8.1 Introduction: the importance of thermal processing

Most foods are submitted to thermal processes such as cooking, baking, roasting, extrusion cooking, pasteurisation or sterilisation. The first processes serving mostly to obtain particular sensory or texture features, the last two to assure microbiological safety and to eliminate some enzymatic activities that reduce food preservation.

The reactions that occur are of great importance for the production of aroma, taste and colour. From this point of view foods can be divided in two classes. In some cases, these modifications must be reduced to a minimum because a natural and fresh appearance is required, as, for example, in drinkable milk or fruit juices. In other cases they are desirable, because they produce the specific sensory and texture features of foodstuffs, such as bread, cereals, chocolate, coffee, nuts, malt and cooked meat. However, when these reactions occur during food preservation, they always have a negative impact on quality.

One of the most important processes involved is the reaction of amino acids, peptides and proteins with reducing sugars and vitamin C, the process generally known as Maillard Reaction (MR) or non-enzymatic browning. This is a cascade of complex competitive reactions and even if most of them are fundamental organic reactions, such as eliminations, aldol condensations, retroaldol fragmentations, oxidations and reductions, the fact that they occur simultaneously and give rise to many reactive intermediates makes difficult their interpretation and control (Yaylayan 1997). For many years these transformations have been studied for their technological impact, but more recently it has been shown that they may be accompanied by a reduction in the nutritive value of foods and by the formation of toxic compounds. The loss in nutritional quality
and potentially in safety is attributed to the destruction of essential amino acids, interaction with metal ions, decrease of digestibility, inhibition of proteolytic and glycolytic enzymes, and formation of anti-nutritional and toxic compounds.

8.2 The importance of the Maillard reaction

The first investigations on the MR were performed around 90 years ago by Maillard (1912). Subsequently, Amadori reported on the formation of a rearranged stable product from glucose and amino acids which was named after him and Heyns reported a similar compound from fructose. An overall picture of the reactions involved was proposed by Hodge (1953). One of the most detailed descriptions of the pathways that lead to the main Maillard Reaction Products (MRPs) can be found in a very complete review by Ledl and Schleicher (1990). Only some relevant points will be discussed here.

Reducing sugars are necessary for this reaction; generally they are a monosaccharide, glucose or fructose, or a disaccharide, maltose or lactose, and in some cases a pentose. Non-reducing disaccharides, such as sucrose, or bound sugars as in glycoproteins, glycolipids, and flavonoids, react only after hydrolysis, a process often facilitated by fermentation. The counterparts are free amino acids or proteins. Fermentation is useful also to increase the concentration of free amino acids, whereas in some cases (e.g. cheese) biogenic amines can react as amino compounds. Small amounts of ammonia can be produced from amino acids during the Maillard reaction and large amounts are added for the preparation of a particular kind of caramel colouring. The mechanism of this reaction has been studied very seldom in real foods, because it is too complex and the separation of non-volatile products is very difficult. On the contrary, most authors have used simple model systems in order to improve control of all the parameters and very often these results have been extrapolated to foods quite efficiently.

Consider now an aldose. The initial step is the condensation of the aldehydic group of the sugar with an amino group to give a relatively unstable glycosylamine 1 which undergoes a reversible rearrangement to give an aminoketose 2 (Amadori compounds) (Fig. 8.1). These intermediates have been fully characterised in model systems and detected in many foods. The equivalent rearrangement of the fructose + amino acid adduct produces an amino aldose which is called Heins product. The reader will find a detailed description of the properties and reactivity of the Amadori Heins compounds in Yaylayan and Huygghues-Despointes (1994).

