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Salvatore Parisi · Weihui Luo

Chemistry of Maillard Reactions in Processed Foods

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Chapter 1
The Importance of Maillard Reaction in Processed Foods

Abstract This chapter concerns the importance of Maillard reaction in the current industry of processed foods from a chemical viewpoint. Historically, the Maillard reaction has been extensively studied in different food ambits because of the influence on chemical and sensorial properties of cooked products. However, Maillard reaction products have been often found in many foods in relation to different processing operations, including cooking procedures. Consequently, currently available food processing operations may have some influence on prepared foods when speaking of Maillard reaction (non-enzymatic browning). This chapter is essentially dedicated to the basic description of current food processing operations in the industry: each process is mentioned with the most known or intended name, and it may explicitly include one or more subsections describing different operations with similar meaning or effects. Each process is also explained with reported effects on foods and beverages when speaking of Maillard reaction and the consequent analytical detection of related products.

Keywords Cooking · Extrusion · Fermentation · Food processing
Heat removal · Maillard reaction · Thermal treatment

Abbreviations

MRP Maillard reaction product

1.1 Food Processing and the Maillard Reaction

The knowledge of food processing options and correlated factors in the modern industry should be recommended when speaking of Maillard reaction products (MRP) in edible products. Because of the complexity of chemistry of foods and beverages, the study of Maillard reaction in foods might be initially discouraging for many interested readers (Mania et al. 2017; Martins et al. 2001; Sharma and Parisi 2017; Singla et al. 2018; Steinka et al. 2017; Zaccheo et al. 2017).

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For these reasons, this chapter would describe the Maillard reaction in strict connection with main food processing operations currently available in the food industry. With reference to each processing operation, the main features of the described argument are briefly discussed when speaking of MRP possible detection. Some processes have not been described here: lyophilisation (or freeze-drying), freeze concentration, modified atmosphere packaging systems, smoking procedures, coating processes and packaging operations, because of the low or negligible influence on MRP production.

Maillard reaction in foods can be observed provided that (Hodge 1953; Martins et al. 2001; Singla et al. 2018; Tressl et al. 1995; Van Boekel and Brands 1998):

(1) The examined food contains nitrogen-based compounds (amino acids, peptides, proteins) and reducing sugars at the same time
(2) Peculiar processing or storage conditions are available. In particular, Maillard reaction—a 'non-oxidative browning' series of reactions—can produce different intermediates and final MRP (5-hydroxymethylfurfural, diacetyl, acetic and formic acids, brownish melanoidins, etc.) if foods or intermediates are exposed to high temperatures and for a prolonged time.

The second condition may tacitly imply cooking processes are the main process with abundant MRP production. On the other hand, industrial productions may have several processes using high-temperature values for a limited time, with similar effects. For this reason, the discussion of the main food processing operations with some influence on Maillard reaction or the reliable determination of MRP should be useful.

1.2 Food Processing Operations—A General Overview

The most common processing operations in the food industry are strictly correlated with the peculiar food sector and intrinsic features such as durability (Parisi 2002). Similar operations may be classified and grouped in a few specific categories in function of their position in the general process flow, or depending on a peculiar feature (Fiorino and Parisi 2016; Lingnert 1990; Marcus 2016; Markowicz et al. 2012).

On these bases, the following food processing operations can be subdivided as follows without relation to the specific food category (Fig. 1.1):

(a) Preliminary room-temperature operations: preliminary cooling; wet and dry cleaning, sorting and grading; peeling
(b) Size reduction
(c) Mixing
(d) Forming
(e) Separation processes

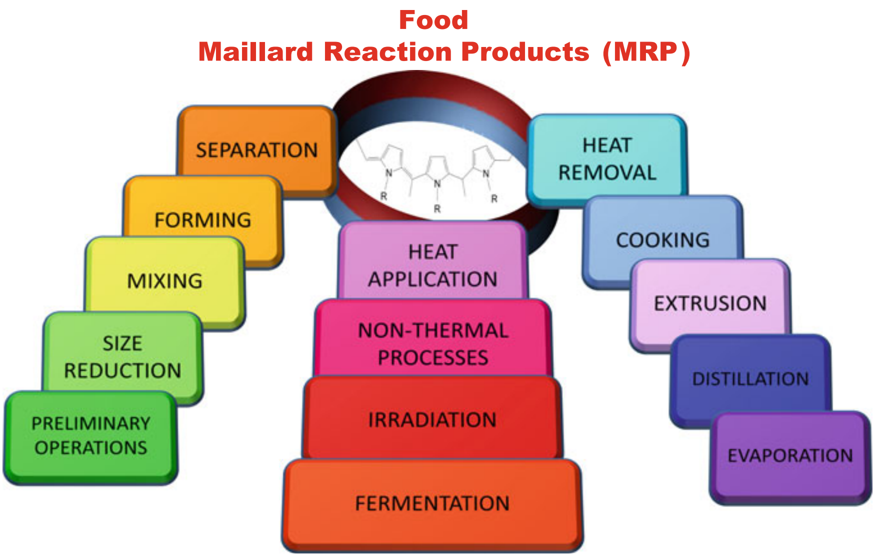

Fig. 1.1 The most common processing operations in the food industry are strictly correlated with the peculiar food sector and intrinsic features such as durability. Similar operations may be classified and grouped in a few specific categories in function of their position in the general process flow, or depending on a peculiar feature. On these bases, the following food processing operations can be discriminated without relation to the specific food category

(f) Fermentation processes
(g) Irradiation processes
(h) Nonthermal processes: high-intensity pulsed electric fields; high hydrostatic pressure; ultrasounds; high-intensity light
(i) Thermal treatments with heat application: blanching; dehydration; dielectric heating; frying; ohmic heating; pasteurisation; sterilisation
(j) Evaporation
(k) Distillation
(l) Extrusion
(m) Cooking procedures
(n) Thermal treatments with heat removal: chilling; freezing.

All above-mentioned processing operations, displayed in Fig. 1.1, are discussed in relation to the following:

(1) The applicability in the food sector, when speaking of peculiar food typologies, and
(2) The possible influence on food products because when speaking of MRP detection in the intermediate food(s) and in the final product(s).

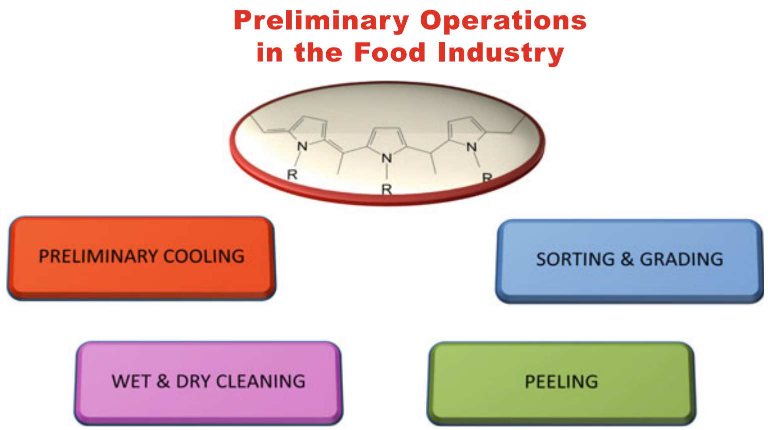

Fig. 1.2 Preliminary operations in the food industry are generally subdivided in four categories, depending on the peculiar process and raw materials to be processed

1.2.1 Preliminary Operations

This section concerns all preliminary operations for raw materials (Fig. 1.2). In general, two reasons justify the existence of preliminary operations in the food industry (Anino et al. 2006; Earle 1983; Fellows 2000; Hartel and Heldman 1998; Martín-Belloso and Soliva-Fortuny 2010):

1.2.1.1 Preliminary Cooling

Vegetable and animal raw materials may be rapidly cooled by means of refrigerated water or chilled air. A general procedure involves the use of refrigerated air on the surface of treated produce without freezing defects. Another system is performed with very low pressures (vacuum cooling), and it may be used for vegetable raw materials such as spinach and cabbage. Should the 'volume/surface area' ratio be notable, the preferred option would be hydrocooling; chilled water is used and recycled with chlorine or ozone addition (Anino et al. 2006; Earle 1983; Fellows 2000; Hartel and Heldman 1998; Martín-Belloso and Soliva-Fortuny 2010).

It should be noted that rapid cooling is not preferred when speaking of animal raw materials immediately after slaughter. The reason is the possible arrest of *rigor mortis* processes with a peculiar phenomenon, 'cold shortening' (it is a typical pre-*rigor mortis* defect at nonfreezing temperatures, reported in relation to red meats), and correlated defects concerning processed meats (in brief, these products tend to be 'tougher' than expected). The solution should be the adequate storage of red-meat carcasses (beef, lamb) above 10 °C. On the other side, some positive results have been reported when speaking of tropical water fish.

Consequently, the following edible raw materials should be considered in this specific ambit:

(a) Vegetable produce and fruits, including apples, beets, broccoli, cantaloupes, carrots, grapes, mushrooms, pears, plums, strawberries, yams (Bernaś and Jaworska 2017; Finkle 1973; Jiro 2002; Serdyuk et al. 2017)
(b) Processed powders obtained from rice, wheat, corn, barley, beans (Toyokura 1995)
(c) Animal raw materials (all types), including animal products such as milk (Jeppson 1975; Tyapugin et al. 2015)
(d) Fish/seafood raw materials: mackerel, S*ardinella moraine*, mussels, etc. (Narumiya and Mikawa 2001; Verkhivker and Altman 2018)
(e) Other food preparations, including processed foods, cheese, boiled rice, sushi preparations, biscuits, noncarbonated and carbonated soft drinks, etc. (Dayakar and Bhargavi 2017; Menin and Mazor 1999; Narumiya and Mikawa 2001).

On the other side, it should be considered that different processing steps applied to heated foods or canned foods are named 'preliminary cooling'; actually, these processes are not applied at the beginning of the food production process, and this distinction should be taken into account (Jeppson 1975).

In general, preliminary cooling treatments have no visible effects on the detection of MRP in foods. On the other hand, the following modifications should be considered from the analytical viewpoint (Anthonius and De Vries 1941; Buldini et al. 2002; De Lathauwer et al. 1981; Kreulen 1976; Le Bail et al. 1999; Menin 2001; Serdyuk et al. 2017):

(1) Food intermediates, especially products and raw materials with high water content and fluids, can be totally or partially crystallised during this treatment. Consequently, should MRP be present in the original raw material(s) or pre-processed food(s) (several situations imply the use of transformed raw materials), the food matrix could suffer a partial displacement of certain nutritional components with consequent inhomogeneity. As a result, the amount of detectable MRP in sampled foods could be affected because the texture of analysed samples is not homogenous
(2) The crystallisation of food matrices should concern sugar solutions, cereal solutions such as maize-starch-melted samples, fruits, etc. In these situations, carbohydrate/lipid complexes could be observed in the crystallised state; the same thing may be observed when speaking of solid and liquid extracts from edible fats and oils, and sugar crystals by separation processes
(3) In addition, partial or total crystallisation may determine the incomplete dissolution of certain proteins, fat matter or amino acids in the analytical procedure. This situation should be considered
(4) The production of MRP may be easily detected and observed after this step. Because of the inhomogeneity of the sample and textural differences in the same food product, the sampling step in the analytical assessment may be important enough.

With these exceptions, it should be affirmed that this process has no predictable effects on the detectability of target analytes (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Nielsen 2003; Vaclavik and Christian 2014; Walstra 2003).

1.2.1.2 Wet and Dry Cleaning

Cleaning processes are carried out with the aim of removing different contaminants from raw materials. The operation may be performed in two different ways: wet and dry procedures (Grandison 2006; Ortega-Rivas 2012).

Wet cleaning processes are considered more effective than dry cleaning processes when speaking of the following removal targets: soil particles, dust, pesticide residues. Warm water is strictly required; in addition, this water can be recycled in the process with consequent additional expenses (filtration, sanitization by means of chlorine addition, etc.). Another (negative) feature is strictly linked with water temperature because chemical reactions and microbial spreading are remarkably accelerated at higher thermal values. By the technological viewpoint, different systems can be considered (spraying, flotation, ultrasonic washing, etc.). Finally, washing water has to be eliminated by means of physical means such as centrifugation; unfortunately, treated fruits and vegetables may suffer superficial damages with enzymatic browning and other defects. By the analytical viewpoint, MRP should not be considered in this ambit; however, the overall appearance of damaged food intermediates is easily correlated with browning effects (Grandison 2006).

Dry cleaning systems are useful when speaking of foods with low-moisture contents, reduced dimensions and notable mechanical resistance. The following equipment—magnetic separators, air or density classifiers and screening devices such as ultraviolet or X-rays detectors—are used in this ambit (please note that the continuous evolution of screening systems proposes also nuclear magnetic resonance imaging, ultrasonic detectors and other imaging techniques, at present). The resulting effluent (food intermediate) is dry enough with reduced microbial risks because of the lower bioavailable water. On the other side, dust production is a serious problem with important safety consequences (including food recontamination).

