap in HiGee distillation, and it has the potential for a bright future in this direction of process intensification.

Summing it up, the replacement of the vertical gravitational force by the centrifugal force has many important benefits, such as [6, 27]:

- Very high volumetric mass-transfer coefficients, leading to reduced size of the equipment. Compact equipment is also convenient for installation, troubleshooting, and maintenance.
- Gas flow velocity can be dramatically increased and the tendency to flood is reduced, thus higher hydraulic capacity is possible.
- The rotor is practically self-cleaning and it does not suffer from plugging, which is especially beneficial to treatments of fouling and solid-containing systems.
- Larger driving force of liquid flow due to high rotational speed allows the use of non-Newtonian or very viscous Newtonian fluids (stripping monomers, polymers solvents).
- Micro-mixing at molecular scale is extremely intensified (useful to make nanoparticles).
- The gas–liquid contact in RPB is characterized by low liquid holdup, thus the time required to reach steady-state operation is drastically reduced. Moreover, the short liquid residence time contributes to avoiding the decomposition of heat-sensitive materials (e.g., thermally unstable).
- The thinner liquid film and small inventories, favor processing of valuable materials.
- The RPB unit is unaffected by moderate disturbance in orientation, which allows its use in ship-mounted or portable units where conventional distillation is not an acceptable option.

8.6 Cyclic Distillation

Cyclic distillation (CyDist) emerged as an important trend for improving distillation performance by process intensification, namely by enhancing the separation efficiency through pseudo-steady-state operation based on separate phase movement (SPM) and providing up to 50 % energy savings [28, 29]. Basically, cyclic

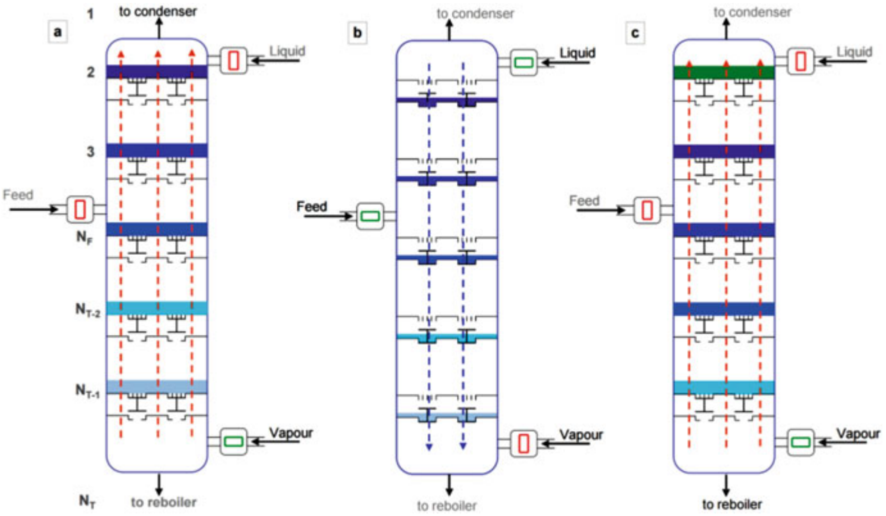


Fig. 8.4 Schematics illustrating the working principle of cyclic distillation: (**a**) vapor flow period; (**b**) liquid flow period; (**c**) beginning of a new vapor flow period

operation can be achieved by controlled cycling, stepwise periodic operation, a combination of these two, or by stage switching. Controlled cycling appears to be the simplest scheme, and it is therefore the preferred option. The cyclic operation was demonstrated on columns equipped with various types of internals: plates (brass, mesh-screen, bubble cap, sieve, packed-plate) and trays with sluice chambers. Essentially, a cyclic distillation column has an operating cycle consisting of two key operation parts: (1) A vapor flow period, when vapor flows upwards through the column and liquid remains stationary on each plate, and (2) A liquid flow period, when vapor flow is stopped, reflux and feed liquid are supplied, and liquid is dropped from each tray to the one below—as shown in Fig. 8.4 [30, 31].

From outside, a cyclic distillation column looks just like a regular tower as part of a chemical plant. However, the cross-section view inside a cyclic distillation column reveals the absence of downcomers and the presence of different internals (Fig. 8.5, courtesy of MaletaCD)—the development of which allowed an efficient SPM in practical operation and therefore the revisit of cyclic distillation technology [29].

As a result of cyclic operation, the achievable throughput is typically over two times higher and lower vapor flow rates are necessary to achieve certain purities. Cyclic distillation can also bring new life to existing distillation columns, by simply changing the internals and operating mode, and therefore providing key benefits, such as increased column throughput, lower energy requirements as well as better separation performance. Moreover, the SPM of the vapor and liquid phases throughout the column provides more degrees of freedom which contribute to excellent process control. Nonetheless, the limitations of cyclic operation must be also taken into account. The application of cyclic operation to vacuum distillation

Fig. 8.5 Cross section of a cyclic distillation column revealing the absence of downcomers and the presence of different types of internals (e.g., trays with sluice chambers)

seems rather difficult, and the performance enhancement critically depends on the complete separation between the liquid and vapor flow periods. However, the more recently proposed sluice-chamber trays seem to avoid the limitations of simple trays [28, 29].

Cyclic distillation was carried out at pilot scale for the separation of benzene/toluene, methanol/water, acetone/water, or methyl-cyclohexane/n-heptane mixtures. At production scale, cyclic distillation is already used in the food industry (Ukraine) for concentrating alcohol, from about 8 % up to 27–45 wt% ethanol. The cyclic distillation column acts mainly as a stripper that increases the alcohol concentration to a higher grade. In the beer production process, a mixture of ethanol–water is obtained by fermentation, but there are also additional components (~30 impurities) constituting less than 0.2 mol% in the feed stream. The concentration of alcohol in the feed stream is 10 vol% (3.29 mol%). The feed stream is supplied on the top tray of the cyclic distillation column (stripping column), while direct steam injection is used in the bottom of the column. The specification for the ethanol concentration in the top distillate varies between 13 and 24 mol%, with a typical value of ~18.25 mol%, while the concentration of ethanol in the bottoms must not exceed 0.004 mol%. MaletaCD implemented several cyclic distillation columns (diameters of 0.4–1.7 m, up to 42 trays), among them one of 15 stages, 0.5 m diameter, 20 m^3/day capacity (see *maletacd.com* for details).

Other potential applications include biofuels (bioethanol, biodiesel, biobutanol), organic synthesis, specialty chemicals, gas processing, petrochemicals, and pharmaceuticals. Furthermore, equipment manufacturers (such as Sulzer, Koch-Glitsch, Julius Montz) are capable of delivering the required internals for the revamping of existing towers into cyclic distillation columns.

Catalytic cyclic distillation is a more advanced combination of cyclic distillation and catalytic distillation in a convenient setup, by placing solid catalyst on the trays and thus allowing reactions to take place in the larger liquid holdup available on the tray due to the cyclic mode of operation. Pătruţ et al. [31] proposed several applications of catalytic cyclic distillation to various chemical processes (e.g., 2-pentene metathesis and dimethyl ether production), but so far no industrial applications have been reported.

8.7 Heat-Integrated Distillation Column

Heat-integrated distillation column (*HIDiC*) is the most radical approach of heat pump design, making use of internal heat-integration [27]. Instead of using a single point heat source and sink, the whole rectifying section of a distillation column becomes the heat source, while the stripping part of the distillation column acts as a heat sink (Fig. 8.6, left), providing a higher potential for energy savings [27, 30]. The internal heat-integration widely enhances the reachable coefficient of performance because the required temperature difference for heat transfer is kept low with gliding temperatures across both parts. The work input is provided by a compressor installed at the top outlet of the stripper section, while the heat pump cycle is closed by the valve flashing the liquid bottom outlet of the rectifier section. The success of HIDiC technology relies actually on good hardware performance for both heat- and mass-transfer tasks, at the same time.

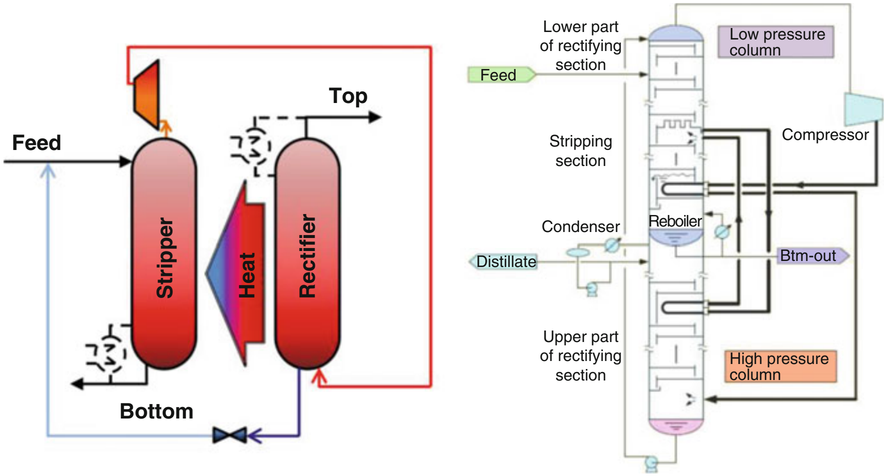


Fig. 8.6 HIDiC configuration (*left*). SuperHIDiC configuration developed by Toyo Engineering Corp. and the National Institute of Advanced Industrial Science and Technology (*right*)

Although HIDiC claims among the highest energy savings possible in distillation, the capital investment costs are higher as compared to conventional distillation—mainly due to the use of an additional compressor and a more complex configuration required for the enhanced heat transfer. Both thermodynamics and bench-scale experimental evaluations proved that HIDiC holds much higher energy efficiency than conventional distillation columns for close-boiling components separations. Several simulation studies and experimental evaluations have further confirmed that the process can be operated very smoothly, with no control difficulties [32].

A number of important issues must be considered during the HIDiC design, as for example: flexibility to changes in the operating conditions, influence of an impurity or a third component, and process dynamics and operation. These impose strict constraints on the energy efficiency that can be potentially achieved by a HIDiC system. Therefore, trade-off between process design economics and process operation appears to be very important, and it has to be carried out with great caution. It is worth noting that among the design and the operating variables, the compression ratio and the heat-transfer coefficient and area are the ones that significantly affect most the performance of a HIDiC. Consequently, an important research task during the recent years was the development of more appropriate configurations, such as multi-tube and multi-shell, plate-type, or even structured-packing HIDiC. The current directions of development are: fractionating heat exchangers (shell-and-tube, plate-fin) or heat exchanging distillation columns (e.g., concentric columns, parallel columns, partitioning-wall columns) [32].

Although there are several pilot-scale installations, the only design of HIDiC that has reached commercialization stage up to date is basically a two-pressure single shell column introduced recently by a Japanese engineering contractor. Toyo Engineering Corporation (www.toyo-eng.co.jp) was successful in overcoming difficulties and managed to develop in collaboration with the National Institute of Advanced Industrial Science and Technology (www.aist.go.jp)—main driver behind all similar projects in Japan—a practical and scalable heat-integrated distillation column configuration named SuperHIDiC, as shown in Fig. 8.6, right [32]. Toyo Engineering Corporation plans to use the novel SuperHIDiC technology in petroleum refining, as well as petrochemicals and fine chemicals production plants.

Compared to other complex separation systems, HIDiC technology has the key advantage of larger energy savings (up to 70 %) although the main problem remains the use of a compressor that adds significantly to the total equipment cost. Therefore, the main challenge of HIDiC technology is to reduce further the investment costs and thus payback times. Anyhow, it is to be expected that with increasing fossil energy prices and availability of low-cost green electrivity, the heat-pump-assisted distillation in general and HIDiC in particular will become more economically competitive in the foreseeable future. The first commercialized configuration so far, i.e., SuperHIDiC, is a serious candidate to make a breakthrough in this respect.

8.8 Dividing-Wall Column

The separation of a zeotropic ternary mixture (ABC) typically requires a direct or indirect sequence of at least two distillation columns. For some mixtures (e.g., when B is the major component and the split between A and B is just as easy as the split between B and C), the direct separation sequence has an inherent thermal inefficiency due to the remixing occurring for the mid-boiling component B—as illustrated in Fig. 8.7, left. Note that a certain amount of energy is used to separate B to a maximum concentration, but B is not removed at this point of high purity—it is actually remixed and diluted to a lower concentration at which it is removed in the bottoms, together with heavy C.

A more energetically favorable alternative configuration that avoids the remixing of internal streams is the so-called Petlyuk distillation or fully thermally coupled distillation columns [33]. However, note that a Petlyuk setup is not always the best choice, as there are mixtures and conditions that may favor implementation of alternative configurations. Although a fully thermally coupled system always has the lowest minimum vapor flow, the energetic optimum strongly depends on the feed composition [34]. As illustrated in Fig. 8.7 (right), certain conventional arrangements (e.g., direct or indirect sequence) provide greater energy savings for lower contents of middle boiling component in the feed, symmetric distribution of high and low boiling components, as well as large differences in relative volatilities [35].

In a Petlyuk setup, the mixture is submitted firstly to pre-fractionation in two liquid and vapor streams and then to the separation of the three components in the main column. The pre-fractionator and the main column are linked by vapor and

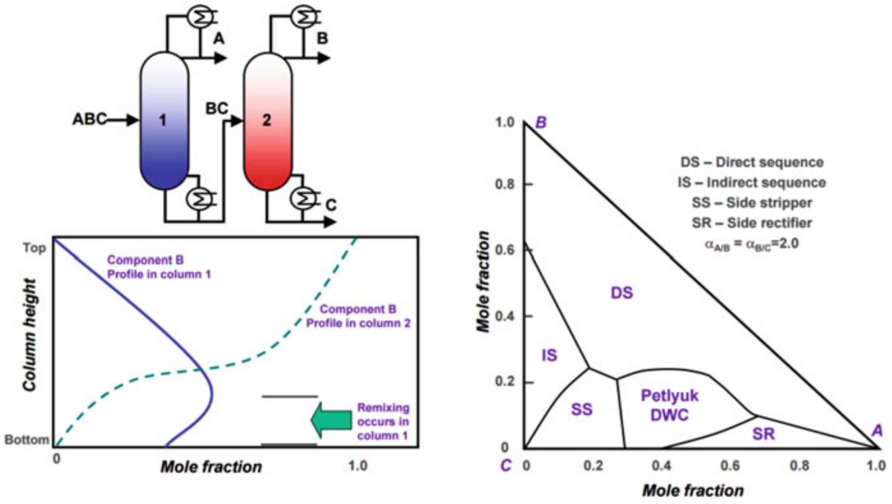


Fig. 8.7 Remixing of mid-boiling component occurs in a direct-sequence arrangement (*left*). Optimality regions of different configurations on the composition space (*right*)

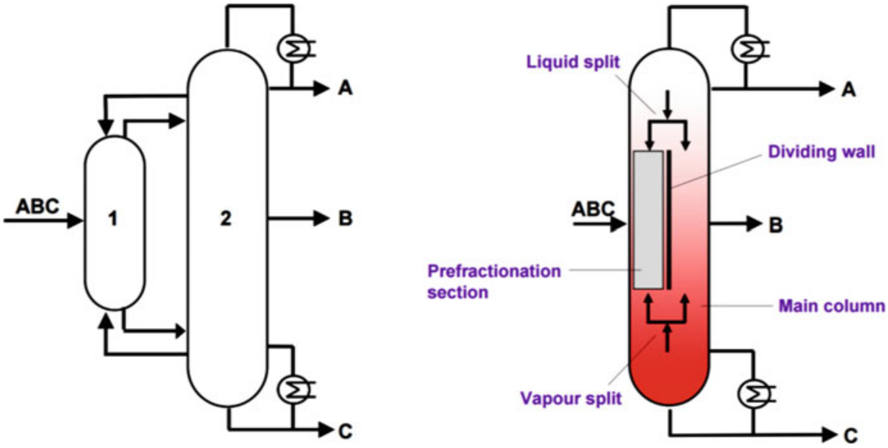


Fig. 8.8 Petlyuk configuration (*left*) and dividing-wall column (*right*)

liquid flows, while the required condenser and reboiler units are attached only to the main column. DWC is a practical implementation that allows further equipment integration and cost savings by integrating the two columns of a Petlyuk configuration into a single shell—as shown in Fig. 8.8 [35–38].

Compared to classic columns with a side draw, a DWC is capable of delivering higher purity side product. The partition wall helps in avoiding the contamination between the feed side and the side-draw section of the column. More details about the specific internals of DWC are available at equipment suppliers (*www.montz.de*), in review papers [34, 39] and specialized monographs [30].

DWC technology found recently great appeal in the chemical industry—with Montz and BASF as leading companies—because it offers major benefits: 25–40 % lower energy requirements (when the feed contains at least 20 % of the mid-boiling component), high purity for all product streams, reduced maintenance costs, small footprint and up to 30 % lower investment costs due to the reduced number of equipment units [30, 35]. Nonetheless, one should keep in mind that DWC has some limitations as well. DWC is operated at the same pressure, which can reduce its cost-effectiveness and practical applicability. For example, one can not combine in a DWC unit, a distillation taking place at vacuum with one at ambient or elevated pressure. Another drawback is that a DWC unit is larger in size (diameter and height) as compared to any single column of a conventional separation sequence—which in certain cases can render the application of DWC as impractical. In addition, the energy required by DWC has to be supplied and rejected at the highest and the lowest temperature levels. This can reduce the overall economy, since more expensive utilities must be used [35].

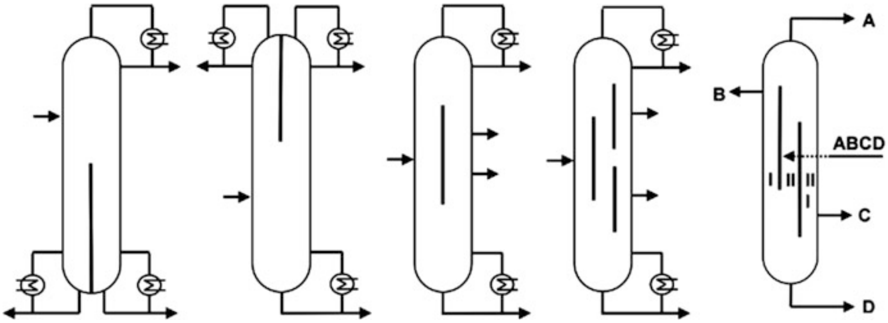


Fig. 8.9 Alternative configurations: bottom and top split column, Kaibel column and multi-partitioned DWC (Sargent and Agrawal arrangements)

8.8.1 DWC Configurations

The original DWC concept was further extended to other useful configurations—such as top and bottom split columns, Kaibel column (two side products) or even multi-partitioned DWC, as shown in Fig. 8.9 [34, 40, 41]. DWC units can also be applied for the separation of more than three components, and a systematic approach was proposed and described by Rong [42]. Of course, the number of possible configurations grows accordingly with the increasing number of components.

For a three-component separation, two different DWC configurations can be applied. The first type (Fig. 8.8) is the most common [34]: the dividing wall and the feed and side draws are placed close to the middle of the column. The second configuration employs a bottom or top split column (Fig. 8.9): the wall is located at the lower or at the upper part of the column.

The bottom split column is referred to as *split shell column with common overhead section and divided bottoms section*, while the top split column is known as *split shell column with divided overhead section and common bottoms section* [34]. Moreover, the wall can be shifted from the center toward the column walls and can have diagonal sections as well. In the *Kaibel column* configuration, the separation is performed in a shell with one dividing wall while the two mid-boiling products accumulate at the right side of the dividing wall. The configuration with only one wall is less thermally efficient, and it can be improved by using more dividing walls. This multi-partitioned setup is referred to as the *Sargent arrangement*. In spite of the theoretical studies carried out so far, no industrial application has been reported so far [35]. In the *Agrawal arrangement*, the feed enters the middle partition of the DWC [34].

Remarkably, the DWC technology is not limited to ternary separations alone, but it could be used also in azeotropic, extractive, and reactive distillation—as shown in Fig. 8.10 [30].

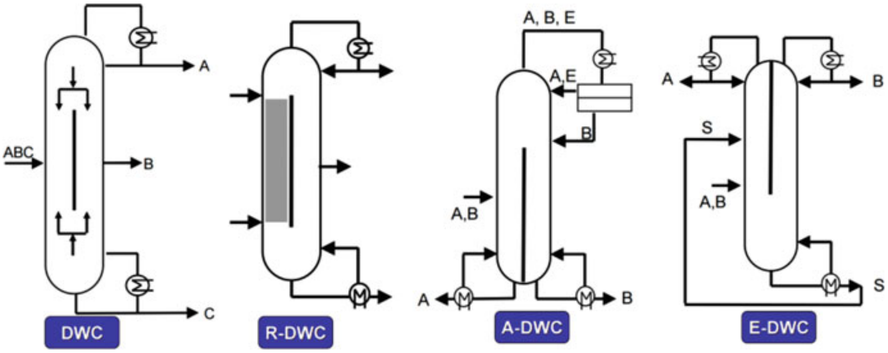


Fig. 8.10 Dividing-wall column used for reactive distillation (R-DWC), azeotropic distillation (A-DWC), and extractive distillation (E-DWC)

8.8.2 Design and Construction Aspects

The design and control of DWC are nowadays quite well established, more information being available elsewhere [30, 35, 43]. Several shortcut and detailed methods are described in literature for the design of DWC, and rigorous DWC simulations can be performed with commercial process simulators (Aspen Plus, ChemCAD, HYSYS, ProSim). The optimal design of a DWC requires adequate models and computer-based simulations. However, commercial process simulators do not include particular subroutines for DWC units. The so-called decomposition method simplifies the design problem, as the existing DWC configuration is replaced by a sequence of conventional distillation columns. The literature reveals that there are several design methods available that concern mostly ternary separations [30]. However, they can be relatively easily extended to cover cases with more components. When designing a DWC system for separation of a three-component feed into three products the number of degrees of freedom (i.e., design parameters) increases as compared to that required in case of designing conventional configurations of two columns in series—where the two columns can be optimized independently of each other [35]. The required design parameters for a DWC are: number of stages in six different sections (e.g., common top and bottom sections, sections above and below the feed stage and side draw, respectively), vapor split ratio, liquid split ratio, reflux ratio, heat input in the reboiler, and the side product flow rate. A proper selection of column internals is necessary to achieve efficient heat and mass transfer and, hence, the required purity. Dividing wall columns can be equipped with trays or packing. Typically, the selection criteria are similar to those for conventional distillation columns, but the wall construction is different for tray and packed columns. Generally, tray DWC is easier to build and the dividing wall that is welded on the column can strengthen the shell stability. The construction of a packed DWC is more complex. Recently, the non-welded wall technology was developed. Using unfixed walls, the column design becomes much simpler.

Other benefits include fewer manholes and lower weight, since the manufacturing requires less metal. The revamping of conventional columns becomes faster, simpler, and cheaper, too. Adopting non-welded partition wall enabled a significant increase of the applications with possibilities for revamping existing columns—so this can be considered as a milestone in the implementation of DWC technology [30].

8.8.3 DWC Operation and Applications

In spite of the clear advantages of DWC and the steady increase of industrial applications, the spreading of DWC was still limited until a few years ago to just a few companies. One reason for this was the insufficient insight on the operation and control of a DWC—this lack of knowledge making most companies reticent to large-scale implementations. Although more difficult to control as compared to conventional columns, the recent studies and the industrial experiences indicate that the control of DWC units is in fact satisfactory [43].

Ever since its first industrial application in 1985, DWC moved from a conceptual to a proven technology, steadily growing in number and size of applications [34, 37]. Table 8.3 conveniently summarizes the DWC applications available at applied research and industrial scale [30]—see the review paper of Yildirim et al. [34] for detailed references. DWC is one of the best examples of proven

Table 8.3 Reported applications of dividing-wall columns [30, 34]

Applied research and industrial applications	Additional information/remarks
Ternary separations	
Benzene–toluene–xylene fractionation	ExxonMobil
Separation of hydrocarbons from the Fischer–Tropsch synthesis unit	Linde AG, Tray column, $H = 107$ m, $D = 5$ m
Separation of benzene from pyrolysis gasoline	Uhde, 170,000 mt/year feed capacity
Separation of C7+ aromatics from C7+ olefin/paraffin	UOP, five DWC, Trap tray
Mostly undisclosed systems	BASF/Montz, over 70 columns, $D = 0.6$–4 m, $P = 2$ mbar to 10 bar
Undisclosed systems	Sumitomo Heavy Ind., Kyowa Yuka, Sulzer Chemtech Ltd. (20 DWC), Koch-Glitsch (10 DWC)
Multipurpose, for various ternary mixtures	Lonza ($H = 10$ m, $D = 0.5$ m, Sulzer Melapak 350Y, Hastelloy C-22)

(continued)

Table 8.3 (continued)

Applied research and industrial applications	Additional information/remarks
Multicomponent separations	
Recovery of four component mixtures of fine chemical intermediates	BASF/Montz, single wall column, $H = 34$ m, $D = 3.6$ m, deep vacuum
Integration of a product separator and an HPNA stripper	UOP, 5 product streams
Retrofit of conventional columns to DW	
Recovers mixed xylenes from reformate motor gasoline	Koch-Glitsch, $D = 3.8$–4.3 m, tray column, over 50 % energy savings
Separation of (iso)paraffins. Production of isohexane	Koch-Glitsch
Separation and purification of 2-ethylhexanol (2-EH)	LG Chem Ltd., dual operation possible
Reactive DWC	
Esterification, transesterification, etherification	Rate-based model/AspenTech ACM, Aspen Plus, Aspen HYSYS, or PRO/II
Azeotropic DWC	
Ethanol dehydration	Entrainer: cyclohexane, *n*-pentane
Extractive DWC	
Separation of toluene and nonaromatics with *N*-formyl-morpholine	Uhde, 28,000 mt/year feed capacity
Crude butadiene from a crude C4 using *N*-methyl-pyrrolidone (NMP) as solvent	BASF, both trays and packing
Bioethanol dehydration	Ethylene glycol used as solvent
Ternary mixture, ethylene glycol as entrainer	Lonza (40 % lower CAPEX)

process intensification technology in distillation, as it allows significantly lower investment and operating costs (typically 25–40 %) while also reducing the equipment and carbon footprint. Considering the number and variety of industrial applications, DWC can already be considered as a success story about PI in distillation, and it will certainly develop into a standard type of equipment in the nearby future. Many applications are known today, mainly concerning separations of ternary mixtures. The development efforts focus nowadays toward the separation of more than three components or applications of extractive, azeotropic, and reactive distillation in a DWC. Nonetheless, DWC has some limitations as well: operation at a single pressure, larger size as compared to any single column of a conventional (e.g., direct or indirect) separation sequence, and larger temperature span as the energy required has to be supplied and rejected at the highest (reboiler) and the lowest (condenser) temperature levels.

8.9 Reactive Distillation

In reactive distillation (RD), significant benefits can be realized by using the reaction to improve separation (e.g., overcoming azeotropes, reacting away contaminants, avoiding difficult separations) or by using separation to improve reactions (e.g., overcoming chemical equilibrium limitations and improving selectivity)—maximum effect being achieved when both aspects apply. Mathematical modeling including rate-based description can be found in the paper of Taylor and Krishna [44]. Theoretical issues and applications are described by various specialists in the monograph edited by Sundmacher and Kienle [45] and Sundmacher et al. [46]. Design, simulation, and control issues are handled in the book of Luyben and Yu [47], while new developments are described in the book of Kiss [30]. Remarkable, over 1100 articles and 800 US patents on RD were published during the past 40 years, covering in total over 235 reaction systems [47].

In a reactive distillation process, the reaction and distillation take place in the same piece of equipment, the reactants being converted with the simultaneous separation of the products and internal recycle of unused reactants. This implies that the boiling points of the products must be different from those of the reactants, preferably highest and lowest in order to remove the products as top and bottom streams. Since both operations occur simultaneously in the same unit, there must be a proper match between the conditions required for reaction and separation [43]. However, the application of RD is somewhat limited by constraints, such as: common operation range for distillation and reaction in terms of temperature and pressure, favorable boiling point sequence (product should be the lightest or heaviest component, while side or by-products the mid-boiling ones) and difficulty in ensuring sufficient residence time by the LV traffic for completing the reaction. The major constraint is set by the LV phase-equilibrium on the chemical reaction, which takes place in liquid phase. By this effect, the actual concentration of reactants in the liquid phase is smaller than in a pure liquid-phase reaction. Accordingly, the reaction rate should be increased by higher temperature and higher pressure, which in many cases is not practical. The best solution is boosting the reaction rate by means of a catalyst. Therefore, employing a (solid) catalyst is inevitable in reactive distillation. For this reason, RD is often designated in industry by the term *Catalytic Distillation*. The catalyst developed for RD should be much faster than for operating a homogeneous liquid-phase reactor, in order to bring the reaction rate compatible with the residence time resulting from the column hydraulics. An example is the zeolite catalyst used in alkylation reactions.

RD setups may consist of multiple catalyst systems, gas and liquid traffic over the catalyst, separation, mass flow, and enthalpy exchange—all of them being optimally integrated in a single processing unit, a key feature of process intensification. By continuously removing the products, reactive distillation makes it possible to use only the stoichiometric reactants ratio (neat operation) and to pull the equilibrium to high conversions [47]. This is in contrast to the typical practice of using an excess of one of the reactants to push the equilibrium toward the desired products, at the penalty of having to recover and recycle the unreacted reactant [30].

8.9.1 Modeling Reactive Distillation

The simulation of RD processes can consider two types of fundamental models: equilibrium stage models (EQ) and non-equilibrium stage modeling (NEQ). The merits and disadvantages of each approach, as well as direct comparison, are discussed in the landmark paper of Taylor and Krishna [44] that is recommended for deeper study. The EQ modeling can be formulated at two levels:

- Simultaneous phase and chemical equilibrium
- Phase equilibrium with chemical kinetics.