At low water content and pH 3–6, they can be considered the main precursors of reactive intermediates in model systems. Deoxydiketoses and deoxyaldoketoses are degradation products of aminoketoses in the pH range 4–7. Ring opening followed by 1, 2 or 1, 3-enolisation are crucial steps in this transformation and are followed by dehydrations and fragmentations with the formation of many very reactive dicarbonyl fragments. One of the most important end products of the reaction of 3-deoxyhexulose is 5-hydroxymethyl-furancarboxaldehyde 3 (HMF).
In the presence of large amounts of primary amines, this compound is suppressed and replaced by pyrrole aldehydes of structure 4 as well as betaines 5 which have been demonstrated to derive from a common intermediate and not from HMF. Compounds 4 and 5 can be obtained also from maltose and lactose. A typical degradation product of 1-deoxydiketoses is furanone 6 which easily splits off formaldehyde to give furanone 7 which is the base for the formation of some relevant low molecular weight coloured compounds. Furanone 7 is produced also from the equivalent reaction of pentoses (Fig. 8.2).

Small C₂, C₃ and C₄ fragments are produced from sugars by retroaldol cleavage (Fig. 8.3). Many of these compounds are very reactive and condense
readily with other retroaldol derivatives or sugar derivatives in which the carbon skeleton is still intact. The reaction with the amino group of amino acids results in the incorporation of nitrogen, a critical step for the formation of melanoidins and important flavour compounds such as pyrazines.

One of the first observations by Maillard was related to the production of CO₂ in the reaction mixture. This process is named Strecker degradation (Fig. 8.4). The mechanism involves the reaction of amino acids with α-dicarbonyl compounds to produce an azovinyllogous beta-ketoacid that is decarboxylated. Thus the amino acid is converted in an aldehyde containing one less carbon than

![Chemical structures](image)

**Fig. 8.2** Relevant end products from 3-deoxydiketoses and 1-deoxydiketoses.

![Chemical structures](image)

**Fig. 8.3** Some of the compounds produced by retroaldol cleavage.
the original amino acid. Most of these aldehydes are very reactive intermediates or have very peculiar sensory properties. In addition to the normal compounds, with cysteine the reaction yields also hydrogen sulfide, with methionine 2-methylthiopropanal and methanethiol. The Strecker degradation is therefore responsible for the incorporation of nitrogen and sulfur in many volatile and non-volatile end products.

In recent years, very detailed experiments on the reaction between $^{13}$C labelled monosaccharides or disaccharides (Tressl et al. 1995; Tressl and Rewicki 1999) and amino acids have clarified the different Maillard pathways of these two important classes of food components, and a revised scheme for the Maillard reaction was proposed. In proteins the most relevant effect of the Maillard reaction is the non-enzymatic glycosylation which involves mostly lysine. The first glycation products are then converted to the Amadori product fructosyllysine that can form cross-links with adjacent proteins or with other amino groups. The resulting polymeric aggregates are called advanced glycation end products (AGEs).

8.3 Thermal processing and food safety

The negative side of thermal processing is the possible formation of potentially carcinogenic MRPs, among which heterocyclic amines (HAs) have attracted a growing interest during the past two decades. HAs include about twenty different derivatives that are primarily found at ppb level in cooked muscle foods (Sugimura et al. 1977). Many HAs have been shown to be carcinogenic in mice, rats, and non-human primates studies. However, epidemiologic studies showed conflicting data: some have shown an association between cooked meat and fish intake and cancer development and others no significant relationship
(Sugimura et al. 1993; Steineck et al. 1993). The International Agency for Research on Cancer (IARC) regards some HAs as possibly or probably carcinogenic to humans, and recommends minimising our exposure to them (IARC 1993). Minimising their formation requires knowledge of precursors, cooking conditions, reaction mechanisms and kinetics, so that the food industry can choose optimal conditions for designing food processes and food process equipments.

HAs are found mostly in the crust of grilled and fried meat and fish and in the pan residue, but to a much lesser extent in the interior of meat (Skog et al. 1995). Cooking time and temperature are critical parameters in determining their amount (Knize et al. 1994). The low concentration of HAs and the complex sample matrix of cooked foods make the analysis of these compounds very difficult. Most data reported in literature refer to polar HAs in cooked muscle foods that are found at low ng/g level (for reviews see Skog 1993; Layton et al. 1995). An improved method for the determination of non-polar HAs has been published recently (Skog et al. 1998). A kinetics model for the formation of polar HAs in a meat model system has been proposed (Arvidson et al. 1998).