With relation to the analytical detection of MRP, wet cleaning procedures should not have direct effects on the detectability of target analytes. On the other side, cleaning means a significant reduction of general contaminants, including processing-derived molecules such as MRP; this situation should be considered. The use of citric acid, ozone or chlorine in washing waters can be observed in certain situations when speaking of peeled and/or size-reduced fruits and vegetables. Interestingly, the so-called enzymatic browning—similar to Maillard reaction—may be avoided or reduced by the visual viewpoint in this way because of microbicidal power of these sanitisers (Ahvenian 2000; Grandison 2006).

The use of technologically advanced systems (ultrasounds, spraying) should not have direct effects on target analytes. The problem of water sources should be solved with appropriate sanitisation; enzymatic browning may be inhibited in this way.

With relation to dry cleaning, the process should not have direct effects on the detectability of target analytes. However, it should be considered that:

(a) Foods with reduced dimensions and notable mechanical resistance could have a higher detection probability if compared with high- and medium-size products (the higher the surface area, the higher the probability of MRP formation)
(b) Aerosolized agglomerations are possible in food production areas. Consequently, powdered particles—possibly containing MRP from different raw materials and lines—may be transported and contaminate easily dry cleaning equipment and the treated food intermediate (Parisi 2012).

Consequently, raw materials treated with dry cleaning systems should be evaluated carefully when speaking of minimally processed foods.

1.2.1.3 Sorting and Grading

Sorting operations aim to discriminate food or food intermediates depending on a well-known and measurable property. The main goal of sorting procedures is the uniformity of food intermediates for subsequent operations; consequently, the removal of peculiar contaminants is not correlated with sorting. On the other hand, should the uniformity of raw materials be important for a selected production, the definition of one or more physical features (defining the perceived ‘quality’) would be needed. For these reasons, sorting systems take into account only four factors: dimensions, shape, colorimetric appearance and weight of the screened raw material (Chen and Sun 1991).

Shape sorting can determine the good or bad evaluation of raw materials (such as raw potatoes) for subsequent processing because regular shapes are desirable. The same thing may be affirmed when speaking of standardised colorimetric appearance and related inspection procedures. Size sorting has the same meaning; in addition, the discrimination of raw materials on the basis of different dimensional features impacts on the effect of subsequent processing activities such as heat processes (smaller bodies may be overheated and bigger materials may be undercooked in a constant heating process, provided that processing parameters are defined for a defined raw material size). Weight screeners are extensively used in the food industry because of the same reasons.

Grading operations mean the concomitant evaluation of foods and food intermediates based on more than one single feature. Consequently, grading is more complex than a simple sorting process because each material is classified (graded) based on many features with enhanced results. Naturally, the negative factor of grading operations is correlated with the remarkable cost of quality control procedures if compared with simple sorting systems.

With reference to the impact on the detection of MRP in foods, sorting and grading procedures may have some importance. The food industry is accustomed to consider the selection of raw materials as one of the main pillars of the allergenic and safety monitoring program (Zhao and Chakrabarty 2012; Rohrbach et al. 1992; Taylor and Baumert 2010; Whyte et al. 2002). In detail, cross-contamination between different production lines (using different raw materials) is avoided or limited by means of extremely drastic controls on entering raw materials.

Dimensions, weight and shape of controlled raw materials have a critical importance because the probability of cross-contamination episodes may be enhanced in products with high superficial areas (little dimensions, low weights, regular shapes): cross-contamination may occur by means of simple contact between different (moisturised or dry) products. Consequently, sorting operations based on different single parameters (including colours) and grading procedures should give more assurance in this ambit (many parameters are considered at the same time). It should be also noted that some MRP have been defined as suspected allergenic substances in certain conditions, and the initial MRP detection may be useful (Chung and Champagne 1999; Gupta et al. 2017). Subsequent processes such as mixing (possible cross-contamination) may significantly increase the probability of MRP detection (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Nielsen 2003; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003). In addition, enzymatic browning (similar to Maillard reaction when speaking of visible colours on food surfaces) may be enhanced because of superficial damages on vegetables and fruits (Sect. 1.2.1.2) (Grandison 2006). On the other side, sorting and grading operations should not have direct effect on Maillard reaction.

1.2.1.4 Peeling

Peeling systems aim to remove undesirable materials from food intermediates (fruits and vegetables) by means of steam processes (high-pressure steam), abrasive surfaces, knives or flames (Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012).

The use of flash steam (high pressure) may be detrimental because of superficial heat penetration; however, current processes are designed with the aim of avoiding overheating (cooking). The use of washing water is also required.

Abrasive surfaces are always correlated with low costs; however, three negative aspects should be considered:

(1) Removed product is more abundant if compared with other peeling systems;
(2) Removed skins require a huge amount of washing water. As a result, the higher the supposed water bioavailability, the higher the risk of enhanced microbial spreading
(3) Finally, production rates (in terms of kilograms of food intermediate per hour or minute) are not excellent, however, some exceptions exist.

Knives may be useful when speaking of fruits with easily removable skin. Finally, flame-peeling systems have been designed for the industry of onions. Substantially, the use of furnaces operating at 1,000 °C and the subsequent removal of charred peel surfaces by means of high-pressure water sprays can determine good results (Srivastava et al. 1997).

Peeling processes should not have direct effects on the analytical detection of target analytes (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Nielsen 2003; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003). However, direct effect on Maillard reaction cannot be excluded. It should be considered that:

(a) The use of abrasive surfaces or knives requires appropriate sanitisation (cross-contamination in industries with many raw materials)
(b) The abundant use of washing water could be detrimental because waters have to be removed (Sect. 1.2.1.2).

On the other side, flame peeling is expected to favour the production of MRP because applied temperatures are approximately 1,000 °C; moreover, flash steam methods may be because of superficial heat penetration. Consequently, the influence of peeling steps may not be negligible in certain situations (Zamora and Hidalgo 2005).

1.2.2 Size Reduction

The reduction in the size of food raw materials and intermediates is extremely desirable in highly automated processes. In general, size reduction is perceived as reduction of solid masses; on the other side, liquid food could need to be dimensionally reduced (Saravacos and Kostaropoulos 2002; Simpson et al. 2012).

Size reduction may be named differently (Fig. 1.3):

- Emulsification (for fluid foods such as milk, butter, margarines, etc.)
- Atomisation (for liquid foods only such as oils)
- Grinding
- Compression
- Impact
- Chopping
- Cutting
- Slicing
- Dicing
- Milling

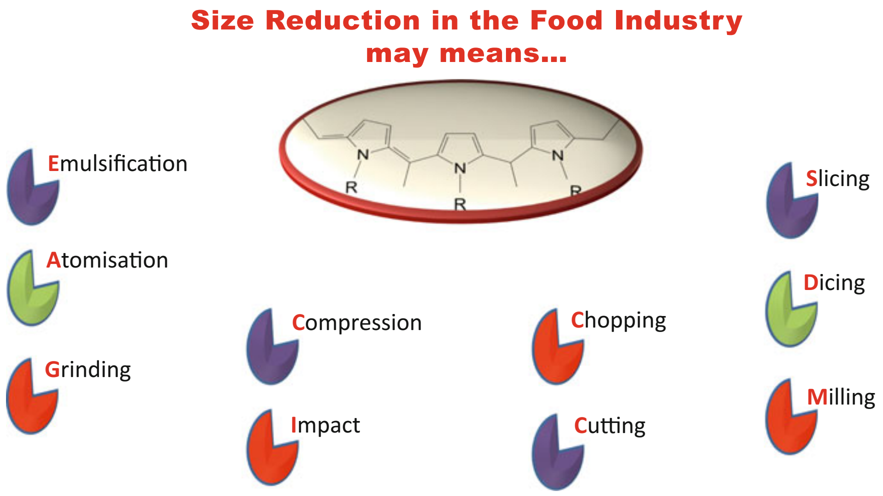

Fig. 1.3 Size reduction may be named differently. As an example, when speaking of solid foods, there are many dedicated systems for virtually each food category. As an example, fibrous foods require generally cutting systems with different features, including parts such as uncoated knives, ultrasonic cutters, pin-and-disc mill, dicers, bowl choppers, etc. In addition, size reduction is normally defined emulsification (or homogenisation) for liquid foods. It has to be noted that emulsification and homogenisation are not exactly synonyms

In general, positive features of size reduction are (Amirante 2013):

(a) Standardisation of raw materials and food intermediates for subsequent operations
(b) The 'volume/surface area' ration tends to lower values with enhanced suitability for heating, drying, cooling, and extraction processes
(c) The definition of a correct 'roundness' index for one specific food unit (this number can roughly be considered as the approximation of possible impact damages between two similar food pieces)
(d) Mixing operations are notably easier depending on reduced size particles.

When speaking of solid foods, there are many dedicated systems for virtually each food category. As an example, fibrous foods require generally cutting systems with different features, including parts such as uncoated knives, ultrasonic cutters, pin-and-disc mill, dicers, bowl choppers, etc. Minimally processed foods could not be obtained without an adequate size reduction step. The important thing is that fibrous foods have the 'right' texture; otherwise, the process could not obtain good results because the efficiency of size reduction is directly dependent on food hardness and friability. Anyway, some negative effects are reported in this ambit:

(a) The augment of food surfaces exposed to air always increase perishability, as stated in the Second Law of Food Degradation (Parisi 2002)
(b) Moderately moist foods may be deteriorated rapidly after size reduction

(c) Microbial spreading is generally accelerated, and biochemical reactions may be notably enhanced
(d) The oxidation of fatty acids and carotenes has to be considered. This fact explains also sensorial modifications for size-reduced products.

When speaking of liquid foods, size reduction is normally defined as emulsification (or homogenisation). It has to be noted that emulsification and homogenisation are not exactly synonyms (Fellows 2000; Hartel and Heldman 1998):

(a) Emulsification is the result of a stable emulsion composed of two physical phases, where the dispersed phase (in the continuous phase) is composed of small droplets
(b) On the other side, homogenisation aims to the size reduction of dispersed phase particles until less than one micrometre.

As a result, homogenization has to be considered as the drastic version of pure emulsification processes.

With relation to emulsification, critical parameters include rheological properties of the continuous phase, and the difference between phase densities. In addition, several emulsifying agents may be required, including ionic chemical substances such as lecithin, salts of oleic acid, certain proteins (egg albumin should be mentioned in this discussion), some stearyl-2-lactylates, nonionic compounds such as glycerol monostearate, and hydrocolloids such as alginates, carboxymethylcellulose, Guar, pectin, etc. (Brennan 2006).

With relation to homogenisation, different systems are available at present: generally, these equipment obtain good results with the application of high speed, pressure, use of colloid mills, ultrasounds, or micro-fluidisers. Unfortunately, each process can determine a different emulsion: as an example, margarine is a simple water-in-oil emulsion while cream for butter production is an oil-in-water system. Anyway, the global network—dispersed and continuous phases—has peculiar viscosity and textural properties depending on many factors. Interestingly, certain emulsions such as ice creams have an important air amount (related air particles may measure less than 100 μm). This reflection should be considered carefully because of the possible abundance of air micro-bubbles in certain sections of the final food product.

With relation to the impact on the analytical determination of MRP, size reduction should be evaluated carefully because of with high superficial areas (little dimensions, low weights, regular shapes): cross-contamination between different production lines and raw materials may occur by means of simple contact between different (moisturised or dry) products. Consequently, size reduction might potentially increase the MRP detection if compared with available information, because of the entering of raw materials. Food intermediates should be evaluated carefully when speaking of minimally processed foods. Subsequent processes such as mixing (possible cross-contamination!) may significantly increase MRP probability of detection (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker

1983; Nielsen 2003; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003).

The standardisation of fruits, vegetables, raw meats, cheeses and other food intermediates can determine enhanced suitability for heating, drying, cooling, extrusion and extraction processes.

1.2.3 Mixing

Mixtures are one of the most critical processes in the food industry (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Nielsen 2003; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003). Similar operations involve two or more ingredients with different physical and chemical features, including rheological properties. In addition, there are several risks correlated with mixing because one or more of mixed ingredients could have low resistance (high friability or resistance to cracks) if compared with other ingredients. As a simple consequence, mixing may give more or less homogenised masses or separated (and visible) phases in the same mixture.

Generally, mixtures of solid foods are not homogenised products: many factors are against this possibility, including differences in particle sizes, density, moisture, shapes, aggregation and rheological properties. Should these properties be similar enough, a good homogeneous product could be obtained. With concern to fluid ingredients, the viscosity has a main role because certain food products or intermediates exhibit non-Newtonian features (irregular viscosity values and turbulent movement). As a result, different mixing processes involve different fluid ingredients and concern different problems. For these reasons, different mixer types are available at present in the food industry depending on the desired process and mixture (small-particle solids and powders, intermediate viscous liquids, high-viscosity liquids, and dispersions) (Brennan 2006). Interestingly, a good or excellent mixing of all components with the virtual homogeneous structure of the final product seems to be correlated with the geometrical shape of these mixers and inner parts, time/temperature features of related processes, and the continuous addition of 'fresh' material in the working mass.