The full equilibrium model requires only thermodynamic knowledge. RCM can greatly help to highlight the range of feasible design in term of pressure, temperature, and separation of products. The simulation is in general easy, but care should be paid to the accuracy of thermodynamic properties, phase equilibrium, and chemical equilibrium. Thus, the model based on phase and chemical equilibrium allows a rapid assessment of feasibility of an RD process [48].

The simulation becomes more realistic adding the knowledge of the chemical kinetics. The progression of reaction on each stage can be followed, and consequently the number of theoretical stages for achieving a target conversion can be obtained. A key parameter in the kinetic approach is the reaction holdup. Accordingly, the selection of internals and hydraulic pre-design are necessary. This topic will be discussed in the next section. It should be stressed that an accurate knowledge of the reaction rate expression is necessary, which can be extrapolated over the interval of composition and temperature. This is a central point in RD and a major source of failure. The reaction rate must be expressed adequately, either on pseudo-homogeneous basis (volume), or per mass of catalyst. Moreover, using concentration instead of activities could introduce large errors, when highly nonideal mixtures are handled, namely when containing water.

In the NEQ modeling, the intensity of the interfacial mass transfer in liquid and vapor phases are counted for, by using the Maxwell–Stefan equations. The availability of specific correlations for calculating the mass-transfer coefficients is necessary, which in turn depend on the selected internals. The potential accuracy of this approach is paid by a much more elaborated procedure that needs customized programming. The comparison with experiments showed that the NEQ modeling gives good results if accurate model parameters are employed [13].

8.9.2 Design and Construction of RD Processes

RD sets specifications on both product compositions and reaction conversion. Consequently, the degrees of freedom (DoF) in an RD column must be adjusted to accomplish these specifications while optimizing an objective function such as the total annual cost (TAC). Several specifications are usually required [13, 30]:

- Column pressure and pressure drop on column or stage. Setting the pressure is constrained by the temperature of top and bottoms, more specifically by the available of on-site cold and hot utilities. If the bottom temperature is excessive, the solution may be the dilution with reactant, which will be recovered separately. In general, working at the highest acceptable temperature is recommended because of its accelerating effect on the reaction rate.
- Number of stages, feed locations of reactants, and exit points of the product streams. In this way, the RD configuration is set up in term of rectification, reaction, and stripping sections.
- Top distillate (liquid, vapor, mixed) or bottom product, absolute or ratio values.
- Condenser and reboiler types.
- Reflux or boilup ratio.
- Holdup distribution on the reactive stages.

A shortcut method for the hydraulic designing of an RD column can be used [13]:

1. Estimate a mean volumetric liquid flow rate for operation.
2. Assume an initial value for the superficial liquid velocity at the "load point" (U_{LP}): recommended 10 $m^3/m^2/h$.
3. Assume an initial value for the number of stages per meter (NSTM).
4. Determine the column diameter. Knowing the packing specifications, estimate the volume of packing and the catalyst holdup per reaction stage.
5. Introduce the above values in simulation, in which the reaction rate is expressed in units compatible with the holdup (mass, molar or volumetric).
6. Determine the total number of reactive stages needed to achieve the target conversion. Pay attention to the profiles of temperatures, concentrations, and reaction rate. Extract liquid and gas flows, as well as fluid properties.
7. Recalculate the load point velocity, the liquid holdup from the above information by using specific correlations and diagrams. Check the hydraulic design by selecting packaging with similar characteristics.
8. Verify if the gas load and the pressure drop are within optimal region.

Afterwards, check all values and repeat the points 4–8 until acceptable values are achieved.

Unlike conventional distillation, the choice of internals for reactive distillation is much more limited [49]. Figure 8.11 presents some examples of catalytic packing. The most important are:

- Catalytic Raschig rings with surface-coated catalyst.
- Catalyst bales, formed by wrapped wire sheets filled with catalyst.
- Structured packing. The elements have the shape of sandwiches manufactured from corrugated wire gauze sheets hosting catalyst bags, assembled as cylinders or rectangular boxes. Conceptually, the packing structure consists of alternating catalyst bags and open channel spaces. For ensuring higher efficiency of combined reaction and diffusion, the catalyst particle should have a diameter of about 0.8–1 mm. The advantages of structured packing are: uniform flow conditions with minimum back-mixing and maldistributions; good radial dispersion, an

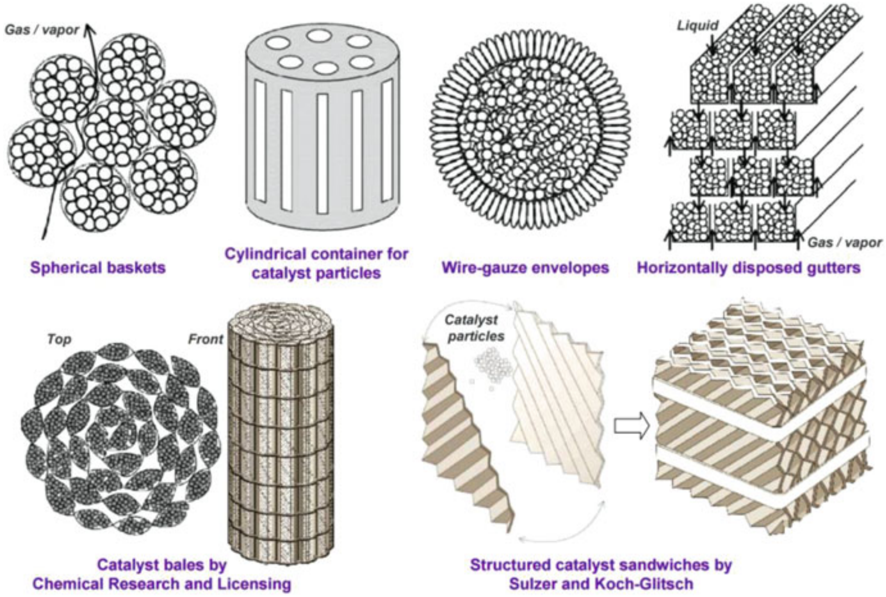


Fig. 8.11 Type of internals (packing) employed in RD [30, 49]

order of magnitude better than in conventional packed beds, ensuring a longer residence time; and efficient maintenance and replacement of catalyst.

Among the commercial offer, one can mention Katapak-S® manufactured by Sulzer ChemTech, and Multipak® supplied by Julius Montz [50].

8.9.3 Applications of Reactive Distillation

Table 8.4 lists the most important applications: (trans-)esterification, hydrolysis, etherification, hydration and dehydration, (trans-)alkylation, isomerization, (de-)hydrogenation, amination, condensation, polyesterification, chlorination, nitration—all being equilibrium limited (for more detailed references, see the books [30, 45, 46]). Figure 8.12 illustrates some reactive distillation configuration alternatives, ranging from a conventional reactive distillation column to reactive DWC, and RD columns combined with a pre-reactor, side reactors, or even membrane separation units [30].

CDTECH (CB&I Lummus Technology), the major commercial reactive distillation technology provider, has licensed until now more than 200 commercial-scale processes operated worldwide at capacities of 100–3000 ktpy for production of ethers (MTBE, TAME, ETBE), hydrogenation of aromatics and light sulfur hydrodesulfurization, ethyl benzene, and isobutylene production. Sulzer ChemTech also

Table 8.4 Main industrial applications of reactive distillation [30]

Reaction type	Catalyst/internals
Alkylation	
Alkyl benzene from ethylene/propylene and benzene	Zeolite β, molecular sieves
Amination	
Amines from ammonia and alcohols	H_2 and hydrogenation catalyst
Carbonylation	
Acetic acid from CO and methanol/dimethyl ether	Homogeneous
Condensation	
Diacetone alcohol from acetone	Heterogeneous
Bisphenol-A from phenol and acetone	N/A
Trioxane from formaldehyde	Strong acid catalyst, zeolite ZSM-5
Esterification	
Methyl acetate from methanol and acetic acid	H_2SO_4, Dowex 50, Amberlyst-15 N/A
Ethyl acetate from ethanol and acetic acid	Katapak-S
2-Methyl propyl acetate from 2-methyl propanol and acid	Cation exchange resin
Butyl acetate from butanol and acetic acid	H_2SO_4, Amberlyst-15, metal oxides
Fatty acid methyl esters from fatty acids and methanol	H_2SO_4, Amberlyst-15, metal oxides
Fatty acid alkyl esters from fatty acids and alkyl alcohols	Ion exchange resin bags
Cyclohexyl carboxylate from cyclohexene and acids	
Etherification	
MTBE from isobutene and methanol	Amberlyst-15
ETBE from isobutene and ethanol	Amberlyst-15/pellets, structured
TAME from isoamylene and methanol	Ion exchange resin
DIPE from isopropanol and propylene	ZSM 12, Amberlyst-36, zeolite
Hydration/dehydration	
Monoethylene glycol from ethylene oxide and water	Homogeneous
Hydrogenation/dehydrogenation	
Cyclohexane from benzene	Alumina-supported Ni catalyst
MIBK from benzene	Cation exchange resin with Pd/Ni
Hydrolysis	
Acetic acid and methanol from methyl acetate + water	Ion exchange resin bags
Acrylamide from acrylonitrile	Cation exchanger, copper oxide
Isomerization	
Iso-paraffins from *n*-parafins	Chlorinated alumina and H_2
Nitration	
4-Nitrochlorobenzene from chlorobenzene + nitric acid	Azeotropic removal of water
Transesterification	
Ethyl acetate from ethanol and butyl acetate	Homogeneous
Diethyl carbonate from ethanol and dimethyl carbonate	Heterogeneous
Vinyl acetate from vinyl stearate and acetic acid	N/A

(continued)

Table 8.4 (continued)

Reaction type	Catalyst/internals
Unclassified reactions	
Monosilane from trichlorosilane	Heterogeneous
Methanol from syngas	$Cu/Zn/Al_2O_3$ and inert solvent
DEA from monoethanolamine and ethylene oxide	N/A
Polyesterification	Autocatalytic

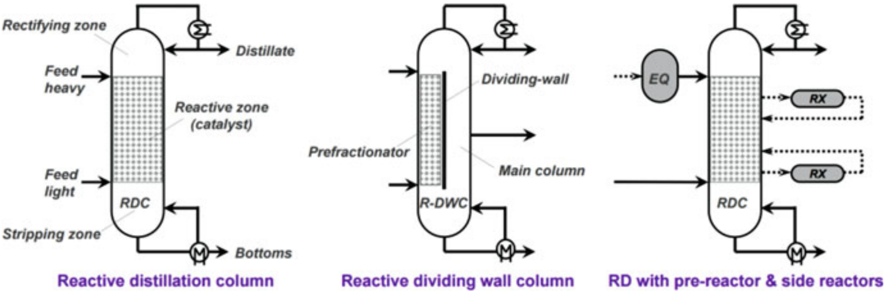


Fig. 8.12 Reactive distillation configurations

reports several industrial-scale applications such as synthesis of ethyl, butyl and methyl acetates, hydrolysis of methyl acetate, synthesis of methylal, and fatty acid esters production [30, 51].

8.9.4 Feasibility and Technical Evaluation

The technical feasibility and economical attractiveness of RD processes can be evaluated using the schemes recently proposed by Shah et al. [52]. The proposed framework for feasibility and technical evaluation of reactive distillation allows a quick-and-easy feasibility analysis for a wide range of chemical processes. Basically, the method determines the boundary conditions (e.g., relative volatilities, target purities, equilibrium conversion, and equipment restriction), checks the integrated process constrains, evaluates the feasibility, and provides guidelines to any potential RD process application. Providing that an RD process is indeed feasible, a technical evaluation is performed afterward in order to determine the technical feasibility, the process limitations, working regime, and requirements for internals as well as the models needed for RD. This approach is based on dimensionless numbers such as Damkohler and Hatta numbers, while taking into account the kinetic, thermodynamic, and mass-transfer constrains [52]. Note that the Damkohler number is the ratio of characteristics residence time (H_0/V) to characteristics reaction time ($1/k_f$), and the Hatta number is the ratio of the maximum possible conversion in the film to the maximum diffusion transport through the film [30].

Summing up, reactive distillation is nowadays an established unit operation in chemical process technology, being also the front-runner in the field of process intensification. At present, there are a variety of models now available in the literature for screening, analysis, design, and optimization of reactive distillation processes. RD brings key benefits to equilibrium-limited chemical systems, resulting in lower investment and operating costs, as well as reduced plant footprint. The industrial applications of RD are flourishing as the scientific community and the technology providers removed the main implementation barriers, developed heuristic process synthesis rules and expert software to identify the techno-economical feasibility of RD [30, 52].

8.9.5 RD Process for Methyl Acetate Production

A small number of industrial applications of RD have been around for many decades, but even today the RD crown is still carried by the Eastman process that reportedly replaced a methyl acetate production plant with a single RD column—process illustrated in Fig. 8.13 [53]—using about 80 % less energy at only 20 % of the investment costs [54, 55].

Methyl acetate is high volume commodity chemical with applications as an intermediate in the manufacture of a variety of polyesters such as photographic film base, cellulose acetate, Tenite cellulosic plastics, and Estron acetate [56]. The industrial process for methyl acetate (MeOAc) synthesis is based on the equilibrium-limited esterification reaction of methanol (MeOH) with acetic acid (AcOH). The reaction takes place in liquid phase in the presence of an acid catalyst, such as sulfuric acid or a sulfonic acid ion exchange resin:

$$\mathrm{MeOH} + \mathrm{AcOH} \leftrightarrow \mathrm{MeOAc} + \mathrm{H_2O} \tag{8.1}$$

The rate expression in the form of activities is strongly preferred since water and methanol have higher polarity than methyl acetate, this leading to a strongly nonideal solution behavior. An activity-based rate model for the reaction chemistry is given by the relation [57]:

$$r = k_{\mathrm{f}}\left(a_{\mathrm{AcOH}}a_{\mathrm{MeOH}} - \frac{a_{\mathrm{MeOAc}}a_{\mathrm{H_2O}}}{K_{\mathrm{eq}}}\right) \tag{8.2}$$

where the reaction equilibrium constant (K_{eq}) and the forward rate constant (k_{f}) are given by:

$$\mathrm{K_{eq}} = 2.32 \times \exp(782.98/T); \quad \text{with } T \text{ expressed in K} \tag{8.3}$$

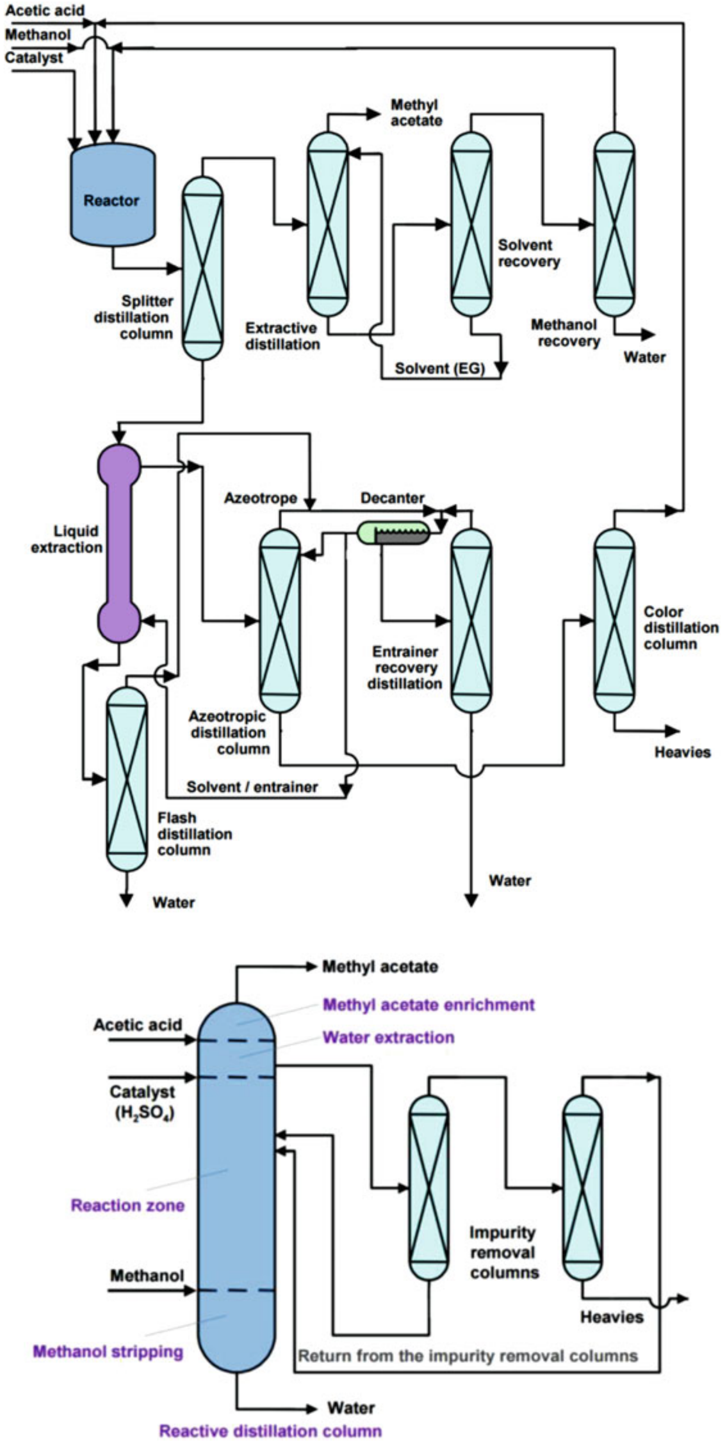


Fig. 8.13 Methyl acetate production: conventional process (top) vs. reactive distillation (bottom)

$$\mathrm{k_f} = 9.732 \times 108 \times \exp(-6287.7/T); \quad \mathrm{h}^{-1} \tag{8.4}$$

Due to the commercial success of the RD process and the potential of the ion exchange resins, a rate expression for an ion exchange resin-catalyzed reaction was proposed [56]. The expression for the reaction rate (r) is based on kinetic data generated over a range of molar feed ratios more typical of reactive distillation conditions:

$$r = \frac{k\left(a_{\mathrm{AcOH}}a_{\mathrm{MeOH}}\left(-a_{\mathrm{MeOAc}}a_{\mathrm{H_2O}}/K_{\mathrm{eq}}\right)\right)}{\left(1 + K_{\mathrm{AcOH}}a_{\mathrm{AcOH}} + K_{\mathrm{MeOH}}a_{\mathrm{MeOH}} + K_{\mathrm{MeOAc}}a_{\mathrm{MeOAc}} + K_{\mathrm{H_2O}}a_{\mathrm{H_2O}}\right)} \tag{8.5}$$

where k is the rate constant, K_{eq} is the equilibrium constant (equal to 5.2 according to Agreda et al. [54]), and K_{i} values (i being the component: AcOH, MeOH, MeOAc, and H_2O) are the adsorption coefficients of the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model. The expression has been successfully used to verify the experimentally observed residue curve maps of this system. The heat of reaction is low ($\Delta H = -3.0165$ kJ/mol), indicating a slightly exothermic reaction that is typical for acetate esterifications. The liquid-phase activity coefficients are well represented by the Wilson model [57]. The reaction can be carried out at 310–393 K and atmospheric pressure. The only main side reaction is the formation of dimethyl ether (DME) by the etherification of methanol, which is predominant at high temperatures [56].

Conventional processes used reactors with large excess of a reactant to achieve high conversion, followed by an energy intensive downstream separation due to the formation of MeOAc/MeOH and MeOAc/H_2O azeotropes. A typical process employed 1–2 reactors, eight distillation columns and one liquid extraction column, thus making it rather complex and capital intensive. Eastman Kodak has developed an RD process that delivers high purity product using a near-stoichiometric ratio of MeOH to AcOH [54]. The RD column (shown in Fig. 8.13) has four sections:

- *Methyl acetate enrichment* section, where acetic acid and methyl acetate are separated above the acetic acid feed, allowing pure methyl acetate to be recovered as overhead product.
- *Water extraction* section, where acetic acid acts as a mass separating agent (extractant) and extracts water (thus breaking the methyl acetate/water azeotrope) and some methanol.
- *Reaction* section, where the reaction occurs in a series of countercurrent flashing stages with sulfuric acid as homogeneous catalyst.
- *Methanol stripping* section, where methanol is stripped from water as the bottom product.

Figure 8.14 shows the composition and temperature profiles along the reactive distillation column [54]. High purity methyl acetate is obtained as distillate, while water by-product is removed as bottom product. Some mid-boiling components are formed due to the impurities present in feed. For this reason, a small side-stream is

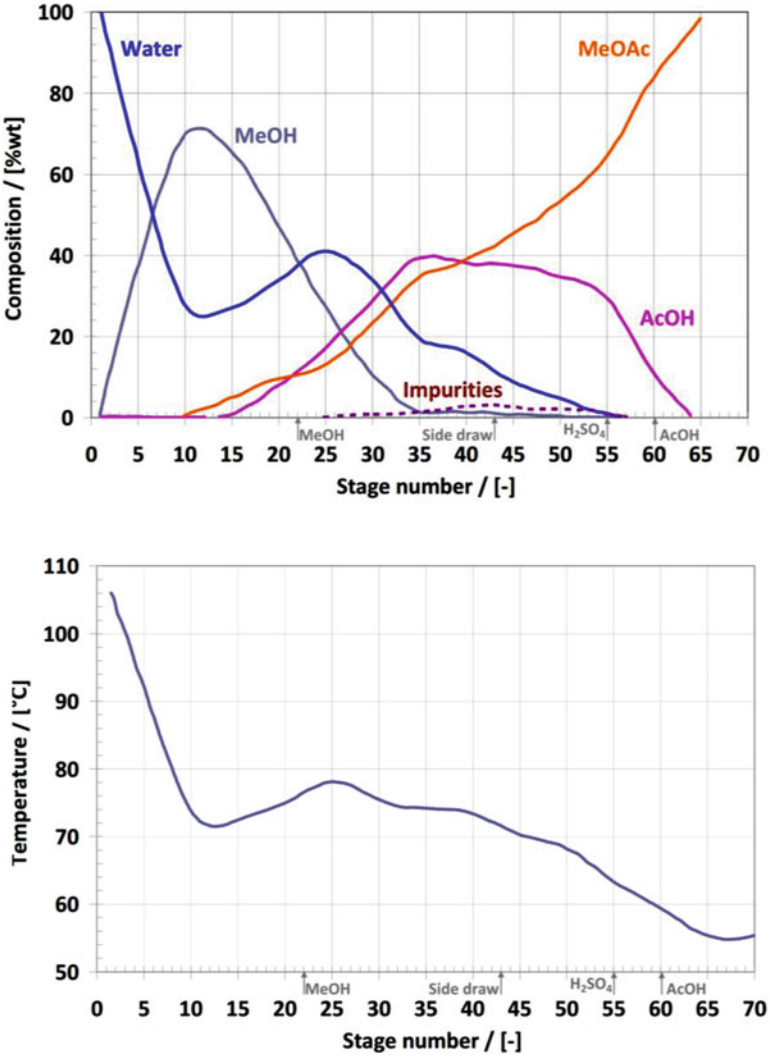


Fig. 8.14 Composition and temperature profiles in the RD column for methyl acetate production

withdrawn above the catalyst feed point and treated separately in an impurity-removal system, where the impurities are stripped and concentrated while a methanol and methyl acetate stream is recycled to the reaction zone of the RD column. Notably, the RD column is operated at a near-stoichiometric molar ratio of acetic acid and methanol, but it is able of yielding high purity methyl acetate as product. The whole process is practically integrated in a single column, thus eliminating the need for a complex distillation column system and recycle of the methanol/methyl acetate azeotrope. Remarkable, a single RD column built at Eastman Kodak's Tennessee plant produces 180 ktpy of high purity methyl acetate [56].

8.10 Concluding Remarks

Significant cost reductions and high energy efficiency can be achieved by employing various approaches based on process intensification principles, e.g., maximized effectiveness, driving forces, and synergy. There are several process intensification technologies that became success stories at industrial scale, as for example: CHE, static mixers, high-gravity technology (HiGee), DWC, and reactive separations (e.g., reactive distillation). The PI development remains of great industrial interest for many reasons [58]:

- *Energy savings and environmental benefits*, which are key features of most PI technologies.
- *Capital cost reduction*, which should be balanced against the risks involved in being an early adopter of novel PI technologies replacing conventional equipment in a process.
- *Enhanced safety*, which can be a strong incentive for new technologies, in cases where it is highly desirable to reduce the in-process inventory of dangerous chemicals (e.g., explosives).
- *Low inventories*, which is particularly important for hazardous substances (e.g., explosives or highly toxic) but also for designing inherently safer chemical process plants.
- *Novel or enhanced products*, which cannot be produced safely or successfully by any other means, as the reactants are too hazardous or the reactions are dangerously exothermic, etc.
- *Improved chemistry*, by controlling the reaction environment in a precise way, thus leading to higher conversions, yields and product purity, while also reducing raw materials losses, energy use, purification requirements, and waste disposal costs.
- *Enhanced processing*, especially in industries based on batch processing (pharma and fine chemicals), where processes are changed frequently as new products are developed, thus providing more opportunities to introduce new technologies.
- *Positive public image*, as most companies want to be seen as highly innovative, sustainable, environmentally friendly. PI can support claims related to doing more with less, sustainable, lower emissions, less carbon footprint, safest available, intensified chemical processing.
- *Value to customers*, as PI allows the implementation of *just-in-time manufacturing* such that whatever the customer wants can be quickly produced, and even at the site of the client.

However, there are also several barriers to the implementation of PI technologies in industry, as for example: fouling in miniaturized devices, slow dynamics of the process industries, conservative plant owners, somewhat limited portfolio of PI unit operations and processes, different solutions required for each driver, new design codes needed for novel PI equipment, insufficient education and publicity regarding

PI. Nonetheless, the adoption of process intensification can be accelerated by a proactive cooperation among industry, academia, research institutes, and regulatory bodies, as well as the engagement of the worldwide PI community. The recommended actions include, but are not limited to [58]: identification and communication of critical needs for PI solutions, publication of successful development and implementation (success stories), education of chemical engineers in PI area, encouragement of development and testing of PI technologies at lab- and pilot-scale, as well as and commercialization of promising but rather risky new PI technologies.