A detailed overview of the risk assessment can be found in a review by Friedman (1996). Data suggest that HAs are the only known animal colon carcinogens that humans (except vegetarians) consume every day and, although very difficult, it would be desirable to control their level in food (Fig. 8.5).

8.4 Thermal processing and nutritional quality

The glycation of protein by sugars affects negatively the nutritional value of proteins (Friedman 1996). In fact, beside the destruction of particularly reactive amino acids, such as lysine, all essential ones must be liberated from food proteins by digestion and factors that decrease digestibility as cross-linking reduces their bioavailability. Loss of nutritional quality has been demonstrated in heat treated casein, casein-glucose, and casein-starch and was explained with decreased nitrogen digestibility, possibly also through impaired intestinal absorption (Gumbmann et al. 1993). On the basis of labelled experiments, Mori and Nakatsuji (1977) affirmed that the reduction of the nutritive value depends on the reduction in intestinal absorption of the Maillard-induced lysine derivatives.

Besides the change in physiological properties of non-enzymatic browning products, there are other factors that could affect the nutritional quality, such as the formation of toxic compounds during the heat treatment of food: heterocyclic amines (HAs), melanoidins and lysinoalanine (LAL). LAL is not exactly an MRP, but a cross-linking product which occurs in proteins treated under alkaline conditions owing to the fact that the ε-amino group of lysine in the protein chain reacts with dehydroalanine, derived from β-elimination of good leaving groups from cystine and O-substituted serine (Friedman 1999). The cross-linking reaction occurs mostly intramolecularly and results in the
Fig. 8.5 Relevant heterocyclic amines.
reduction of digestibility of the proteins involved. The loss of nutritional quality is particularly relevant in infant nutrition where milk is the only source of proteins and amino acids. Erbersdobler (1989) observed other adverse effects in experiments with animals fed with thermally treated proteins, in particular, damage of the renal function, but these negative influences do not seem to be significant in practical conditions.

Another important nutritional consequence of the MR in food is the formation of antioxidative materials. Chiu et al. (1991) carried out studies on the formation of antioxidants in the reaction between tryptophan and glucose or fructose. These MRPs have a positive effect in preventing lipid oxidation in foods and the scavenging of active oxygen species has been related to these antioxidative effects. Chelation of metals is another important contribution.

There are also some scattered data on the formation of antibacterial materials (Einarsson et al. 1983, 1988). Products deriving from arginine/glucose and arginine/xylose seemed particularly efficient. However, the reported data refer only to model systems and it is not clear if these compounds really contribute to the preservation of foods.

8.5 Thermal processing, food flavour and colour

The MR is responsible for most colour formation during thermal processing of food, e.g. bread baking, roasting of coffee and nuts, roasting of meat, kiln-drying of malt. Although nobody can deny its importance in determining the quality of foods, the progress of knowledge in this field has been slowed by many methodological difficulties, because most of the colour is due to high molecular weight polymers, which are named melanoids. Some attempts have been made to isolate melanoids from foods, e.g. soy sauce (Hashiba 1973; Lee et al. 1987), dark beer (Kuntcheva and Obretenov 1996), malt or roasted barley (Milic et al. 1975; Obretenov et al. 1991), coffee (Maier and Buttle 1973; Steinhart and Packert 1993), but their very complex, probably non-repetitive, structure has limited their structural characterisation. Until now the only coloured compounds which have been fully characterised are some low molecular weight ones (Ames and Nursten 1989; Arnoldi et al. 1997; Ravagli et al. 1999; Hofmann 1998b, 1998d; Tressl et al. 1998a, 1998b; Wondrack et al. 1997). Figure 8.6 shows the structure of some coloured compounds isolated in recent years.

Generally foods contain proteins and more rarely free amino acids. In a recent work (Hofmann 1998c), it was demonstrated that different compounds are produced reacting glucose with glycine and alanine or β-casein. With free amino acids the majority of coloured compounds were shown to have molecular weight below 1000 amu, whereas the reaction between glucose and casein leads to a drastic increase of the molecular weight. Hofmann (1998a) has proposed colour dilution analysis, a method that permits selection of the compounds of a mixture that contribute mostly to colour. Another very important consequence of the MR is the formation of flavour, a complex sensory feature related both to taste and
smell sensations. From the viewpoint of taste, there is a generalised shift from sweet to bitter sensations in part from the destruction of sugars and in part the formation of bitter compounds. The latter aspect has not been studied in detail yet, partly for methodological difficulties.