With reference to the influence on the analytical detection of target analyte(s), the mixing step should be evaluated carefully because the probability of analytical detection may be enhanced in mixtures where one or more components have high superficial areas (little dimensions, low weights and regular shapes).

Obtained mixtures should be homogeneous depending on particle sizes, density, moisture, shapes, aggregation and rheological properties of involved components.

The geometrical shape of mixers (and inner parts), time and temperature, and the continuous addition of 'fresh' material in the working mass are important parameters. In certain situations, the production of food emulsions can be observed; however, food matrices are not thermodynamical equilibrium systems, in general. Consequently, the higher the viscosity of intermediate masses during mixing, the higher the possible heat transfer during the production (intermolecular friction is partially turned into thermal dissipation) (Brennan 2006; McClements 2015; Metcalfe and Lester 2009). However, no direct correlations between mixing operations and MRP have been demonstrated so far.

The possibility of non-Newtonian behaviours with turbulence in the mixer has to be considered; as a result, obtained masses could be not homogeneous (air micro-bubbles, coexistence of different phases, isolated clumps, macroscopic aggregations, etc.). As a result, the more irregular the matrix, the most erratic (variable) the distribution of potential MRP in the food. Subsequent processes could not modify the distribution of potential MRP, unless another mixing process is needed (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Nielsen 2003; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003).

1.2.4 Forming

This operation is critical in the food industry because the final appearance of the food product depends partially on the performance of related forming systems. Actually, there are a number of possible forming options, virtually one per each food product (and raw materials for the food industry). Essentially, solid products are 'formed' by means of specific metallic, plastic, or hybrid moulders after filling (by pressure) and subsequent removal (by means of cutting rollers, knives, wire-cut machines, etc.). Naturally, the texture of intermediately formed masses has to be evaluated; in certain situations, cooling is strictly required if masses are fluid enough and cannot maintain the desired geometrical shape. This problem may also be observed when speaking of certain packaged food immediately after forming procedures. In addition, it should be mentioned that certain foods are formed by extrusion processes (Sect. 1.2.13) and immediately packaged; consequently, forming may be also named 'extrusion' in these cases. The geometrical shape and speed of forming are the critical factors in this ambit (Björck et al. 1984; Noguchi et al. 1982).

With reference to the analytical detection of MRP, this process has no predictable effects in general (Belitz et al. 2009; Coupland 2014; Fennema 1996; Saravacos and Kostaropoulos 2002; Vaclavik and Christian 2014; Walstra 2003). Possible non-homogeneity issues are probably caused in other processing steps (example: mixing). Maillard reaction is favoured under drastic thermal conditions; the forming operation does not appear to be able to determine thermal dissipation in food intermediated during this step, with the important exclusion of 'pure' extrusion processes and the use of high pressures. Actually, the addition of food plasticisers (water, glycerol, sucrose, etc.) to high-protein content masses may avoid thermal modifications (Hernandez-Izquierdo and Krochta 2008; Hernandez-Izquierdo et al. 2008). However, no direct correlations between forming operations and MRP have been demonstrated so far.

1.2.5 Separation Processes

Separation processes are always required in the food industry. One or more reasons may be considered. In general, the separation of different food constituents from one single matrix may mean the production of one or more high quality and cheap food products, and one or more by-products with some significant feature for the food industry (or other non-food sectors). Certain substances such as soy lecithin may be described as good examples, although the list is surely longer and heterogeneous, including rennet casein for cheese productions, peculiar proteins such as milk albumins, etc. This section could also include the removal of different contaminants (Sect. 1.2.1) or the partial removal of water (evaporation, Sect. 1.2.10).

Anyway, separation processes aim to obtain (Belitz et al. 2009; Coupland 2014; Fennema 1996; Lerici and Lercker 1983; Saravacos and Kostaropoulos 2002; Tamime 2009; Vaclavik and Christian 2014; Walstra 2003):

(a) The removal of solid or liquid matters of high importance from fluid or dry food intermediates, or liquids of low importance by different viewpoints (nutritional, economic purposes, etc.), or
(b) The recovery of very important compounds in little quantities from a food intermediate (enzymes are a good example). In this situation, low yields are always considered a success depending on the cost of the 'very important' food product.

Five different separation processes are known at present (Fig. 1.4):

1. Centrifugation, intended as separation of immiscible liquids, or removal of solids (low quantities) from liquids (also named clarification), or recovery of solids with some economic importance
2. Filtration (intended as the removal of suspended and insoluble particles from a liquid medium) by means of systems using vacuum or pressure filters
3. Oil or juice extraction by means of batch or continuous presses. Basically, a liquid medium is separated from the original fruit or vegetable raw material by fragmentation or rupture of cellular walls and subsequent (or concomitant) separation by means of semiautomatic presses or continuous 'expellers'
4. Solid/liquid extraction of important food constituents by means of peculiar solvents. The targeted substance has to be organic and chemically compatible with the chosen solvent (water, organic solvents such as cyclohexane, etc.)
5. Membrane filtration processes: hyperfiltration (separation of water from molecules with low molecular weight, ideally <300 Da), nanofiltration (removed particles have a molecular weight between 300 and 1,000 Da), ultrafiltration (molecular weights < 300,000 Da), and microfiltration (molecular weight are >300,000 Da). Other processes are electrodialysis and ion exchange separation systems.

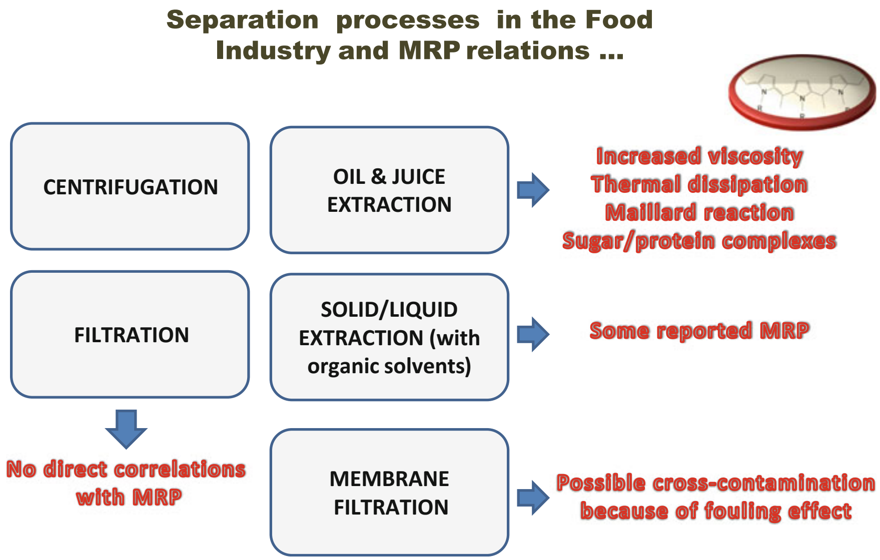

Fig. 1.4 Five main different separation processes are known at present: centrifugation (also named clarification when speaking of removal of solid particles); filtration; oil or juice extraction; solid/liquid extraction of important food constituents by means of peculiar solvents; and membrane filtration processes (hyperfiltration, nanofiltration, ultrafiltration and microfiltration). These techniques can have their own positive properties and some negative features when speaking of MRP in edible products

These techniques can have their own positive properties and some negative features. Centrifugation performances are measured based on recovered materials; substantially, results depend on the constant composition of entering materials on the one side (thermal values may have some influence), and the cleanliness of used systems on the other side (cross-contamination is always possible). The same thing may be affirmed when speaking of filtration techniques; obtained performances are good enough, but results depend on the quantity and quality of entering substances (with relation to insoluble solids), related processing temperatures, and the status of used filters. Oil and juice extraction systems may be conducted with good results; however, the best extraction is normally obtained in a two-stage process (first, rupture of cellular walls; second, effective extraction). In addition, the use of higher temperatures diminishes oil viscosity and extraction yields are naturally enhanced. On the other hand, heat-conducted extraction processes may be detrimental for the obtained product in terms of viscosity, excessive oxidation because of the reduction of active polyphenols, browning defects, etc.

Matured vegetables and fruits give better results in relation to extraction processes; on the other side, observed defects are similar to those obtained with heat-conducted processes.

Extraction with solvents is favoured at high temperatures, but food substances may be partially destroyed in these situations with increased viscosity values; in addition, the superficial area of raw materials determines the performance of these processes (the higher the surface area, the higher the theoretical extraction). Solvents should be easily removable, and this performance may depend on the purity of selected solvents.

Finally, membrane concentration systems are different enough with relation to aims and technological features. In general, it may be observed that the main limitations of these procedures are correlated with the composition of feeding (entering) fluids on the one hand, and with the maximum capacity of removable solid matters (it should be less than one-third of the total amount of entering fluids). Additionally, all used membranes are subject to the deposition of 'fouling' powders after a certain time; consequently, it has to be considered that predictable performances should decrease, and that deposed polymers could interfere with filtration by means of possible contamination.

With concern to MRP detection, centrifugation and filtration have not direct effects with the exception of some problem related with the rheology of entering matters, the presence of insoluble solids, and incorrect sanitisation procedures (cross-contamination is possible). However, no direct correlations between these operations and MRP have been demonstrated so far.

On the other hand, heat-conducted oil and juice extraction could give unexpected problems in terms of increased viscosity, thermal dissipation/consequent Maillard reaction with possible complexes involving sugars and proteins, and separation between different phases depending on the presence of relevant lipid amounts. Extraction with solvents might cause some problem (Sims and Morris 1987); for this reason also, the use of microwave filtration systems has been proposed as a valid alternative method when speaking of organic oils extracted from fruits (Ahmad and Langrish 2012).

Finally, membrane filtration systems might have some effect because of the known 'fouling' defect. Should a dedicated equipment be used alternatively for different productions, the cleanliness of all interested machine parts would be assured; otherwise, cross-contamination episodes could be expected erratically (Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Belitz et al. 2009; Tamime 2009). On the other side, membrane filtration is often proposed as one of the most powerful systems for the prevention of enzymatic browning (no Maillard reaction) of raw fruit juices (Gökmen et al. 1998; Sapers 1991).

1.2.6 Fermentation Processes

Fermentation is a well-known process in the food industry: it is part of historical food traditions worldwide. Many processed foods are or contain fermented food intermediates such as baked products, cheeses (Goff 2017), alcoholic beverages, etc. Selected cultures are used with the aim of modifying food textural properties, colours, aromas, and enhancing related durabilities. Actually, the last objective is reached by means of other preservative treatments; however, fermentation processes are used today on a large scale worldwide (Fellows 2000; Hartel and Heldman 1998). In addition, enzymatic reactions may be considered in different environments with excellent results in terms of obtained yields, nutritional values, and production costs (if compared with traditional fermentative processes).

With relation to fermentation processes, selected culture are used with the aim of performing homo-or hetero-fermentative reactions depending on the final product (one or more compounds respectively, including) from organic substrates; anyway, final molecules are ethyl alcohol and carbon dioxide or organic acids. The discussion would require many pages; consequently, the reader should consult more specific literature papers. By the technological viewpoint, one element at least should be mentioned. Several lactic acid bacteria have been recently made available in the fermentation industry and widely appreciated because of peculiar stabilising (rheological) properties. In particular, the use of stabilising and emulsifying agents may be limited or avoided if used lactic acid bacteria are able to produce 'firm'-fermented masses.

In general, fermented foods are different from the original raw material because of the modified composition of proteins, lipids and carbohydrates. The concomitant transformation of these molecules in simple compounds modifies the entire chemical and physical state of the fermented food with increased viscosity, incorporation of gaseous molecules, and in general with the possibility of irregular (non-homogeneous) sections in the tridimensional structure of the fermented food.

The utilisation of peculiar enzymes in food productions aims to eliminate these irregular results. As a result, pectic enzymes such as polygalacturonase can be used with the aim of avoiding gelatinization in certain fruit and vegetable preparations.

Fermentation processes are reported to favour the production of MRP, probably because of prolonged treatments and correlated temperatures. For this reason, the detection of MRP in fermented foods has to be expected (Amarowicz 2009).

1.2.7 Irradiation Processes

Food irradiation is used in the industry with the aim of preserving food commodities against different menaces: degradative and pathogen agents, insects, larvae, etc. Irradiation may reduce effects of normal (natural) chemical reactions in foods such as ripening (the inhibition of sprouting is also reported). Food commodities are exposed to ionising radiations (X-rays and electrons) without direct contact (Fellows 2000; Hartel and Heldman 1998; Lerici and Lercker 1983).

With reference to the aims of this document, it should be noted that ionisation may potentially hydrolyse and oxidise carbohydrates and fatty molecules with modifications of the complete food structure. Actually, ionising treatments are designed and implemented with the aim of avoiding or limiting similar defects. However, it has been reported that foods with high lipid concentrations are not suitable for irradiation (Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Lerici and Lercker 1983).

Irradiation processes determine MRP production in treated foods: in particular, the production of brown MRP (pigments) has been demonstrated under ultraviolet irradiation at 420 nm when speaking of whey proteins. Gamma irradiation is responsible for MRP generation (different products) in irradiated foods up to 100 kGy; similar effects have been reported with relation to microwave irradiation (Chawla et al. 2009; Rao et al. 2011; Yeo and Shibamoto 1991). As a result, the impact of irradiation cannot be excluded when speaking of Maillard reaction in modern foods.