References

1. Stankiewicz A (2003) Reactive separations for process intensification: an industrial perspective. Chem Eng Process 42:137–144
2. van Gerven T, Stankiewicz A (2009) Structure, energy, synergy, time—the fundamentals of process intensification. Ind Eng Chem Res 48:2465–2474
3. Harmsen GJ (2010) Process intensification in the petrochemicals industry: drivers and hurdles for commercial implementation. Chem Eng Process 49:70–73
4. Sanders JPM, Clark JH, Harmsen GJ, Heeres HJ, Heijnen JJ, Kersten SRA, van Swaaij WPM, Moulijn JA (2012) Process intensification in the future production of base chemicals from biomass. Chem Eng Process 51:117–136
5. Boodhoo K, Harvey A (eds) (2013) Process intensification technologies for green chemistry: innovative engineering solutions for sustainable chemical processing. Wiley, New York
6. Reay D, Ramshaw C, Harvey A (2013) Process intensification—engineering for efficiency, sustainability and flexibility, 2nd edn. Butterworth-Heinemann, Oxford
7. Lutze P, Babi DK, Woodley JM, Gani R (2013) Phenomena based methodology for process synthesis incorporating process intensification. Ind Eng Chem Res 52:7127–7144
8. Commenge J-M, Falk L (2014) Methodological framework for choice of intensified equipment and development of innovative technologies. Chem Eng Process 84:109–127
9. Freund H, Sundmacher K (2008) Towards a methodology for the systematic analysis and design of efficient chemical processes—part 1: from unit operations to elementary process functions. Chem Eng Process 47:2051–2060
10. Kays WM, London AL (1998) Compact heat exchangers, 3rd edn. Krieger Pub Co, Malabar
11. Hesselgreaves JE (2001) Compact heat exchangers: selection, design and operation. Pergamon, oxford
12. Shah RK, Kraus AD, Metzger D (1990) Compact heat exchangers. Taylor & Francis, New York
13. Dimian AC, Bildea CS, Kiss AA (2014) Integrated design and simulation of chemical processes, 2nd edn. Elsevier, Amsterdam
14. Edward PL (2004) Handbook of industrial mixing-science and practice. Wiley, Hoboken
15. Thakur RK, Vial C, Nigam KDP, Nauman EB, Djelveh G (2003) Static mixers in the process industries—a review. Chem Eng Res Des 81:787–826
16. Doble M (2008) Green reactors. Chem Eng Prog 104(8):33–42
17. DeRosa T (2014) Engineering green chemical processes: renewable and sustainable design. McGraw-Hill Professional, New York
18. Ehrfeld W, Hessel V, Löwe H (2000) Microreactors: new technology for modern chemistry. Wiley-VCH, Weinheim
19. Wirth T (ed) (2013) Microreactors in organic chemistry and catalysis. Wiley-VCH, Weinheim

20. Reschetilowski W (ed) (2013) Microreactors in preparative chemistry: practical aspects in bioprocessing, nanotechnology, catalysis and more. Wiley-VCH, Weinheim
21. Ramshaw C (1983) HiGee distillation—an example of process intensification. Chem Eng (London) 389:13–14
22. Rao DP, Bhowal A, Goswami PS (2004) Process intensification in rotating packed beds (HiGee): an appraisal. Ind Eng Chem Res 43:1150–1162
23. Reddy KJ, Gupta A, Rao DP (2006) Process intensification in a HIGEE with split packing. Ind Eng Chem Rese 45:4270–4277
24. TU Dormund (2015) www.fvt.bci.tu-dortmund.de/cms/en/research/research_topics/Process_intensification_by_unit_operation_design/index.html. Accessed 24 June 2015
25. Wang GQ, Xu ZC, Ji JB (2011) Progress on Higee distillation—introduction to a new device and its industrial applications. Chem Eng Res Des 89:1434–1442
26. Stankiewicz A, Moulijn JA (2004) Re-engineering the chemical processing plant: process intensification. Marcel Dekker, New York
27. Kiss AA (2014) Distillation technology—still young and full of breakthrough opportunities. J Chem Technol Biotechnol 89:479–498
28. Maleta VN, Kiss AA, Taran VM, Maleta BV (2011) Understanding process intensification in cyclic distillation systems. Chem Eng Process 50:655–664
29. Maleta BV, Shevchenko A, Bedryk O, Kiss AA (2015) Pilot-scale studies of process intensification by cyclic distillation. AIChE J 61:2581–2591
30. Kiss AA (2013) Advanced distillation technologies—design, control and applications. Wiley, New York
31. Pătruţ C, Bildea CS, Kiss AA (2014) Catalytic cyclic distillation—a novel process intensification approach in reactive separations. Chem Eng Process Process Intensif 81:1–12
32. Kiss AA, Olujic Z (2014) A review on process intensification in internally heat-integrated distillation columns. Chem Eng Process 86:125–144
33. Petlyuk FB (2004) Distillation theory and its application to optimal design of separation units. Cambridge University Press, Cambridge
34. Yildirim O, Kiss AA, Kenig EY (2011) Dividing wall columns in chemical process industry: a review on current activities. Sep Purif Technol 80:403–417
35. Dejanović I, Matijašević L, Olujić Ž (2010) Dividing wall column—a breakthrough towards sustainable distilling. Chem Eng Process 49:559–580
36. Wright RO (1949) Fractionation apparatus. US Patent No. 2471134
37. Kaibel G (1987) Distillation columns with vertical partitions. Chem Eng Technol 10:92–98
38. Asprion N, Kaibel G (2010) Dividing wall columns: fundamentals and recent advances. Chem Eng Process 49:139–146
39. Olujić Ž, Kaibel B, Jansen H, Rietfort T, Zich E, Frey G (2003) Distillation column internals/configurations for process intensification. Chem Biochem Eng Quart 17:301–309
40. Agrawal R (2001) Processes for multicomponent separation. US Patent No. 6286335
41. Ghadrdan M, Halvorsen IJ, Skogestad S (2011) Optimal operation of Kaibel distillation columns. Chem Eng Res Des 89:1382–1391
42. Rong B-G (2011) Synthesis of dividing-wall columns (DWC) for multicomponent distillations—a systematic approach. Chem Eng Res Des 89:1281–1294
43. Kiss AA, Bildea CS (2011) A control perspective on process intensification in dividing-wall columns. Chem Eng Process 50:281–292
44. Taylor R, Krishna R (2000) Modelling reactive distillation. Chem Eng Sci 55:5183–5229
45. Sundmacher K, Kienle A (eds) (2003) Reactive distillation: status and future directions. Wiley-VCH, Weinheim
46. Sundmacher K, Kienle A, Seidel-Morgenstern A (eds) (2005) Integrated chemical processes: synthesis, operation, analysis, and control. Wiley-VCH, Weinheim
47. Luyben WL, Yu CC (2008) Reactive distillation design and control. Wiley-AIChE, New York
48. Noeres C, Kenig EY, Gorak A (2003) Modelling of reactive separation processes: reactive absorption and reactive distillation. Chem Eng Process 42:157–178

49. Krishna R (2002) Reactive separations: more ways to skin a cat. Chem Eng Sci 57:1491–1504
50. Hoffman A, Noeres C, Gorak A (2004) Scale-up of reactive distillation columns with catalytic packings. Chem Eng Process 43:383–395
51. Harmsen GJ (2007) Reactive distillation: the front-runner of industrial process intensification: a full review of commercial applications, research, scale-up, design and operation. Chem Eng Process 46:774–780
52. Shah M, Kiss AA, Zondervan E, de Haan AB (2012) A systematic framework for the feasibility and technical evaluation of reactive distillation processes. Chem Eng Process 60:55–64
53. Kiss AA (2012) Applying reactive distillation. NPT Procestechnol 19(1):22–24
54. Agreda VH, Partin LR, Heise WH (1990) High-purity methyl acetate via reactive distillation. Chem Eng Process 86:40–46
55. Siirola JJ (1996) Industrial applications of chemical process synthesis. Adv Chem Eng 23:1–62
56. Mahajani SM, Chopade SP (2000) Reactive distillation: processes of commercial importance. In: Wilson ID, Edlard TR, Poole CA, Cooke M (eds) Encyclopedia of separation science. Academic, London, pp 4075–4082
57. Huss RS, Chen F, Malone MF, Doherty MF (2003) Reactive distillation for methyl acetate production. Comput Chem Eng 27:1855–1866
58. Tsouris C, Porcelli JV (2003) Process intensification: has its time finally come? Chem Eng Prog 99(10):50–55

Chapter 9
Stochastic Optimization for Process Intensification

Claudia Gutiérrez-Antonio and Adrián Bonilla-Petriciolet

Abstract This chapter describes and discusses stochastic optimization methods for solving problems involved in process intensification, given an emphasis in multiobjective optimization due to its increasing importance in the chemical engineering community. A brief description of the multiobjective optimization strategies such as genetic algorithms, simulated annealing, tabu search, differential evolution, ant colony and particle swarm optimization is provided, including several applications of evolutionary optimization methods in the intensification of separation processes.

9.1 Introduction

Optimization is a relevant tool for the intensification of chemical engineering processes. Optimization problems abound in the context of chemical engineering, and, during last decades, there have been significant developments in this field including several applications for process intensification. The systematic study in the optimization field has conducted to the development of a large family of methods and algorithms, which can be applied in different stages of process design, see Table 9.1. Books published during last years have documented these advances in the chemical engineering context, e.g., [1–3].

Traditionally, optimization problems in chemical engineering have been handled using a single objective function, which is associated to an attribute or characteristic to be minimized or maximized for the system under analysis. This type of optimization problems encouraged the development of novel and powerful numerical

---

C. Gutiérrez-Antonio (✉)
Facultad de Química, Universidad Autónoma de Querétaro, Av. Cerro de las Campanas s/n, Col. Las Campanas, Santiago de Querétaro, Querétaro 76010, Mexico
e-mail: claugtez@gmail.com; claudia.gutierrez@uaq.mx

A. Bonilla-Petriciolet
Instituto Tecnológico de Aguascalientes, Aguascalientes, Mexico
e-mail: petriciolet@hotmail.com

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_9

Table 9.1 Illustration of optimization problems involved in process system engineering

Stage	Optimization problem	Example
Process model building	Global and multiobjective optimization problems	Parameter identification in thermodynamic and kinetic models
		Phase equilibrium calculations
Process design and synthesis	Global and multiobjective optimization problems	Heat exchanger network design
Process operations	Global and multiobjective optimization problems	Scheduling batch plants and managing supply chains

strategies. In fact, the literature devoted to the optimization in chemical engineering has mainly focused on the solving of single optimization problems. Nowadays, the design of chemical processes must consider different objectives simultaneously; for instance, the energy consumption, environmental impact, social impact, among others. Several years ago, the implementation of a chemical process relied almost exclusively on the value of the internal rate of return. Now, this value is used with other indicators in order to consider the impact on environment, social and sustainability aspects. All these considerations make the chemical process synthesis a more complex problem, since different criteria must be considered simultaneously to have an optimal solution. Moreover, the chemical processes usually have a multiobjective nature, since normally there are several objectives in conflict between them; which are also restrained to requirements, physical or economical limitations. It is important to note that these multiobjective problems have been the topic of several studies during last years in the chemical engineering community [1–3].

To date, a wide variety of optimization methods have been used in process system engineering. Available methods include algorithms with local and global convergence properties for handling one or several objective functions simultaneously. The characteristics, convergence properties, capabilities, and limitations of these optimization tools may vary significantly depending on the problem at hand. However, stochastic optimization methods have an outstanding performance and offer several advantages for solving problems involved in process intensification. Deterministic methods search systematically for the optimum value within the prescribed range of the decision variables, while stochastic methods employ a random search and heuristics to find the solution of the optimization problem. Although deterministic methods may offer theoretical and computational guarantees to find the optimum solution, stochastic methods retain several advantages. They do not require any assumptions for the problem at hand, are capable of addressing the nonlinearity and non-convexity of the objective function as a black box problem, and they are relatively easier to program and implement. Moreover, most of these methods have their extrapolations to multiobjective optimization, and they are proper to parallelization to efficiently handle large-scale optimization problems. Also, from the perspective of practical applications, they reduce significantly the optimization time as compared to deterministic methods, especially for problems with several decision variables.

To date, several stochastic methods have been proposed and studied for solving (single and multiobjective) optimization problems in process intensification. They include simulated annealing, genetic algorithms, differential evolution, particle swarm optimization, harmony search, ant colony optimization, and other new or hybrid algorithms. These methods are based on the application of exploration and exploitation strategies, which have been developed from principles of natural phenomena and artificial intelligence. The numerical performance and convergence behavior of stochastic optimization methods are determined by both the intensification and diversification strategies, which guide and modify the numerical operations to efficiently explore the search space of decision variables in order to find (near-) the optimal solutions. Specifically, the diversification (exploration) stage is devoted to exploring the search space, and for the computation of the objective function value of very different points in the search domain to find the promising area. On the other hand, the intensification (exploitation) stage investigates the promising area to locate, as near as possible, the global optimum solution that the algorithm is looking for.

Two categories are commonly used for the classification of stochastic optimization methods: population-based methods and point-to-point methods. In point-to-point methods, the algorithm uses only one solution at the end of each iteration, from which the search will start in the next iteration. On the other hand, population-based methods employ a set of solutions at the end of each iteration. Hybrid optimization strategies have also been developed by combining two or more metaheuristics, to improve reliability and efficiency of traditional stochastic optimization methods.

In particular, this chapter describes and discusses stochastic optimization methods for solving optimization problems involved in process intensification, given an emphasis on multiobjective optimization due to its increasing importance in the chemical engineering community. A brief description of these methods is provided including several applications of evolutionary optimization methods in process intensification of separation processes.

9.2 Definition of an Optimization Problem for Process Intensification

In general, an optimization problem (single or multiobjective) involved in process intensification can be defined as follows

$$\text{Optimize}[f_1(x), f_2(x), \ldots, f_k(x)] \tag{9.1}$$

subject to m inequality constraints

$$g_i(x) \geq 0 \quad i = 1, 2, \ldots, m \tag{9.2}$$

and the p equality constraints

$$h_i(x) = 0 \quad i = 1, 2, \ldots, p \tag{9.3}$$

considering the bounds on the optimization variables

$$x_{\mathrm{L}} < x < x_{\mathrm{U}} \tag{9.4}$$

where k is the number of objective functions f_i, while $x = [x_1, x_2, \ldots, x_n]^{\mathrm{T}}$ is the vector of n decision variables with lower x_{L} and upper x_{U} bounds. The objective is to determine, from among the set $\mathfrak{F}$ of all vectors, which satisfy (9.2)–(9.4), the particular set of values $x_1^*, x_2^*, \ldots, x_n^*$ that yields the optimum values of all the objective functions [4].

The objective functions f_i involved in the optimization of chemical processes are indicators of their characteristics, operation, and performance. They can be related to the different metrics including the process effectiveness, economic indicators, environmental impact, safety and reliability, control properties and other attributes/characteristics of interest to be improved/analyzed, including any combination of them. For the case of the process model building, these objective functions can be related to thermodynamics calculations or parameter identification problems.

If the problem at hand involves only one objective to be optimized; it is solved as a single optimization problem. This optimization can be classified in subfields depending on the characteristics of the objective function, type of decision variables, and constraints. In this scenario, the target is to identify the set of values for the decision variables that provides the (global) maximum or minimum value of the objective function used.

On the other hand, when two or more objective functions should be optimized simultaneously, the problem is handled as a multiobjective optimization. In these problems, the objectives are in conflict between them, thereby a simple solution is not desirable or in some cases even not feasible. For this kind of problems, a set of optimal solutions that represents the best trade-off between these objectives is the goal, instead of a single solution. This set of optimal designs can be achieved by means of Pareto front, which is a set of optimal non-dominated solutions [5]. In this way, the Pareto front allows having not just one optimal solution, but a set of optimal solutions that represents the best compromises between the objectives in consideration. In particular, the Pareto front is defined as follows: we say that a vector of decision variables $x^* \in \mathfrak{F}$ is Pareto optimal if there does not exist another $x \in \mathfrak{F}$ such that $f_i(x) \leq f_i(x^*)$ for all $i = 1, 2, \ldots, k$, and $f_i(x) < f_i(x^*)$ for at least one j. This definition says that x^* is Pareto optimal if there is no feasible vector of decision variables $x \in \mathfrak{F}$, which would decrease some criterion without causing a simultaneous increase in at least one other criterion [5]. The set of Pareto optimal is called as Pareto front. Note that this is the most commonly adopted notion of optimality, originally proposed by Francis Ysidro Edgeworth [6], and later generalized by Vilfredo Pareto [7]. Traditionally, the objective functions involved in the intensification of chemical engineering processes are highly non-linear, multivariable, and potentially non-convex. The complexity and the difficulty of solving optimization problems, including the analysis of their solutions, are likely to increase with the number of objective functions considered. The optimization variables used for the intensification of chemical processes are degrees of freedom related to the operation, configuration, and physical characteristics of the system under analysis. These variables can be continuous and discrete. However, the presence of discrete optimization variables increases the problem complexity due to the optimization space is disjoint and potentially non-convex. Additionally, the constraints impose limits for the feasible values of optimization variables. The feasible search space of the optimization problem is determined by these constraints. The inequality and equality constraints may be derived from physical restrictions for the processes, or they are defined considering an expected/desired performance or characteristic for the system. The presence of these constraints increases the optimization problem complexity and they are considered to define the strategy that should be used for the resolution of the optimization problem. In summary, the difficulty and complexity of optimization problems are determined by the properties and mathematical relationships among the objectives or performance criteria to be optimized, the type of decision variables, and the presence and properties of the constraints.

9.3 Stochastic Optimization Algorithms for Process Intensification

Evolutionary algorithms are a powerful tool to tacked mono- and multiobjective problems, which are based on an imitation of the evolutionary principles of nature in order to reach optimal solutions. The principal difference of evolutionary algorithms with the classical methods is that the first ones consider a set of solutions instead of a single one. In order to generate the Pareto, the classical methods address the multiobjective problem making a single objective problem [8]. This is done using two approaches. One is to consider the optimization of an objective, while the rest of them are treated as restrictions [9]. The other approach is performing a weighted sum of the different objectives, by grouping them into a single function [10]. In contrast, evolutionary algorithms have been recognized to be well suited for multiobjective optimization, because of their capability to evolve a set of non-dominated solutions distributed along the Pareto front [11]. This ability of an evolutionary algorithm to find multiple optimal solutions in one single simulation run makes evolutionary algorithms unique in solving multiobjective optimization problems [12].

Among the evolutionary algorithms, genetic algorithms are, without any doubt, the most popular technique for this kind of strategies. Genetic algorithms (GA) are an optimization technique proposed by Holland [13] that mimics the process of natural selection. In this algorithm, the decision variables are codified to constitute a chromosome; there are different kinds of codifications, being the binary one the most popular. Then, starting from an initial encoded solution, an entire population is generated. This population is evaluated according to its fitness function, which emulates the survival capacity of the species. Based on the value of the fitness function, individuals are sorted and selected to become the parents of the next generation. The selected parents are combined to generate a new generation of children, which partially replace the current population basis. Children are mutated, in order to ensure getting trapped in a local optimum. Also, the elitism operator allows keeping the best solution during the optimization process. The entire population evolves, with the fitness improving over the generations [14].

A considerable number of techniques to solve multiobjective optimization problems using genetic algorithms have been proposed. For instance, we can mention the Vector Evaluated Genetic Algorithm, VEGA [15], Multiobjective Genetic Algorithm, MOGA [16], the Non-dominated Sorting Genetic Algorithm, NSGA [17], the Niched Pareto Genetic Algorithm, NPGA [18], the Non-dominated Sorting Genetic Algorithm II, NSGA-II [19], and the Micro-Genetic Algorithm, MGA [20, 21]. Nevertheless, one of the most popular multiobjective genetic algorithms is the NSGA-II [19], which is a very robust tool and it is easy to implement.

The NSGA-II [19] is a multiobjective genetic algorithm with low computational requirements, elitist approach, and parameters-less sharing approach with respect to NSGA [17]. This algorithm builds a population of competing individuals, ranks and sorts each individual according to non-domination level, applies evolutionary operations to create a new pool of offspring, and then combine the parents and offspring before portioning the new combined pool into fronts [22]. By far, this is the most used multiobjective genetic algorithm, and it is usually taken as reference when new algorithms are presented.

The genetic algorithms are, without any doubt, the representative technique of the evolutionary strategies, which are inspired by nature. However, recently new techniques, also inspired by nature, are proposed; these approaches are known as metaheuristics. A metaheuristic is an algorithm designed to solve approximately a wide range of hard optimization problems, without having to deeply adapt to each problem [23]. Metaheuristics are characterized because they are inspired by nature, using stochastic elements, and have various parameters that must be tuned for each problem. A metaheuristic is successful if there is an appropriate balance between diversification and exploitation stages; as stated, the first one allows you to explore a large part of the search space, while the second one concentrates the efforts on those areas the search space which are more promising. If a metaheuristic gives more weight to diversification, then you could not be close to the global optimum; but if more weight is given to exploitation then you could fall into a local optimum. Several metaheuristics have been proposed; being the most popular and used: simulated annealing, tabu search, differential evolution, ant colony, and particle swarm optimization. Next, we described briefly each one of them.

Simulated annealing is an optimization technique inspired by the process of annealing of metals. In this process, first the metal is heated by raising the energy of the molecules, and allowing them to move freely. Subsequently, a cooling process is performed, which minimizes the energy of the particles by their accommodation in a crystalline structure. If the cooling is done very quickly then an amorphous structure is obtained, which leads to a higher energy state. The simulation of the annealing of metals was proposed, through an algorithm, by Metropolis et al. [24]; however, Kirkpatrick et al. [25] and Cerny [26] pointed out the analogy between this process and the optimization strategies: the objective function is represented by the energy of the particles, while the temperature and the cooling path are the operators. Unlike genetic algorithms, simulated annealing (SA) does not use populations but instead it uses only one solution; thereby, the acceptance of a new individual is based on a probability value. In spite of this, different multiobjective simulated annealing approaches have been developed. The critical step for using simulated annealing for multiobjective optimization relies on the form of calculations in the probability of acceptance when more objectives are considered. Several authors have proposed different approaches to use simulated annealing for multiobjective problems, such as $L\infty$-Tchebycheff norm [27], weighted sum of probabilities for all objectives for a single solution [28–33] and entire populations [33, 34], Pareto dominance [35, 36], or normalized aggregation functions [37]. Another metaheuristic strategy is tabu search (TS), which was proposed by Glover [38]. This algorithm is similar to simulated annealing, since a unique solution is evolved through admissible movements, that allow decreasing or not the objective (in case of minimization). However, reverse movements are not allowed, in order to avoid falling in a local optima; these positions are registered in a list, called Tabu list. Therefore, the main operators are three kinds of memory arrays: short-term, intermediate-term, and long-term. These memories register the information about recent visited points, optimal or near-optimal points and explored regions, respectively [22]. There are different proposals to manage multiobjective optimization with tabu search, as can be found in the works of Gandibleux et al. [39], Hansen [40, 41], Hertz et al. [42], Baykasoğlu [43], Baykasoğlu et al. [44], Ho et al. [45], Jaeggi et al. [46], Kulturel-Konak [47], Xu et al. [48], among others.

The ant colony (AC) is another metaheuristic that was developed by Marco Dorigo, inspired by colonies of real ants [49–52]. In real colonies, the ants secrete a chemical substance called pheromone, which is used to communicate between them: the ants tend to take the paths where large amounts of pheromone are present. From a computer science perspective, the ant colony is a multi-agent system where low level interactions between single agents (artificial ants) result in a complex behavior of the entire ant colony [22]. In this way, at the beginning of the searching process all the ants are dispersed, looking for food; as the optimization process progresses, ants begin to follow a common path, the one with higher levels of pheromones. In the end, the whole colony follows the same path, which is the shortest. The first algorithm for ant colony was proposed by Gambardella and Dorigo [53], Ant-Q, which in reality is a family of algorithms; this for single optimization. However, several multiobjective approaches have been developed in order to use ant colony for this kind of problems. We can mention the works of Mariano and Morales [54, 55], Gambardella et al. [56], Iredi et al. [57], Gagné et al. [58, 59], McMullen [60], and T'kindt et al. [61].

Moreover, differential evolution is a metaheuristic proposed by Storn and Price [62, 63] and Price et al. [64]; and it was originally developed for continuous optimization, sharing some similarities with traditional evolutionary algorithms. However it does not use binary encoding as a simple genetic algorithm [65], and it does not use a probability density function to self-adapt its parameters as an Evolution Strategy [66]. Instead, differential evolution performed mutation based on the distribution of the solutions in the current population [22]. Therefore, several variants of the differential evolution algorithm are possible, depending on the type of selection, the recombination, and mutation operators. For instance, the work of Mezura-Montes et al. [67] present eight variants of this strategy. Also, several multiobjective differential evolution approaches have been developed by Chang et al. [68], Bergey [69], Abbass et al. [70], Abbass and Sarker [71], Sarker et al. [72], Madavan [73], Xue et al. [74], Xue [75], Babu and Jehan [76], Parsopoulos et al. [77], Iorio and Li [78] and Sharma and Rangaiah [79]. On the other hand, based on the movements of a bird flock when they try to find food, Kennedy and Eberhart [80] proposed an approach called Particle Swarm Optimization. This strategy is similar to the evolutionary algorithms, since there is a population which performance is measured with a function similar to fitness function. Additionally, this approach introduces the use of flying potential solutions through hyperspace, used to accelerated convergence [22]. Also, the historical of past movements can be used to improve the current individuals on the population, similar to tabu search. Moreover, there are a great amount of proposals to use this strategy to address multiobjective optimization problems. Some of these works were developed by Moore and Chapman [81], Ray and Liew [82], Parsopoulus and Vrahatis [83], Hu and Eberhart [84], Coello Coello and Salazar Lechuga [85], among others. The evolutionary algorithms have been used to solve different problems to solve complex problems in industry and services, in areas ranging from finance to production management and engineering [23]; the problems consider single and multiple objectives, with constraints in most of the cases. Next, we are going to present the applications of these strategies in Chemical Engineering, especially in Process Intensification.

9.4 Applications of Evolutionary Optimization Algorithms for Intensification of Chemical Engineering Processes

As was mentioned before, chemical processes have a multiobjective nature along with different constraints that must be considered in the problem statement. Traditional design of chemical processes considers a set of sequence unit operations, where each equipment is devoted to perform just one type of modification to the process stream. These modifications generate changes in composition, energy content, or the amount of movement. Even in traditional chemical processes, the optimal design problem is very complex, highly nonlinear, with several constraints. Therefore, evolutionary algorithms have been used successfully for the single and multiobjective optimization of traditional chemical processes in the areas of process design, control, reaction systems, and separation [86]. These efforts conduct to better processes, with less energy consumption or more production rates. However, the decreasing in these objectives has a limit. If we want to get decreases with several magnitude orders, then we have to intensify the process. Process intensification significantly enhances transport rates, giving every molecule the same processing experience [87]. For instance, this involves combining two or more unit operations, reducing the size of equipment to control the transport phenomena, or the use of new technologies (such as ultrasound or microwaves). In turn, this leads to having processes with reduced capital costs and investment, greater efficiencies, and increased production. The new intensified process units must have optimal designs, in order to take advantage of all the benefits. However, the design of these new intensified units is more complex, since there are smaller physical spaces, reduced operating conditions due to the existence of physic and reactive equilibria, or the incorporation of technologies like microwave or ultrasound. Thereby, the modelling of these processes is even more complex than the modelling of traditional chemical processes, but keeping the multiobjective nature. So, the lack of design methodologies allowed that optimization strategies become an important tool to reach the optimal design of intensified processes; especially the evolutionary algorithms since complete models of the processes are not required. Next, we are going to present a review of some works where multiobjective evolutionary algorithms are used to reach the optimal design of intensified separation processes. These applications have been selected to illustrate the application of stochastic optimization methods in process system engineering.

Cheng et al. [88] performed the multiobjective optimization of catalytic membrane reactor for the production of methanol and hydrogen. They used the elitist non-dominated sorting genetic algorithm (NSGA-II) [19], along with a non-isothermal model. Otherwise, Gómez-Castro et al. [89] performed the multiobjective optimization of multiple dividing wall columns using a multiobjective genetic algorithm with handling constraints. Also, they proposed a methodology for sizing multiple dividing wall columns.

The problem of optimal design Petlyuk sequences was addressed by Gutiérrez-Antonio et al. [90] using a multiobjective genetic algorithm with handling constraints, coupled to Aspen Plus process simulator. Their strategy allows generating, in just run, the complete Pareto front for the defined objectives: heat duty and number of stages in each distillation column. Also, for the purification of quaternary mixtures, Vázquez-Castillo et al. [91] proposed the use of a multiobjective genetic algorithm for the optimization of energy and total of number of stages of different thermally coupled sequences. They found that the best options in terms of energy consumption, total annual cost, thermodynamic efficiency, and CO_2 emissions also show the best control properties.

The use of reactive distillation, both conventional and thermally coupled, for the production of biodiesel was proposed by Miranda-Galindo et al. [92]. In this work, the authors employ a multiobjective genetic algorithm with handling constraints in order to generate the Pareto front. They considered as objectives the total energy consumption and the total number of stages. Also, Behroozsarand and Shafiei [93] realized the multiobjective optimization of a transesterification reactive distillation column with thermally coupling. They employed the elitist non-dominated sorting genetic algorithm (NSGA-II) [19], along with HYSYS process simulator, for minimization of reboiler energy cost, maximization of *n*-butyl acetate molar flow as reactive distillation productivity, and maximization of methanol molar flow as nonreactive distillation column productivity.

Miranda-Galindo et al. [94] used a multiobjective differential evolution to address the optimal design problem of a distillation with reactor-side for hydrodesulfurization process of diesel. The results obtained in the Pareto Fronts indicate competition between total annual cost, CO_2 emissions, and the amount of sulfur compounds of the hydrodesulfurization process. These Pareto Fronts were useful to identify proper conditions for the operation of this process.

Torres-Ortega et al. [95] proposed the use of extractive thermally coupled sequences for the separation of ethane and carbon dioxide mixture. They used a multiobjective differential evolution algorithm. The proposed sequences were simultaneously optimized by minimizing the total annual cost (TAC) and maximizing the acid gas removal. Also, the optimal design problem for hybrid distillation/melt crystallization using thermally coupled distillation schemes was proposed by Bravo-Bravo et al. [96]. The design and optimization were carried out using, as a design tool, a multiobjective genetic algorithm with restrictions coupled with the process simulator Aspen Plus.

Cadavid et al. [97] tackled the interesting topic of performing the biodiesel production in a counter-current reactive extractive column. Therefore, the reaction and separation are realized in the same vessel. In order to find the operating conditions that maximize the biodiesel production and process productivity they used a multiobjective evolutionary algorithm. Moreover, the design of hybrid distillation/melt crystallization processes was addressed by Micovic et al. [98]. They present a design methodology that employs the Aspen Custom Modeler; and also, it includes the multiobjective optimization of the proposed hybrid separation using evolutionary algorithms.

Beierling et al. [99] continued their work on the multiobjective optimization of hybrid distillation/melt crystallization processes. They used a complex layer melt crystallization model, and validated their results with experimental data. On the other hand, the optimization of alternative distillation sequences for natural gas sweetening was performed with a multiobjective differential evolution method [100]. The authors consider cryogenic extractive distillation sequences, conventional and thermally coupled, in comparison with the traditional system of absorption. Results show a superior performance of the thermally coupled extractive sequences in terms of energy consumption and dynamic behavior. Also, Micovic et al. [101] worked on the optimal design of hybrid separations combining nanofiltration and distillation for wide boiling mixtures. They performed an optimization under uncertainty using multiobjective evolutionary algorithms for the design of this intensified separation alternative.

Recently, a combined method for optimal design of intensified distillation sequences has been proposed [102]. This methodology considers the use of the sequential design method along with a multiobjective differential evolution algorithm. The combination of these powerful tools allows getting optimal designs decreasing in 36 % the computational time, and limiting error propagation. Moreover, the production of ethyl *tert*-butyl ether was tackled using reactive distillation systems [103]. In order to get the optimal design of this intensified reaction–separation process, a multiobjective evolutionary algorithm with a nonlinear solver was used. They compare genetic algorithms and particle swarm optimization, finding that both strategies are capable of solving this kind of problem.

Woinaroschy [104] studied the multiobjective optimization of a biodiesel process production, considering as raw material soybean oil. They coupled the stochastic tool with SuperPro Designer, in order to optimize three objectives: maximize the net profit, minimize volatile organic compounds (VOC) emissions, and maximize the number of chemical operators' jobs.

Recently, Gutiérrez-Antonio et al. [105] proposed the use of thermally coupled distillation sequences for the intensification of a hydrotreating process to produce biojet fuel. They used a multiobjective genetic algorithm with handling constraints, coupled to Aspen Plus process simulator. They found an interesting reduction in energy consumption; also, they proposed the use of a turbine, so electricity can be generated in the process. In the same year, Gómez-Castro et al. [106] considered the multiobjective optimization of thermally coupled distillation sequences using the non-equilibrium model. They compared the obtained results with those obtained from using the equilibrium model, finding that equilibrium and non-equilibrium designs show similar heat duties but differences on configurations.

From the revision of the previous works, we note that different intensified processes have been designed using multiobjective evolutionary algorithms. The used strategies include genetic algorithms, particle swarm, and differential evolution. However, other strategies are still missing to be applied for this kind of problems, such as cuckoo search which has just been applied for the nonlinear estimation of parameters in phase equilibria [107, 108]. The application of multiobjective optimization strategies for process intensification can be extended to other topics covered in this book.