Much more can be said about aroma. Odorous compounds must be relatively small in size and lack polarity, therefore they can be studied by GC-MS much more easily than any other MRP. Hundreds of compounds have been identified. Nursten (1980–81) has suggested dividing them into three groups:

**Fig. 8.6** Examples of low molecular weight coloured compounds recently reported in literature: 19 (Ravagli et al. 1999); 20 (Hofmann 1998d); 21 (Hofmann 1998a); 22 (Hofmann 1998b); 23 (Tressl et al. 1998a); 24 (Tressl et al. 1998b).
1. simple sugar dehydration/fragmentation products, such as furans, pyrones, cyclopentenes, carbonyls, acids (Fig. 8.7);
2. simple amino acid degradation products, Strecker aldehydes and sulfur compounds;
3. volatiles produced by other interactions: pyrroles, pyridines, imidazoles, pyrazines, oxazoles, thiazoles, aldol condensation products (Fig. 8.8).

Pyrazines give a major contribution to roasted and cooked aroma (Maga 1982; Arnoldi 1992); their organoleptic properties depend strictly on structure and quantitative structure-activity relationships (QSARs) have been proposed.

Flavours developed by using thermal treatment of selected precursors have become standard commercial flavours sold all over the world, and they are generally known in Europe as 'process flavours' (Manley 1994). They are generally sold as the final flavour, however microwave flavours may be sold as precursor mixtures prior to the development of flavour.

Of course not only the absolute concentration, but also the typical note and the odour thresholds of flavour are important in determining the sensory properties of a food. The reader will find many sensory data of MRPs in a very complete compilation by Fors (1983). Threshold values can sometimes be relatively high (ppm range) or extraordinarily low (ppb level or less), for example 3-sec-butyl-2-methoxypyrazine can be perceived in water at 0.001 ppb, and 1,3,5-trithiane in water at 0.04 ppb.

Although MRPs are relevant impact compounds in foods, the presence of a odour-active volatile is not a direct measure of its importance to aroma. Specific techniques have been developed to solve this problem: the most common are the gas-chromatography-olfactometry (GCO) technique (Cunningham et al. 1986) and the aroma extraction dilution analysis (AEDA) (Schieberle et al. 1990). The
GCO bioassay characterises potent odour-active volatiles by sniffing the gas chromatograph effluent. Using a sniffing port, a trained operator notes the presence of an odour at a particular retention index and records the sensory characteristics. In subsequent runs the sample is diluted by factors of three and the analysis is repeated until the odour is no longer perceivable. The combination of these runs produces a corrected chromatogram with odour potency defined as the area of the chromatographic peaks. Using this technique, for example, it was possible to determine the major odour potent compounds in glucose-proline model systems (Roberts and Acree 1994) which are burnt caramel, cotton candy and popcorn. They are diacetyl, 2-acetyl-1-pyrroline, 2-acetyl-1,4,5,6-tetrahydropyridine, 2-acetyl-3,4,5,6-tetrahydropyridine and furaneol, and all of them are very small and apparently irrelevant peaks in the FID chromatogram.

8.6 Maillard reaction and lipid oxidation

Another important reaction which occurs in processed and cooked foods and influences the aroma is lipid degradation. The intermediates of these reactions are involved in the formation of food flavour. Experiments carried out with
model systems added with fat have demonstrated that several volatile compounds are product by the interaction between MRPs and lipid oxidation products (Whitfield 1992). Most of them are heterocyclic compounds containing nitrogen or sulfur such as alkylthiazoles, long-chain alkylpyrazines (Chiu et al. 1990; Huang et al. 1987), pyridines and thiophenes.

Phospholipids were added to model systems to mimic the formation of meat aroma (Farmer and Mottram 1990; Farmer et al. 1989), and recently it was demonstrated that some edible oils can affect the pyrazine profile (Negroni et al. 2000).

