Nutritional and Toxicological Aspects of the Chemical Changes of Food Components and Nutrients During Heating and Cooking

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Abstract

Heating and cooking is one of the oldest methods of food treatment that can be used to increase the shelf life and improve the palatability, aroma, taste, appearance, and texture of food. It also provides safe food to the consumer by inactivation of pathogenic organisms/microorganisms, toxins, or enzymes and production of additional antimicrobial substances or enzymes. However, heating of foods may also have undesirable consequences, e.g., the loss of nutrients such as vitamins, essential amino acids, unsaturated fatty acids, and minerals. Heat treatments also affect the allergenicity of food, either reducing or increasing it. Moreover, thermal treatment of food also produces harmful substances and toxic compounds like Maillard reaction products, furan, heterocyclic aromatic amines, acrylamide, acrolein, and *trans* fatty acids. These toxic compounds are considered as carcinogenic, mutagenic, genotoxic, and teratogenic properties and are a concern from a human health risk point of view.

Introduction

Heating is one of the oldest methods of food treatment. The various thermal treatments (like boiling, drying, grilling, frying, and roasting) affect quality of food in many ways. This treatment can alter the aroma, taste, color, appearance, and texture and can also increase the shelf life of food thus contributing decisively to acceptance of foods. The shelf life of food can be improved by inactivation of pathogenic organisms/microorganisms, toxins, or enzymes and production of additional antimicrobial substances or enzymes. The thermal processing either activates or inactives the food allergens depending upon types of foods, presence of ingredients, and type of heating. Heating of foods often is a condition for intended consumption. The foods like raw vegetables, potatoes, and rice need to be cooked to render them palatable while thermal processing can be applied to produce edible foods like bread and bakery products. Heating of foods may also have undesirable consequences, e.g., the loss of nutrients such as vitamins, essential amino acids, and unsaturated fatty acids. Moreover, thermal treatment of food also produces harmful substances and toxic compounds like furan, heterocyclic aromatic amines, and acrylamide (Gerhard et al. 2007).

Acrylamide may be formed by baking, frying, and roasting of foods, particularly of cereal products (e.g., roasted cereals, bread, and bakery products), potato products (e.g., chips, fried potatoes, and crisps), coffee, and cocoa. It is formed on heating of foods above 120 °C by the Maillard reaction, preferentially by condensation of the asparagine (amino acid) with fructose and glucose (reducing sugars). Acrylamide is considered a probable human carcinogen, implying that its metabolite epoxypropanamide (glycidamide) is the actual active genotoxic agent. In animal experiments with rodents, glycidamide-DNA adducts were found in all tissues investigated at high dosage. Furthermore, animal experiments have shown that acrylamide exhibits toxic effects to the nervous system and the reproductive organs (Gerhard et al. 2007).

Heterocyclic aromatic amines (HCAs/HAAs) are formed in varying concentrations by frying or grilling or by comparable methods of heating meat and fish, depending on the type of protein, the temperature, and the heating time. Two main types of HCAs are formed in varying amounts, depending on the temperature and precursor compounds: isoquinoline (so-called IQ compounds) and carboline derivatives. Many HAAs show a mutagenic potential in bacterial and mammalian cell-based test systems and are carcinogenic in animal experiments. In humans, bioactivation of HAAs to carcinogenic metabolites varies greatly between individuals. Furan is a volatile compound that has been detected in heated food products like coffee, bread, vegetable, and meat preserves, as well as in baby food. Its presence in widely different types of foods suggests that it is formed by different routes. Oral application of furan to rats and mice led to different tumor patterns. 3-Monochloro-1,2-propanediol (3-MCPD) is regarded as a reference substance for a series of undesirable compounds known as chloropropanols. 3-MCPD may be produced in the ppb (μg/kg) range during manufacture of seasoning sauces from hydrolyzed vegetable protein as well as by baking or toasting of bread, cereals, and coffee beans. 3-MCPD is formed at temperatures significantly above 100 °C by various formation mechanisms. More recent studies show that certain foods may contain not only chloropropanols but also their esters in quantities that can be 50 to 150 times higher than those of 3-MCPD. 3-MCPD has caused tumors in animal experiments when applied at high dosage (Gerhard et al. 2007).

Effect of Various Nutrients During Cooking and Heating of Foodstuffs

Cooking, an important food processing, increases the flavor, appearance, texture, stability, and digestibility of foods as well as destroys pathogens and deactivates toxic substances. The heat-induced chemical changes in amino acids, proteins, sugars, carbohydrates, lipids, minerals vitamins, and other food components reduce nutritive values and even the formation of some toxic chemical compounds (discussed under subsequent section).