9.5 Conclusions

Stochastic optimization methods are powerful numerical tools for the intensification of chemical engineering processes. In particular, evolutionary algorithms offer several advantages for solving multiobjective design problems. The interest in this type of multi-criteria design problems has increased substantially during last years in the chemical engineering community; specially in the development of process intensification area. In this approach, dramatic decreasing in energy consumption or size of the equipment can be achieved; however, the design task is more complex. Different strategies including genetic algorithms, particle swarm, and differential evolution have been used for the design of intensified process. However, other strategies are still missing to be applied for this kind of problems. Therefore, it is expected that stochastic multiobjective optimization methods can play a relevant role for development of novel intensified systems.

References

1. Rangaiah GP (ed) (2009) Multi-objective optimization: techniques and applications in chemical engineering. World Scientific, Singapore
2. Rangaiah GP (ed) (2010) Stochastic global optimization: techniques and applications in chemical engineering. World Scientific, Singapore
3. Rangaiah GP, Bonilla-Petriciolet A (eds) (2013) Multi-objective optimization in chemical engineering: developments and applications. Wiley, Chichester
4. Coello-Coello CA (2005) Evolutionary multiobjective optimization: current state and future challenges. In: Proceedings of the fifth international conference on hybrid intelligent systems, 0-7695-2457-5/05, IEEE
5. Mezura-Montes E (2001) Uso de la técnica multiobjetivo NPGA para el manejo de restricciones en Algoritmos Genéticos. Maestría en Inteligencia Artificial, Thesis, Universidad Veracruzana
6. Edgeworth FY (1881) Mathematical physics. P. Keagan, London
7. Pareto V (1896) Cours D'economie Politique, vol I, II. F. Rouge, Lausanne
8. Croicu AM (2005) Single and multiple-objective stochastic programming models with application to aerodynamics. Electronic theses, treatises and dissertations, paper 3027
9. Caramia M, Dell'Olmo P (2008) Multi-objective management in freight logistics increasing capacity, service level and safety with optimization algorithms. Springer, New York
10. Chankong V, Haimes YY (1983) Multiobjective decision making theory and methodology. Elsevier, New York
11. Sarkar D, Modak JM (2005) Pareto-optimal solutions for multiobjective optimization of fed-batch bioreactors using nondominated sorting genetic algorithm. Chem Eng Sci 60 (2):481–492
12. Deb K (2001) Multi-objective optimization using evolutionary algorithms. Wiley, Chichester
13. Holland JH (1975) Adaptation in natural and artificial systems. University of Michigan Press, Ann Arbor
14. Bhaskar V, Gupt, SK, Ray AK (2000) Application of multiobjective optimization in chemical engineering, National University of Singapore
15. Schaffer JD (1985) Multiple objective optimization with vector evaluated genetic algorithms. In: Genetic algorithms and their applications: proceedings of the first international conference on genetic algorithms. Lawrence Erlbaum, London, pp 93–100
16. Fonseca CM, Fleming PJ (1993) Genetic algorithms for multi-objective optimization: formulation, discussion and generalization. In: Forrest S (ed) Proceedings of the fifth international conference on genetic algorithms. University of Illinois at Urbana-Champaign, Morgan Kauffman, Los Altos, pp 416–423
17. Srinivas N, Deb K (1994) Multiobjective optimization using nondominated sorting in genetic algorithms. Evol Comput 2(3):221–248

18. Horn J, Nafpliotis N (1993) Multiobjective optimization using the niched pareto genetic algorithm. Technical report IlliGAL report 93005, University of Illinois at Urbana Champaign, Urbana
19. Deb K, Agrawal S, Pratap A, Meyarivan T (2000) A fast elitist non-dominated sorting genetic algorithm for multiobjective-optimization: NSGA-II, KanGAL report 200001. Indian Institute of Technology, Kanpur
20. Coello Coello CA, Toscano Pulido G (2001a) A micro-genetic algorithm for multiobjective optimization. In: Zitzler E, Deb K, Thiele L, Coello Coello CA, Corne D (eds) First international conference on evolutionary multi-criterion optimization (Lecture notes in computer science no. 1993). Springer, Berlin, pp 126–140
21. Coello Coello CA, Toscano Pulido G (2001b) Multiobjective optimization using a micro-genetic algorithm. In: Lee S, Goodman ED, Wu A, Langdon WB, Voigt H-M, Gen M, Sen S, Dorigo M, Pezeshk S, Garzon MH, Burke E (eds) Proceedings of the genetic and evolutionary computation conference (GECCO'2001). Morgan Kaufmann, San Francisco, pp 274–282
22. Coello Coello CA, Lamont GB, Van Veldhuizen DA (2007) Evolutionary algorithms for solving multi-objective problems, 2nd edn. Springer, New York
23. Boussaïd I, Lepagnot J, Siarry P (2013) A survey on optimization metaheuristics. Inform Sci 237:82–117
24. Metropolis N, Rosenbluth A, Roseblunth M, Teller A, Teller E (1953) Equation of state calculations by fast computing machines. J Chem Phys 21(6):1087–1092
25. Kirkpatrick S, Gellatt C, Vecchi M (1983) Optimization by simulated annealing. Science 220 (4598):671–680
26. Cerny V (1985) A thermodynamic approach to the traveling salesman problem: an efficient simulation algorithm. J Optimiz Theory Appl 45(1):41–51
27. Serafini P (1994) Simulated annealing for multiple objective optimization problems. In: Tzeng G, Wang H, Wen U, Yu P (eds) Proceedings of the tenth international conference on multiple criteria decision making: expand and enrich the domains of thinking and application, vol 1. Springer, New York, pp 283–292
28. Ulungu E (1993) Optimisation Combinatoire multicritere: Determination de l'ensemble des soltions efficacies et methods interactives. PhD thesis, Faculté des Sciences, Université de Mons-Hainaut, Mons
29. Ulungu E, Teghem J, Fortemps P (1995) Heuristics for multi-objective combinatorial optimization by simulated annealing. In: Gu J, Chen G, Wei Q, Wang S (eds) Multiple criteria decision making: theory and applications. Proceedings of the 6th national conference on multiple criteria decision making. Sci-Tech, Windsor, pp 228–238
30. Ulungu E, Teghem J, Fortemps P, Tuyttens D (1999) MOSA method: a tool for solving multiobjective combinatorial optimization problems. J Multi Crit Decis Anal 8(4):221–236
31. Ulungu E, Teghem J, Ost C (1998) Efficiency of interactive multi-objective simulated annealing through a case study. J Oper Res Soc 49:1044–1050
32. Ray T, Gokarn R, Sha O (1995) A global optimization model for ship design. Comput Ind 26:175–192
33. Czyzag P, Jaszkiewicz A (1997) Pareto simulated annealing. In: Fandel G, Gal T (eds) Multiple criteria decision making. Proceedings of the XIIth international conference. Springer, Hagen, pp 297–307
34. Czyzag P, Jaszkiewicz A (1998) Pareto simulated annealing—a metaheuristic technique for multi-objective combinatorial optimization. A thermodynamic approach to the traveling salesman problem: an efficient simulation algorithm. J Multi Crit Decis Anal 7:34–47
35. Ruiz-Torres AJ, Enscore EE, Barton RR (1997) Simulated annealing heuristics for the average flow-time and the number of tardy jobs bi-criteria identical parallel machine problem. Comput Ind Eng 33(1–2):257–260
36. Nam D, Park CH (2000) Multiobjective simulated annealing: a comparative study to evolutionary algorithms. Int J Fuzzy Syst 2(2):87–97

37. Hansen MP (1997) Generating a diversity of good solutions to a practical combinatorial problem using vectorized simulated annealing. Technical report. Institute of Mathematical Modelling, Technical University of Denmark
38. Glover F (1986) Future paths for integer programming and links to artificial intelligence. Comput Oper 13(5):533–549
39. Gandibleux X, Mezdaoui N, Fréville A (1997) A tabu search procedure to solve combinatorial optimization problems. In: Caballero R, Ruiz F, Steuer RE (eds) Advances in multiple objective and goal programming, vol 455. Springer, New York, pp 291–300
40. Hansen MP (1998) Tabu search in multiobjective optimization: MOTS. In: Proceedings of the 13th international conference on multiple criteria decisions making, Cape Town, South Africa
41. Hansen M (2000) Tabu search for multiobjective combinatorial optimization: TAMOCO. Control Cybernet 29(3):799–818
42. Hertz A, Jaumard B, Ribeiro C, Filho WF (1994) A multi-criteria tabu search approach to cell formation problems in group technology with multiple objectives. RAIRO/Oper Res 28 (3):303–328
43. Baykasoğlu A (2001) Goal programming using multiple-objective tabu search. J Oper Res Soc 52(12):1359–1369
44. Baykasoğlu A, Owen S, Gindy N (1999) A taboo search based approach to find the Pareto optimal set in multiple objective optimization. Eng Optim 31(6):731–748
45. Ho S, Yang S, Ni G, Wong H (2002) A tabu method to find the Pareto solutions of multiobjective optimal design problems in electromagnetics. IEEE Trans Magn 38 (2):1013–1016
46. Jaeggi D, Asselin-Millerm C, Parks G, Kipouros T, Bell T, Clarkson J (2004) Multi-objective parallel tabu search. In: Parallel problem solving from nature (Lecture notes in computer science), vol 3242. Springer, New York, pp 732–741
47. Kulturel-Konak S, Smith AE, Norman BA (2006) Multi-objective tabu search using a multinomial probability mass function. Eur J Oper Res 169:918–931
48. Xu J, Sohoni M, McCleery M, Bailey TG (2006) A dynamic neighborhood based tabu search algorithm for real-world flight instructor scheduling problems. Eur J Oper Res 169:978–993
49. Dorigo M, Caro GD (1999) The ant colony optimization metaheuristic. In: Corne D, Dorigo M, Glover F (eds) New ideas in optimization. McGraw-Hill, New York
50. Colorni A, Dorigo M, Maniezzo V (1992) Distributed optimization by ant colonies. In: Varela FJ, Bourgine P (eds) Proceedings of the first European conference on artificial life. MIT, Cambridge, pp 134–142
51. Dorigo M, Maniezzo V, Colorni A (1996) The ant system: optimization by a colony of cooperating agents. IEEE Trans Syst Man Cybernet Part B 26(1):29–41
52. Dorigo M, Stützle T (2004) Ant colony optimization. MIT, Cambridge
53. Gambardella LM, Dorigo M (1995) Ant-Q: a reinforcement learning approach to the travelling salesman problem. In: Prieditis A, Russell S (eds) Proceedings of the 12th international conference on machine learning. Morgan Kaufmann, San Francisco, pp 252–260
54. Mariano CE, Morales E (1999) MOAQ an ant-Q algorithm for multiple objective optimization problems. In: Banzhaf W, Daida J, Eiben AE, Garzon MH, Honavar V, Jakiela M, Smith RE (eds) Genetic and evolutionary computing conference, vol 1. Morgan Kaufmann, San Francisco, pp 894–901
55. Mariano CE, Morales E (1999b) A multiple objective ant-Q algorithm for the design of water distribution irrigation networks. Technical Report HC-9904, Instituto Mexicano de Tecnología del Agua
56. Gambardella LM, Taillard É, Agazzi G (1999) MACS-VRPTW: a multiple ant colony system for vehicle routing problems with the time windows. In: Corne D, Dorigo M, Glover F (eds) New ideas in optimization. McGraw-Hill, New York, pp 63–76
57. Iredi S, Merkle D, Middendorf M (2001) Bi-criterion optimization with multi colony ant algorithms. In: Zitzler E, Deb K, Thiele L, Coello Coello CA, Corne D (eds) First

international conference on evolutionary multi-criterion optimization (Lecture notes in computer science no. 1993). Springer, Berlin, pp 358–372
58. Gagné C, Gravel M, Price WL (2000) Scheduling a single machine where set up times are sequence dependent using an ant colony heuristic. In: Abstract proceedings of ANTS'2000, pp 157–160
59. Gagné C, Price WL, Gravel M (2001) Scheduling a single machine with sequence dependent setup time using Ant Colony Optimization. Technical report 2001-003. Faculté des Sciences de L'Administration, Université Laval
60. McMullen PR (2001) An ant colony optimization approach to addressing a JIT sequencing problem with multiple objectives. Artif Intell Eng 15:309–317
61. T'kindt V, Monmarché N, Tercinet F, Laügt D (2002) An ant colony optimization algorithm to solve a 2-machine bi-criteria flowshop scheduling problem. Eur J Oper Res 142 (2):250–257
62. Storn R, Price K (1995) Differential evolution: a simple and efficient adaptive scheme for global optimization over continuous spaces. Technical Report TR-95-012. International Computer Science Institute
63. Storn R, Price K (1997) Differential evolution—a fast and efficient heuristic for global optimization over continuous spaces. J Global Optim 11:341–359
64. Price KV, Storn MR, Lampinen JA (2005) Differential evolution. A practical approach to global optimization. Springer, Heidelberg
65. Goldberg DE (1989) Genetic algorithms in search, optimization and machine learning. Addison-Wesley, Boston
66. Schwefel HP (1995) Evolution and optimum seeking. Wiley, New York
67. Mezura-Montes E, Velázquez-Reyes J, Coello Coello CA (2006) Comparing differential evolution models for global optimization. In: Cattolico M et al. (ed) 2006 genetic and evolutionary computation conference, vol 1. ACM Press, Seattle, pp 485–492
68. Chang C, Xu D, Quek H (1999) Pareto-optimal set based multiobjective tuning of fuzzy automatic train operation for mass transit system. IEEE Proc Electr Power Appl 146 (5):577–583
69. Bergey P (1999) An agent enhanced intelligent spreadsheet solver for multi-criteria decision making. In: Proceedings of the fifth Americas conference on information systems, Milwaukee, pp 966–968
70. Abbass HA, Sarker R, Newton C (2001) PDE: a pareto-frontier differential evolution approach for multi-objective optimization problems. In: Proceedings of the congress on evolutionary computation 2001, vol 2, pp 971–978
71. Abbass HA, Sarker R (2002) The Pareto differential evolution algorithm. Int J Artif Intell Tools 11(4):531–552
72. Sarker R, Abbass HA, Newton CS (2003) Solving two multi-objective optimization problems using evolutionary algorithm. In: Mohammadian M, Sarker RA, Yao X (eds) Computational intelligence in control. Idea Group Publishing, Hershey, pp 218–232
73. Madavan NK (2002) Multiobjective optimization using a Pareto differential evolution approach. In: Congress on evolutionary computation, vol 2, pp 1145–1150
74. Xue F, Sanderson AC, Graves RJ (2003) Pareto-based multiobjective differential evolution. In: Proceedings of 2003 congress on evolutionary computation, vol 2. IEEE Press, Canberra, pp 862–869
75. Xue F (2004) Multi-objective differential evolution: theory and applications. PhD thesis, Rensselaer Polytechnic Institute
76. Babu B, Jehan MML (2003) Differential evolution for multi-objective optimization. In: Proceedings of 2003 congress on evolutionary computation, vol 4. IEEE Press, pp 2696–2703
77. Parsopoulos K, Taoulis D, Pavlidis N, Plagianakos V, Vrahatis M (2004) Vector evaluated differential evolution for multiobjective optimization. In: Proceedings of 2004 congress on evolutionary computation, vol 1. IEEE Press, pp 204–211

78. Iorio AW, Li X (2004) Solving rotated multiobjective optimization problems using differential evolution. In: AI 2004: advances in artificial intelligence proceedings (Lecture notes in artificial intelligence), vol 3339. Springer, New York, pp 861–872
79. Sharma S, Rangaiah GP (2013) Multi-objective optimization of a bio-diesel production process. Fuel 103:269–277
80. Kennedy J, Eberhart RC (1995) Particle swarm optimization. In: Proceedings of the 1995 I.E. international conference on neural networks, 1942-1948
81. Moore J, Chapman R (1999) Application of particle swarm to multiple objective optimization. Department of Computer Science and Software Engineering, Auburn University
82. Ray T, Liew K (2002) A swarm metaphor for multiobjective design optimization. Eng Optim 34(2):141–153
83. Parsopoulus K, Vrahatis M (2002) Particle swarm optimization method in multiobjective problems. In: Proceedings of the 2002 ACM symposium on applied computing. ACM Press, pp 603–607
84. Hu X, Eberhart R (2002) Multiobjective optimization using dynamic neighborhood particle swarm optimization. In: Congress on evolutionary computation, vol 2, pp 1677–1681
85. Coello Coello CA, Salazar Lechuga M (2002) MOPSO: a proposal for multiple objective particle swarm optimization. In: Congress on evolutionary computation, vol 2, pp 1051–1056
86. Bhaskar V, Gupta SK, Ray AK (2000) Applications of multiobjective optimization in chemical engineering. Rev Chem Eng 16(1):1–54
87. Reay D, Ramshaw C, Harvey A (2008) Process intensification. Engineering for efficiency, sustainability and flexibility. Elsevier, Amsterdam
88. Cheng S-H, Chen H-J, Chang H, Chang C-K, Chen Y-M (2008) Multi-objective optimization for two catalytic membrane reactors—methanol synthesis and hydrogen production. Chem Eng Sci 63(6):1428–1437
89. Gómez-Castro FI, Rodríguez-Ángeles MA, Segovia-Hernández JG, Gutiérrez-Antonio C, Briones-Ramírez A (2008) Optimal designs of multiple dividing wall columns. Chem Eng Technol 34(12):2051–2058
90. Gutiérrez-Antonio C, Briones-Ramírez A (2009) Pareto front of ideal petlyuk sequences using a multiobjective genetic algorithm with constraints. Comput Chem Eng 33(2):454–464
91. Vázquez-Castillo JA, Venegas-Sánchez JA, Segovia-Hernández JG, Hernández-Escoto H, Hernández S, Gutiérrez-Antonio C, Briones-Ramírez A (2009) Design and optimization, using genetic algorithms, of intensified distillation systems for a class of quaternary mixtures. Comput Chem Eng 33(11):1841–1850
92. Miranda-Galindo EY, Segovia-Hernández JG, Hernández S, Gutiérrez-Antonio C, Briones-Ramírez A (2011) Reactive thermally coupled distillation sequences: Pareto front. Ind Eng Chem Res 50(2):926–938
93. Behroozsarand A, Shafiei S (2011) Multiobjective optimization of reactive distillation with thermal coupling using non-dominated sorting genetic algorithm-II. J Nat Gas Sci Eng 3 (2):365–374
94. Miranda-Galindo EY, Segovia-Hernández JG, Hernández S, Bonilla-Petriciolet A, Rangaiah GP (2012) Multiobjective optimization in distillation with reactor-side for hydrodesulfurization process of diesel. Comput Aided Chem Eng 30:682–686
95. Torres-Ortega CE, Segovia-Hernández JG, Gómez-castro FI, Hernández S, Bonilla-Petriciolet A, Rong BG, Errico M (2013) Design, optimization and controllability of an alternative process based on extractive distillation for an ethane–carbon dioxide mixture. Chem Eng Process Process Intensif 74:55–68
96. Bravo-Bravo C, Segovia-Hernández JG, Hernández S, Gómez-castro FI, Gutiérrez-Antonio C, Briones-Ramírez A (2013) Hybrid distillation/melt crystallization process using thermally coupled arrangements: optimization with evaluative algorithms. Chem Eng Process Process Intensif 67:25–38

97. Cadavid JG, Godoy-Silva RD, Narvaez PC, Camargo M, Fonteix C (2013) Biodiesel production in a counter-current reactive extraction column: modelling, parametric identification and optimisation. Chem Eng J 228:717–723
98. Micovic J, Beierling T, Lutze P, Sadowski G, Górak A (2013) Design of hybrid distillation/melt crystallisation processes for separation of close boiling mixtures. Chem Eng Process Process Intensif 67:16–24
99. Beierling T, Micovic J, Lutze P, Sadowski G (2014) Using complex layer melt crystallization models for the optimization of hybrid distillation/melt crystallization processes. Chem Eng Process Process Intensif 85:10–23
100. Torres-Ortega CE, Segovia-Hernández JG, Gómez-Castro FI, Hernández S, Bonilla-Petriciolet A, Rong BG, Errico M (2014) Optimization of alternative distillation sequences for natural gas sweetening. Comput Aided Chem Eng 33:1201–1206
101. Micovic J, Werth K, Lutze P (2014) Hybrid separations combining distillation and organic solvent nanofiltration for separation of wide boiling mixtures. Chem Eng Res Des 92 (11):2131–2147
102. Errico M, Pirellas P, Torres-Ortega CE, Rong BG, Segovia-Hernández JG (2014) A combined method for the design and optimization of intensified distillation systems. Chem Eng Process Process Intensif 85:69–76
103. Domingues L, Pinheiro CIC, Oliveira NMC (2014) Optimal design of reactive distillation systems: application to the production of ethyl tert-butyl ether (ETBE). Comput Chem Eng 64:81–94
104. Woinaroschy A (2014) Multiobjective optimal design for biodiesel sustainable production. Fuel 135:393–405
105. Gutiérrez-Antonio C, Gómez-Castro FI, Hernández S, Briones-Ramírez A (2015) Intensification of a hydrotreating process to produce biojet fuel using thermally coupled distillation. Chem Eng Process Process Intensif 88:29–36
106. Gómez-Castro FI, Segovia-Hernández JG, Hernández S, Gutiérrez-Antonio C, Briones-Ramírez A, Gamiño-Arroyo Z (2015) Design of non-equilibrium stage separation systems by a stochastic optimization approach for a class of mixtures. Chem Eng Process Process Intensif 88:58–69
107. Sushil K, Datta D, Babu BV (2011) Estimation of equilibrium parameters using differential evolution in reactive extraction of propionic acid by tri-n-butyl phosphate. Chem Eng Process Process Intensif 50(7):614–622
108. Jaime-Leal JE, Bonilla-Petriciolet A, Bhargava V, Fateen SEK (2015) Nonlinear parameter estimation of e-NRTL model for quaternary ammonium ionic liquids using Cuckoo search. Chem Eng Res Des 93:464–472

Chapter 10
Process Intensification in the Production of Liquid Biofuels: Strategies to Minimize Environmental Impact

**Fernando I. Gómez-Castro, Irene Cano-Rodríguez,
and Zeferino Gamiño-Arroyo**

Abstract Process intensification is a branch of Chemical Engineering which has taken importance in the last decades, because through its application it is possible to obtain alternative processes with smaller/multitask equipment and reduced energy requirements. Such reductions may have a positive benefit to the environment, since smaller equipment implies less use of material for its construction; while reductions on energy requirements imply lowering direct emissions of greenhouse gases to the atmosphere. In this contribution, examples of intensification alternatives recently proposed for enhancement of processes is presented. In particular, process intensification in the production of liquid biofuels is analyzed. The application of such tool in the production of biofuels, which are expected to reduce environmental impact when compared to the use of fossil fuel, has both energy savings and further reductions in terms of pollutant emissions.

10.1 Introduction

It is well known that human population is growing at an accelerated rate. Estimated human population in the year 2015 is about 7.2 billion, and it has been predicted that by the year 2050, the number of individuals will increase to 9.15 billion [1]. To keep the lifestyle of modern populations in big cities, several products and services are required. Nevertheless, any human activity intended to obtain useful products and/or services will have a direct impact on the environment. A clear example is the production of different forms of energy. Electricity is produced mainly through the generation of steam by burning fossil fuels. Heating

---

F.I. Gómez-Castro (✉) • I. Cano-Rodríguez • Z. Gamiño-Arroyo
Division de Ciencias Naturales y Exactas, Departamento de Ingenieria Quimica, Universidad de Guanajuato, Noria Alta s/n Col. Noria Alta, Campus Guanajuato, Guanajuato, Mexico
e-mail: fgomez@ugto.mx; irene@ugto.mx

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_10

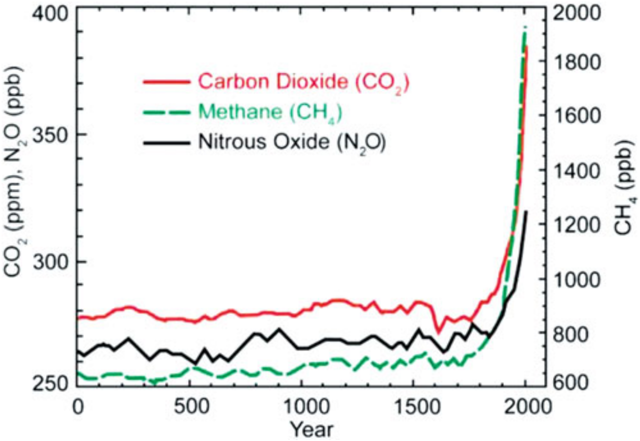


Fig. 10.1 Variations in the concentration of greenhouse gases in the atmosphere [2]

requirements in industrial processes are usually satisfied through the use of steam, which is once more obtained by burning fossil fuels. Transportation sector has a great dependence on the derivatives of petroleum, since the engines of many vehicles (terrestrial or aerial) require burning fossil fuels to work. When combustion of fossil fuels occurs, many gases are released and accumulated into the terrestrial atmosphere. Among those gases (also known as greenhouse gases), carbon oxides, nitrogen oxides, sulfur oxides, and methane are the most important, and particulate matter (PM) is also released. Changes in greenhouse gases concentration with time can be seen in Fig. 10.1. An important increase in the concentration of such components is observed from around 1700 to 1800, when the Industrial Revolution began. It is also worthy to observe that from the beginning of Industrial Revolution, no visible reduction in greenhouse gases concentration is perceived.

The high concentration of the aforementioned gases on the atmosphere has as consequence that only a small fraction of the solar radiation entering into the planet is released back into the outer space. This phenomenon is known as greenhouse effect. Due to the accumulation of energy, the temperature on the surface of the planet is increased, and global warming occurs (Fig. 10.2). Of course, human activity is not the only source of CO_x, NO_x, etc., but it has contributed to its accelerated generation.

Many options have been proposed to reduce the environmental impact of human activities. The use of renewable energy sources is an option which must be explored in the next decades in order to reduce the emissions of greenhouse gases into the atmosphere. Production of biofuels from biomass is considered as one of the most promissory alternatives in the transportation sector. Of course, it is also important to educate the population about the need of living in a more sustainable way.

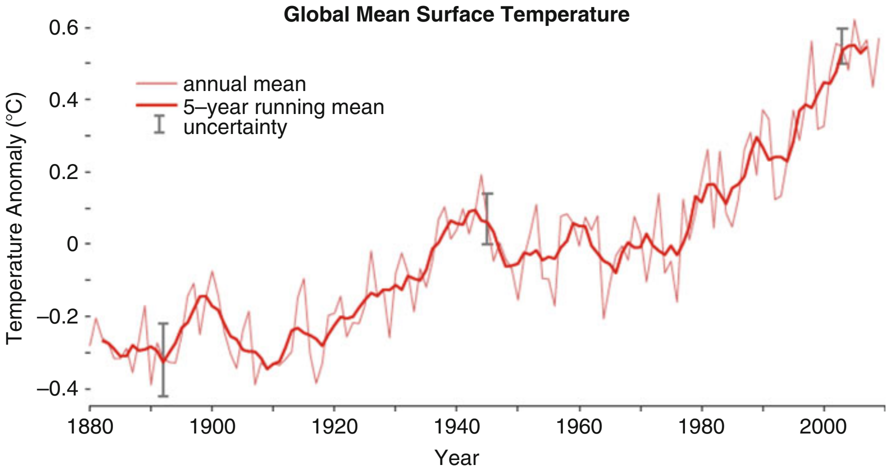


Fig. 10.2 Increase in the mean temperature on surface, 1880–2000 [3]

In the area of process engineering, it is of particular interest to design processes with low energy requirements and the use of a minimal number of equipment. This is the basis from which the area of process intensification arises. Process intensification is a branch of Chemical Engineering which main objective is to propose production processes in plants as small as possible and with low total energy requirements. To reduce the size of the plants, the scope is reducing the size of equipment or the number of operations in the process, or using multifunction equipment. To reduce energy requirements, the proper use of energetic sources inside the process is mandatory. Since energy requirements of industrial processes are usually satisfied with steam, for which production is necessary to burn some kind of fuel (usually fossil fuels), by reducing energy requirements a direct reduction on environmental impact is obtained.

In this chapter, a review of intensification proposals for processes intended to produce environment friendly products is presented. The analysis is focused to liquid biofuels, in particular biodiesel, bioethanol, and bio-jet fuel. Different intensification alternatives are discussed, and their main characteristics are commented. It is clear that biofuels are clean and renewable products, thus if process intensification is applied to their production processes, their global environmental footprint will be even lower.

10.2 Process Intensification in the Production of Liquid Biofuels

Biofuels are alternative sources of energy, which are intended to partially substitute the traditional petroleum-derived fuels. Such alternative fuels must be renewable to ensure their availability; and they must also have lower environmental impact than

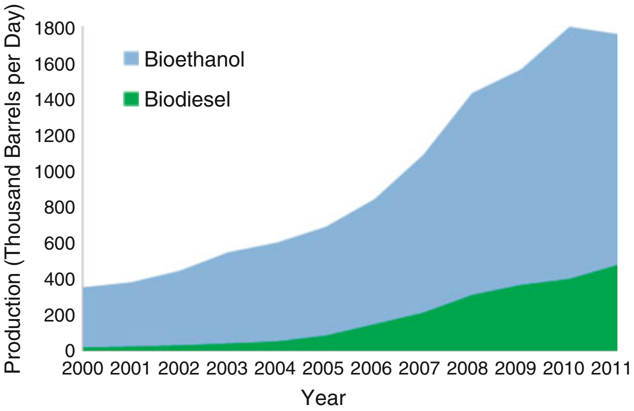


Fig. 10.3 World biofuels production, 2000–2011 [4]

its fossil counterparts. Biofuels are usually obtained from biomass, which is treated to obtain solid, liquid, or gaseous fuels. An important limitation which must be mentioned is that the biomass used as raw material must not be also used for human alimentation. Liquid biofuels are considered as mid-term substitutes for the fossil fuels used in the transport sector, so they have gained interest over the last years. In Fig. 10.3, world production of biodiesel and bioethanol is shown.