1.2.8 Non-thermal Processes

This section is specifically dedicated to processes for the production of 'minimally processed' foods and their influence on Maillard reaction and the analytical detection of MRP. The demand for these products has increased constantly in the last years because of the following (desired) properties:

(a) Minimally processed foods are obtained with little or completely absent thermal processes
(b) Organoleptic features of the original food are virtually unchanged, with special reference to colorimetric appearance and aroma; microbial spreading, responsible for the rapid degradation of fresh fruits and vegetables, is inhibited
(c) The general consumers' appreciation is high and in constant increase.

Many 'non-thermal' processes may be described; this document is focused on four main technologies because of their positive results and the current state of the art (Ahmed et al. 2016; Barbosa-Cánovas and Juliano 2008; Fellows 2000; Hartel and Heldman 1998; Lerici and Lercker 1983; Saravacos and Kostaropoulos 2002; Simpson et al. 2012):

(1) High-intensity pulsed electric fields
(2) High hydrostatic pressure
(3) Ultrasounds
(4) High-intensity light.

1.2.8.1 High-Intensity Pulsed Electric Fields

High-intensity pulsed electric fields (electrolysis) can be used with good results in the industry of liquid foods (Heinz et al. 2001) because of the following advantages:

(a) Vegetative life forms are practically destroyed
(b) Sensorial features of treated foods and food intermediates are practically unchanged
(c) There are not reported toxicological adverse effects.

On the other side, the following disadvantages have to be considered carefully:

(1) Enzymes are not affected by this method; consequently, enzymatic reactions may take place
(2) This treatment cannot be used for solid foods
(3) Heat treatments should be used in conjunction with this technology. Consequently, one of the main prerequisites for minimally processed foods does not appear satisfied
(4) Electrolysis effects have to be evaluated carefully. In fact, the general modification of foods is not reported yet, but there are not reports with relation to normal (continuous) or large-scale productions with several batches or sub-lot units.

1.2.8.2 High Hydrostatic Pressure

High-pressure systems are well known in the food industry (Barbosa-Cánovas and Juliano 2008), because vegetative life forms can be destroyed or inactivated at pressure values exceeding 350 MPa at least (spores can be destroyed at 400 MPa with a coupled and moderate heating). High pressures may be applied statically or with pulsed treatments (the last systems appears more useful). In general, related advantages of this method are the following:

(a) Elimination/inactivation of vegetative life forms and spores (depending on treatments)
(b) Sensorial features of treated foods and food intermediates are practically unchanged
(c) There are not reported toxicological adverse effects
(d) The result of this treatment is virtually constant and uniform into all ideal sections of the products.

On the other side,

(1) Certain enzymes are not affected by this method (apparently, more than 1,000 MPa could be requested in some cases); consequently, enzymatic reactions might take place
(2) This treatment cannot be used for foods where free water is <40%
(3) Heat treatments could be used in conjunction with this technology
(4) It has been reported that some microorganism could survive
(5) Finally, this process should be performed as a discontinuous system, with some management problems on the practical level.

1.2.8.3 Ultrasounds

The use of high-intensity ultrasound waves with applied frequency $\leq$ 2.5 MHz can be useful in certain ambits because of the following effects on foods (Soria and Villamiel 2010):

(a) Tissues are physically demolished; consequently, present vegetative cells, enzymes and spores are eliminated
(b) Selected chemical reactions such as oxidation can be promoted
(c) The process can be discontinuous (batch processing) or continuous, depending on exigencies.

On the opposite hand, it should be mentioned that:

(1) Ultrasound waves may be partially impeded in their action depending on the physical composition of the food and the possible air presence
(2) Texture can be compromised
(3) Heat treatment is required in conjunction with this technology.

1.2.8.4 High-Intensity Light

High-intensity light systems can effectively destroy microorganisms by means of photothermal and photochemical reactions. The emitting light source works in the ultraviolet spectrum and in the visible spectrum at the same time; as a result, ultraviolet rays cause photochemical effects, while radiations in the visible spectrum cause thermal destruction. The application of pulsed light radiation requires very short temporally cycles: sensorial features of treated foods are reported to be substantially unmodified. On the other side, microbicidal effects are reported only on the surface of treated foods, while inner layers could be not affected.

With reference to Maillard reaction and the reliable MRP analytical detection in treated foods, discussed processes may have some effects (Ahmed et al. 2016; Barbosa-Cánovas and Juliano 2008; Belitz et al. 2009; Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012).

High-intensity pulsed electric fields (electrolysis) do not alter enzymatic activity; on the other side, heat treatments may be required in connection with this system. In general, thermal procedures may favour the modification of proteins (example: serum albumin) in connection with carbohydrates (example: dextran); Maillard reaction should be expected in these situations. Pulsed electric fields have been reported to promote potentially MRP production (Guan et al. 2010); however, the comparison between heat treatments and this system on different food intermediates has demonstrated that non-enzymatic browning is reduced in the second situation (Cortés et al. 2008). With relation to analytical detection, the distribution of target analytes in the sample should not be altered.

High-pressure systems could diminish the allergenic danger on condition that applied pressures are very high because enzymatic activity is inhibited over 1,000 MPa (no significant reports are available at present). Heat treatments may be a problem, similarly to pulsed electric fields. With relation to detectability, the distribution of target analytes in the sample should not be altered in a negative way because high pressure is applied on all the food intermediate without differences; consequently, inhomogeneity should not be observed.

With concern to ultrasounds, heat treatments are required in connection with this method: possible problems should be expected, similarly to pulsed electric fields. For these reasons, the application of ultrasounds and heat treatments can notably enhance Maillard reaction in different food intermediates, especially with relation to the production of glycated proteins (Chen et al. 2016); in addition, the texture of food intermediates may be modified (inhomogeneity of the final product?). As a result, ultrasounds should be evaluated carefully.

High-intensity light should not have important effects with relation to the reliable MRP detection because this treatment appears useful only on the surface of treated foods, while inner layers do not appear modified. Thermal effects should be limited to surfaces only. On the other side, this method is reported to have effects on colour, taste, and aroma of certain yellow cheeses (Kim et al. 2003). Consequently, the possible effect of high-intensity light should be evaluated in connection with other non-thermal systems, although sensorial results may appear more favourable in comparison with light-pasteurised products (Caminiti et al. 2012).

1.2.9 Thermal Treatments with Heat Application

Thermal treatments with heat application are one of the basic pillars in the industry of foods: many reasons, the tradition above all, can justify this reflection. The main difference between historical heat treatments and the modern application and improvement is correlated with the remarkable number of food categories and sub-categories available at present (Grandison 2006).

Many processed foods mean many possible processing problems (and related solutions). The current state of the art in the field of heat treatments could be explained in a simplified way by means of the following list (Fellows 2000; Hartel and Heldman 1998 Lerici and Lercker 1983; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Schoeninger et al. 2017; Tamime 2009):

- Blanching (with steam or hot water)
- Dehydration (with hot air)
- Dielectric heating
- Frying (with hot oils)
- Ohmic heating
- Pasteurisation and sterilisation.

Each treatment may have slightly different goals; however, the basic aims of thermal treatments with heat applications can be summarised as follows:

(a) Modification of organoleptic features of the food product with hedonistic importance by means of the chemical and physical transformation of proteins, fat substances, carbohydrates, starches, etc.
(b) Preservation of foods against degradative life forms, pathogen agents, enzymatic action and other living contaminants (insects, larvae, parasites, etc.)
(c) Shelf-life enhancement without additional storage treatments (refrigeration, etc.).

The description of each thermal treatment is not among the aims of this document. However, the following subsections give a simplified description of each process with information concerning risks and advantages.

1.2.9.1 Blanching

Blanching is used for vegetable and fruit raw materials with the aim of blocking enzymatic activity and limiting microbial spreading in harvested materials. For this reason, it should be considered as a preliminary operation. Raw materials are heated rapidly, maintained at the chosen thermal value for a very limited time, and then rapidly cooled. Steam or hot-water blanching systems can be used (temperature: 70–105 °C); differences are correlated with the effective blanching of the product: steam blanchers do not assure the complete treatment in all external and inner layers of the food; consequently, some section may be over-blanched, and other sections may remain under-blanched. In addition, washing (and adequate sanitised water) is required, and some part of the raw material may be lost. With relation to hot-water systems, thermophilic bacteria may survive; the use of sanitised water is remarkable. Anyway, blanching water may contain calcium chloride with the aim of enhancing texture firmness of raw materials after the treatment (the formation of calcium pectate networks can help). The use of different calcium salts (gluconate, lactate, etc.) as firmness enhancers has been reported, although these substances may be used for fruit impregnation instead of water blanching (Alzamora et al. 2005).

1.2.9.2 Dehydration

Dehydration aims to remove the most part of the aqueous content by heat application. Consequently, food durability is extended because degradative and pathogen agents are notably inhibited (bioavailable water is much reduced). Hot-air systems are used for this operation. Some risk exists when speaking of dehydration processes: in fact, the physical structure of the food matrix may notably reduce the performance of similar processes because a relevant part of removable water molecules remains linked to cellular structures. Consequently, size reduction or mechanical cutting operations or atomization (spraying of foods as concentrated fine droplet dispersions) should enhance the process performance. Another problem is the load of treated foods into driers: the higher the amount of treatable units (blocks, single vegetables, etc.), the lower the water removal within a specified time (for a given temperature).

1.2.9.3 Dielectric Heating

Dielectric heating is the application of microwave or radio frequency electric fields to foods with the aim of increasing inner temperature. Actually, the basic aim is to heat preservation by means of low-pressure drying or defrosting operations (when speaking of microwave fields), or simple moisture removal with radio frequency fields. In addition, baking operations may be improved with a supplementary dielectric heating process. The basic problem of this system, widely diffused as household treatment, appears linked with the extreme variability of foods, heating machines, and advices for time and temperature conditions (they depend on the food producer) (Zhao et al. 2000).

1.2.9.4 Frying

Frying is a peculiar process similar to cooking operations, except for the use of hot oils during the process and the thermal increase extended only to external food layers. In fact, water amounts on the external surfaces are rapidly removed when foods are immersed in hot oils, while inner sections may remain moisturised enough. For this reason, fried foods should require other preservation treatments, normally by heat removal (refrigeration, etc.), although the shelf life can be improved depending on the dimensional structure (reduced thickness) and size of foods. Thermal conductivity of foods, applied temperatures (200 °C are often reported as a good superior limit), the type of frying oil, and the peculiar frying method (deep-fat or swallow) have a critical importance. Anyway, the final product is the sum of the initial food intermediate and the adsorbed oil (it may easily exceed one-third of the total product amount). Consequently (Dobraszczyk et al. 2006),

(a) The content of anti-oxidant compounds in the oil (tocopherols) is expected to be lower in ‘old’ oils, while frequently changed oils in the process should assure a good protection against oxidation
(b) Fried foods could be seen as a two-layer structure: a superior layer (the crust) and the inner network. Fats, proteins and carbohydrates are heavily modified in the superficial crust (Maillard reaction has to be considered), and a relevant fat amount is of ‘external’ (oil) origin. In the inner ‘network’, chemical and physical modifications could be lower than expected because frying is not cooking or baking; however, the partial moisture removal may determine a

network-like structure in the food with interesting inhomogeneity. It has to be considered that water removal is inhibited by the crust formation (it acts as a sealing layer), while oil is allowed to diffuse from the surface to the inner layer (and the higher the entrained oil, the lower the moisture content.

1.2.9.5 Ohmic Heating

Ohmic heating is substantially the application of alternating electric currents to a food, with the consequent heat dissipation and thermal augments. Differently from dielectric heating, this process appears more suitable for continuous processing, and many difficulties such as overheating (burning) are solved. On the other hand, foods should be defined carefully in terms of moisture content, rheological properties, pH, thermal conductivity and dimensional features (length, width, height).

1.2.9.6 Pasteurisation

Pasteurisation and sterilisation are the most known thermal treatments in the food industry (Fellows 2000; Hartel and Heldman 1998).

The first process, pasteurisation, is applied at temperatures < 100 °C; basic goals are the extension of shelf-life values (in terms of several months) for acidic foods, while low-acid foods can be effectively treated with the aim of destroying pathogens and extending durability (in terms of several days) at the same time. Times and temperatures are variable enough: two good examples can be 65 °C (time: 30 min) for fruit juices (acid foods), or 71.5 °C (time: 15 s) for milk (low-acid food). With reference to negative effects, some minimal effect on sensorial properties can be observed because thermal values are not excessive, and the same thing can be affirmed for cycle times. Probably, observed defects are mainly related to local overheating problems caused by incorrect design and implementation of processes.

1.2.9.7 Sterilisation

Sterilisation and the subsequent evolution, ultra-high temperature (UHT) treatment, are more drastic processes, aiming to the complete destruction of alternative and pathogen agents, with additional inactivation of enzymes. Different time and temperature cycles may be decided on condition that critical factors have been established. Interestingly, the effect of sterilisation treatments depends also on the decided time on the basis of a few factors such as pH (of the food intermediate), container sizes, microbial resistance to heat and the characterization of food intermediates (solid, liquid, colloid appearance, etc.).