Food is essential to life. Food is a mixture of chemical components, and nutrients account for more than 99.9 % of the food. Nutrients are the building blocks of the human body needed for growth, to maintain and repair the body tissues, to regulate body processes, to furnish energy for the body's functions, as well as reproduction of living organisms. The main classes of nutrients are carbohydrates, proteins, fats, vitamins, and minerals. The macronutrients (e.g., carbohydrates, proteins, fats) are the major sources of energy and building materials for the living cells. The micronutrients (vitamins and minerals) are equally very important but needed in small amounts (Karmas and Harris 1988). Food also contains some antinutritive substances. Antinutritives are mainly found in plant material. These antinutritive substances induce toxic effects indirectly, by interference with the functioning and utilization of nutrients or causing nutritional deficiencies. There are mainly three types of antinutritives like antiproteins (e.g., protease inhibitors and lectins),

antiminerals (e.g., phytic and oxalic acid), and antivitamins (e.g., ascorbic acid oxidase and antithiamine). The antiproteins and antiminerals interfere with the digestion, absorption, or metabolic utilization of protein (amino acids) and minerals respectively whereas antivitamins inactivate or destroy vitamins.

The food processing techniques like heating (pasteurization, sterilization) and cooking (boiling, baking, broiling, microwaving, roasting, frying, steaming, stewing, and smoking) are considered as practice to transform raw foods into ready for consumption. The heating or cooking is employed in food to ensure safe, nutritive, high quality of food products to the consumers. The primary objective of cooking is to increase the palatability of the food. Heating helps in better food digestibility and enhances the bioavailability of bioactive food components through changes in the physicochemical structure of food matrix (Burri et al. 2009), while blanching, pasteurization, and sterilization are meant to increase storage life of the foodstuff and to minimize foodborne diseases. The major nutritional benefits of heating of foods include formation of color, aroma, and taste active compounds as well as antioxidants; improving the palatability of the raw materials; and elimination or reduction of microbial load, natural toxins, and enzyme inhibitors. The formation of taste, aroma, and color via the Maillard reaction in foods and beverages (e.g., bread, breakfast cereals, roasted meat, soy sauce, malted beverages, and coffee) is a typical peculiarity of these products. Melanoidins formed during final stage of the Maillard reaction contribute brown color to the product. The various Maillard reaction products have shown beneficial chemoprotective properties in both in vitro and in vivo studies. The number of factors will influence the nutritional content of the food. The level of nutrient in food will depend on various conditions like oxygen, pH, heat, and light which can be prevailed during food processing (Burri et al. 2009). Depending on the nature of food being processed and the amount of nutrient presence in the food, retention of nutrient content varies. For example, sensitivity of vitamin C to heat varies with pH. The vitamin and macronutrient contents of foods are more likely to be affected by processing.

Blanching is a heat process frequently applied to tissue systems prior to freezing, drying, or canning. It is a mild heat treatment and important step in the processing of fruits and vegetables. Blanching is used to (i) inactivate enzymes which would contribute to undesirable changes in color, flavor, or nutritive value during storage; (ii) wilt the tissue to facilitate packing, removing tissue gases prior to container filling, increasing the temperature of the tissue prior to container closing, and inactivating or activating enzymes; and (iii) reduce microbial loads prior to further processing (Karmas and Harris 1988). Blanching in hot water results in large losses of water-soluble vitamins by leaching thermally labile nutrients and bioactive compounds. However, inactivation of oxidative and other degradative enzymes (e.g., lipoxygenase for carotenoids, polyphenol oxidase for flavonoids, ascorbic acid oxidase for vitamin C) during blanching will prevent further and greater losses by enzyme-catalyzed degradation during processing and storage. Due to heat treatment, considerable losses of carotenoids and flavonoids have been found in fruits and vegetables juices. Heat treatment, on the other hand, also increases

bioavailability of carotenoids presumably by softening or breaking cell walls and membranes. Heating conditions (time-temperature combination) should therefore be optimized so that bioavailability is increased, but without provoking significant degradation.

The term "nutritional losses in food processing" is generally taken to refer to all nutrients; the most sensitive by far are vitamin C and to a lesser extent B_1 – the other nutrients are much more stable, and very little is lost in most processes. Where losses of nutrients take place, the relative importance of the food in question as a source of the particular nutrient must be taken into account. The losses from the poorer sources of the nutrient in question are of little significance, e.g., vitamin C of milk is largely destroyed during pasteurization, but milk, even if consumed untreated, is not an important source of this vitamin. Biological measures of protein quality will show a fall only when the limiting amino acid is affected, e.g., milk, meat, and fish are limited by methionine plus cystine (sulfur-containing amino acids) and contain a relative surplus of lysine. If the amount of available lysine is reduced, there will be no change in the biological measure until the damage is severe enough to make lysine limiting (Bender 1978).