A positive trend in production of biofuels is observed in Fig. 10.3, and it is expected that production keeps growing in the next years, together with the efforts looking for more efficient raw materials.

Production of liquid biofuels involves several stages, from obtaining the renewable biomass, its transportation, the production process of the biofuel, and then delivering the product to the consumer. In this chapter, the focus will be on the processes for obtaining biofuels and the proposals for the intensification of such processes.

10.2.1 Biodiesel

Biodiesel is a renewable fuel, which can be used to partially substitute fossil diesel. It is mainly obtained from vegetable oils and/or animal fats. The use of renewable oils as fuels is not new. In the Paris Exposition of 1900, Rudolph Diesel used peanut oil to test one of the engines he designed [5]. Nevertheless, vegetable oils were not able to compete with the low prices of fossil fuels. Furthermore, the direct use of vegetable oils in diesel engines caused some issues, mainly due to their high viscosity. Nowadays, with the increase in the prices of fossil fuels, the interest on using renewable sources of energy has grown. Thus, methods to reduce the viscosity of the oils have been developed. Is through those methods that biodiesel is

Table 10.1 Properties of fossil diesel and biodiesel [6]

	Diesel (no. 1-D)	Diesel (no. 2-D)	Biodiesel
Flash point (minimum, °C)	38	52	130
Water and sediment, % max.	0.05	0.05	0.05
90 % distilled, °C	288	338	360
Viscosity at 40 °C (minimum, mm^2/s)	1.3	1.9	1.9
Ash, % max	0.01	0.01	0.02
Sulfur, % max	0.05	0.05	0.05
Cetane number, minimum	40	40	47

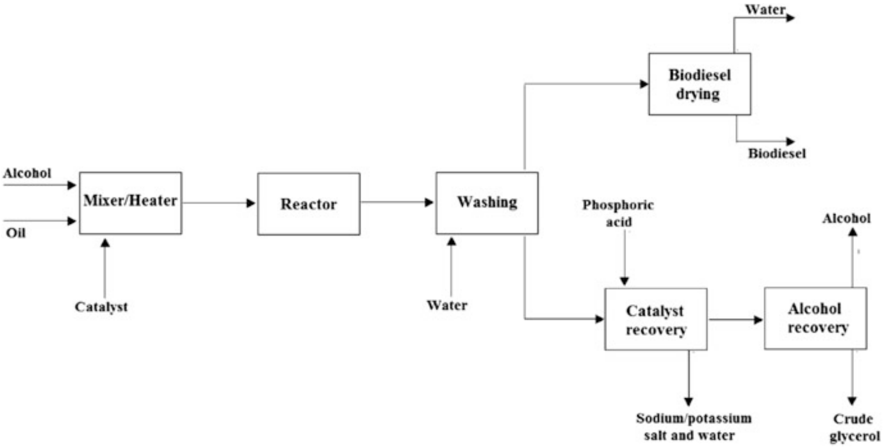


Fig. 10.4 Simplified flowsheet for the catalytic biodiesel process. Adapted from [7]

obtained. A comparison between physical properties of fossil diesel and biodiesel is presented in Table 10.1.

The most common method to produce biodiesel involves the transesterification of the triglycerides (and esterification of the fatty acids) contained in vegetable oils and animal fats, obtaining alkyl esters and glycerol. The reaction is catalyzed with basic catalysts, such as sodium or potassium hydroxide, although some approaches uses sulfuric acid to promote the reaction. Nevertheless, basic catalysts are very sensitive to the presence of free fatty acids and water in the raw material, and saponification reactions may compete with transesterification, reducing the biodiesel yield and increasing the number of purification steps. Figure 10.4 shows a simplified flowsheet of the conventional, basis-catalyzed process for biodiesel production.

The use of novel reaction technology is one of the explored areas in process intensification for biodiesel production. Boucher et al. [8] proposed a laminar flow system for the simultaneous production of biodiesel and separation of the by-products. In particular, the formation of two phases allows the separation of biodiesel in the upper layer and glycerol in the lower layer. Other work reported the use of a static mixer reactor enhanced by ultrasound for the esterification of an oil with a 12.785 wt% of free fatty acids [9]. The use of microchannel reactors has also been reported for the production of biodiesel. Such reactors are small and their scale-up can be achieved by adding more reactors in parallel [10]. It has been reported that microchannel reactors achieve high heat transfer rates, reducing energy consumption when compared with a conventional batch stirred reactor [10, 11]. Microchannel reactors also enhance mass transfer [12], which is one of the main limitations in the traditional biodiesel production due to the formation of two phases. The use of rotating tube reactors has also been reported for the production of biodiesel, where temperatures of 40–60 °C and pressure of 1 atm is required. Such reactors require little space and are easy to scale-up [10]. The use of microstructure reactors under supercritical conditions has also been reported. Such systems may achieve full conversion in less than 30 s of residence time over a heterogeneous catalyst [13].

Another approach for the intensification of the biodiesel processes involves simultaneous reaction and separation. Example of this philosophy are the membrane reactors, where while the reaction occurs, the small molecules selectively passes through the membrane and the oil is retained [14]. It has been reported that, for a membrane reactor, the required concentration of basic catalyst is considerable lower than that employed in the traditional process [15]. Different kinds of membranes have been proposed for those reactors, such as biocatalytic membranes [16], microporous membranes [17], and composite membranes [18], among others.

It has also been reported that the use of reaction systems combined with staged separation processes. A clear example of this approach is reactive distillation. In reactive distillation, reaction(s) occur in a distillation tower, with trays or packed, while simultaneously, the by-products are separated. This causes the reaction equilibrium to be shifted to the products side, enhancing conversion and selectivity. Kiss et al. [19] proposed the use of reactive distillation by using a heterogeneous catalyst. They established that zeolites and ion-exchange resins are not suitable for the production of biodiesel by reactive distillation. Different catalysts have been proposed as good alternatives, such as sulfated zirconia [19], sulfated titania, and sulfated tin oxides [20]. Heat integration for a reactive distillation column with sulfated zirconia has also been proposed [21]. Other advantages of using catalytic reactive distillation are that no excess of alcohol is required and there is no need for a catalyst neutralization step [22]. Heterogeneous reactive distillation, nevertheless, requires a high active catalyst and has hydraulic constraint that limits the maximum residence time of the liquid phase [20]. Research has also been conducted to obtain biocatalysts for the production of biodiesel by reactive distillation or reactive extraction. The use of lipases immobilized on magnetic structures [23, 24] is an example of such approaches. Nevertheless, it has been established that the cost of the lipase is one of the main limitations to its use at industrial level, and more research is required to define a systematic study on the immobilization technology and the determination of optimal operation conditions [25]. On the other hand, homogeneous reactive distillation has also been proposed for the esterification of fatty acids after a hydrolysis step in a supercritical process [26].

Other combined approaches for simultaneous reaction/separation involves the use of reactive absorption in a tower with solid acid catalyst. In such an operation, required temperatures are lower than in reactive distillation, thus there is lower risk of thermal decomposition of biodiesel [27]. In other work, the reactive absorption process is enhanced by heat integration [28].

In the case of catalytic reactive distillation, further energy savings can be achieved by using thermally coupled structures. In general, thermally coupled distillation systems make use of the composition profiles of the column and the energy contents of the streams to further reduce energy requirements. One of the most known thermally coupled systems is the dividing wall column, because it has the highest energy savings among the thermally coupled sequences for many cases. The use of a reactive dividing wall column (RDWC) for the production of biodiesel has been recently proposed. Kiss et al. [29, 30] presented the proposal of a RDWC for an industrial application at Akzo Nobel. They claim that the RDWC structure has the capacity to solve the problem of production shifts required by market demand changes. RDWC are complex systems, and its design is not a trivial task. Rigorous optimization of a RDWC for the production of biodiesel has been reported through the use of genetic algorithms [31] and simulated annealing [32]. Another proposal is using a dividing wall column for the separation of the mixture methanol/water/glycerol, usually obtained in biodiesel synthesis [33].

As it can be seen, many alternatives for the intensification of processes for the production of biodiesel have been proposed. There are approaches on which the design of the reactor is modified to reduce its size. Nevertheless, almost all the existent reports are only at laboratory or pilot level. The other approaches involve the simultaneous transesterification/esterification and purification, for which industrial application has already been proven.

10.2.2 Bioethanol

Bioethanol is intended to partially substitute gasoline in terrestrial transportation. It is nothing more than ethanol obtained from renewable sources. It is one of the most promising biofuels, with the capacity of acting as an additive for gasoline, reducing emissions of greenhouse gases. The first reported uses of ethanol as fuel date back to 1907. By the first years of the twentieth century, mixtures of alcohol and gasoline were used on farms in the United States. Nevertheless, with the reductions on gasoline prices, the use of ethanol as fuel was minimized and petroleum-based gasoline turned into the main fuel for vehicle engines [34]. With comparison purposes, some properties of ethanol and gasoline are presented in Table 10.2.

Bioethanol can be produced using raw material with high contents of sugars, such as sugarcane, sweet sorghum, and sugar beet; starchy material, such as wheat or corn; or lignocellulosic biomass, such as wood, straw, and grasses [36]. Algae have been recently proposed as biomass with high contents of starch [37]. The use of lignocellulosic materials appears to be the best option because such materials are

Table 10.2 Properties of ethanol and gasoline [35]

	Ethanol	Gasoline
Density (g/cm^3)	0.785	0.737
Normal boiling point (°C)	78.00	38–204
Lower heating value (kJ/g)	26.87	43.47
Sulfur content (ppm)	0.00	~200
Vapor pressure at 37.8 °C (kPa)	17	65
Flash point (°C)	13	−40
Autoignition temperature (°C)	366	300
Flammability limits (°C)	13–42	−40 to 18

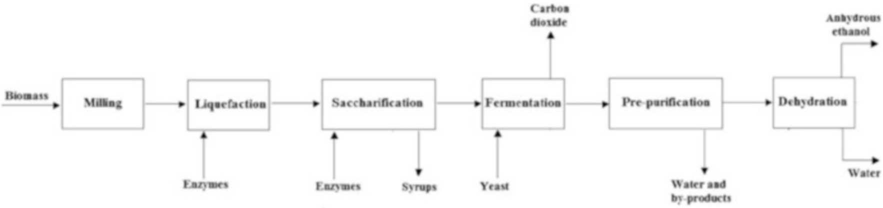


Fig. 10.5 Simplified flowsheet for the bioethanol process. Adapted from [7]

usually considered agricultural waste. Furthermore, lignocellulosic materials don't compete with human alimentation, as occurred with first-generation ethanol sources as corn and sugarcane.

In general, bioethanol production takes place in three steps, but the required number of operations depends on the nature of the components of raw material. In a first stage, a thermochemical pretreatment takes place. This stage is necessary for raw materials with high content of lignin, because the presence of that component makes difficult, the enzymatic activity. The most common pretreatment implies using sulfuric acid [38]. In a second stage, cellulases and hemicellulases are saccharified through enzymatic procedures. Finally, the released sugars are fermented into ethanol by specialized enzymes [38].

Once fermentation occurred, a mixture of components is obtained, mainly ethanol and water. Nevertheless, to use ethanol as fuel in engines, it must be basically anhydrous. Thus, a purification process is required. Nevertheless, an additional issue appears when purifying ethanol, because the binary mixture ethanol–water presents an azeotrope at 96 wt% of ethanol [39]. Some methods which are used for the dehydration of ethanol are heterogeneous azeotropic distillation, extractive distillation, adsorption, and pervaporation [40, 41]. Nevertheless, the most common purification process implies the use of conventional distillation to take the mixture to a composition close to the azeotrope (about 95 wt% of ethanol), and then, in a second column, using extractive distillation to obtain high-purity ethanol, over 99.8 wt% [42]. In Fig. 10.5, a general process flowsheet for the production of bioethanol from non-lignocellulosic material is shown.

For the pretreatment of lignocellulosic material, different combinations of processes have been proposed with positive results. To mention some examples, the use of sulfuric acid combined with ball milling [43, 44], hot-compressed water with ball milling [45], and microwave irradiation with ionic liquid treatment [46] have been reported.

Some intensification alternatives in the reactive step are discussed now. Ben Chaabane [47] proposed the use of a two-stage bioreactor with cell-recycle, reporting an ethanol productivity of 40 g/L h with no residual substrate concentration. Masuda et al. [48] proposed a reactor with a Taylor–Couette flow for the continuous gelatinization and hydrolysis of starch. Ikwebe [49] proposed performing simultaneously saccharification and fermentation in an oscillatory baffled reactor. According to the reported results, the proposed system increased significantly the yields when compared to a stirred tank reactor. In order to achieve simultaneous optimal conditions for both reactions, the use of thermotolerant yeasts has been proposed [50]. The use of ultrasound has also been reported to enhance enzymatic hydrolysis [51]. It has been reported that ultrasound helps yield to be increased, reducing processing time and enzyme consumption. Novy et al. [52] have established that strain evolution can be a tool for the intensification of ethanol production, since through this approach the consumption rate of sugars into ethanol is increased, while yield of by-products is reduced.

Dehydration of ethanol is a step with high energy demand in the bioethanol process [53], mainly due to the inherent low thermodynamic efficiency of distillation. Thus, in this stage of the process intensification, efforts have been focused to reduce energy requirements. Errico and Rong [54] proposed thermally coupled arrangements alternative to the conventional distillation/extractive distillation/entrainer recovery sequence. Different degrees of coupling produce a set of configurations. According to the reported results, all the proposed configurations have small reductions on energy requirements when compared to the base case, but high reductions in total annual cost. Similar results have been reported for sequences with dividing wall columns [55]. Nevertheless, non-DWC sequences with side stream have better control properties [56]. Kiss and Ignat [57] proposed the combination of extractive distillation and thermally coupled distillation, resulting in an extractive dividing wall column for the separation of the mixture water/ethanol. For a mixture with 10 wt% of ethanol, energy savings of about 17 % are reported. Kiss and Suszwalak [58] proposed the use of extractive and azeotropic dividing wall columns for the purification of bioethanol. For a mixture of 85 mol% of ethanol (about 93.5 wt%, close to the azeotropic composition), it has been reported that the extractive dividing wall column allows energy savings of about 10 % over the conventional configuration, while 20 % of energy savings are achieved with the azeotropic dividing wall column. Other intensification proposal for the purification of ethanol involves the use of reactive distillation [59]. In this approach, water reacts with ethylene oxide, producing ethylene glycol, which can be easily separated from ethanol. According to the results reported by Tavan and Hosseini [59], the use of reactive distillation shows advantages in terms of energy requirements and total annual costs over a traditional scheme based on azeotropic distillation.

10.2.3 Bio-jet fuel

Bio-jet fuel is a biofuel which is intended to partially substitute commercial jet fuel (Jet-A and Jet-A1). It consists on linear and branched hydrocarbons with 8–16 carbons, obtained from renewable sources. Bio-jet fuel is a special case of biofuel, because it must have a chemical composition very similar to its fossil counterpart. In the case of biodiesel and bioethanol, their chemical composition is quite different from diesel and gasoline, respectively. Nevertheless, due to the low temperature and low pressure occurring on flights, bio-jet fuel must have almost the same properties (particularly freezing and flash temperatures) of fossil jet fuel. Furthermore, since bio-jet fuel contains no aromatics, it must be used in mixtures with fossil jet fuel to keep the desired properties. Properties for conventional jet fuels are shown in Table 10.3. Bio-jet fuel must accomplish with very similar properties.

There are many proposed strategies for the production of bio-jet fuel. The process developed by UOP Honeywell is in an advanced stage of development, with technology used in a refinery which produces 30 million gallons (about 115 million liters) of renewable fuels per year [62]. Bio-jet fuel obtained by this method accomplishes the characteristics required for an aviation fuel. The process consists in two reactive steps. In the first one, the raw material (usually a vegetable oil) reacts with hydrogen in a hydrotreating reactor, where linear hydrocarbons are obtained as products, together with carbon dioxide and water. Linear hydrocarbons are then treated in a hydroisomerization/hydrocracking reactor, where desired chain lengths are obtained and a proportion of the linear hydrocarbons are ramified. Then, the mixture of linear and ramified hydrocarbons is refined in a distillation train, where fractions of light hydrocarbons, bio-jet fuel, and green diesel are obtained. A simplified flowsheet for the production process of bio-jet fuel from vegetable oils is shown in Fig. 10.6.

Since the production of bio-jet fuel is a relatively recent area of interest, there are only few proposals for its intensification. For the reactive steps, Sinha et al. [64] proposed the use of microchannel and monolithic reactors to enhance the mass and heat transfer in the hydroprocessing reactions. Using a Ni–Mo catalyst supported by gamma alumina, the authors report a higher selectivity to kerosene. Furthermore, it has been reported that the monolithic reactor shows lower yield of oligomeric products when compared to the microchannel reactor.

Table 10.3 Properties of jet fuels [60, 61]

	Jet-A	Jet-A1
Boiling range (°C)	170–300	170–300
Freezing temperature (°C)	−40	−47
Flash temperature (minimum, °C)	38	38
Density at 15 °C (kg/m^3)	775–840	775–840
Viscosity at 20 °C (maximum, mm^2/s)	8.0	8.0
Energy content (MJ/kg)	43.28	43.28

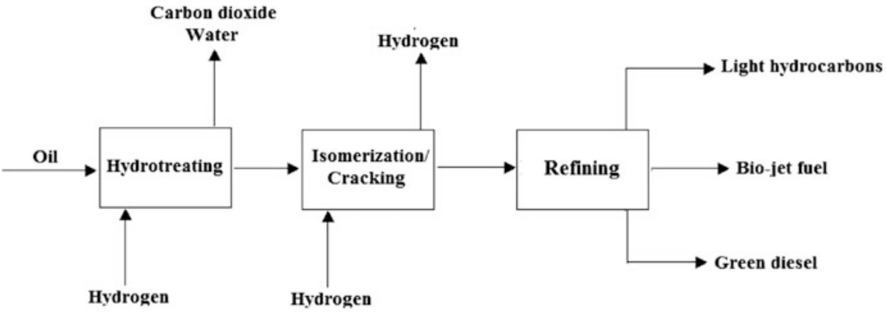


Fig. 10.6 Simplified flowsheet for the bio-jet fuel process. Adapted from Gutiérrez-Antonio et al. [63]

In the case of the refining section, Gutiérrez-Antonio et al. [63] proposed the use of thermally coupled distillation sequences to perform the separation of the stream leaving the isomerization reactor into the three main fractions (light hydrocarbons, bio-jet fuel, and green diesel). The authors performed the design and optimization of the distillation sequences through a stochastic approach. It is reported that a thermally coupled direct sequence is the best option in terms of energy requirements to obtain the desired fractions, with energy savings around 15–20 % when compared to conventional distillation sequences. Furthermore, reported results show that the use of a dividing wall column is not recommendable for the mixture under analysis.

10.3 Conclusions

Process intensification is a tool which can be helpful for the development of low-cost processes with better use of physical spaces and low energy requirements. Those reductions in energy requirements have a direct impact on greenhouse emissions, because lower quantities of fossil fuels are burned and thus less carbon dioxide, methane, and other gases are released to the atmosphere. Thus, application of process intensification principles can be useful to reduce environmental footprints in the production industry. In this contribution, examples of intensification application on processes for the production of biofuels are presented. Such approaches are an important effort to reduce environmental impact on both sides: the product itself and its production process.

References

1. Goldstone JA (2010) The new population bomb: the four megatrends that will change the world. http://www.foreignaffairs.com/articles/65735/jack-a-goldstone/the-new-population-bomb. Accessed 8 Dec 2014

2. Environmental Protection Agency (2014) Climate change science overview. http://www.epa.gov/climatechange/science/overview.html. Accessed 10 Dec 2014
3. Riebeek H (2010) Global warming. http://earthobservatory.nasa.gov/Features/GlobalWarming/printall.php. Accessed 10 Dec 2014
4. Energy Information Administration (2014) International energy statistics. http://www.eia.gov/cfapps/ipdbproject/IEDIndex3.cfm. Accessed 11 Dec 2014
5. Altin R, Cetinkaya S, Yücesu HS (2001) The potential of using vegetable oil fuels as fuel for diesel engines. Energy Convers Manage 42:529–538
6. Schobert HH (2013) Chemistry of fossil fuels and biofuels. Cambridge University Press, New York
7. Drapcho CM, Nhuan NP, Walker TH (2008) Biofuels engineering process technology. McGraw-Hill, New York
8. Boucher MB, Weed C, Leadbeater NE et al (2009) Pilot scale two-phase continuous flow biodiesel production via novel laminar flow reactor-separator. Energy Fuels 23:2750–2756
9. Somnuk K, Smithmaitrie P, Prateepchaikul G (2013) Two stages continuous process of methyl ester from high free fatty acid mixed crude palm oil using static mixer coupled with high-intensity of ultrasound. Energy Convers Manage 75:302–310
10. Qiu Z, Zhao L, Weatherley L (2010) Process intensification technologies in continuous biodiesel production. Chem Eng Process 49:323–330
11. Wen Z, Yu X, Tu ST et al (2009) Intensification of biodiesel synthesis using zigzag micro-channel reactors. Bioresour Technol 100:3054–3060
12. Dai JY, Li DY, Zhao YC et al (2014) Statistical optimization for biodiesel production from soybean oil in a microchannel reactor. Ind Eng Chem Res 53:9325–9330
13. Schürer J, Thiele R, Wiborg O et al (2014) Synthesis of biodiesel in microstructures reactors under supercritical reaction conditions. Chem Eng Trans 37:541–546
14. Kiss AA, Bildea CS (2012) A review of biodiesel production by integrated reactive separation technologies. J Chem Technol Biotechnol 87:861–879
15. Dube MA, Tremblay AY, Liu J (2007) Biodiesel production using a membrane reactor. Bioresour Technol 98:639–647
16. Machsun AL, Gozan M, Nasikin M et al (2010) Membrane microreactor in biocatalytic transesterification of triolein for biodiesel production. Biotechnol Bioprocess Eng 15:911–916
17. Baroutian S, Aroua MK, Raman AAA et al (2011) A packed bed membrane reactor for production of biodiesel using activate carbon supported catalyst. Bioresour Technol 102:1095–1102
18. Shi W, He B, Cao Y et al (2013) Continuous esterification to produce biodiesel by SPES/PES/NWF composite catalytic membrane in flow-through membrane reactor: experimental and kinetic studies. Bioresour Technol 129:100–107
19. Kiss AA, Omota F, Dimian AC et al (2006) The heterogeneous advantage: biodiesel by catalytic reactive distillation. Top Catal 40:141–150
20. Kiss AA, Dimian AC, Rothenberg G (2008) Biodiesel by catalytic reactive distillation powered by metal oxides. Energy Fuels 22:598–604
21. Kiss AA (2011) Heat-integrated reactive distillation process for synthesis of fatty esters. Fuel Process Technol 92:1288–1296
22. de Lima da Silva N, Garcia Santander CM, Batistella CB et al (2010) Biodiesel production from integration between reaction and separation system: reactive distillation process. Appl Biochem Biotechnol 161:245–254
23. Xie W, Ma N (2009) Immobilized lipase on Fe3O4 nanoparticles as biocatalyst for biodiesel production. Energy Fuels 23:1347–1353
24. Dussan KJ, Cardona CA, Giraldo OH et al (2010) Analysis of a reactive extraction process for biodiesel production using a lipase immobilized on magnetic nanostructures. Bioresour Technol 101:9542–9549
25. Robles-Medina A, González-Moreno PA, Esteban-Cerdán L et al (2009) Biocatalysis: towards ever greener biodiesel production. Biotechnol Adv 27:398–408

26. Gómez-Castro FI, Rico-Ramírez V, Segovia-Hernández JG et al (2013) Simulation study on biodiesel production by reactive distillation with methanol at high pressure and temperature: impact on costs and pollutant emissions. Comput Chem Eng 52:204–215
27. Kiss AA (2009) Novel process for biodiesel by reactive absorption. Sep Purif Technol 69:280–287
28. Kiss AA, Bildea CS (2011) Integrated reactive absorption process for synthesis of fatty esters. Bioresour Technol 102:490–498
29. Kiss AA, Pragt JJ, van Strien CJG (2009) Reactive dividing-wall column—how to get more with less resources? Chem Eng Commun 196:1366–1374
30. Kiss AA, Pragt JJ, van Strien CJG (2009) Reactive dividing-wall column—defying equilibrium restrictions. Chem Prod Process Model 4:1–13
31. Miranda-Galindo EY, Segovia-Hernández JG, Hernández S et al (2011) Reactive thermally coupled distillation sequences: Pareto front. Ind Eng Chem Res 50:926–938
32. Kiss AA, Segovia-Hernández JG, Bildea CS et al (2012) Reactive DWC leading the way to FAME and fortune. Fuel 95:352–359
33. Kiss AA, Ignat RM (2012) Enhanced methanol recovery and glycerol separation in biodiesel production—DWC makes it happen. Appl Energy 99:146–153
34. Karuppiah R, Peschel A, Grossmann IE et al (2008) Energy optimization for the design of corn-based ethanol plants. AIChE J 54:1499–1525
35. Prasad S, Singh A, Jain N et al (2007) Ethanol production from sweet sorghum syrup for utilization as automotive fuel in India. Energy Fuels 21:2415–2420
36. Martinez-Hernandez E, Sadhukhan J, Campbell GM (2013) Integration of bioethanol as an in-process material in biorefineries using mass pinch analysis. Appl Energy 104:517–526
37. John RP, Anisha GS, Madhavan Nampoothiri K et al (2011) Micro and macroalgal biomass: a renewable source for bioethanol. Bioresour Technol 102:186–193
38. Gray KA, Zhao L, Emptage M (2006) Bioethanol. Curr Opin Chem Biol 10:141–146
39. Martinez Avilés A, Saucedo-Luna J, Segovia-Hernandez JG et al (2012) Dehydration of bioethanol by hybrid process liquid-liquid extraction/extractive distillation. Ind Eng Chem Res 51:5847–5855
40. Frolkova AK, Raeva VM (2010) Bioethanol dehydration: state of the art. Theor Found Chem Eng 44:545–556
41. Gil ID, Gómez JM, Rodríguez G (2012) Control of an extractive distillation process to dehydrate ethanol using glycerol as entrainer. Comput Chem Eng 39:129–142
42. Vázquez-Ojeda M, Segovia-Hernández JG, Hernández S et al (2013) Design and optimization of an ethanol dehydration process using stochastic methods. Sep Purif Technol 105:90–97
43. Teramoto Y, Tanaka N, Lee SH et al (2008) Pretreatment of eucalyptus wood chips for enzymatic saccharification using combined sulfuric acid-free ethanol cooking and ball milling. Biotechnol Bioeng 99:75–85
44. Teramoto Y, Lee SH, Endo T (2008) Pretreatment of woody and herbaceous biomass for enzymatic saccharification using sulfuric acid-free ethanol cooking. Biotechnol Technol 99:8856–8863
45. Inoue H, Yano S, Endo T et al (2008) Combining hot-compressed water and ball milling pretreatments to improve the efficiency of the enzymatic hydrolysis of eucalyptus. Biotechnol Biofuels 1:2
46. Ha SH, Mai NL, An G et al (2011) Microwave-assisted pretreatment of cellulose in ionic liquid or accelerated enzymatic hydrolysis. Bioresour Technol 102:1214–1219
47. Ben Chaabane MF (2006) Intensification de la production d'éthanol biocarburant dans un bioréacteur bi-étagé avec recyclage cellulaire: Modélisation et Stratégie de conduite. Dissertation, L'Institut National des Sciences Appliqueés de Touluse
48. Masuda H, Horie T, Hubacz R et al (2012) Process intensification of continuous starch hydrolysis with a Taylor-Couette flow reactor. In: Proceedings of the 14th European conference on mixing, Warszaw, Poland, 10-13 September 2012

49. Ikwebe J (2012) Intensification of bioethanol production by simultaneous saccharification and fermentation in an oscillatory baffled reactor. Dissertation, Newcastle University
50. Ballesteros M, Oliva JM, Negro MJ et al (2004) Ethanol from lignocellulosic materials by a simultaneous saccharification and fermentation process (SFS) with Kluyveromyces marxianus CECT 10875. Process Biochem 39:1843–1848
51. Subhedar PB, Gogate PR (2013) Intensification of enzymatic hydrolysis of lignocellulose using ultrasound for efficient bioethanol production: a review. Ind Eng Chem Res 52:11816–11828
52. Novy V, Krahulec S, Wegleiter M et al (2014) Process intensification through microbial strain evolution: mixed glucose-xylose fermentation in wheat straw hydrolyzates by three generations of recombinant Saccharomyces cerevisiae. Biotechnol Biofuels 7:49
53. Pacheco-Basulto JA, Hernández-McConville D, Barroso-Muñoz FO et al (2012) Purification of bioethanol using extractive batch distillation: simulation and experimental studies. Chem Eng Process 61:30–35
54. Errico M, Rong BG (2012) Synthesis of new separation processes for bioethanol production by extractive distillation. Sep Purif Technol 96:58–67
55. Errico M, Rong BG, Tola G et al (2013) Optimal synthesis of distillation systems for bioethanol separation. Part 2. Extractive distillation with complex columns. Ind Eng Chem Res 52:1620–1626
56. Segovia-Hernandez JG, Vázquez-Ojeda M, Gómez-Castro FI et al (2014) Process control analysis for intensified bioethanol separation systems. Chem Eng Process 75:119–125
57. Kiss AA, Ignat RM (2012) Innovative single step bioethanol dehydration in an extractive dividing wall column. Sep Purif Technol 98:290–297
58. Kiss AA, Suszwalak DJPC (2012) Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing wall columns. Sep Purif Technol 86:70–78
59. Tavan Y, Hosseini SH (2013) A novel integrated process to break the ethanol/water azeotrope using reactive distillation—part I: parametric study. Sep Purif Technol 118:455–462
60. Chevron (2000) Aviation fuels: technical review. Chevron Product Company, Chevron U.S.A. Inc.
61. Agosta A (2002) Development of a chemical surrogate for JP-8 aviation fuel using a pressurized flow reactor. Dissertation, Drexel University
62. International Air Transportation Association (2013) IATA 2013 report on alternative fuels, Montreal-Geneva
63. Gutiérrez-Antonio C, Gómez-Castro FI, Hernández S et al (2015) Intensification of a hydrotreating process to produce biojet fuel using thermally coupled distillation. Chem Eng Process 88:29–36
64. Sinha AK, Sibi MG, Naidu N et al (2014) Process intensification for hydroprocessing of vegetable oils: experimental study. Ind Eng Chem Res 53:19062–19070

Chapter 11
Dynamics, Controllability, and Control of Intensified Processes

Rafael Maya-Yescas, Ricardo Aguilar-López, and Gladys Jiménez-García

Abstract The arts of design, optimize, and control of chemical processes should be considered simultaneously [Chem Eng Sci 38:1881–1891, 1983; Chem Eng Process Process Intensif 52:1–15, 2012]. Nevertheless, in the case of process intensification the most common situation is that design is performed as first stage (following mass/energy integration guidelines), secondly processes are optimized (costs, profit, environmental impact), and finally a control scheme is adopted. Additionally, it is necessary to consider that intensification generates new process dynamics (different responses and characteristic times) and reduces, notoriously, the number of manipulate variables available for control. Hence, the original difficult tasks of partial control and stability of both, process and control [Chem Eng J 92:69–79, 2003], becomes more complicated. This chapter is devoted to the analysis of the problems mentioned above, which are inherent to any chemical process although more evident during process intensification. Some special features of the control are identified and some suggestions are given to enface problems that arise after the intensification of some separation and reaction/separation examples.