8.7 Controlling factors in the Maillard reaction

Understanding the factors that influence the MR is critical for achieving its control. The formation of colour and flavour and the loss in nutritional value are the aspects that have been studied in detail. The most important parameters that affect the MR are: temperature, pH, water activity, and the structure of amino acids and sugars involved. However, most of the information available has been collected in model systems and not in real foods.

The effect of temperature is particularly strong and involves every aspect of the MR. For example, several experiments have shown that an increase in temperature and/or time of heating leads to an increase of colour development and aroma profile. Not only the amount of the MRPs is increased, but also their nature is modified. For example it has been demonstrated that the carbon-to-nitrogen ratio, the degree of unsaturation and the chemical aromaticity of the melanoidins formed in model systems increase with temperature and time. The formation of undesired compounds as HAs (see Section 8.3) is particularly sensitive to high temperature and a careful choice of the cooking conditions allows them to be reduced to a minimum.

Considering flavour, at intermediate temperatures caramel or cooked flavours are produced, while at higher temperatures the aroma profile is toasted or roasted. Nevertheless, the MR proceeds slowly also at room temperature and browning and off-flavour formation are responsible for the deterioration of food during storage.

The MR proceeds faster at low moisture level (Nursten 1980–81), and it is generally accepted that moisture values corresponding to a water activity around 0.65–0.75 are the most favourable. The differences in colour and flavour of the outer part (where fast dehydration occurs) and wet inner part of baked or roasted foods are a very clear proof of these effects. However, not all the MRPs are sensitive in the same way and studies on flavour have demonstrated that different classes of volatile components are more or less sensitive depending on whether or not water is required for their formation. The complex network of reactions that produce browning is far from being disclosed, but certainly many condensations and dehydrations are involved and water activity is a critical parameter of the reaction kinetics.
pH is another important parameter. Browning is much greater at pH above 7 and the rate of colour formation can be reduced by decreasing pH. Flavour is also influenced, for example pyrazines reductones and fission products are preferred at high pH values, while furans, especially furfurals, prevail at lower pH. Nevertheless, mixtures of compounds are formed at each pH. Careful control of the pH is necessary in model systems because of acid formation, whereas food pH is more stable because they have a buffered environment.

Another important parameter is the structure of the reactants: pentoses react more quickly than hexoses, that react faster than disaccharides, and aldoses react faster than ketoses. Non-reducing sugars such as sucrose, dextrines and bound sugars are involved only after hydrolysis. Aspartic and glutamic acids are relatively unreactive, whereas lysine, the most reactive free amino acid, is reactive also in proteins owing to the ε-amino group. The structure of the amino acids determines the formation of particular MRPs such as sulfur compounds from cysteine and methionine, that, however, react only after hydrolysis or fermentation.

8.8 Methods of measurement

Browning is certainly a macroscopic effect of the MR and sometimes it is directly measured to determine the progress of the reaction. However, recently much more sophisticated parameters have been suggested and used.

Non-enzymatic glycosylation of proteins is one of the most important nutritional consequences and many methods have been developed for its estimation. The first glycation product or Schiff base rearranges to a more stable ketoamine or Amadori product. The Amadori product can form cross-links between adjacent proteins or with other amino groups. The resulting polymeric aggregates are called advanced glycation end products (AGEs).

During acid hydrolysis of proteins, the glucose derived Amadori product fructosyllysine reacts to give furosine in about 30% yields and a small amount of pyrroldidine, whereas 50% reverts to lysine. Furosine was first detected by Erbersdobler and Zucker (1966) in foods and it can be easily analysed by HPLC with 280 nm detection. The corresponding reaction in milk and milk products produces lactulosyllysine that can be estimated by the furosine method, too. The furosine test has been used by several authors to study the progress of the Maillard reaction in different foods (Chiang 1983; Hartkopf and Erbersdobler 1993, 1994; Henle et al. 1995; Resmini et al. 1990).