1.2.9.8 Impact on Maillard Reaction and MRP Analytical Detection

Different situations have to be discussed here, as displayed in Fig. 1.5 (Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Belitz et al. 2009; Tamime 2009; Schoeninger et al. 2017). Blanching is a low-thermal treatment, and its main aim is to block enzymatic activity and inhibit microbial spreading in harvested raw materials. For these reasons, blanching may have good results when speaking of low MRP, in particular, acrylamide in French fries, probably because of microstructural modifications in the original potatoes, and the consequent uniform diffusion of asparaginase (Pedreschi et al. 2011). The problem of enhanced Maillard reaction appears linked to prolonged heat treatments only (Puupponen-Pimiä et al. 2003). Interestingly, the use of firmness enhancers such as calcium chloride is reported to reduce acrylamide levels (Mestdagh et al. 2008). On the other hand, the intermediate mass may show low weights and reduced firmness when speaking of potato cubes, while dried papaya products may show enhanced textural properties (Severini et al. 2003).

Dehydration aims to remove the most part of the aqueous content by heat application. Consequently, a relevant part of water-soluble food allergens should be theorically removed. Consequently, Amador compounds and MRP, in general, are often correlated with dehydrated products such as orange juices, raisins, onions, garlic, etc. (Del Castillo et al. 1999).

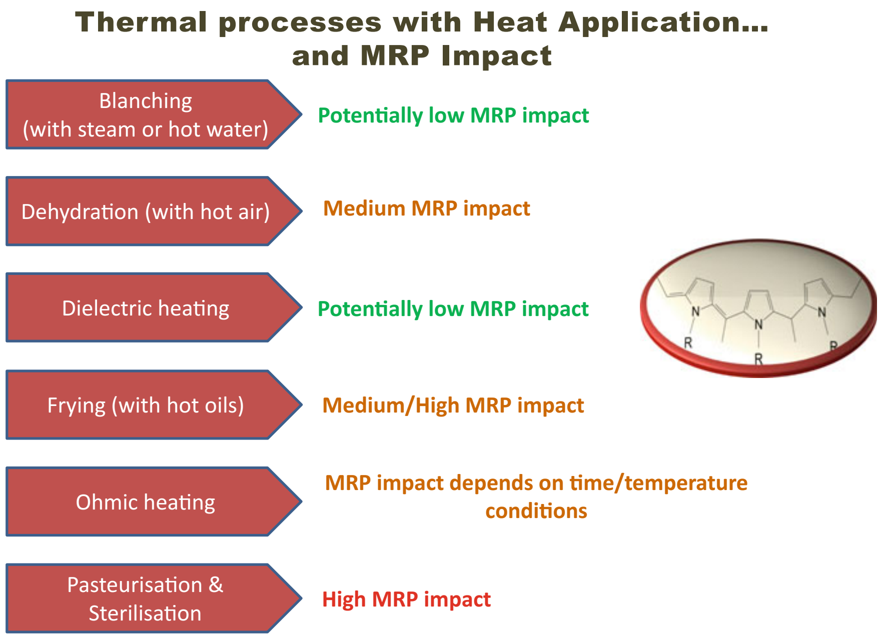

Fig. 1.5 The influence of thermal food processing with heat application in relation to MRP detection

With reference to dielectric heating, related systems for food applications have not been apparently evaluated in connection with Maillard reaction. On the other side, frying techniques appear to be in strong connection with MRP production, especially acrylamide in deep-fried fries (Gertz and Klostermann 2002). Boiling processes are reported to favour Maillard reaction when speaking of products such as beers, milk and rice wines (Van Boekel 1998).

With relation to sampling, the structure of fried foods such as potato strips should be also considered. The two-layer distribution (hard crust/ soft core) is not homogeneous (Pedreschi et al. 2001).

The influence of ohmic heating on MRP production in foods depends mainly on time/temperature combinations. At present, it may be assumed that the denaturation of proteins and MRP production are similar if classical heating systems and ohmic heating processes are carried out in products such as model infant formulae and milks (Roux et al. 2009).

Pasteurisation and sterilisation are generally reported to have notable influence on MRP production in all possible food ambits. The most part of scientific papers have shown these processes are the main cause of reactions and effects including the thermal destruction of caseins, MRP formation, overburning/overcooking, production of various complexes involving allergenic foods, and inhomogeneity in treated foods because of technical malfunction (agitation failures) or non-Newtonian behaviour of the treated fluid (Singla et al. 2018). Actually, pasteurisation is reported to cause denaturation of β-lactoglobulin and α-lactalbumin in certain situations. Caseins cannot be denatured: these proteins may be partially demolished. Anyway, alternative processes concerning heat treatments are generally evaluated in comparison with sterilisation and pasteurisation because these techniques are recognised to enhance MRP production and have notable microbicidal power at the same time (Jaeger et al. 2010).

1.2.10 Evaporation

Evaporation treatments have the basic aim of removing partial water content from liquid foods only by vapourization (Fellows 2000; Hartel and Heldman 1998). In other terms, food intermediates have to be treated at the boiling point for water, with two main consequences: reduction of water activity values, and concentration of non-volatile components. For these reasons (including the exclusive application for liquid foods only), the treatment is different from other above-discussed separation systems. Steam is required: the process may be performed increasing pressure and steam temperature, or lowering thermal values of the boiling liquid (water) under partial vacuum conditions. Anyway, surfaces of evaporation equipment may be covered by fouling deposits, similarly to agglomerations found on membrane separation systems. In this ambit, the main causes of similar deposits have to be considered (a) the natural degradation (denaturation) of proteins, (b) the deposition of certain polymers (polysaccharides) and (c) chemical and physical differences between treated foods (rheological properties, thermal values, etc.) and evaporator surfaces. Anyway, the higher the concentration, the higher the resistance of treated foods (in terms of non-uniform heat transfer, heat damages or burning) because of increasing viscosity values. Maillard reaction has to be considered carefully; evaporated foods often suffer darkening effects.

Evaporation treatments are reported to have important effects when speaking of Maillard reaction in liquid foods, similarly to pasteurisation and sterilisation (Belitz et al. 2009; Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Schoeninger et al. 2017; Tamime 2009).

1.2.11 Distillation

Distillation treatments have the basic aim of removing one or more volatile components with different volatility degrees of a liquid mixture by means of selective evaporation and subsequent condensation (Fellows 2000; Hartel and Heldman 1998; Lerici and Lercker 1983; Saravacos and Kostaropoulos 2002; Simpson et al. 2012). The main product, the condensed 'distillate', contains more volatile substances, preferably separated the one from the other, while compounds with lower vapour pressure remain as residual substances at the base of the so-called distillation column. Modern industrial systems do not operate batch distillation; economic reasons suggest the continuous addition of liquid mixtures and the concomitant separation of most volatile fractions, with additional partial reflux (recycling) of a limited distillate amount for ameliorated separation.

Naturally, defects of distilled products are correlated with the thermal augment with all possible options (partial destruction or modification of most volatile compounds because of partial heat dissipation into the column).

Distillation treatments might have some effects when speaking of Maillard reaction in liquid foods, similarly to pasteurisation and sterilisation (Belitz et al. 2009; Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012). However, it has to be considered that the separation of most volatile components excludes molecules with notable molecular weight. These molecules—including high-molecular weight MRP—would remain in the residual mass instead of distilled solutions. Apparently, there are not dedicated researches concerning Maillard reaction and distillation in foods at present.

1.2.12 Extrusion

Extrusion processes aim to realise a new product from intermediate food pastes (fluids), granular masses or powders (Fellows 2000; Hartel and Heldman 1998). Basically, the flow of entering food intermediate is forced to enter into a single unit, the 'extruder': here, the mass is mixed, kneaded, sheared, compressed, possibly cooked, shaped and formed at the same time. A peculiar type of machine, cooking extruders, generally work at temperatures above 100 °C and up to 250 °C (time: 2 min). The new plasticised mass getting out of the extruder, subjected to expansion and directed to the final forming and/or packaging step, is really hotter than the entering mass because of the additional heat treatment and dissipation by friction forces. Anyway, the extruded product has to be cooled. On the other hand, cold extrusion occurs at temperatures < 100 °C; therefore, only heat dissipation by friction forces into the extruded may augment the inner temperature of the final extruded product (confectionery, breakfast cereals, crispbread, melted cheeses, *surimi*, etc.).

In general, these processes are rapid enough; however, the common opinion that extrusion by means of single- or two-screw extruders produces foods with no microbial spreading is incorrect. In fact, foods with low water activity (≤ 0.4) are well preserved because microbial agents cannot operate in similar conditions; on the other side, extruded cheeses with water activity ≥ 0.9 have not a similar justification. In the last situation, main causes for these good performances are the reduced or virtual absence of manipulation in this step, the similarity of extruders with a locked reactor, the absence of process effluents, and the constant or increasing temperature of entering/final masses.

On the other side, extrusion can work well depending on the viscosity of entering food intermediates. In other terms,

(a) The entering mass has to have a constant and well-defined moisture (the presence of this solvent influences heavily the operational viscosity)
(b) The type of entering material(s) has to be correctly defined: particulates, granulated matters (and related size dimensions), fluid materials (melted cheeses), etc.
(c) Chemical and physical features of the entering mass should be known (pH, etc.). Should one or more features be modified after the process, something would be surely gone wrong. As an example, gelatinisation of certain pastes or protein denaturation may be induced by pH variations, increased moisture, unexpected raising temperatures during the process, use of undeclared food additives, etc.

Because of the immediate expansion of extruded masses getting off extruders, the product glassy state tends to set up a new structure when cooled. Consequently, each possible failure in the process would probably remain without solution; this is the situation for partially gelatinised extruded masses with high moisture content and enhanced viscosity, although modern extruders may correct the defect in some way (but the elimination is not assured).

Ideally, cereal-based foods tend to absorb water; there is a certain relationship between thermal values for extrusion and water absorption. Consequently, the higher the severity of thermal extrusion, the higher the aqueous absorption with the possibility of ‘ruling’ starch solubility in some way.

With relation to food containing large natural polymers such as caseinates, gluten or soy proteins, the extrusion process should give cross-linked and oriented polymeric matrices (a sort of fibrous structure) in the direction of the processing flow. This reflection highlights the role of initial, unmodified proteins; these molecules have to be partially demolished during the process. Otherwise, the plasticized structure could not be easily obtained.

Other defects are often caused by the addition of flavours (they could give some sticking effect), non-enzymatic browning and food colourants (should the extrusion process be unable to give perfectly homogenised masses, the dissolution of food colourants in the intermediate mass would give strange lines or fading effects). The production of hydroxymethylfurfural has been reported in some study concerning extrusion processes (cereal products), and the amount of this molecule depends on the concentration of sugars in the entering food intermediate.

With relation to Maillard reaction in extruded foods, the following points have to be considered and carefully evaluated (Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Belitz et al. 2009):

(1) Viscosity is critical; as a consequence, should the entering mass be not constant, the possible inhomogeneity would be expected even in the single food product (if realised with notable weights).
(2) The presence of particulates, clumps, etc., should affect negatively the process and the homogeneity of the final food (example: centre sections are different from external surfaces)
(3) pH variations may induce the partial gelatinisation of certain pastes or protein denaturation. These irregular structures in the final food product may not be corrected. On the other side, high carbohydrate contents may inhibit gelatinisation
(4) Foods containing caseinates (from milk), gluten (from cereals) or soy proteins tend to give cross-linked and oriented polymeric matrices (a sort of fibrous structure) in the direction of the processing flow. This behaviour may be observed if these proteins are not abundant in the food, with possible inhomogeneity in a theoretically plasticised food
(5) Extrusion may require heat treatment or be carried out on heat-treated masses. The reported presence of 5-hydroxymethylfurfural in some study concerning extrusion processes (cereal products), and the amount of this molecule demonstrates the importance of Maillard reaction. Anyway, different researches have reported MRP production in heat-treated and extruded food intermediates (model food systems, pasta, chestnut and rice flour-based doughs, etc.).

1.2.13 Cooking Procedures

Cooking, also intended ‘roasting’ or ‘baking’, aim to remove moisture from certain foods by means of hot-air transfer; however, the main objective is to modify the food itself for palatability purposes (Lerici and Lercker 1983). Naturally, microbial spreading is at least inhibited and durability values could be enhanced, although cooked product needs adequate refrigerated storage before consumption. The term 'baking' is often correlated to the production of flour-based foods, while 'roasting' is associated with meats, vegetables and other non-flour-based products. Thermal conductivity of treated foods is important; at the same time, thickness and other dimensional features of food intermediates have to be considered. The crust formation has to be also evaluated, similarly to frying processes (in fact, frying is a moderate cooking process). Moisture is eliminated by evaporation and conduction (capillary flow phenomena).