R. Maya-Yescas (✉)
Faculty of Chemical Engineering, Universidad Michoacana de San Nicolás de Hidalgo,
Ciudad Universitaria, Av. Francisco J. Mugica, s/n., Morelia, Michoacan 58030, Mexico
e-mail: rafaelmayayescas@yahoo.com.mx; rmayay@umich.mx

R. Aguilar-López
Centre of Research and Advanced Studies, Instituto Politécnico Nacional,
Mexico City, Mexico

G. Jiménez-García
Instituto Tecnológico Superior de Pátzcuaro, Pátzcuaro, Mexico

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0_11

11.1 Introduction

11.1.1 Dynamics and Controllability of Simple Processes

A common question that arises during design of any chemical process is: Will it be controllable? The answer is not easy, and has been a topic of research for more than five decades. The first formal development about this topic was the "Relative Gain Array" [1–3] which explains the probable interactions between control actions on manipulate variables for "Multiple Input Multiple Output" (MIMO) processes. Following the guidelines of this methodology it is possible to assess two important characteristics of the control to be developed: (a) desirable control loops; (b) general changes in the behavior of the closed loop process with respect to the open loop one.

Research about other characteristics of the closed loop operation has been intensive, for example, the effect of the sign of the disturbance with respect to the dynamics of the process [4], the effect of characteristic time of process response with respect to control actions [2, 5] nonlinear controllability and its comparison with linear analysis [6, 7]. Most advanced techniques are those that consider a simple model of the process and try to generate a quasi-linear Proportional-Integral-Derivative Control, such as the Internal Model Control [8], differential algebraic controllers [9], geometric controllers [10], and so on. In most cases conclusions are that it should be a proper set of control actions that generate some evolving path for the process, so that after reasonable time a new stable steady state has been reached [11]. However, in industrial practice linear control is used for most of the processes, and not many theoretical analyses are performed [12]; also fuzzy controllers are gaining acceptation [13].

11.1.2 Number of Manipulate Variables Before and After Integration

One of the classic problems during controllers design is that a process contains lots of operating variables, many of them nonmeasurable and sometimes unknown. Hence, a proper model for the process could be a difficult task and, at the end of the modeling stage, there are many sources of uncertainty [14]. This process model is the base to select the set of control variables, which is desirable to be as large as possible, say n variables. In contrast, manipulate variables are only a small subset of those process variables, say $m < n$ variables, and many of them are related to process inputs. This situation constraints the control design to the number of manipulate variables available, and the largest MIMO subsystem to be controlled exhibits dimension $m \times m$. Therefore, there are $(n - m)$ operating variables that remain without control; this situation is known as "partial control of uncertain processes"; it is not very satisfactory but often is "the best to be done."

Additionally, the role of pairing between manipulate and control variables is paramount important. Maya-Yescas and Aguilar [6] analyzed a much intensified industrial process known as “fluidized-bed catalytic cracking” (see example 3 below). They followed the easiness of the regulation of important states that depend on dynamic features related to operating conditions, design, control, and the relationship among them. One of the most important characteristics that have to be analyzed when a reacting system is to be controlled is the stability of the zero dynamics [15]. For this analysis, a dynamic nonlinear model for the system under study, (11.1), which consists of mass balances, energy balances, and equilibrium relationships, is the starting point.

$$\dot{x}(t) = f(x(t))G(x(t))u(t) \tag{11.1}$$

Here $x(t) \in \mathfrak{R}^n$, $f(x(t)) := \{f : \mathfrak{R}^n \to \mathfrak{R}^n\}$, $G(x(t)) := \{G : \mathfrak{R}^n \to \mathfrak{R}^{n\times m}\}$, $u(t) \in \mathfrak{R}^m$. Dimensions n and m correspond to number of states in the model and number of manipulate variables, respectively. Vector function f contains all nonlinear terms in the model and G matrix contains linear relationships among system states and vector of manipulate variables u.

Now, the zero dynamics of a system are defined as the minimal order dynamics of its inverse [15, 16]. For nonlinear systems the realization of this inverse could be very complicated or even impossible. However for control affine systems (control vector u appears in linear form) that are partially controlled, it is possible to assess the stability features of the zero dynamics following the dynamics of the uncontrolled (or dynamic) states, x_D, (11.2b), while the system is partially controlled by the regulation of a subset of states, x_C, (11.2a). Notice that explicit dependence with time has been dropped in order to simplify notation.

$$\dot{x}_\mathrm{C} = f_\mathrm{C}(x) + G_\mathrm{C}(x)u \tag{11.2a}$$

$$\dot{x}_\mathrm{D} = f_\mathrm{D}(x) + G_\mathrm{D}(x)u \tag{11.2b}$$

In order to ensure controllability, or resilience [17], the goal is to find the vector of manipulated inputs u (common to both subsets x_C and x_D) assuming that the regulated variables will remain steady at the desired set point, sp (11.3). Then it is possible to substitute the vector of manipulated inputs, u^sp, into the balances for dynamic variables, (11.2b), to obtain the dynamic behavior of those variables that are not directly controlled, see (11.4).

$$\dot{x}_\mathrm{C}^\mathrm{sp} = 0 \Leftrightarrow u^\mathrm{sp} = -G_\mathrm{C}^{-1}(x)f_\mathrm{C}(x) \tag{11.3}$$

$$\dot{x}_\mathrm{D}^\mathrm{sp} = f_\mathrm{D}(x) - G_\mathrm{D}(x)G_\mathrm{C}^{-1}(x)f_\mathrm{C}(x) \tag{11.4}$$

Here, $\dot{x}_\mathrm{D}^\mathrm{sp} \in \mathfrak{R}^{n-m}$ represents the dynamics of uncontrolled variables; $f_\mathrm{D}(x) := \{f_\mathrm{D} : \mathfrak{R}^{n-m} \to \mathfrak{R}^{n-m}\}$ is the nonlinear part of the model associated with uncontrolled variables, but depending on the complete set of state variables; $G_\mathrm{D}(x) := \left\{G_\mathrm{D} : \mathfrak{R}^{n-m} \to \mathfrak{R}^{(n-m)\times m}\right\}$ is the matrix containing linear relationships between uncontrolled variables and manipulate variables of the closed loop system; and $u^{\mathrm{sp}} \in \mathfrak{R}^m$ is the vector of manipulate inputs. If the evolution of the dynamic behavior of the uncontrolled variables is stable when operating under this particular set of inputs u^{sp}, it is possible to conclude that zero dynamics are stable as well. Therefore, in order to ensure complete stability of the zero dynamics and of the control, each balance for the uncontrolled variables should tend to an attractor at the desired set point. The proposed policy is to ask for all dynamic balances $\dot{x}_{\mathrm{D}}^{\mathrm{sp}}$ to exhibit negative sign at the operating set point.

Proposition A controller of the system, (11.1), is stable $\forall t > 0$, if and only if:

$$f_{\mathrm{D}}(x) - G_{\mathrm{D}}(x)u^{\mathrm{sp}} < 0, \quad \text{i.e. } \dot{x}_{\mathrm{D}}^{\mathrm{sp}} < 0, \forall t > 0 \tag{11.5}$$

It is important to note that this analysis is performed for *any* type of controller at *any* operating region; therefore this methodology is applicable to *any* system that exhibits control affine structure, at *any* operating point. This analysis complements the relative gain array developed by Bristol [1]. A sketch of proof of this proposition can be found in Aguilar-López and Maya-Yescas [18]; it is used in the second example of this chapter.

11.2 Observability and Control

After integration of two or more process units in a single one, or after optimization of an intensified process, the number of manipulate inputs could be reduced even more [11]. Moreover, uncertainties of the model could be increased because of the hidden of input multiplicities or weird responses inside the new process unit. This situation commonly provokes rejection by operators. On the other hand, integration of process units avoids the use of intermediate utility operations, such as heating or cooling, pumping or decompressing, and so on. Therefore, some control difficulties of the individual processes can be absorbed inside of the new integrated one, improving process responses to control actions. This argumentation favors consideration of intensified process; if it is possible to prove that the partial control of the process will work effectively, as demonstrated by uncontrolled (and sometimes unmeasured) variables. Hence, it is necessary to introduce a methodology to "observe" the behavior of the complete system, even without enough measurements.

The purpose of this section is to discuss some conditions required on the system for possible solutions to observability issues. Such conditions above all correspond to what are usually called "observability conditions." Consider the following state-space representation of the dynamics of a process system, (11.6a) and (11.6b).

$$\dot{x}(t) = f(x(t)) \cdot u(t) \tag{11.6a}$$

$$y(t) = h(x(t)) \tag{11.6b}$$

Here, x denotes the vector of states taking values in certain domain X, which is a connected manifold of dimension n; u denotes the vector of known external (manipulate) inputs, taking values in some open subset U; and y denotes the vector of measured outputs taking values in some open subset Y. Functions f and h will, in general, be assumed to be C^{∞} in their arguments, and input manipulate functions $u(\cdot)$ to be locally essentially bounded and measurable functions in a set U. The system will be assumed to be forward complete.

A fundamental question to the analysis of physical systems is whether the state of the system (x) can be uniquely determined from its output data (y). Specifically, given the dynamic description of the system and the observation process, how to find such conditions that are able to determine uniquely the current state of the system from an initial state and a given time interval on the basis of the observed output. This problem is called the inverse or observability problem. The test of a system's observability is a necessary prerequisite to the estimation of states and parameters from the output of the system. In short, they must express that there is indeed a possibility that the purpose of the observer can be achieved, namely that it might be possible to recover $x(t)$ from the only knowledge of u and y up to time t. At first glance, this will be possible only if $y(t)$ bears the information on the full state vector when considered over some time interval: this roughly corresponds to the notion of observability. Observability, in control theory, is a measure for how well internal states of a system can be inferred by knowledge of its external outputs. Hence, observability and controllability of a system are mathematical duals.

Formally, a system is said to be observable if, for any possible sequence of state and control vectors, the current state can be determined in finite time using only the outputs (this definition is slanted towards the state space representation). Less formally, this means that from the system outputs it is possible to determine the behavior of the entire system. If a system is not observable, then current values of some of its states cannot be determined through output sensors. This implies that their value is unknown to the controller and, consequently, that it will be unable to fulfill the control specifications referred to these outputs.

11.2.1 Linear Observability Approach

For nonlinear systems, a way to test the observability for an equilibrium point and its neighborhood is to transform the original nonlinear problem into a linear system; this transformation is done via Taylor series linearization and it is valid as said in the Grobman–Hartman theorem [19]. As background, consider the linear system given by (11.7a) and (11.7b).

$$\dot{x} = Ax + Bu \tag{11.7a}$$

$$y = Cx \tag{11.7b}$$

Here x is the vector of state variables and y is the vector of measured outputs. Now, consider expansion of (11.7a) by Taylor series, see (11.8).

$$\frac{dx}{dt} = A\overline{x} + B\overline{u} \tag{11.8}$$

Vectors A and B are functions of x, defined as, see (11.9a) and (11.9b).

$$A(\overline{x}) = \left(\frac{\partial f}{\partial x}\right)_{x=\overline{x}} \tag{11.9a}$$

$$B(\overline{u}) = \left(\frac{\partial f}{\partial u}\right)_{u=\overline{u}} \tag{11.9b}$$

Now, from a general framework, let's consider the finite set $Y = \left(y, y', y'', \ldots\right)^{\mathrm{T}} \in \Re^m$ related to the derivatives of the vector of finite time system outputs. By substitution of (11.9a) into (11.7b), it is possible to construct the following linear dynamic system, see (11.10).

$$\begin{bmatrix} y \\ y' \\ y'' \\ \vdots \\ y^{n-1} \end{bmatrix} = \begin{bmatrix} Cx \\ CAx \\ CA^2x \\ \vdots \\ CA^{n-1}x \end{bmatrix} \tag{11.10}$$

Equation (11.10) can be written in vector form using (11.11a) and by defining N, (11.11b).

$$Y = NX \tag{11.11a}$$

$$N = \left[C, CA, CA^2, \ldots, CA^{n-1}\right] \tag{11.11b}$$

Notice that if the matrix N (named 'observability matrix') is invertible (full rank), then state vector X can be easily obtained using (11.12). In this case, "the state vector X is observable with respect to the measurable output Y."

$$X = N^{-1}Y \tag{11.12}$$

Local observability analysis is condensed by the following theorem [20]:

Local Observability Theorem. A continuous time linear (or linearized) system is *observable* if and only if the state reconstruction system, (11.11a) and (11.11b), exhibits $\text{rank}(N) = n$; here n is the order of the system.

Sometimes systems exhibit unobservable subspaces ($\text{rank}(M) < n$); in order to determine if this unobservable equilibrium point of the studied system is stable, a detectability analysis is performed. This analysis is done via the Popov–Belevitch–Hautus (PBH) theorem [19], which uses the following matrix representation given by (11.13).

$$M = \begin{bmatrix} C - \lambda I \\ A \end{bmatrix} \tag{11.13}$$

Here λ are the eigenvalues of the matrix C, and I is the identity matrix.

Local Detectability Theorem (*PBH*). A continuous time linear (or linearized) system, (11.13), is *detectable* if and only if $\text{rank}(M) = n$ [21].

11.2.2 Nonlinear Observability Approach

The study of observer design algorithms began with the works by Luenberger [22] for dynamic linear systems. Their methodology has been proven extremely useful, especially for online monitoring, fault detection, and observer-based-control design; however for nonlinear systems the theory is very scarce. Nowadays, nonlinear observer design is the subject of research for many groups, several estimation techniques have been developed and the application to industrial systems is increasing. A first classification of state observers could be based on the full/partial knowledge of the model structure [23]. In the first case, a drawback is present; the uncertainty in the model parameters can generate possibly large bias in the estimation of the unmeasured states. The second case, the observers are named asymptotic observers, these are based on the hypothesis that the uncertainty in the model system lies within the highly nonlinear structures, so that the observers are designed employing the phenomenological approaches, not necessarily needing the main nonlinear structure information.

A second classification for the designed observers is based on the robustness of the estimator algorithm against disturbances, noise output, or dynamic uncertainties. High gain and sliding mode observers satisfied some of the above criteria. The high gain observer was developed first by [24] and it robustly estimates the unmeasured states against non-modeled dynamics while asymptotically attenuating disturbances with the drawback of noise amplification through its own observer gain and peaking phenomenon. The sliding mode observer was introduced by Drakunov and Utkin [25, 26] and Slotine and Li [27], taking as objective to maintain stability and performance in the presence of discrepancies between the plant and its corresponding model. Generally speaking, the sliding mode observer, instead of feeding back the output error between the observer and the system linearly (linear innovative term), the output error is fed back via a discontinuous switched signal (*sign* function term). This has the advantage of robustness to disturbances, insensitivity to unknown inputs and a finite time convergence, but with the disadvantage of chattering, increasing the system's relative degree and in some cases destabilize the closed loop system. In order to diminish the chattering problem and improve the corresponding observer's performance, higher order sliding mode observers (HOSM) were developed in the nineties by Edwards and Spurgeon [28] and are still being researched [29], however, the chattering phenomenon is still present (for a complete revision of state of the art see [30]).

11.2.2.1 Nonlinear Observers Design

Consider the following nonlinear system representation given by (11.14a) and (11.14b).

$$\dot{x} = f(x, u) + \Delta f \tag{11.14a}$$

$$y = Cx \tag{11.14b}$$

Here $y \in \mathfrak{R}^m$ is the measured output vector, $x \in \mathfrak{R}^n$ is the vector of state variables, $u \in \mathfrak{R}^q$ is the manipulate inputs vector, $f(\bullet) : \mathfrak{R}^{n+q} \rightarrow \mathfrak{R}^n$ is a nonlinear smooth vector function that satisfies a Lipschitz condition in x and is uniformly bounded in u, Δf is the additive bounded either modeling or measuring error. The general structure of state observer for system, (11.14a), is given by (11.15).

$$\dot{\hat{x}} = \hat{f}(\hat{x}, u, y) \tag{11.15}$$

Usually, it is required that at least $\|x - \hat{x}\| \rightarrow 0$ as $t \rightarrow \infty$; exponential convergence could be also required in some cases [31].

Proposition 1 The dynamic system, (11.16), is a robust observer for system in (11.15):

$$\dot{\hat{x}} = \hat{f}(\hat{x}, u) + g_1 \varepsilon + g_2 \left(\frac{\varepsilon}{\sqrt{1 + \varepsilon^2}} \right) \tag{11.16}$$

Here $\varepsilon = x - \hat{x}$. A similar analysis for the demonstration of this proposition could be found in [32].

Now, let's consider the following robust observer design, (11.17a), under lack model information and unknown disturbances for a specific nonlinear representation of the system, (11.6a) and (11.6b), with linear measured output given by (11.17b).

$$\dot{x} = Ax + \Psi(x) + (g_0 + \Delta g)u + j(x)d \tag{11.17a}$$

$$y = h(x) = Cx \tag{11.17b}$$

Here $x \in \mathfrak{R}^n$ is the vector of states, $\varPsi(x) := \mathfrak{R}^n \to \mathfrak{R}^n$ is a nonlinear smooth vector function, $u \in \mathfrak{R}^q$, $q \leq n$ is the control input, $j(x) := \mathfrak{R}^n \to \mathfrak{R}^m$, $m \leq n$, g_0 is the nominal control input coefficient, Δg is the bounded additive uncertainty of the control input and $d \in \mathfrak{R}^z$, $z \leq n$, is the bounded input disturbance vector.

Now, because $\varPsi(x)$, Δg, and $j(x)d$ are unknown, the following change of variable is proposed, see (11.18). Notice that the new variable, w, contains all uncertainties related to the process.

$$w = \varPsi(x) + \Delta g u + j(x) d \tag{11.18}$$

Equation (11.17a) is now changed by the following extended system, (11.19a) and (11.19b).

$$\dot{x} = Ax + g_0 u + w \tag{11.19a}$$

$$\dot{w} = \wp(x, \overline{u}) \tag{11.19b}$$

Here $\overline{u} = (u, d)$, $\wp := \mathfrak{R}^{n+q+z} \to \mathfrak{R}^n$ is an unknown vector field, which is assumed to satisfy a Lipschitz condition, with respect to the vector x, (11.20), and is bounded $|\wp| \leq \varOmega \ll \infty$.

$$\|w(x - \overline{u}) - \hat{w}\,(\hat{x} - \overline{u})\| \leq L\|x - \hat{x}\,\| \tag{11.20}$$

As mentioned before, for control purposes it is necessary to estimate the uncertain term w in order to make the control realizable, therefore the following uncertainty observer is proposed [33, 34]. Consider the following assumptions:

- w is observable with respect to $\{u, y\}$, that is to say, w satisfies a differential polynomial in terms of $\{u, y\}$ and some of their time derivatives: $P(w, u, \dot{u}, \ldots, y, \dot{y}, \ldots) = 0$.
- K_1 is selected from the following Ricatti algebraic equation, which has P as symmetric and positive definite solution for some $\rho > 0$:
- K_i is selected to satisfy $\lambda_{\min}(PK_iC) \geq 0$, for $2 \leq i \leq m - 1$.

Proposition 2 The dynamic system, (11.21a) and (11.21b), is an asymptotic observer for the system given by (11.14a) and (11.14b).

$$\dot{\hat{x}} = A\hat{x} + g_0 u + \hat{w} + \sum_{j=1}^{m} K_i (y - C\hat{x}\,)^{2i-1} \tag{11.21a}$$

$$\dot{\hat{w}} = \sum_{j=1}^{m} \overline{K}_l (y - C\hat{x}\,)^{2i-1} \tag{11.21b}$$

Finally, the estimation error, (11.22a), can be evaluated as given by (11.22b) and (11.22c).

$$\vec{\varepsilon} = \begin{bmatrix} \varepsilon_x \\ \varepsilon_w \end{bmatrix} = \begin{bmatrix} x - \hat{x} \\ w - \hat{w} \end{bmatrix} \tag{11.22a}$$

$$\dot{\varepsilon}_x = (A - K_1 C)\varepsilon_x - \sum_{i=2}^{m} K_i (C\varepsilon_x)^{2i-1} + (w - \hat{w}) \tag{11.22b}$$

$$\dot{\varepsilon}_w = \wp - K_1(y - C\hat{x}) - \sum_{i=2}^{m} K_i (y - C\hat{x})^{2i-1} \tag{11.22c}$$

Demonstration of this proposition could be found in [33, 34].

11.3 Examples of Partial Control and Its Implications on Intensified Processes

As it was pointed out, “complete control” of any process is impossible; nevertheless in order to ensure that operation will be stable, unmeasured internal information has to be estimated from external measurements. This situation yields to the dual problem of observer design as system controllability approach. In the following subsections some examples of intensified process are given.

11.3.1 Loosing of Manipulate Variables After Energy Integration in Reactive Distillation

Biodiesel is the common name for fatty acid methyl esters, obtained by esterification (acid catalysis) or trans-esterification (basic catalysis) of vegetable or animal oils with alcohols, and used as liquid fuel. Production involves the reaction, under mild conditions, between the oil and, typically, excess of methanol. Traditional production of biodiesel exhibits some handicaps, such as the shift of equilibrium to fatty acids by using excess of alcohol that must be separated and recycled. As alternative, it is possible to integrate reaction/separation operations into a single intensified unit, a reactive distillation column, followed by a second separation unit. Esterification reactions are exothermal; therefore there is additional heat production by chemical reaction that can be integrated to the separation system. These configurations exhibit several advantages such as shifting equilibrium in the reactive region and, because of the thermal integration with the second unit, energy savings during products separation [35].

In order to design production sequences taking advantage of steady state knowledge (energy savings) and considering dynamic performance, this example compares control capability of two possible configurations, a reactive distillation column followed by conventional indirect separation sequence (Fig. 11.1) and a

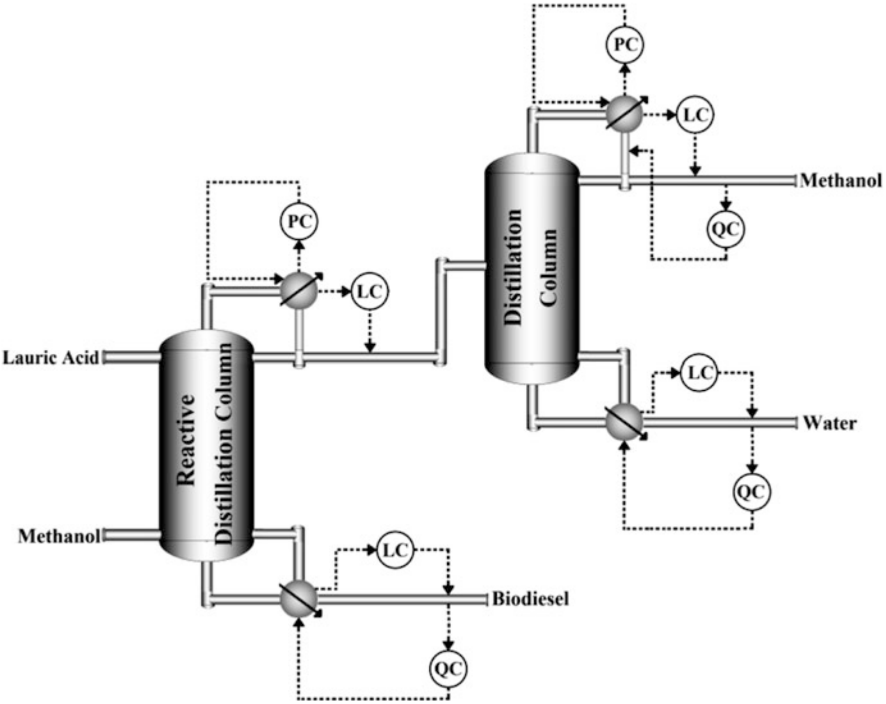


Fig. 11.1 Reactive distillation and conventional separation indirect sequence

reactive distillation column without reboiler, followed by a nonadiabatic flash and coupled to a stripper (Fig. 11.2). Esterification of lauric acid using methanol was considered as model reaction, following kinetics and phase equilibrium already studied [35, 36]. In both cases, steady-state systems were designed using ASPEN-Plus™ and then transported to ASPEN-Dynamics™. Control tuning was performed by minimizing the Integral of Accumulated Error (known as IAE), and PI controllers were used.

Firstly, notice that reactive distillation column in the second configuration differ because of the lack of reboiler (Fig. 11.2); also second separators are completely different, being interesting that in the integrated option the stripper lacks of reflux ratio control (Fig. 11.2). Open loop dynamics revealed that both configurations are feasible [37]. PI controllers were implemented, following the classic LV scheme, pairing methanol purity (>97.5 %) with reflux ration of the second column (Fig. 11.1) and with reflux ratio of the first column (Fig. 11.2). Purity of biodiesel product (>98.5 %) was paired with heating duty of the reactive distillation column (Fig. 11.1) and with heating duty of the flash (Fig. 11.2). Purity of water product (>98.5 %) was paired with the reboiler heating duty (Fig. 3.1a) and with the heating duty of the side stripper (Fig. 11.2).

Energy requirements were evaluated by simulation (Table 11.1); as it is possible to notice cooling services of integrated process is about 91.8 % and heating services

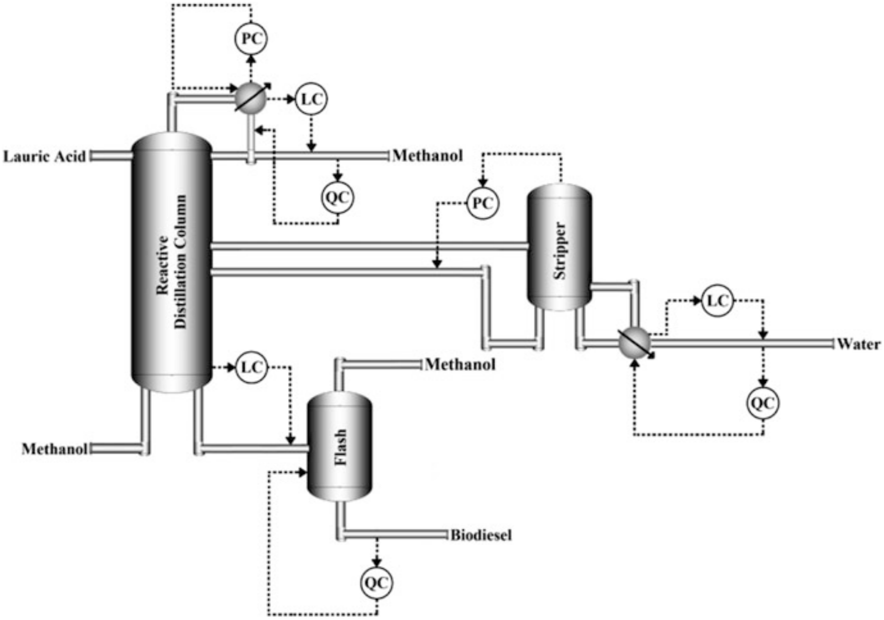


Fig. 11.2 Reactive distillation, flash and stripper after sequence intensification

Table 11.1 Energy requirements for selected configurations

Figure 11.1	Cooling (kW)	Heating (kW)	Figure 11.2	Cooling (kW)	Heating (kW)
First column	1460.4	674.0	First column	1523.6	n.a.
Second column	199.1	221.8	Stripper	n.a.	158.1
Total	1659.5	895.8	Flash	n.a.	538.7
			Total	1523.6	696.8

are about 77.8 % with respect to the conventional one. Open-loop control properties, evaluated by single value decomposition, are probed by implementing PI controllers to the system [37].

In order to test control capability of these sequences, two drastic disturbances were supplied: 10 % step decrease and 10 % step increase of the acid feedstock to the reactive distillation column.