Carboxymethyllysine is another useful parameter. It was detected for the first time in milk by Büser and Erbersdobler (1986) and an oxidative mechanism was proposed for its formation (Ahmed et al. 1986). Hewedy et al. (1991) have compared several damage indicators for the classification of UHT milk, but have shown that it is suitable only for monitoring very severe damage because it is formed only in small amounts.

Another useful parameter is 5-hydroxymethylfurfuraldehyde (HMF). Its formation in foods has been explained in two ways: via the Amadori products
through enolisation (in the presence of amino groups) and via lactose isomerisation and degradation, known as the Lobry de Bruyn-Alberda van Ekenstein transformation (Ames 1992). Owing to this, recently it has been proposed to measure separately the HMF formed only by the acidic degradation of Amadori products, called bound HMF and directly related to the MR, and total HMF related also to the degradation of other precursors (Morales et al. 1997). This method is more reliable than the previous spectrophotometric one (Keeney and Bassette 1959).

ε-Pyrrolyllysine is another parameter that has been proposed to measure the MR in foods. It was observed for the first time in the reaction between glucose and lysine (Nakayama et al. 1980). It is particularly useful in dry foods because it is very stable. Resmini and Pellegrino (1994) have proposed a method to measure protein-bound ε-pyrrolyllysine in dried pasta. The formation of this MRP parallels very well the formation of furosine.

LAL, though not deriving from the MR, can be a useful parameter in cheese where the very low residual concentration of lactose impairs the MR and makes other decomposition routes not involving sugars more probable. Pellegrino et al. (1996) have proposed a very sensitive method to detect the addition of caseinates to mozzarella cheese based on LAL determination by HPLC with fluorimetric detection.

8.9 Application to the processing of particular foods

As indicated above, the MR is of critical importance for the production of aroma, taste and colour of foods, that can be roughly divided into two classes. The first class contains foods where a natural and fresh appearance is required such as, for example, drinkable milk or fruit juices. In this case, the thermal treatment is applied to sterilise and the modifications induced by the MR must be reduced to a minimum. Typical cooked, roasted or baked foods such as bread, cereals, chocolate, coffee, nuts, malt, and cooked meat belong to the second class. In this case, the MR is the tool to attain the specific sensory and texture features. In this chapter three foods are discussed as examples of a very mild process (milk), a medium temperature process (bread), and a very drastic one (coffee).

8.9.1 Milk

Milk is heated to improve its shelf-life and to kill disease-causing microorganisms and viruses. Three processes are used:

1. pasteurisation at 85°C for 2–3 s or at 72–75°C for 15–30 s in a plate heater;
2. UHT treatment in coils or plate at 136–138°C for 5–8 s or by steam injection at 140–145°C for 2–4 s;
3. autoclave sterilisation in closed bottles.
In each of them the time and temperature conditions must be selected carefully to reduce the MR to a minimum.

Drinkable milk is probably one of the foods that has been more studied from this point of view and great importance is attributed to the preservation of its nutritional value. Many parameters can be used to identify correctly the different milk classes and some of them are based on the MR. Although the pH is neutral and the sugar concentration is around 3.5%, the recent industrial technologies of the production of pasteurised and UHT milk are rather mild and milk contains only lactose, a disaccharide relatively slow to react. In these conditions only the first steps of the MR occur and lysine glycation is the main consequence, while aroma and colour remain practically unchanged. The main product is therefore lactulosyllysine, that can be quantified indirectly after acid hydrolysis as furosine. Many methods have been proposed for its quantification, on one of the best being proposed by Resmini \textit{et al.} (1990). In raw and pasteurised milk, the level of furosine is around 3–5 mg/100 g protein, in UHT milk is 5–220 mg/100 mg, in sterilised milk is \textgreater{} 300 mg/100 g. Abnormal values indicate fraud, for example the addition of reconstituted milk powder.

Great interest has been dedicated to the nutritional value of dry milk powder, whose most important use is for the preparation of infant formulas. The main processes used include preconcentration using film evaporating systems to 40–50% solids and spray drying. An alternative method is drum drying where the liquid is applied in a thin layer to a heated cylinder and after some time removed by a knife. With the latter method, however, the thermal exposure is much higher.