The cooking process may be performed with many different systems: direct and indirect-heating ovens, batch or continuous ovens, heated tunnels, etc. The final result depends on the final desired product. Anyway, the following phenomena have to be considered:

(a) Fatty molecules are dispersed in the food and/or are drained off
(b) Proteins are normally denatured and/or are subjected to coagulation
(c) The inner layers become crispy and porous, similarly to a tridimensional network (frying, Sect. 1.2.9.4)
(d) A typical crust is formed as the result of starch gelatinization
(e) Sensorial features (aroma, colour) are completely modified.

Cooking processes are intrinsically connected with Maillard reaction in all foods. In general, MRP production is observed in many researches, in particular when speaking of non-enzymatic browning and aroma modifications (Martins et al. 2001). Substantially, the most part of cooked foods show a variable amount of detectable MRP; for this reason, cooking steps should be always considered when speaking of browning limitation (or enhancement, in certain situations) as the result of Maillard reaction.

1.2.14 Thermal Treatments with Heat Removal

Heat removal can surely increase shelf-life values of produced foods and beverages. Biochemical reactions and microbial activity increase their speed (and correlated effects) at moderate thermal values; on the other hand, thermal reduction means slow biochemical reactions and inhibition of microbial spreading. Consequently, adequate storage procedures can be performed by means of heat removal. Naturally, similar processes should be considered as post-processing systems, although each raw material in the industry is stored at low temperatures more and more times before its use. Chilling and freezing procedures are briefly described here (Fellows 2000; Hartel and Heldman 1998; Lerici and Lercker 1983; Tamime 2009).

1.2.14.1 Chilling

Chilling (or refrigeration) concerns all possible processes with environmental heat removal and consequent food storage between −1 and 8 °C. Shelf-life extension is notable, but it is dependent on the peculiar food product. By the technological viewpoint, the main observed effect is the solidification of fat and oil molecules; this fact means that microbial spreading is only inhibited; in addition, normal physical and chemical reactions (or displacements of certain phases into the product, including water movement) remain possible. Consequently, refrigerated foods are not 'frozen' products, and many possible complaints in the modern industry depend on the confusion between 'chilling' and 'freezing' (Raison and Lyons 1986).

1.2.14.2 Freezing

Freezing (temperatures are usually between −20 and −30 °C, although −40 °C can be easily observed in the industry) is a more drastic procedure if compared with chilling. Frozen foods are a well-established category of food products nowadays: their importance is correlated with the virtual absence of food degradation and microbial activity during freezing, if thermal values are effectively and continually maintained until the end of claimed shelf-life periods. With reference to frozen foods, the normal problem is correlated with ice crystal formation and the dimension of these ice crystals; should crystallisation generate too big agglomerations, tissues would be partially destroyed, and the re-absorption of water molecules in the defrosting step would be difficult enough. In addition, a section of frozen foods remains unfrozen and 'glassy' during the initial treatment (one to several hours) with little damages, although the type of food may influence this behaviour.

Chilling and freezing have no effects on Maillard reaction because of (a) the removal of heat from treated foods, and (b) kinetic considerations dependent on low-storage thermal values. On the other side, freezing treatments could have some effect (Belitz et al. 2009; Fellows 2000; Hartel and Heldman 1998; Saravacos and Kostaropoulos 2002; Simpson et al. 2012; Tamime 2009) because of the production of ice crystals, the possible volumetric expansion during the process, and the subsequent rehydration (defrosting process). Generally, the initial structure is not obtained because ice crystals are not completely re-absorbed; as a result, the original food sample (example: carrots) should be expected to be modified with possible inhomogeneity effects (Préstamo et al. 1998). As a result, sampling may be a critical operation from the analytical viewpoint when speaking of MRP determination in high- and medium-moisturised foods.

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Chapter 2
Maillard Reaction in Processed Foods—Reaction Mechanisms

Abstract The 'Maillard reaction' is one of the most exciting research areas in the field industrial and artisanal food production. Many of the most known and marketed packaged foods in the current market may be correlated with Maillard reaction, especially when speaking of desired aroma, taste and colour modifications. In other words, the 'non-enzymatic browning' can be a distinctive advantage in certain situations, and an important challenge in other ambits, depending on two antithetical factors: the hedonistic expectations of common food consumers, and the demonstrated toxicity and undesired health effects of Maillard reaction products on the human being. Marketing and hedonistic desires on the one side, and health risks on the other side define the current situation with relation to Maillard reaction in foods. Processing operations can be classified and grouped in a few specific categories with relation to non-enzymatic browning in foods: 'strong', 'possible' or 'exclusion of' influence. This classification is chemically explained here by means of basic Maillard reaction steps, from the production of Amadori or Heyns compounds to the final melanoidins (and other intermediate products).

Keywords Acrylamide · Advanced glycation end · Amino compound
5-Hydroxymethylfurfural · Maillard reaction · Melanoidin · Reducing sugar

Abbreviations

AGE Advanced glycation end
HMF 5-hydroxymethylfurfural
MRP Maillard reaction product

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2.1 Maillard Reaction Mechanisms and Food Processing—An Overview

The ‘Maillard reaction’ is one of the most exciting research areas in the field industrial and artisanal food production. Many of the most known and marketed packaged foods in the current market may be correlated with Maillard reaction, especially when speaking of desired aroma, taste and colour modifications. In other words, the ‘non-enzymatic browning’ can be a distinctive advantage in certain situations, and an important challenge in other ambits, depending on two antithetical factors (Singla et al. 2018):

(a) The hedonistic expectations of normal (common) food consumers, and
(b) The demonstrated toxicity and undesired health effects of Maillard reaction products (MRP) on the human beings.

Marketing and hedonistic desires on the one side, and health risks on the other side define the current situation with relation to Maillard reaction in foods.

In addition, the influence of food processing operations on raw materials should be considered and carefully evaluated. The most common processing steps in the food industry are correlated with one or more peculiar food categories; the appearance of the final food has also a certain weight on the ‘right’ process, when speaking of different technological options and choices (Fiorino and Parisi 2016; Lingnert 1990; Marcus 2016; Markowicz Bastos et al. 2012). These operations can be classified and grouped into a few specific categories with relation to the possible MRP production and detection in food products (Sect. 1.2):

(1) Strong influence (probable or demonstrated enhancement of Maillard reaction and MRP production):
(2) Possible influence with relation to the analytical MRP detection because of non-Maillard reaction-related causes
(3) Exclusion of influence with concern to the analytical MRP detection because of non-Maillard reaction-related causes.

The first group—probable or demonstrated enhancement of Maillard reaction and MRP production—should consider at least the following steps (Sect. 1.2, Fig. 2.1):

(a) Fermentation
(b) Irradiation
(c) Non-thermal processes: high-intensity pulsed electric fields; high hydrostatic pressure; ultrasounds
(d) Thermal treatments with heat application: dehydration; dielectric heating; frying; pasteurisation; sterilisation

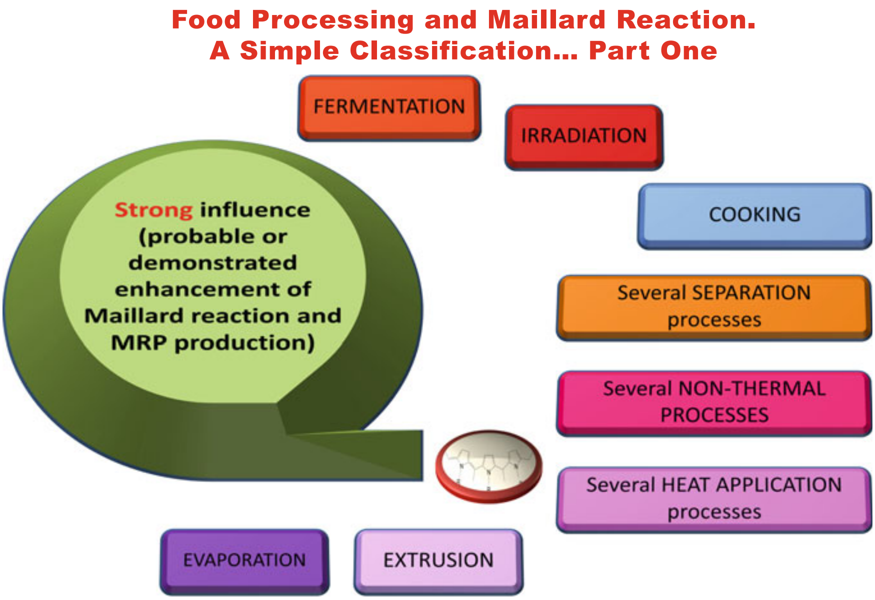

Fig. 2.1 The most common processing operations in the food industry are strictly correlated with the peculiar food sector and intrinsic features. The influence of food processing operations on raw materials should be considered and carefully evaluated. The most common processing steps in the food industry are correlated with one or more peculiar food categories. These operations can be classified and grouped in a few specific categories with relation to the possible MRP production and detection in food products. Several processes have a probable or demonstrated enhancement of Maillard reaction and MRP production

(e) Evaporation
(f) Separation processes: oil or juice extraction; extraction with solvents;
(g) Extrusion
(h) Cooking procedures.

The second group—possible influence with relation to the analytical MRP detection because of non-Maillard reaction-related causes—should consider at least the following processes (Sect. 1.2, Fig. 2.2):

(a) Preliminary room-temperature operations: preliminary cooling, dry cleaning; sorting and grading; peeling
(b) Size reduction
(c) Mixing
(d) Forming
(e) Separation processes: centrifugation; filtration; membrane filtration
(f) Thermal treatments with heat application: dehydration; ohmic heating.

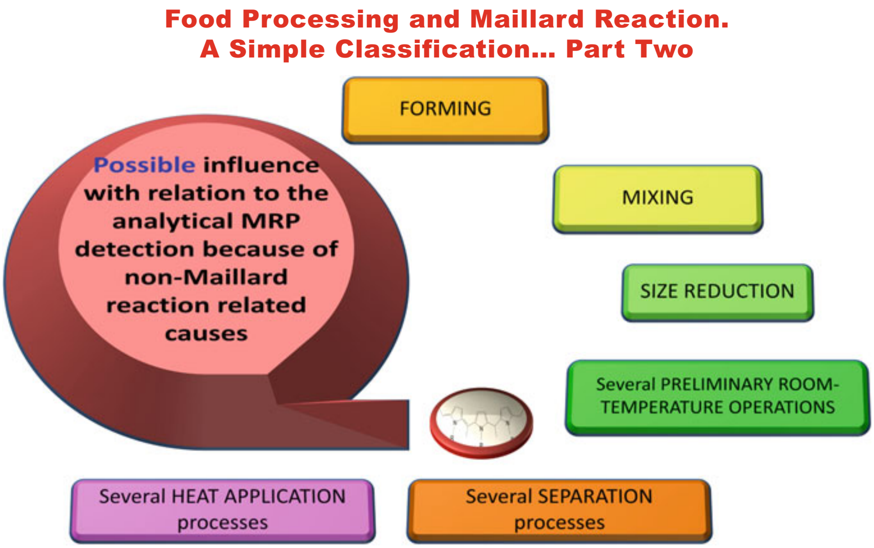

Fig. 2.2 The most common processing operations in the food industry are strictly correlated with the peculiar food sector and intrinsic features. The influence of food processing operations on raw materials should be considered and carefully evaluated. The most common processing steps in the food industry are correlated with one or more peculiar food categories. These operations can be classified and grouped in a few specific categories with relation to the possible MRP production and detection in food products. Several processes may potentially influence the analytical MRP detection because of non-Maillard reaction-related causes

Finally, the third category—exclusion of influence with concern to the analytical MRP detection because of non-Maillard reaction-related causes—should consider these processed (Sect. 1.2, Fig. 2.3):

(a) Preliminary room-temperature operations: preliminary cooling; wet cleaning
(b) Non-thermal processes: high-intensity light
(c) Distillation
(d) Thermal treatments with heat removal: chilling; freezing.