Firstly, comparing the effect of the direction of the disturbance on the first sequence (Fig. 11.1), it is possible to note that a decrease of feedstock is followed by decrease of heating and reflux ratio (Fig. 11.3). This happens because the second column is overdesigned for this new flow of feedstock. In contrast, if the disturbance is an increase of feedstock, opposite direction, then the separation tower increases the heat duty in the reboiler about 30 % and also modifies the reflux ratio

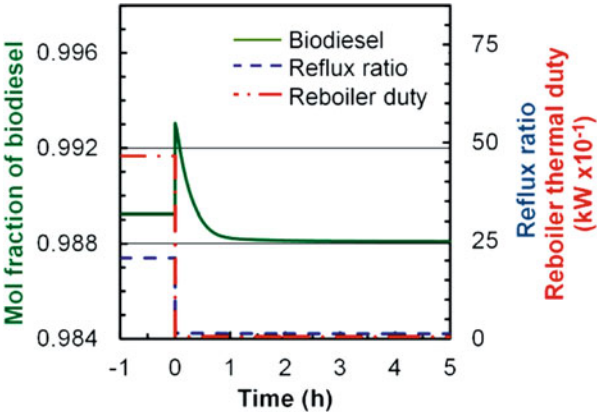


Fig. 11.3 Response and control effort of the conventional configuration to a disturbance of −10 % in feedstock flow

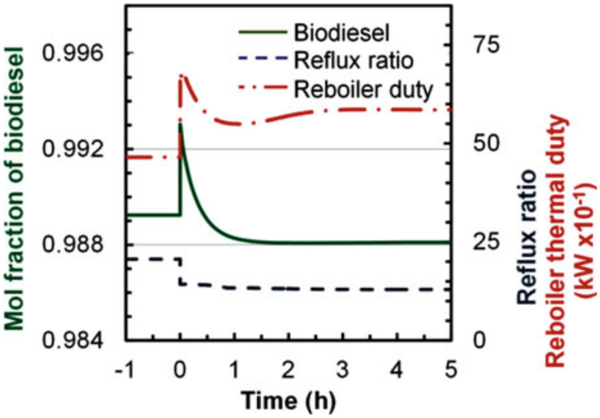


Fig. 11.4 Response and control effort of the conventional configuration to a disturbance of +10 % in feedstock flow

until stabilization of the system (Fig. 11.4). In both cases, if the second column is a conventional distillation unit, the system is able to reject both disturbances.

On the other hand, when the second separation unit consists of a coupled stripper (Fig. 11.2), it is possible to note that a decrease of feedstock changes instantaneously both, heating duty and reflux ratio, but at the end these two manipulate variables return to its initial values, approximately (Fig. 11.5). In this case, the stripper is working in its limit, and the energy management of the reacting distillation column is able to compensate the disturbance and to stabilize the system. In contrast, an increase in feedstock provokes that reflux ratio increases to values out of the operating region, larger than 70 (Fig. 11.6), which means that the reactive distillation column is almost not producing distillate. Therefore, although the system is rejecting the disturbance and recovering the purity of the product, it is not able to operate because the accumulation of distillate products in the reactive distillation column that takes it to flood in about 5.5 h (not shown).

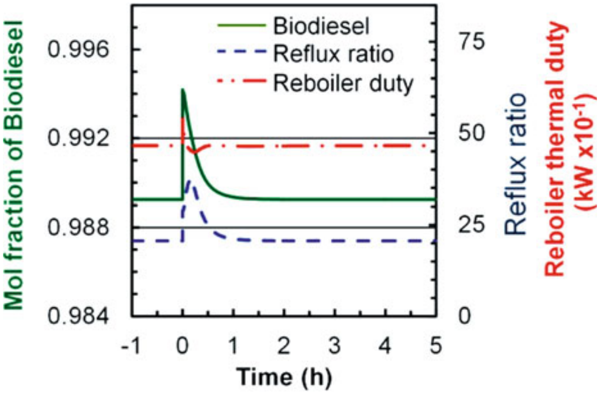


Fig. 11.5 Response and control effort of the integrated configuration to a disturbance of −10 % in feedstock flow

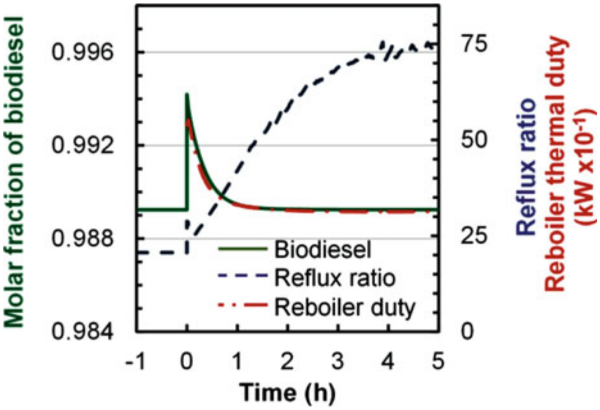


Fig. 11.6 Response and control effort of the integrated configuration to a disturbance of +10 % in feedstock flow

Comparison between both systems show that the sequence with conventional column (Fig. 11.1) is able to reject both disturbances, meanwhile integrated sequence (Fig. 11.2) is not. The difference, in terms of control, is that integration of the second column with the first one loose two important manipulate variables:

- Only one reboiler remains, instead of two in the conventional case [11]. Reboiler function is to manage energy balance by energy supply; and because of its characteristic slow dynamics this management is “slow.” However, in the previous case, this variable did not show to be crucial for the disturbance rejection.
- Additionally, the second column in the integrated sequence, now a stripper, lacks the control of the reflux ratio. This control also manages the energy balances by changing the flow to the top of the column, and also sending a fluid that has been cooled down. Hence the management that control actions on this manipulate variable provoke on the energy balance are “very fast.” In the previous case, this variable played a crucial role in the disturbance rejection role; because of its absence, the integrated sequence was not able to reject the increase of feedstock disturbance.

To sum up, reacting distillation columns are much intensified processes that, frequently, help to save energy in reaction-separation schemes. If additional separation operations are required, there is always possibility to integrate the column downstream with the reacting distillation one. Nevertheless, not all possible integrations are feasible [37] and, more important, the number of manipulate variables decreases [11]. This last situation provokes that the "partial control" of the system transforms into a weaker one and, in some cases, it could be a notorious disadvantage in terms of disturbance rejection. At this point of the example, it is possible to suggest different pairing of control and manipulate variables, such as the one obtained after the RGA analysis [38]; however, LV configuration is highly preferred in industrial practice.

11.3.2 Fluidized-Bed Catalytic Cracking: An Intensified Industrial Process

Fluidized-bed catalytic cracking (FCC) is, currently, the heart of many refineries; its mission has been changing along the years depending on product demands and, now, on environmental concerns. It is a process that has been intensified since its beginning, because of the great amount of energy that manages. This process is divided into a section called "converter" that consists of two coupled reactors [39], called riser and regenerator; between them there is a catalyst stripper (inside it there are also chemical reactions) and pipes. The converter is followed by a section devoted to separate the products using an atmospheric distillation tower.

The main mission of FCC converters (Fig. 11.7) is to crack large hydrocarbon molecules (C_{30}s–C_{60}s), boiling point about (280–545) °C coming from blends (called feedstock) of gas oils and residua into added value shorter molecules; this feedstock could be hydrotreated. Typical products in case of nonhydrotreated feedstock are light cycle oil (LCO, used in production of diesel and fuel oil; b.p. >221 °C), 48%p–50%p gasoline (C_5s–C_{12}s; 38.5 °C $<$ b.p. $<$ 221 °C), and 12%p–14%p liquid petroleum gas (LPG, C_3s–C_4s); there are additional products such as 4%p–6%p dry gas (DG, H_2–C_2s), sour gas (H_2S), heavy cycle oil (HCO, considered as unconverted feedstock), and 5%p–6%p solid coke; this compound remains adsorbed on the catalyst surface decreasing effective reaction rates, phenomena known as "catalyst deactivation" [*e.g.* 40, 41]. Most reactions take place in the vapor phase inside the riser.

After preheating (to about $T_a = 200$ °C), partially evaporated feed is aspersed by steam at the bottom of the riser, where it contacts hot catalyst coming from the regenerator. The heat absorbed by the catalyst during regeneration provides the energy to evaporate and heat the feed to its desired reaction temperature, about (560, 580) °C; the average heat of reaction, resulting from feedstock evaporation plus cracking reactions, is endothermic. Riser outlet temperature (T_{ro}) is controlled at about (510, 545) °C, depending on production objectives; in order to maintain

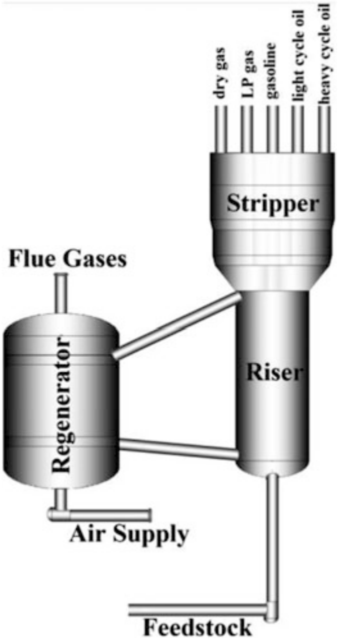


Fig. 11.7 Schematics of a typical FCC converter with single feed [39]

yields at the desired value, catalyst circulation rate from the regenerator to the bottom of the riser, measured as catalyst-to-oil (C/O) mass ratio, is the manipulated variable. After stripping, catalyst moves back to the regenerator, where coke is burned, at about (680, 710) °C, in order to recover activity and to be heat and used as a vehicle for the energy necessary at the riser; either operating temperature in the regenerator (T_{rg}) or excess of oxygen in flue gases $\left(y_{\mathrm{O}_2}\right)$ is controlled by manipulating airflow rate (F_{a}) at the regenerator inlet [6].

The product stream arrives to a distillation tower (Fig. 11.8) at about 5 °C below T_{ro}, and supplies the energy required for the distillation operation; therefore this tower does not have reboiler. Additionally, this tower is thermally coupled to a side rectifier for LCO and HCO separation.

This highly intensified process exhibits the following advantages in terms of energy management:

- The main energy generator is the regenerator reactor, due to the coke burning. This coke is generated in the riser reactor and sent, straight, to the regenerator top as a solid deposit on catalyst particles.
- Similarly, regenerated catalyst particles (without coke) are sent back straight to the riser bottom, at very high temperature (T_{rg} about 690–700 ° C) and without cooling.
- Products stream is sent to the distillation tower at T_{ro}, supplying the energy necessary to separate the heaviest products from those of greater added value and without a reboiler.

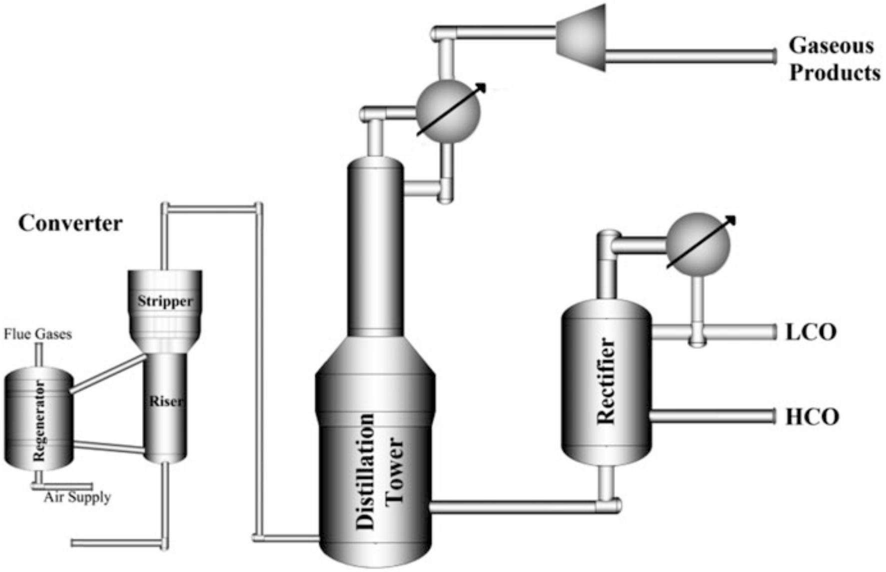


Fig. 11.8 Schematics of the distillation tower after the converter in a typical FCC unit

On the other hand, the process exhibits control issues as consequence of intensification, such as:

- Regenerator reactor is subject to the cokized-catalyst load from the riser, feedstock that arrives at T_{ro}, and limits manipulate variables to air supply, only. A failure in air supply devices obligates to emergency stop the complete unit. Additionally, riser operation also establishes the amount of catalyst that is taken from the bottom of regenerator.
- Riser reactor is controlled by changing the catalyst flow rate from the regenerator, which is a very useful degree of freedom for control. Because feedstock flow rate remains approximately constant, riser control is not difficult.
- For the distillation column, instead of the two common control actions for the energy balance (reflux ratio and reboiler heating duty), there is only one available (reflux ratio) because of the lack of reboiler.
- Finally, the side rectifier is completely dependent on the energy received by flow from the distillation column, and also counts with reflux ratio control.

11.3.2.1 Pairing of Control and Manipulate Variables

The mathematical model used was conceptually similar to (11.1)–(11.4); details can be found in [6]. In this section the control implications of pairing of variables is considered. In order to analyze the problem of pairing manipulate-control variables, using the idea of the inverse of the process, Maya-Yescas and Aguilar [6] and

Aguilar-López and Maya-Yescas [32] followed, firstly, the behavior of the "$\dot{x}_{\mathrm{D}}$ variables," (11.4), when the unit is subject to the control of the regenerator using the airflow rate ($u = F_{\mathrm{a}}$, external input) and the riser and the distillation tower exhibit internal control only. It was considered that the unit operates in full combustion mode, defined as the case when operation does not allow presence of carbon monoxide in the regenerator flue gases.

Two options of control variable were considered, either y_{O_2} in regenerator effluent (Fig. 11.9a) or temperature of catalyst in the regenerator, T_{rg} (Fig. 11.9b). Secondly, it was considered that it is possible to manipulate, also as independent variable, the mass catalysis flow that arrives to regenerator from the catalyst stripper; this option is expected to be easier to control. Catalyst flow was used to control coke on regenerated catalyst in both cases and airflow rate was used to control either y_{O_2} fraction in regenerator effluent (Fig. 11.10a) or temperature T_{rg} in the regenerator (Fig. 11.10b).

As it can be noticed, if the unit is operated at full combustion mode, the pairing $\left[F_{\mathrm{a}} - T_{\mathrm{rg}}\right]$ is not stable; this has been commonly found in operation as inverse

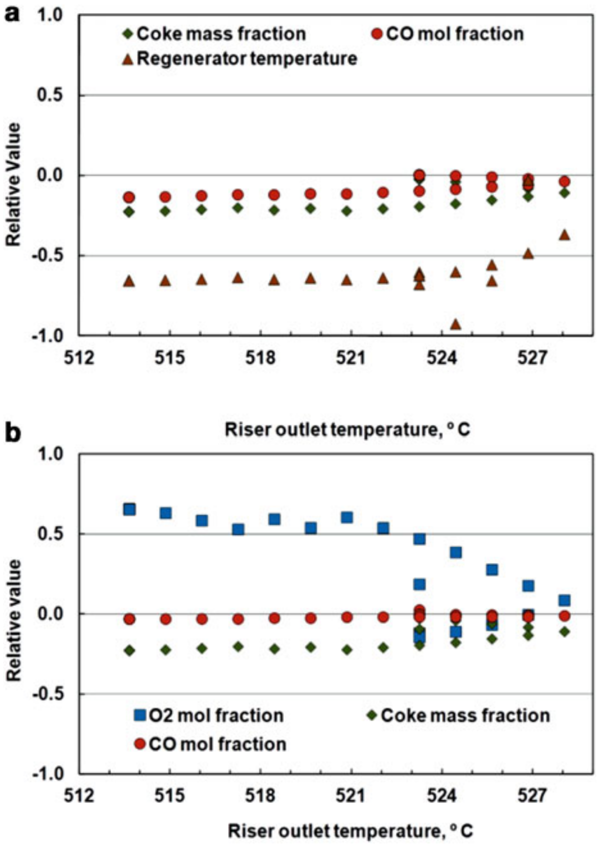


Fig. 11.9 Relative values of the balances for $\dot{x}_{\mathrm{D}}$ in the region of maximum gasoline production. (**a**) Manipulation of F_{a} to control y_{O_2} fraction in regenerator effluent. (**b**) Manipulation of F_a to control T_{rg} [6]

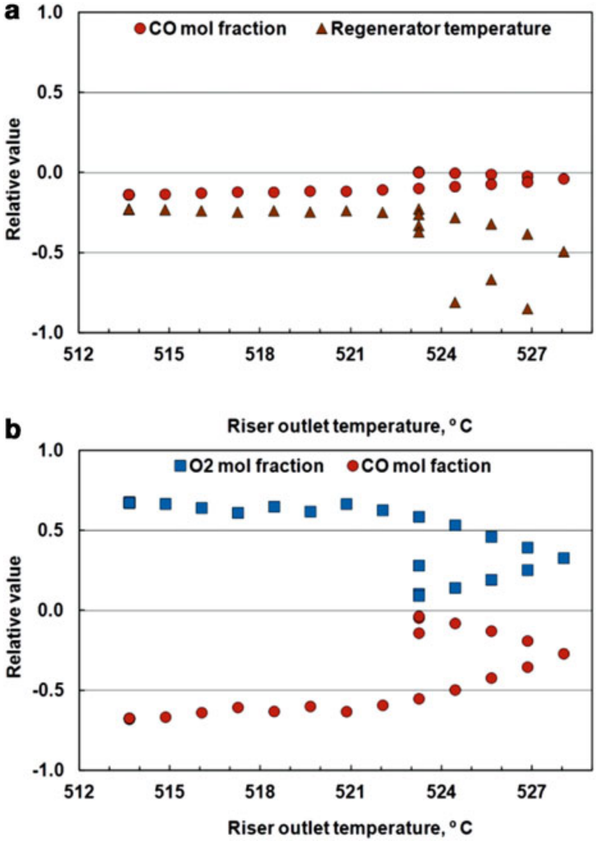


Fig. 11.10 Relative values of the balances for $\dot{x}_D$ in the region of maximum gasoline production. (**a**) Manipulation of airflow rate to control y_{O_2} fraction in regenerator effluent. (**b**) Manipulation of airflow rate to control T_{rg} [6]

response to the control action [6]. Even if more manipulate variables are available, as in the case of the flow of catalyst to the regenerator, the control of T_{rg} continues being instable. Therefore, the availability of manipulate variables cannot warranty easy control of intensified (or any other) processes; the pairing of manipulate-control variables is very important. It is emphasized that this analysis is valid for *any* type of control in systems that exhibit control affine structure.

To sum up, the high degree of intensification {[converter (regenerator – riser reactors)] – [separation (distillation tower plus side rectifier)]} enables the process to manage large amounts of energy without intermediate cooling/heating operations. Consequently, regenerator reactor and distillation tower are limited in control actions because of the loss of degrees of freedom due to the integration with the riser reactor. On the other hand, control of the energy balance depends on several design and operating variables; it was pointed out that the pairing of manipulate-control variables plays a crucial role.

11.3.2.2 The Dual Problem Control: Observability

Recently, new approaches to estimate online uncertainty terms developed for modeling and control of chemical reactors have employed filtering techniques and calorimetric balances [42, 43]. The advantage of this kind of methods is their easy computational implementation and that their structure exhibits strong physical meaning; additionally they take advantage of the nonlinear properties of chemical kinetics. Details of the mathematical models are similar to (11.6a) and (11.6b) and can be found in [18].

For control purposes, let's consider partial combustion mode defined as the case when operation allows presence of carbon monoxide in the regenerator flue gases. A common choice of variables to be regulated is riser outlet temperature (T_{ro}) and temperature of regenerator's dense bed (T_{rg}). Because products distribution at the riser outlet is determined by reaction temperature inside the riser, there is good incentive to control both temperatures, T_{ro} and T_{rg}. Additionally, control of T_{rg} is critical to avoid irreversible deactivation of the catalyst during coke burning and/or cyclone damage. A common choice of manipulate variables is the regenerated catalyst flow at riser inlet (F_{S}) and the airflow rate at regenerator inlet (F_{a}). If the pairings $[F_{\mathrm{S}} - T_{\mathrm{ro}}]$, $\left[F_{\mathrm{a}} - T_{\mathrm{rg}}\right]$ are selected to design a decentralized control strategy, which is a classical riser-regenerator control structure [16, 44] is obtained.

This section is devoted to visualize the control structure that is obtained when temperature regulation of T_{rg} and T_{ro} is performed by input-output linearizing state feedback [45, 46]. As first approach, it is assumed that all parameters and reaction rates are known; in addition it is supposed that all states are available for online measurements. Of course these are not realistic assumptions; however they will be used as intermediate assumptions towards the final control law to be designed.

Control of T_{rg}. The energy balance equation for the regenerator can be expressed as (11.23).

$$\frac{dT_{\mathrm{rg}}}{dt} = L_{\mathrm{rg}} + D_{\mathrm{rg}}F_{\mathrm{a}} + Q_{\mathrm{rg}} + \varpi_{\mathrm{rg}} \tag{11.23}$$

Here L_{rg} includes the linear terms, D_{rg} is the coefficient of the control input F_{a}, and Q_{rg} is the heat generated by the burning of coke in regenerator's dense bed. The new term $\varpi_{\mathrm{rg}} \sim N\left[0, B_{\mathrm{rg}}\right]$ is the model of the corresponding error of measurement due to white noise, with mean zero and covariance B_{rg}.

The following step is to employ a linearizing state feedback law to regulate T_{rg}, so the following expression is obtained:

$$F_{\mathrm{a}} = \left(-L_{\mathrm{rg}} - Q_{\mathrm{rg}} - g_{\mathrm{rg}}\left(T_{\mathrm{rg}} - T_{\mathrm{rg}}^{\mathrm{sp}}\right)\right)/D_{\mathrm{rg}} \tag{11.24}$$

Here $g_{\mathrm{rg}} > 0$ is the control gain and $T_{\mathrm{rg}}^{\mathrm{sp}}$ is the desired regenerator temperature (set point). Note that D_{rg} never becomes zero in operating conditions.

This feedback linearizes the dynamics of the temperature of the regenerator's dense bed; hence the closed loop dynamics behave as asymptotically stable linear system:

$$\frac{dT_{\mathrm{rg}}}{dt} = -g_{\mathrm{rg}}\left(T_{\mathrm{rg}} - T_{\mathrm{rg}}^{\mathrm{sp}}\right) \tag{11.25}$$

Control of T_{ro}. The dynamic behavior of the riser reactor is governed by a distributed parameter model (it is a plug flow reactor), and then energy balance is spatially discretized in order to derive a linearizing feedback controller. A first order discretization of the spatial derivative, (11.26), using the reactor outlet conditions, provides an approximation to the dynamics of the temperature at the riser reactor outlet.

$$\frac{dT_{\mathrm{ro}}}{dt} = \frac{F_{\mathrm{S}} - F_{\mathrm{f}}}{W_{\mathrm{ri}}}\left(\frac{\Delta T_{\mathrm{ro}}}{\Delta z} + \varpi_{\mathrm{ro}}\right) + Q_{\mathrm{ri}} \tag{11.26}$$

The new term $\varpi_{\mathrm{ro}} \sim N[0, B_{\mathrm{ro}}]$ is the model of the corresponding error of measurement due to white noise, with mean zero and covariance B_{ro}. The original derivative has been replaced by a ratio of changes plus the uncertainty and Q_{ri} is the term of heat generation due to chemical reaction.

In order to calculate the control action F_{S}, the following consideration has to be done: $T_{\mathrm{ro}}^{\mathrm{sp}}$ is the set point temperature at the riser outlet, therefore the control objective is regulation error $\varepsilon_{\mathrm{ro}} = T_{\mathrm{ro}}(t) - T_{\mathrm{ro}}^{\mathrm{sp}}$ to exhibit closed-loop exponentially stable dynamic behavior. Re-grouping the dimensionless consumption of heat by reaction, it is possible to derive (11.27), given in terms of measurable quantities. Next, the control input is calculated in terms of the same quantities, (11.28); therefore state feedback, and consequently T_{ro}, should converge asymptotically to desired temperature $T_{\mathrm{ro}}^{\mathrm{sp}}$.

$$\overset{v}{Q}_{\mathrm{ri}} = Q_{\mathrm{ri}} + \frac{F_{\mathrm{S}} - F_{\mathrm{f}}}{W_{\mathrm{ri}}}\varpi_{\mathrm{ro}} \tag{11.27}$$

$$F_{\mathrm{S}} = -F_{\mathrm{f}} + W_{\mathrm{ri}}\left(-\overset{v}{Q}_{\mathrm{ri}} - g_{\mathrm{ri}}\left(T_{\mathrm{ro}} - T_{\mathrm{ro}}^{\mathrm{sp}}\right)\right)\frac{\Delta z}{\Delta T_{\mathrm{ro}}} \tag{11.28}$$

Note that during industrial practice, riser temperature measurements are only available at inlet and outlet of the reactor, therefore for practical controller implementation it is considered $\Delta z = L$, being L the reactor length, and $\Delta T_{\mathrm{ro}} = T_{\text{riser-outlet}} - T_{\text{riser-inlet}}$.

Up to here, the control law has assumed perfect knowledge of reaction rates. In practice this is impossible, particularly for the FCC process where the conversion of feedstock to lighter compounds and the burning of coke during catalyst regeneration follow complex reaction networks [39], which are poorly known. Nonetheless, for temperature regulation, the exact knowledge of the reaction rates functionalities is not necessary. Instead, a control strategy that has access to the instantaneous temperatures of input and output flows and to instantaneous heat production rates due to reaction inside the reactors is enough. In most cases, it is suitable to assume that the convective transport of energy is known, therefore in order to obtain good performance by temperature regulation, a problem of estimating (observing) heat production rate has to be confronted.

Uncertainty Estimation by Kalman filtering. The methodology proposed to estimate heat generation rates is to use a Kalman filter, considering that uncertainty terms can be expressed as one additional state variable (which structure is unknown, of course) to build a new system of higher dimension ($n+1$).

In the energy balance equation for the regenerator, (11.24), the dynamic behavior of the uncertain terms can be expressed as (11.29).

$$\dot{\hat{Q}}_{\mathrm{rg}} = \frac{d\left(Q_{\mathrm{rg}} + \varpi_{\mathrm{rg}}\right)}{dt} = f\left(T_{\mathrm{rg}}, O_{\mathrm{d}}, C_{\mathrm{rc}}\right) \tag{11.29}$$

Here O_{d} is the oxygen used to burn coke, therefore related to heat generation by chemical reaction, and C_{rc} is the amount of coke in the catalyst leaving the regenerator.

By taking regenerator temperature T_{rg} as the system output, the subsystem given by (11.24) and (11.25) can be written in observability form [47], which satisfies the uniform observability condition; moreover, in practice, Q_{rg} can be reconstructed by means of a state observer. Such observer would be structured as a copy of the subsystem, (11.24) and (11.25), corrected by an observation error. However, this typical observer structure is not realizable because the functionality $f(\bullet)$ in (11.28) is unknown. Then in order to develop an estimate of the uncertain term, a Kalman filter is proposed [42, 47] to transform (11.24) into (11.30).

$$F_{\mathrm{a}} = \left(-L_{\mathrm{rg}} - \hat{Q}_{\mathrm{rg}} - g_{\mathrm{rg}}\left(T_{\mathrm{rg}} - T_{\mathrm{rg}}^{\mathrm{sp}}\right)\right)/D_{\mathrm{rg}} \tag{11.30}$$

By using a similar methodology for the riser, the dynamics of the uncertainty estimator is given by (11.31) and the Kalman filter is used to transform (11.28) into (11.32).

$$\dot{\check{Q}}_{\mathrm{ri}} = K_{\mathrm{ro}}\left(T_{\mathrm{ro}} - \hat{T}_{\mathrm{ro}}\right) \tag{11.31}$$

$$F_{\mathrm{S}} = -F_{\mathrm{f}} + W_{\mathrm{ri}}\left(-\check{Q}_{\mathrm{ri}} - g_{\mathrm{ri}}\left(T_{\mathrm{ro}} - T_{\mathrm{ro}}^{\mathrm{sp}}\right)\right)\frac{\Delta z}{\Delta T_{\mathrm{ro}}} \tag{11.32}$$

Both control laws mentioned above serve as practical stabilizers for the reactors. Practical stability means that controllers, (11.30) and (11.32), are able to drive temperature trajectories as close to the set-points as desired, in a finite period of time. In addition to the above developments, we assume that control inputs are subjected to (*not modeled*) actuator dynamics, see (11.33). The block diagram for

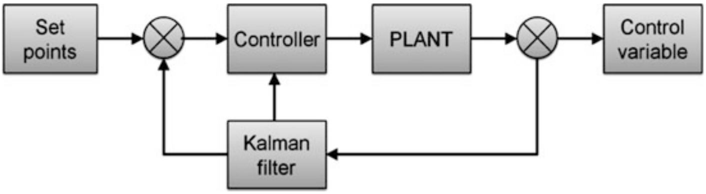


Fig. 11.11 Block diagram of the proposed controller

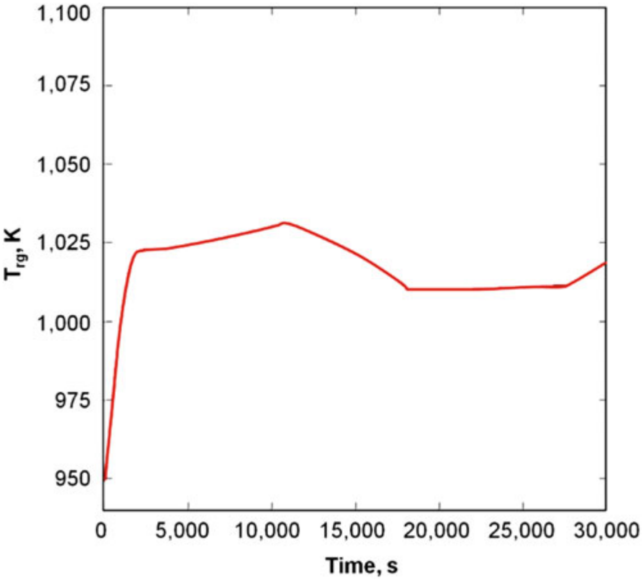


Fig. 11.12 Behavior of regenerator temperature during open-loop simulation

the proposed controller is shown in Fig. 11.11, including the position of the filtering process.

$$\tau_r \frac{dF_{ar}}{dt} + F_{ar} = F_{ao} \tag{11.33}$$

Here, F_{ar} and F_{ao} are the actual and the calculate airflow rate values at the regenerator inlet, respectively.