\subsection*{8.9.2 Baked products}

Wheat flour contains only very small amounts of free sugars and the fermentation process is very important to generate glucose and maltose that are indispensable MR precursors. This can be improved by the addition of flour from malted grains very rich in $\alpha$-amylase. Bread baking time and temperatures vary very much as a function of the bread dimensions and constituents, in general small products (about 45 g) may be heated for 18–20 min at 240–250°C, while big products (1000 g) may be heated at 240–220°C for 55–65 min. Naturally, especially in the case of large products, the heat transfer occurs slowly and there is a temperature gradient from the outer to the inner part of the dough. Water evaporates efficiently only in the crust, while the inner part remains softer and colder. The extent of the MR and its consequences are not homogeneous: the differences in colour, flavour and texture of the crumb and the crust are probably part of the hedonistic pleasure of bread consuming. In crumb the most important flavours are autoxidation products of linoleic acid, methional and diacetyl, while 2-methyl-3-ethylpyrazine, 2-acetylpyrazine, 2-acetyl-1-pyrroline and 5-methyl-(5H)cyclopenta(b)pyrazine and furaneol are responsible for the caramel, malty and roasty notes of crust. Free proline is the precursor of many volatile compounds that have been characterised in detail.
(Tressl et al. 1985). The pleasant colour of crust is due in part to the MR and in part to caramelisation of sugars.

8.9.3 Coffee
During roasting, coffee beans undergo many pyrolytic reactions, which lead to the substances responsible for its particular colour and flavour. The knowledge of green coffee composition is still incomplete and during roasting other reactions take place besides the MR, so that the composition of roasted coffee, especially the non-volatile part, is still far from being clear. The process can be divided into two phases: drying and roasting. An important parameter is heat transfer which is correlated with time and temperature of roasting. The intensity of colour is correlated with the final roasting temperature. The taste changes from slightly sweet (green coffee) to bitter.

Most of the constituents are transformed, with some exceptions such as caffeine. Free amino acids and sucrose, which is around 8.0% in arabica green coffee and 4.0% in robusta green coffee, disappear completely, but also polysaccharides are transformed, together with other compounds not directly involved in the MR like chlorogenic acid. Any effect that changes the concentration of the precursors in green beans before roasting influences the quality of the roasted material. At the end the condensation and caramelisation products are about 25%. More than 700 volatile compounds have been identified in coffee aroma: important classes deriving from the Maillard reaction are pyrans, pyrazines, pyridines, pyrones, pyrroles, thiazoles and thiophenes (Illy and Viani 1995).

8.10 Future trends
Extrusion cooking is a high-temperature/short-time technique was introduced in 1930s in the cereal industries. Nowadays this process is used extensively in the food industry for the production of expanded snacks, breakfast cereals, textured soy protein, and other foods. Due to the nature of this technique, involving high temperatures, pressures and shear forces, the food matrix is subjected to chemical changes (gelatinisation of starch molecules, cross-linking of proteins) and the production of flavours can be induced by the Maillard reaction (Riha et al. 1996).

Another recent technique for food processing is microwave heating. As experienced also during domestic cooking, the aroma profile of foods cooked in this way is a very critical point. The lack of volatiles is due to the speed of heating and surface moisture and temperature; actually many aroma compounds are steam volatile and during microwave heating they evaporate rapidly; moreover the surface $a_{ss}$, that generally is around 1.0, is very unfavourable for the Maillard reaction. In order to enhance the flavour profile of microwaved foods several approaches have been attempted, e.g. addition of commercial
flavourings or Maillard precursors, use of microwave absorbing susceptor sheets, combination of heating treatment (van Eijk 1992).

8.11 Sources of further information and advice

The reader will find a useful discussion of the consequences of thermal treatment of the most relevant foods in Belitz and Grosch (1999). Every 3–4 years the researchers meet for international symposia, whose proceedings are a very useful source of information (Waller and Feather 1983; Fujimaki et al. 1986; Finot et al. 1990; Parliment et al. 1994; O’Brien et al. 1998).

8.12 References


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