However, the above-shown discrimination of food processing operations is mainly based on the demonstration of Maillard reaction in selected foods, while reaction mechanisms are not mentioned. Because of the multifaceted nature of Maillard reaction—it should be considered as a complex group of concomitant and cascade reactions (Hodge 1953; Martins et al. 2001; Singla et al. 2018), the description of involved reactions should be considered in connection with the particular food category or categories, and with relation to above-considered processes. The aim of this Chapter is to describe Maillard reaction steps—three different stages—in relation to processed belonging to the first group (Fig. 2.1), where

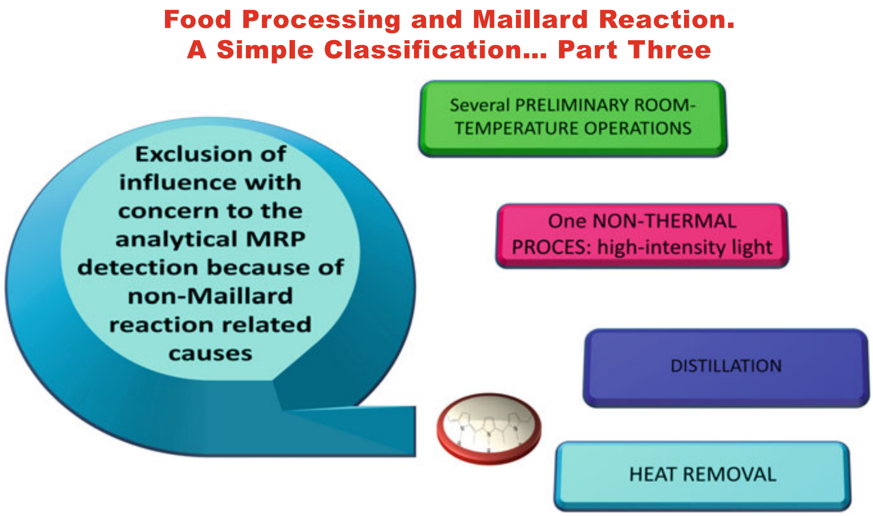

Fig. 2.3 The most common processing operations in the food industry are strictly correlated with the peculiar food sector and intrinsic features. The influence of food processing operations on raw materials should be considered and carefully evaluated. The most common processing steps in the food industry are correlated with one or more peculiar food categories. These operations can be classified and grouped in a few specific categories with relation to the possible MRP production and detection in food products. Several processes have no direct or indirect influence with relation to the analytical MRP detection in foods

a direct influence on MRP production is demonstrated or highly probable. Different non-Maillard reaction pathways—caramelisation, ascorbic acid production, lipid oxidation—are not considered here.

2.2 Maillard Reaction and Food Processing—The First Step

The first equation in the Maillard reaction is a condensation involving two partners (Gupta et al. 2017; Simpson et al. 2012):

(a) A molecule containing a primary amino group, especially amino acids (lysine and arginine above all because of an available free ε-amino group), polypeptides and proteins
(b) A reducing sugar with a carbonyl group.

Results of this condensation are a water molecule and a Schiff's base, in equilibrium with a *N*-substituted glycosylamine (Fig. 2.4); the last intermediate is not stable, and the subsequent transformation—named Amadori rearrangement—gives a 1-amino-1-deoxi-2-ketose (Amadori compound) by means of an intermediate

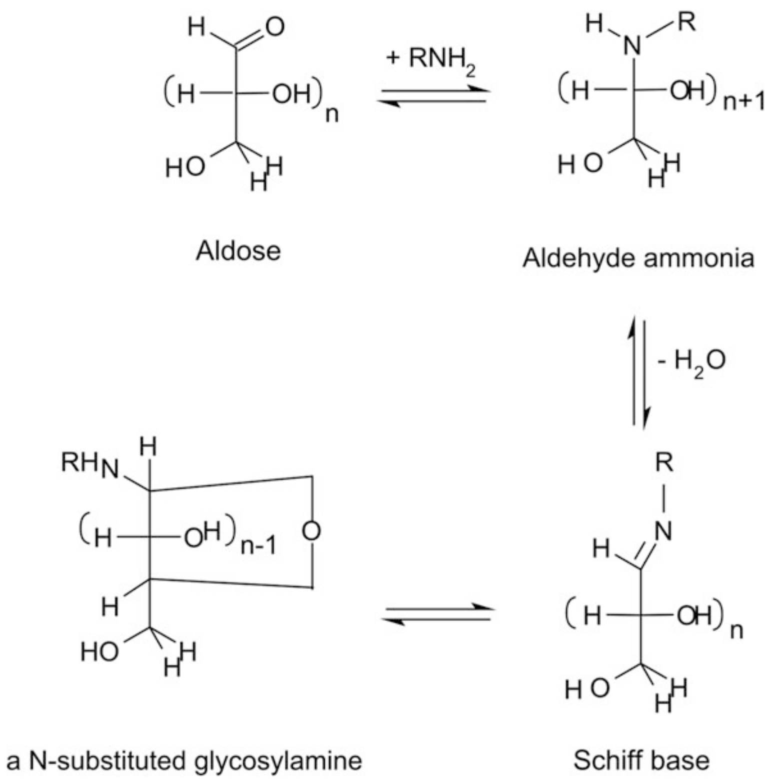

Fig. 2.4 The first equation in the Maillard reaction is a condensation involving a molecule containing a primary amino group and a reducing sugar with a carbonyl group. Results of this condensation are a water molecule and a Schiff's base, in equilibrium with a *N*-substituted glycosylamine; the last intermediate is not stable, and the subsequent transformation—named Amadori rearrangement—gives a 1-amino-1-deoxi-2-ketose (it is not displayed here)

enaminol (Gupta et al. 2017; Li et al. 2014; Simpson et al. 2012). Should the involved sugar be a ketose, the product would be named Heyns compound. Interestingly, this reaction is carried out at high temperatures, and without the production of brownish colours (in fact, the reaction medium remains colourless). Figure 2.4 shows this reaction for a general aldose and a general primary amine.

The obtained Amadori compound is not thermostable, and prolonged storage periods are also a cause of demolition. For these reasons, ketoamines may be subsequently degraded in different ways (Corzo-Martínez et al. 2010; Hodge 1953; Marcus 2016). In general, the first step of Maillard reaction occurs in all foods containing needed partner molecules on condition that high temperatures are provided. In addition, high pressures do not seem to influence the production of Amadori products (Simpson et al. 2012; Singla et al. 2018). On these bases, the first step may be observed in all processes belonging to the first group (Fig. 2.2):

(i) Fermentation
(j) Irradiation
(k) Non-thermal processes: high-intensity pulsed electric fields; high hydrostatic pressure; ultrasounds
(l) Thermal treatments with heat application: dehydration; dielectric heating; frying; pasteurization; sterilization
(m) Evaporation
(n) Separation processes: oil or juice extraction; extraction with solvents;
(o) Extrusion
(p) Cooking procedures.

In relation to interested foods, it could be difficult to operate a reliable discrimination because many foods and food preparations are produced with one or more of above-mentioned processes.

2.3 Maillard Reaction in Acid or Neutral Conditions

The obtained Amadori (or Heyns) compounds may be degraded in different ways, depending on the original reducing sugar and pH conditions (Arnoldi 2001; Corzo-Martínez et al. 2010; Hodge 1953; Marcus 2016; Singla et al. 2018).

In particular, acidic or neutral conditions (actually, pH is reported to be between 4 and 7) determine the transformation or Amadori compounds in the Schiff's base of 5-hydroxymethylfurfural (HMF) or furfural, depending on nature or reducing sugars (hexoses for HMF, pentoses for furfural). Chemically, a 1,2- or 1,3-enolisation mechanism is required (after ring opening), and three water molecules are generated (Corzo-Martínez et al. 2012; Martins et al. 2001). The subsequent addition of one water molecule can turn the Schiff's base into different molecules because of concomitant fragmentations and other complex mechanisms (an amino compound is eliminated):

(a) HMF, or
(b) Furfural.

The production of these intermediates is extremely important for food safety reasons. In addition, these molecules can give—after different steps—brownish polymers called melanoidins. Moreover, the glycation reaction between sugars and amino compounds (proteins) can alter the nutritional amount (Arnoldi 2001; Simpson et al. 2012; Singla et al. 2018).

On these bases, above-mentioned MRP have been found so far in foods as a cause of one or more of heating procedures (Fig. 2.3), including (Aguiló-Aguayo et al. 2009; Belitz et al. 2009; Corzo-Martínez et al. 2010; Guerra-Hernández et al. 2002; Martins et al. 2001; Morales et al. 1996; O'Brien et al. 1989; Porretta 1991;

Rada-Mendoza et al. 2004; Serra-Cayuela et al. 2014; Singh et al. 2009; Zhu et al. 2009):

(a) Heating (product example: pasteurised milk, pasteurised fruit juices, baked rye bread, treated honeys, roasted coffee)
(b) Hydrolisation of vegetable proteins and starch
(c) Dehydration of certain vegetables.

Substantially, each process involving high temperatures, a prolonged time cycle and pH values $\leq$ 7.0 is potentially able to determine the production of HMF, furfural, dycarbonyl compounds and other MRP suitable for the subsequent production of melanoidins. Therefore, each heating process shown in Fig. 2.3 is involved, including also fermentation, irradiation and extrusion (Adams 2005; Nursten 2007; Rao et al. 2011; Van Rooijen et al. 2014).

2.4 Maillard Reaction in Alkaline Conditions—The Formation of Advanced Glycation End Products

The obtained Amadori (or Heyns) compounds may be also degraded at pH values > 7 with the production of the following molecules (Corzo-Martínez et al. 2012; Martins et al. 2001; Nursten 2007; Singla et al. 2018):

(a) Reductones, in equilibrium with the correspondent dehydroreductones.
(b) Dicarbonyl molecules, including glyoxal, methylglyoxal, glycolaldehyde, 1- and 3-deoxyglucosones, etc.

Interestingly, reductones may be also converted into fission (carbonyl) products. Subsequently (Gupta et al. 2017),

(1) Dehydroreductones may give melanoidins (Fig. 2.5) and/or amino ketones by means of the presence of a single amino compound
(2) At the same time, dehydroreductones may react with fission molecules via Strecker degradation. The obtained Strecker aldehydes may be converted into amino ketones (an amino molecule is required in the last option)
(3) Consequently, dicarbonyl products may be turned into amino ketones and (subsequently) melanoidins. It has to be noted that amino ketones may react with HMF and/or furfural at the same time.

Finally, furfural and HMF may be turned into aminoketones, aldimines and ketimines, and final melanoidins (Fig. 2.5) with the important contribution of amino compounds. Actually, brownish melanoidins can be obtained with the production of other small and medium-molecular-weight polymers able to give distinctive colours or fluorescence to food products; the cooperation of reductones, furfural/HMF and mentioned aldehydes is required and abundantly reported (Gupta et al. 2017; Hofmann 1998; Led and Schleicher 1990). The complete discrimination of

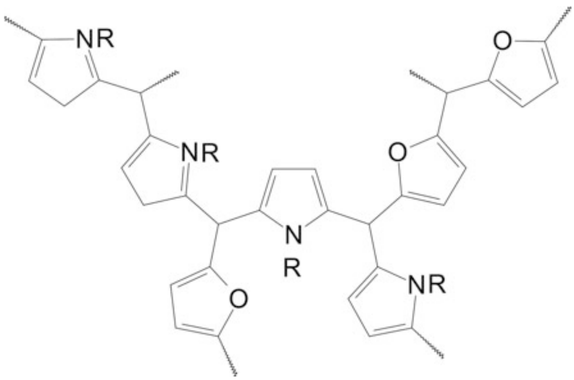

Fig. 2.5 Melanoidins are coloured substances with low or high molecular weight. Originally, small molecules are formed with a peculiar property: the ability of creating high-molecular weight copolymers via cross-linking reactions. Molecular weight can reach 100,000 Da. The other partner is generally a protein with free ε-amino groups (of arginine or lysine or arginine residues). The final brown-coloured compounds have not a definite structure. The displayed molecule is only a fragment; in addition, it represents only one of the many possibilities (Simpson et al. 2012)

involved reactions—cyclisation, dehydration, isomerisation, retroaldolisation, and condensation steps—is difficult enough (Martins et al. 2001); the variety of possible products and by-products does not help the work of involved researches.

Anyway, all possible products obtained with the reaction of fission (dicarbonyl) products and other molecules such as amino compounds are compounds of interest from the medical angle. In relation to in vivo reactions these MRP are named 'advanced glycation end' (AGE) products (Kokkinidou 2013; Singh et al. 2001). AGE are responsible for peculiar protein-AGE adducts and AGE-protein-AGE cross-linked systems (Gkogkolou and Böhm 2012). AGE are normally studied in relation to worrying effects on human health.

The production of AGE and final MRP, in general, can be favoured (and accelerated) on condition that pH of foods and/or food intermediates are 7 or higher values in some point of the production flowchart, or after production (and before expiration date) (Gupta et al. 2017; Simpson et al. 2012). With exclusive relation to heating procedures, different processes might be considered based on thermal conditions and pH values, but the demonstration of a clear and undoubtable connection between processing features and MRP/AGE formation is not assured. For example,

(a) Alkaline fermentation can be considered when speaking of MRP/AGE production. Example: Pidan fermentation (Li and Hsieh 2004; Wang and Fung 1996)
(b) On the other side, irradiation on alkaline sugar–glycine solutions does not appear linked with MRP/AGE production, at present (Oh et al. 2006).

For these reasons, the problem is not the 'right' or 'bad' process, but the treated food depending on pH values. Consequently, the following foods and beverages should be considered when speaking of heating processes and MRP production at pH equal or higher than 6.90 (this list is not exhaustive; pH = 7.00 has been lowered to 6.90 with the aim of including certain products with pH close to neutrality) (Anonymous 1962; Bridges and Mattice 1939; Warren et al. 1995):

- Bird's nest soup
- Boiled flounder
- Camembert cheese
- Clams
- Conch
- Cooked crab meat
- Cooked hominy
- Corn, corn starch, corn flakes, frozen cooked corn
- Cooked spinach
- Egg (white)
- Fresh coconut, coconut milk and coconut preserves
- Graham crackers
- Grass jelly
- Lobster bisque, cooked lobster
- Lotus root
- Olives (black and ripe types)
- Peanut soup
- Peptonised milk
- Sauteed smelts
- Shrimp sauce
- Soy infant formula
- Soybean milk
- Tea
- Tofu (soybean curd)
- Wax gourd drink.