Performance of control and manipulate variables are shown by numerical simulations, comparing open loop behavior, closed loop behavior under PI-IMC control [8], and closed loop behavior using controllers, (11.30) and (11.32). It is considered that temperatures and flows are available for measurement, as it is routinely done during operation of FCC units. Additionally, $a \pm 1$ K offset by noise in measurements is considered (Figs. 11.12 and 11.13).

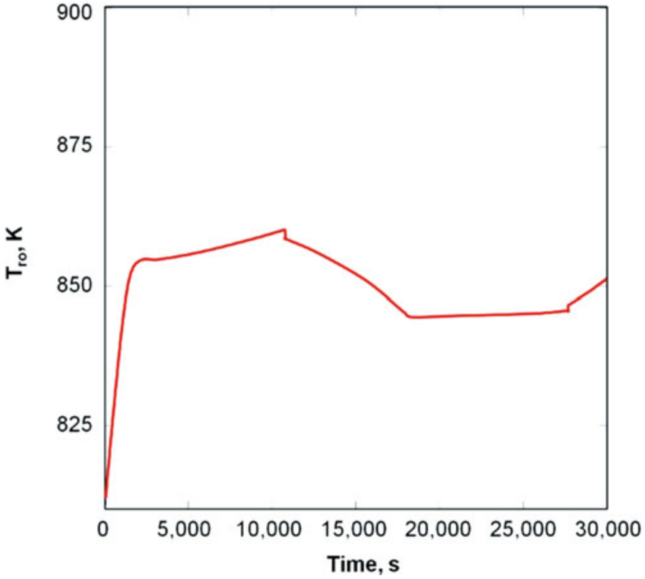


Fig. 11.13 Behavior of riser temperature during open-loop simulation

During simulations, the following sequence of step disturbances entering the regenerator and riser reactors are considered: A 5 K step increase in T_a occurs at $t = 30$ min, a 5 K step decrease in T_f occurs at $t = 180$ min, a 2.5 % increase in K_C occurs at $t = 270$ min and, finally, a 4 kg/min decrease in F_f occurs at $t = 390$ min. These step disturbances are expected during industrial operation [32]. Additionally, several changes in set points occur for both reactors: the original set point for regenerator temperature (T_{rg}) changes from 970 to 965 K at $t = 85$ min and from 965 to 960 K at $t = 250$ min, both in step way. For the riser outlet temperature (T_{ro}), the set point changes from 765 to 770 K at $t = 165$ min and step-changes again from 770 to 760 K at $t = 333$ min.

If PI control is used to regulate temperatures, during the first minutes a trajectory faring from the set points (T_{rg} in Fig. 11.14 and T_{ro} in Fig. 11.15) are noticed. Moreover, after the period of stabilization the control is saturated for the airflow rate (Fig. 11.16) and it is not able to eliminate the offset that has been produced since the first disturbance arrived to the system. Control of T_{ro} is, even, worse due to the lack of proper response of the manipulate variable (F_S, Fig. 11.17); this difficult to control arises because of the higher energy inventory in the regenerator, which manipulates riser temperature additionally to the change of catalyst flow rate. During industrial practice this situation is faced by the elimination of automatic control actions and manual adjusting of the desired steady state, which is not the most adequate control strategy.

In contrast, controller proposed by (11.30) stabilizes very fast regenerator temperature (Fig. 11.18), eliminating immediately any offset. T_{ro} also stabilizes very fast and does not exhibit offset after any disturbance or set point change (Fig. 11.19). This situation is the result of the estimation of the actual value of

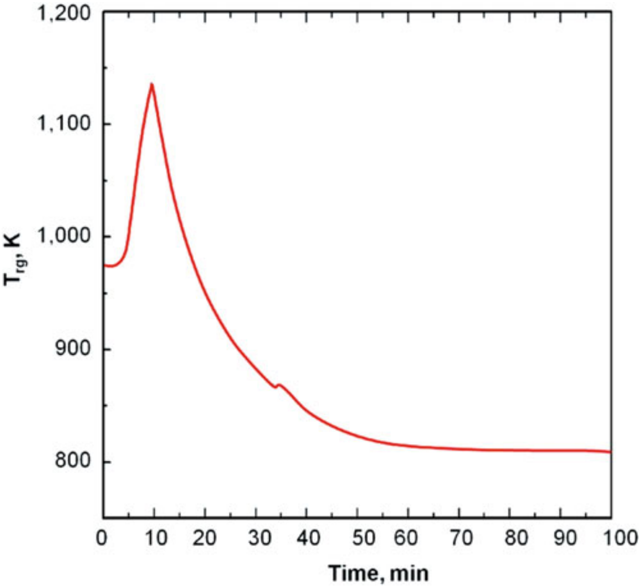


Fig. 11.14 Closed-loop performance of regenerator temperature using the PI-IMC

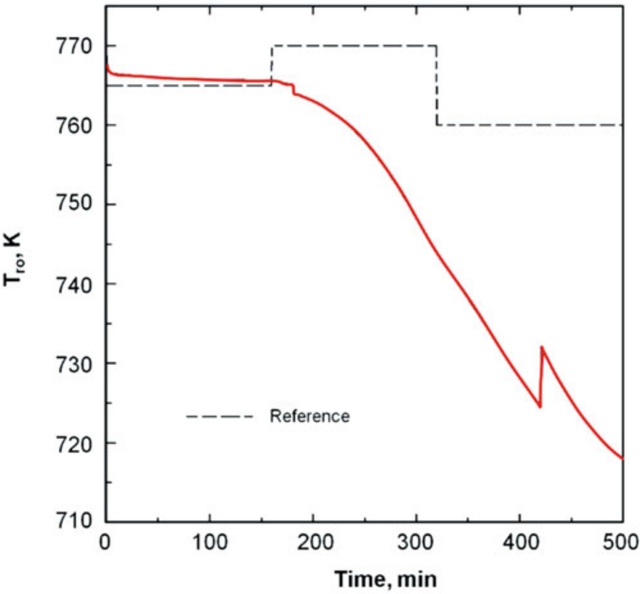


Fig. 11.15 Closed-loop performance of riser temperature using the PI-IMC

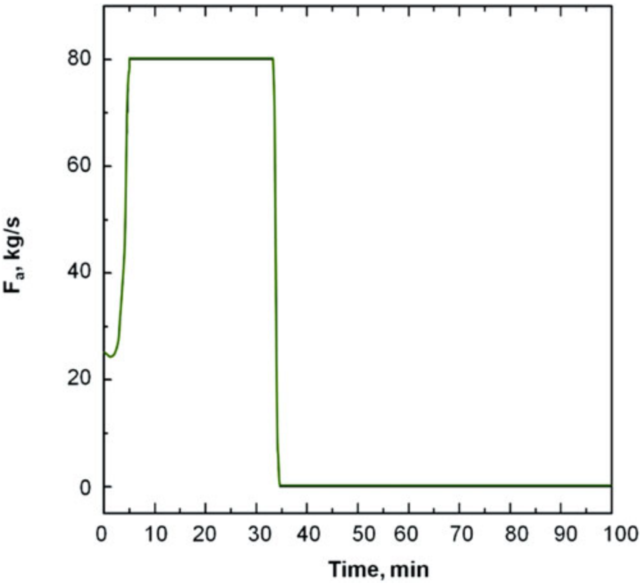


Fig. 11.16 Closed-loop performance of manipulate variable in the regenerator using the PI-IMC

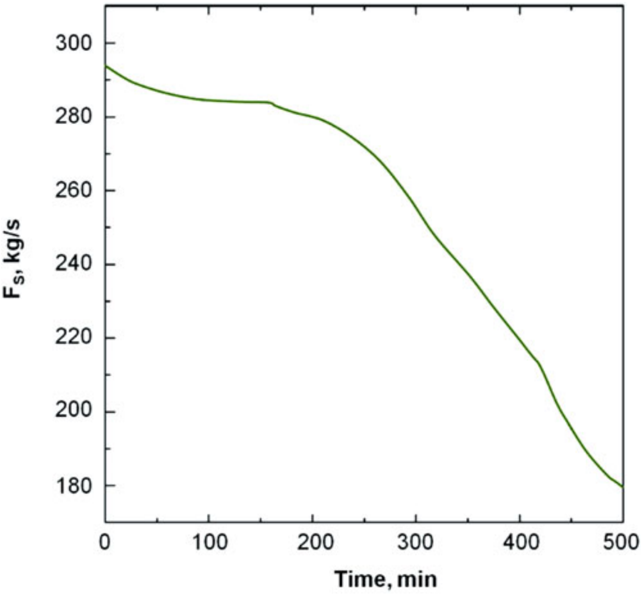


Fig. 11.17 Closed-loop performance of manipulate variable in the riser using the PI-IMC

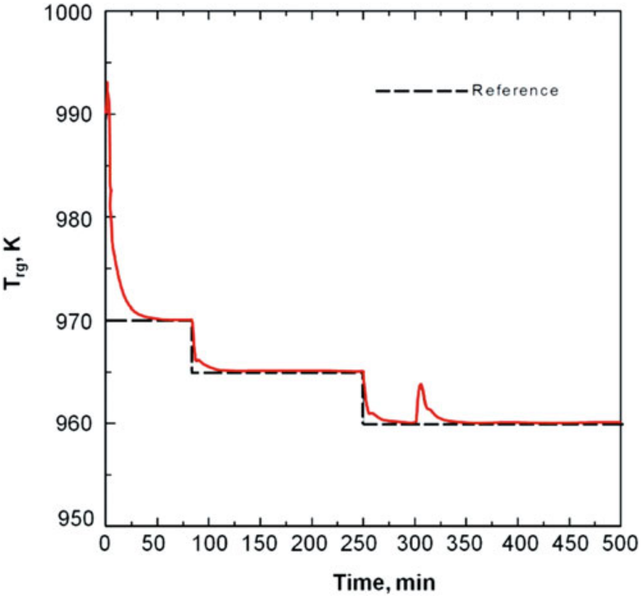


Fig. 11.18 Closed-loop performance of regenerator temperature using the controller proposed

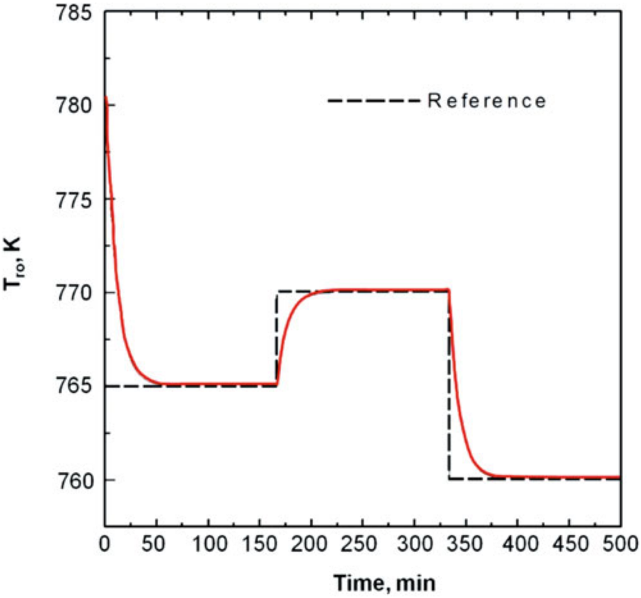


Fig. 11.19 Closed-loop performance of riser temperature using the controller proposed

the energy balance instead of the use of the crude measurement of T_{rg}; consequently, the control considers this balance in its actions.

Another important advantage of the controller proposed in (11.30) and (11.32) can be noticed following the control actions that are taken. It is important to notice that both controllers use the same measures to change airflow rate, Fig. 11.16 for the PI and Fig. 11.21 for (11.30), or catalyst flow rate, Fig. 11.17 for the PI and Fig. 11.21 for (11.32), in order to reject disturbances and keep the temperatures at their set points. Nevertheless, manipulate variables behavior is completely different in the two cases. For the PI controller airflow rate shows a continuous increasing, independently of the disturbance; this situation might be consequence of the complex behavior of the energy balance that has been analyzed several times [44, 48–50].

PI control does not receive information about the energy inventory in the regenerator, which encloses the control inside the operating region in which it was tuned. In contrast, for the case of the linearizing control developed in this chapter, the 5 K step increase in T_a (at $t = 30$ min) is detected by (11.29) as excess of energy entering to the regenerator. To reject this disturbance, the controller, (11.30), increases the airflow rate F_a (Fig. 11.20), so more heat is extracted from the regenerator via output convective flow. Now, when a 2.5 % increase in K_C occurs at $t = 270$ min, more coke is produced increasing heat generation in the

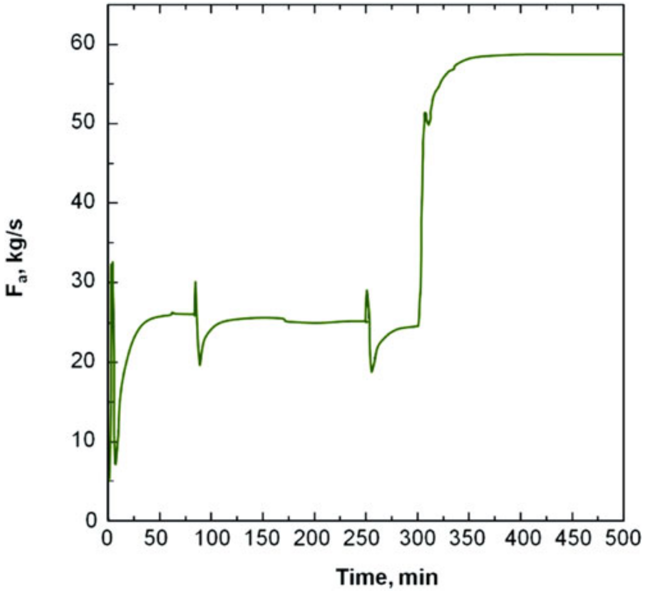


Fig. 11.20 Closed-loop performance of regenerator control input using the controller proposed

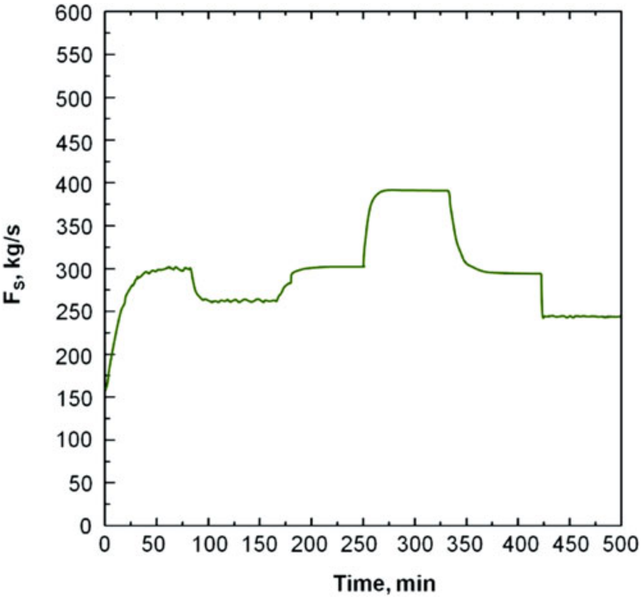


Fig. 11.21 Closed-loop performance of riser control input using the controller proposed

regenerator. To reject the effect of this perturbation, controller, (11.32), increase catalyst flow rate FS (Fig. 11.21) and control, (11.30), increases airflow rate F_a (Fig. 11.20). When a step change in the set point occurs in both reactors, the main effect consist of excess or lack of energy in the process, these disturbances are detected by the estimation algorithm and the information generated is used for the controllers that counteracts to increase or diminish airflow rate and catalyst flow rate in order to keep temperatures at their set points.

Dynamics of the estimation of uncertainties by the Kalman-like observer, heat generation in riser (Fig. 11.22) and in regenerator (Fig. 11.23), are shown. In the riser, the effect of the noisy temperature measurements is transmitted to the estimation scheme, which gives a noisy estimate for the uncertainty term (Fig. 11.22). However the control law is able to regulate temperature in spite of this situation; moreover, this regulation is reached without large control effort. In the regenerator case, the uncertainty is estimated in a smooth way (Fig. 11.23), which supports controller performance.

Finally, when a time delay in the control action of the regenerator is considered, it acts like a filter of the peaking phenomena that occurs every time a disturbance arrives to the process, producing smooth behavior in the airflow rate control action. In this case the process can be controlled using an observed-based approach, a novel design of a PI control.

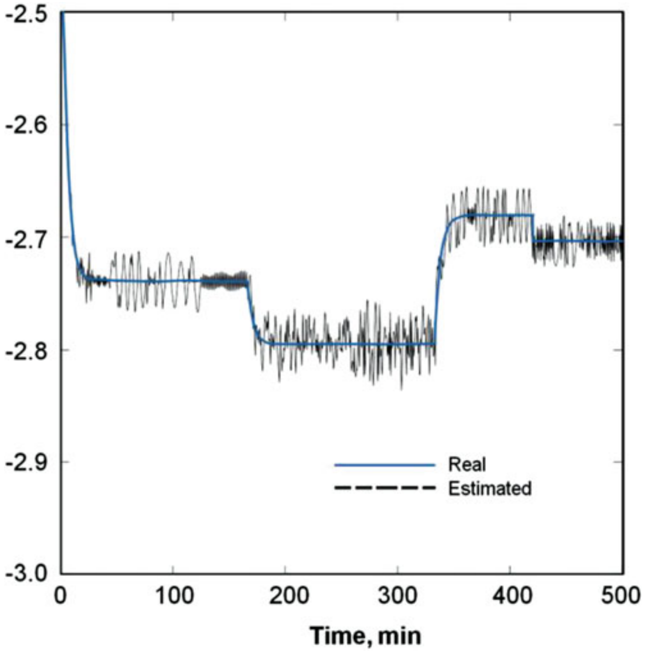


Fig. 11.22 Closed-loop estimation of the uncertainty (heat of reaction) in riser

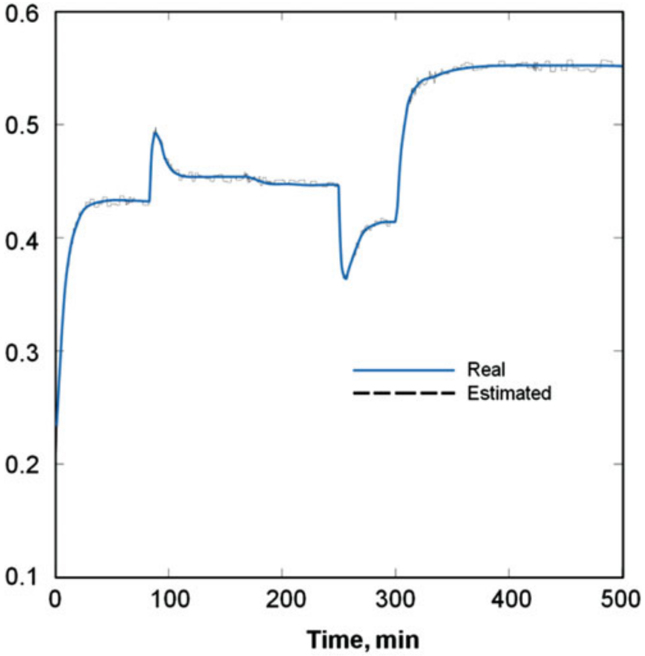


Fig. 11.23 Closed-loop estimation of the uncertainty (heat of reaction) in regenerator

11.4 Conclusions of the Chapter

Process intensification offers significant advantages in material and energy efficient management and savings. Further advances in economic and operating performance can be achieved if operation and control of a whole process are considered simultaneously and systematically. Intensification exhibits some handicaps as the loosing of manipulate variables as consequence of the reduction of equipment. Additionally, non-common control options could be considered. Therefore, design, optimization and control of intensified (and any other) processes should be performed simultaneously, because some controllability issues could be provoked during integration/intensification.

Process Control is not a panacea; currently, the most used control is the linear Proportional-Integral, classic and innovative types. As described, each process can be considered as exhibiting a proper personality. One of the most challenging aspects of control is pairing of n-control variables (interesting for production purposes) with a set of $m < n$ manipulate variables. This situation drives the control engineer to develop a particular control for each particular operating case. The subset of "Intensified Process" exhibits similar properties; in fact, every time that a design strategy is practiced in engineering, some intensification is used. Therefore, the aim of this chapter is to show that, although control engineering is "easy-to-apply," there is not a "universal" approach to develop each control; always ad-hoc controllers have to be developed for each process if they have to be operated satisfactorily. Hence, an intensified process could be as, more or less difficult to control than any other equivalent; but our goal is to analyze (properly) and to develop the right control for it. And, unfortunately, there is no certainty that the best effort will succeed during operation, but fortunately, using current simulation tools, it is possible to prevent it before plant crashing.

Finally, there is an alternative way to analyze controllability, which consists of the dual observability problem; although complicated, this approach could help to solve control problems in complex intensified systems.

Acknowledgments Authors thank a lot grants provided by the National System of Researchers (CONACYT) that helps to support this work.

References

1. Bristol EH (1966) On a new measure of interaction for multivariable process control. IEEE Trans Autom Control AC-11:133–134
2. Grosdidier P, Morari M, Holt BR (1985) Closed-loop properties from steady-state gain information. Ind Eng Chem Fundam 24:221–235
3. Skogestad S, Morari M (1987) Implications of large RGA elements on control performance. Ind Eng Chem Res 26:2323–2330
4. Skogestad S, Morari M (1987) Effect of disturbance directions on closed-loop performance. Ind Eng Chem Res 26:2029–2035

5. Morari M (1992). Effect of design on the controllability of chemical plants. In: IFAC workshop on interactions between process design and process control, September 6-8, London, UK
6. Maya-Yescas R, Aguilar R (2003) Controllability assessment approach for chemical reactors: nonlinear control affine systems. Chem Eng J 92:69–79
7. Economou CE, Morari M (1986) Internal model control. 5. Extension to nonlinear systems. Ind Eng Chem Process Des Dev 25:403–411
8. Rivera DE, Morari M, Skogestad S (1986) Internal model control. 4. PID controller design. Ind Eng Chem Process Des Dev 25:252–263
9. Aguilar-López R, Martínez-Guerra R, Maya-Yescas R (2003) State estimation for partially unknown nonlinear systems: a class of integral high gain observers. IEE Proc Control Theory Appl 150:240–244
10. Daoutidis P, Soroush M, Kravaris C (1990) Feedforward/feedback control of multivariable nonlinear processes. AIChE J 36:1471–1484
11. Nikačević NM, Huesman AEM, Van den Hof PMJ, Stankiewicz AI (2012) Opportunities and challenges for process control in process intensification. Chem Eng Process Process Intensif 52:1–15
12. Ogunnaike BA (1986) Controller design for nonlinear processes via variable transformations. Ind Eng Chem Process Des Dev 25:241–248
13. Precupa R-E, Hellendoorn H (2011) A survey on industrial applications of fuzzy control. Comput Ind 62:213–226
14. Aguilar-López R, Maya-Yescas R (2005) State estimation for nonlinear systems under model uncertainties: a class of sliding-mode observers. J Process Control 15:363–370
15. Daoutidis P, Kravaris C (1991) Inversion and zero dynamics in nonlinear multivariable control. AIChE J 37:527–538
16. Isidori A (1995) Nonlinear control systems, 3rd edn. Springer, London
17. Morari M (1983) Design of resilient processing plants-III. A general framework for the assessment of dynamic resilience. Chem Eng Sci 38:1881–1891
18. Aguilar-López R, Maya-Yescas R (2008) Inverse dynamics: a problem on transient controllability for industrial plants. Inverse Probl Sci Eng 16:811–827
19. Perko L (2001) Differential equations and dynamical systems, 3rd edn. Springer, New York
20. Aguilar-Lopez R, Mata-Machuca J, Martinez-Guerra R (2010) On the observability for a class of nonlinear (bio) chemical systems. Int J Chem Reactor Eng 8(1): Article 3
21. Hespanha JP (2009) Linear systems theory. Princeton University Press, Princeton
22. Kalman RE (1960) A new approach to linear filtering and prediction problems. J Basic Eng: 82:35–45
23. Bastin G, Dochain D (1990) On-line estimation and adaptive control of bioreactors. Elsevier, Amsterdam
24. Tornambé A (1992) High-gain observers for nonlinear systems. Int J Syst Sci 23:1475–1489
25. Drakunov SV, Utkin VI (1995). Sliding mode observers. Tutorial. In: Proceedings of the 34th conference on decision 81 control, New Orleans, USA, December 1995, pp 3376–3378
26. Drakunov SV, Utkin VI (1992) Sliding mode control in dynamic systems. Int J Control 55:1029–1037
27. Slotine J, Li W (1991) Applied non-linear control. Prentice Hall, Englewood Cliffs
28. Edwards C, Spurgeon SK (1998) Sliding mode control. Taylor & Francis, London
29. Fridman L, Shtessel YB, Edwards C, Yan X-G (2008) Higher-order sliding-mode observer for state estimation and input reconstruction in nonlinear systems. Int J Robust Nonlinear Control 18:399–412
30. Shtessel Y, Edwards C, Fridman L, Levant A (2013) Sliding-mode control and observation. Control engineering. Springer, New York
31. Gauthier JP, Hammouri H, Othman S (1992) A simple observer for nonlinear systems application to bioreactors. IEEE Trans Autom Control 37:875–880

32. Aguilar-López R, Maya-Yescas R (2006) Robust temperature stabilization for fluid catalytic cracking units using extended Kalman-type estimators. Chem Prod Process Model 1:1–20, Article 3
33. Aguilar-Sierra H, Martinez-Guerra R, Mata-Machuca J (2011) Fault diagnosis via a polynomial observer. In: 8th international conference on electrical engineering computing science and automatic control, Merida, pp 121–126
34. Mata-Machuca J, Martinez-Guerra R, Aguilar-Lopez R (2010) An exponential polynomial observer for synchronization of chaotic systems. Commun Nonlinear Sci Numer Simulat 15:4114–4130
35. Vázquez-Ojeda M, Segovia-Hernández JG, Hernández S, Hernández-Aguirre A, Maya-Yescas R (2012) Optimization and controllability analysis of thermally coupled reactive distillation arrangements with minimum use of reboilers. Ind Eng Chem Res 51:5856–5865
36. di Felice R, de Favery D, de Andreis P, Ottonello P (2008) Component distribution between light and heavy phases in biodiesel processes. Ind Eng Chem Res 47:7862
37. Cornejo-Jacob JL, Vázquez-Ojeda M, Segovia-Hernández JG, Hernández S, Maya-Yescas R (2013) Comparación de gasto energético y desempeño a lazo cerrado de secuencias de destilación reactiva y térmicamente acopladas para producción de biodiesel (in Spanish). In: X International Congress on Innovation and Technologic Development (CIINDET 2013), Cuernavaca, Morelos, México, March 13–15, 2013: Article # 621
38. Segovia-Hernández JG, Hernández-Vargas EA, Márquez-Muñoz JA, Hernández S, Jiménez A (2005) Control properties and thermodynamic analysis of two alternatives to thermally coupled distillation systems with side columns. Chem Biochem Eng Quart 19:325–332
39. Jiménez-García G, Aguilar-López R, Maya-Yescas R (2011) The fluidized-bed catalytic cracking unit building its future environment. Fuel 90:3531–3541
40. Corella J (2004) On the modelling of the kinetics of the selective deactivation of catalysts. Application to the fluidized catalytic cracking process. Ind Eng Chem Res 43:4080–4086
41. Froment GF, Bishoff KB, de Wilde J (2011) Chemical reactor analysis and design, 3rd edn. Wiley, New York
42. Aguilar-López R, Alvarez-Ramírez J (2002) Sliding-mode control scheme for a class of continuous chemical reactors. IEE Proc Control Theory Appl 149:263–268
43. Alvarez-Ramirez J, Aguilar R, López-Isunza F (1996) Robust regulation of temperature in reactor-regenerator fluid catalytic cracking units. Ind Eng Chem Res 35:1652–1659
44. Hovd M, Skogestad S (1993) Procedure for regulatory control structure selection with application to the FCC process. AIChE J 39:1938–1953
45. Aguilar-López R (2003) Integral observers for uncertainty estimation in continuous chemical reactors: differential-algebraic approach. Chem Eng J 9:113–120
46. Kravaris C, Palanki S (1988) Robust nonlinear state feedback under unstructured uncertainty. AIChE J 7:1119–1127
47. Deza F, Busvelle E, Gauthier JP, Rakotopara D (1992) High gain estimation for nonlinear systems. Syst Control Lett 18:295–299
48. Grosdidier P, Mason A, Aitolahti A, Vanhumaki V (1993) FCC unit regenerator-reactor control. Comput Chem Eng 17:165–179
49. Kurihara H (1967) Optimal control of fluid catalytic cracking process. PhD dissertation, MIT, Cambridge
50. Taskin H, Kubat C, Uygun Ö, Arslankaya S (2006) FUZZY-FCC: fuzzy logic control of a fluid catalytic cracking unit to improve dynamic performance. Comput Chem Eng 30:850–863

Index

J.G. Segovia-Hernández, A. Bonilla-Petriciolet (eds.), *Process Intensification in Chemical Engineering*, DOI 10.1007/978-3-319-28392-0