2.5 Maillard Reaction and Alternative Pathways—The Acrylamide Way

It has recently been reported that acrylamide, one of the most known food intermediates with safety importance, has been found in grilled, baked and toasted foods in notable amounts (Corzo-Martínez et al. 2012; Martins et al. 2001). Probably, the reaction of certain amino acids such as asparagine with reducing sugars may give the related Schiff's base with the final production of melanoidins and acrylamide after several steps. Acrylamide is reported to be an important marker for Maillard reaction in certain foods, especially grilled, baked and toasted products (Corzo-Martínez et al. 2012; Fiorino and Parisi 2016; Martins et al. 2001). In addition, Mediterranean-diet foods could be analysed with a presence of this toxin (Delgado et al. 2017).

In general, acrylamide is produced after the formation of a Schiff's base from a reducing sugar (glucose, fructose) and a specific amino acid, asparagine (Mottram et al. 2002; Simpson et al. 2012; Singla et al. 2018; Swedish National Food Administration 2002). Subsequently, the obtained Amadori compound, *N*-(D-glucos-1-yl)-L-asparagine, is decomposed by means of several steps with the elimination of carbon dioxide, ammonia and the production of acrylamide over 5 μg/kg in certain products (Simpson et al. 2012).

Actually, subsequent studies have demonstrated that (Borda and Alexe 2011; Simpson et al. 2012; Singh et al. 2007):

(a) 'High' (over 150 μg/kg) or notable acrylamide amounts are usually found after the following processes: frying, grilling, baking and toasting, with the exclusion of remaining heating procedures (at present). The combination of 'old' and new heating processes such as dielectric heating may diminish acrylamide levels, while extrusion might determine the increase of this molecule
(b) Apparently, heating processes should reach at least 120 °C
(c) Asparagine is not essential. Other amino acids, including alanine, cysteine, glutamine, methionine, etc.—might give low acrylamide quantities
(d) The amount of acrylamide in cookies may be correlated with brown colours by means of colorimetric testing methods, and this research confirms the Maillard characterisation of this probably carcinogenic substance (the first stage is common to normal MRP and acrylamide).

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Chapter 3
Maillard Reaction and Processed Foods—Main Chemical Products

Abstract The multifaceted nature of Maillard reaction—a complex group of concomitant and cascade reactions—imposes the description of involved reactions in connection with the particular food category or categories, and with relation to the above-considered processes. In addition, discussed reaction chains give several final products or intermediates normally found in foods or beverages. The aim of this Chapter is to describe briefly the probability of analytical detection of main Maillard reaction products when speaking of the production of Amadori or Heyns compounds, advanced glycation end products and the formation of acrylamide. Consequently, the nonenzymatic browning is discussed by the chemical viewpoint with the correlation between the peculiar Maillard compound (intermediate molecule and/or final melanoidins) and food categories as produced by means of particular processing operations and pertinent conditions (time, temperature, pH values, etc.).

Keywords Acrylamide · Amadori compound · Amino compound
Maillard reaction · Melanoidin · Processed food · Reducing sugar

Abbreviations

HMF 5-Hydroxymethylfurfural
MRP Maillard reaction product

3.1 The Detection of Main Maillard Reaction Products Depending on Processed Foods and Production Methods

The recent interest in the 'Maillard reaction' is one of the most distinctive features of the modern research in food science. Many of the most known and marketed foods may be correlated with Maillard reaction, especially when speaking of desired aroma, taste and colour modifications. The 'non-enzymatic browning' can

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be a distinctive advantage in certain situations, and an important challenge in other ambits, depending on two antithetical factors (Singla et al. 2018a):

(a) The hedonistic expectations of normal (common) food consumers, and
(b) The demonstrated toxicity and undesired health effects of Maillard reaction products (MRP) on the human being.

The influence of food processing operations on raw materials should be considered and carefully evaluated, as discussed in Chaps. 1 and 2. In particular, these processes can be classified and grouped in a few specific categories (Figs. 2.1, 2.2, and 2.3) with relation to the possible MRP production and detection in food products (strong influence, possible influence or no involvement (Sect. 1.2). Other classifications are strictly dependent on their position in the general process flow, or on a peculiar feature (Fiorino and Parisi 2016; Lingnert 1990; Marcus 2016; Markowicz Bastos et al. 2012).

The multifaceted nature of Maillard reaction—a complex group of concomitant and cascade reactions (Hodge 1953; Martins et al. 2001)—imposes the description of involved reactions in connection with the particular food category or categories, and with relation to the above-considered processes. In addition, discussed reaction chains give several final products or intermediates normally found in foods or beverages. The aim of this Chapter is to describe briefly the probability of analytical detection of some main MRP when speaking of main Maillard reaction pathways: the production of Amadori or Heyns compounds, the production of advanced glycation end (AGE) products, and the formation of acrylamide.

3.2 Maillard Reaction and Processed Foods from Amadori Compounds to 5-Hydroxymethylfurfural, Furfural and Acrylamide

After the first stage of Maillard reaction—a condensation involving a molecule containing a primary amino group and a reducing sugar with a carbonyl group, giving a Schiff's base and the subsequent Amadori rearrangement into a 1-amino-1-deoxy-2-ketose—the Schiff's base may be turned into 5-hydroxymethylfurfural (HMF), furfural, and other products if pH is ≤ 7.0 (Sect. 2.2). The analytical detection of these products as cause of one or more of heating procedures (Figs. 2.1 and 2.2) has been extensively studied (Aguiló-Aguayo et al. 2009; Belitz et al. 2009; Guerra-Hernández et al. 2002; Martins et al. 2001; Morales et al. 1996; O'Brien et al. 1989; Rada-Mendoza et al. 2004; Serra-Cayuela et al. 2014; Singh and Heldman 2009; Zhu et al. 2009).

Each process involving high temperatures, a prolonged time cycle, pH values ≤ 7.0 and raw materials with the abundance of reducing sugars and nitrogen-containing compounds, is potentially able to determine the production of HMF and furfural (Singla et al. 2018b). Interestingly, certain metal ions such as calcium and magnesium may favour HMF production. Unfortunately, HMF may be also obtained from monosaccharides via a complex pathway including the Lobry de Bruyn–Alberda–van Ekenstein transformation in acidic conditions at high temperatures (Kowalski et al. 2013). Consequently, caramelisation could be kinetically studied by means of the analytical determination of HMF in certain situations (Kroh 1994).

The analytical detection of HMF (an unstable molecule) has been reported so far in the following products (Baglio 2017; Kowalski et al. 2013; Singla et al. 2018b):

(1) Processed fruits, vegetables and bakery foods: treated jams (as ingredients for infant foods), juices, apple purees, dried fruits (plums, pears, apricots, etc.), tomato products, cereals, breakfast cereals, bread, dried pasta, coffee, etc. Interestingly, the addition of ammonium bicarbonate has been reported to be correlated with unexpected HMF in high amounts in cookies. With reference to some cereal-based products, HMF has been found in high quantities with acrylamide
(2) Milk-based foods: processed milk, infant milk, heat-treated and cooked cheeses
(3) Commercial honey, and honey as ingredients for other products (example: Spanish *turron*)
(4) Other foods: alcoholic beverages (normal wines, Chinese rice wines, etc.), syrups,

With reference to the simple furfural obtained, if the reducing sugar is a pentose instead of a hexose (Singla et al. 2018a), it can be found in the same way of HMF because of the same basic conditions for HMF and furfural production. Furfural is not stable, similarly to HMF.

There is another product with important safety-related features. This molecule, acrylamide, is obtained after the formation of a Schiff's base from a reducing sugar (glucose, fructose) and a specific amino acid, asparagine (Simpson et al. 2012; Singla et al. 2018a; Swedish National Food Administration 2002). Subsequently, the obtained Amadori compound is decomposed by means of several steps with the elimination of carbon dioxide, ammonia, and the production of acrylamide in grilled, baked, toasted foods and several 'Mediterranean-Diet' products (Delgado et al. 2017; Singla et al. 2018a). With relation to interested foods—baked foods, potato chips, other fried foods, crackers, breakfast cereals, cookies, etc.—it should be considered that asparagine is not strictly required (other amino acids have been reported to be important when speaking of low acrylamide production in cooked foods). In addition, acrylamide and HMF may be found at the same time in toasted bread, cookies and Spanish specialties (*churros* and *rosquillas)* as originated from different chain reactions in the general ambit of the Maillard reaction (Kowalski et al. 2013; Simpson et al. 2012).

3.3 Maillard Reaction and Processed Foods—Melanoidins

Amadori or Heyns compounds may be degraded in alkaline conditions or at pH = 7.0 in foods. In these conditions, the following molecules would be easily obtained as an alternative pathway—the way of advanced glycation end (AGE) products—if compared with HMF, furfural or acrylamide production (Martins et al. 2001; Nursten 2007):

(a) Dicarbonyl molecules. Several of these intermediates are glyoxal, methylglyoxal, glycolaldehyde, 1- and 3-deoxyglucosone and butanedione
(b) Reductones, in equilibrium with the correspondent dehydroreductones.

Interestingly, these intermediates are important enough for different reasons, including also for the following:

(1) The aroma of foods. The cause is correlated with pyrazine derivatives obtained from Strecker aldehydes. These intermediates are obtained from dicarbonyl products and dehydroreductones
(2) The production of melanoidins as the final compounds of the Maillard reaction.

With relation to HMF, furfural, fission products and reductones, these molecules are substantially unstable; for this reason also, the Maillard reaction should go on with a multidirectional framework until the formation of stable MRP (and AGE, when speaking of in vivo reactions). On the other hand, aroma and colour are basic sensorial features concerning foods; consequently, the interest of food technologists in these factors is high.

Among all possible MRP, the production of melanoidins (Fig. 2.5) should be considered as the most evident proof of Maillard reaction, intended as nonenzymatic browning. Interestingly, these compounds may alter the functions of certain nitrogen-based molecules, in particular, proteins (Gupta et al. 2017). These large molecules may also have prebiotic properties.

Actually, these molecules may be obtained by means of non-Maillard reaction pathways such as the enzymatic oxidation of monohydroxyphenol and *o*- and *p*-dihydroxyphenols (Simpson et al. 2012). As a result, the abundance of melanoidins in food products could be explained by means of different reasons and reagents.

By the chemical viewpoint, melanoidins (Fig. 2.5) are coloured substances with low or high molecular weight (Simpson et al. 2012). Originally, small molecules are formed with a peculiar property: the ability of creating high-molecular weight copolymers via cross-linking reactions (molecular weight can reach 100,000 Da); the other partner is generally a protein with free ε-amino groups (of arginine or lysine or arginine residues). The final brown-coloured compounds have not a definite structure, although the following three suggestions have been reported so far (Simpson et al. 2012):

(1) The polymeric skeleton is mainly composed of polycondensated furan and/or pyrrole rings

(2) Alternatively, melanoidins are based on a carbohydrate structure with low-molecular nitrogen-based fragments, a few unsaturated heterocycles and undemolished carbohydrates
(3) In addition, observed melanoidins could be linked to small chromophores via bonds with protein skeletons.

Anyway, it seems that these copolymers in the final and high-molecular-weight complex structure are largely dependent on the amount and characterization of initial reagents. Carbohydrates can react with proteins and produce melanoidins; however, the role of oxidised lipids (instead of carbohydrates) in association with proteins cannot be excluded, although it has been reported that the nature of obtained melanoidins can be different enough depending on pH and thermal values (Simpson et al. 2012). Interestingly, browning may be inhibited if pH is low enough and moisture amounts are high: in these situations, caramelisation is the competitor reaction with more success, and obtained sulphur-like odours are ascribed to this phenomenon. Should pH arrive to 6.0 and moisture be low enough, Maillard reaction would be favoured in general (Simpson et al. 2012).

Melanoidins (Fig. 2.5) can be easily found in the majority of heat-treated foods, as the final products of Maillard reaction. Basic conditions are, as previously discussed in Chaps. 1 and 2, the abundance of Maillard reaction partners, adequate pH and thermal values, and a reduced moisture amount. In particular, their presence has been reported in the following products at least (Adams 2005; Brudzynski and Miotto 2011; Chandra et al. 2008; Coca et al. 2004; Papetti et al. 2006; Simpson et al. 2012; Van Boekel et al. 2010; Vignoli et al. 2011):

- Roasted coffee and water-soluble coffee
- Roasted barley (coffee surrogates)
- Sugarcane molasses
- Toasted and cooked bread
- Cookies
- Breakfast cereals
- Beers
- Beers
- Breakfast cereals
- Cocoa
- Cooked cheese
- Cookies
- Honey
- Milk
- Processed fruit juices
- Processed tomato sauces
- Sugar beet juices
- Sugarcane molasses (and derived distillery effluents)
- Roasted coffee and water-soluble coffee
- Roasted barley (coffee surrogates)
- Toasted and cooked bread.

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