Most legumes contain a number of toxins and other substances that inhibit digestive enzymes. Destruction of them increases the nutritional value of the proteins. Legumes contain toxins like goitrogens and phytohaemagglutinins (agglutinate the red blood cells) that lead to death of animals if fed raw beans. The raw kidney beans cause nutritional muscular dystrophy in pregnant ewes due to a heat-labile vitamin E antagonist. Cottonseed meal contains gossypol which is both toxic and combines with lysine so reducing the nutritional value of the protein. When these toxins are themselves proteins, they are inactivated by heat. Raw egg white contains mucoprotein and avidin that combine with the vitamin, biotin, and render it unavailable. Some types of fish contain thiaminase which can destroy thiamin if the fish is eaten raw. Heat treatment destroys them. Many cereals contain a bound form of niacin which is not biologically available but can be liberated during baking/heating and under alkaline conditions. Phytate present in cereal bran and in mature legumes can reduce the absorption of calcium, phosphate, and iron by forming insoluble salts which can be reduced during processing. The heating of cereal grains increases feed conversion efficiency and palatability due to the destruction of peroxidase, lipoxygenase, and esterase. The Maillard reaction is responsible for a small nutritional loss in return for the desirable flavors and color produced in foods like roasted meat, crust of bread, and biscuits (Bender 1978).

There are mainly two kinds of nutrient losses in meat, viz, loss of juices containing protein and vitamin B in solution and reduced availability of amino acids and partial destruction of thiamin. There is difference between the temperature of the oven, outer parts, and inner parts of a piece of meat. The extent of the losses will vary with temperature, time, type of cooking, size of the portion, and content of connective tissue (Bender 1978). Many processed foods are enriched by vitamins and minerals as nutrients. The stability of naturally present nutrients may differ from those added nutrients. This may be due to difference in chemical form of added nutrient as well as physical protection afforded to the natural nutrients by the

other food ingredients. During enrichment, the stabilized forms of vitamins are added which may be more stable than those naturally present. Consequently, added nutrients can be more stable or less stable than the natural ones. In protein-enriched soya, added methionine (a sulfur-containing amino acid) was more sensitive than the naturally present protein (Bender 1978).

There are number of books and papers available on nutrient aspects. Readers are advised to refer some of the excellent books such as Bender (1978), Karmas and Harris (1988), Gerhard et al. (2007), Burri et al. (2009) for further information.

Changes in Proteins and Amino Acids

The essential building blocks for proteins are the amino acids which can be stabilized by various forces and bonds involved in primary, secondary, tertiary, and quaternary structures. Among the 22 amino acids that make up most proteins, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine are considered as essential amino acids. The nutritional value of proteins is dependent on the quantity, digestibility, and availability of essential amino acids. Proteins have complex molecular structure that can undergo various changes during thermal treatments. During thermal processing, both positive and negative effects occur in proteins. It improves the digestibility and availability by denaturation of protein structure. Various enzymes (proteinous in nature) such as lipases, lipoxygenases, and hydrolases as well as trypsin inhibitors have abilities to destabilize the foods or decrease the digestibility of food items. The denaturation of proteins during thermal processing deactivates these enzymes as well as the inhibitors and improves the quality of food products. Upon denaturation, peptide bonds of the protein are more readily available for hydrolysis by proteolytic enzymes. The excessive heat applied to the outside of foods of the puffing exploding type of processing used in popcorn or breakfast cereals causes severe protein damage. The amino acids are completely decomposed or produce cross-linkages forming polyamino acids leading to destruction of amino acids. Protein denaturation, on the other hand, also imposes a greater risk of rapid subsequent microbial contamination under poor hygienic or storage conditions, respectively, imposing the risk of food poisoning. Immunological properties of β-lactoglobulin (whey protein) may be altered by heat denaturation which can be less efficiently transported than the native form (Gerhard et al. 2007).

The Maillard reaction product like *N*-α- acetyl-carboxymethyl-L-lysine/pronyl-L-lysine exhibits an antioxidative capacity fivefold higher than that of ascorbic acid. The amino acid reacts with reducing sugar in the Maillard reaction and reduces the protein quality. The lysine, as one of the essential amino acids, is involved in this reaction, and bioavailability is lost (Burri et al. 2009). The transformation of the side chains of protein-bound amino acids in basic conditions leads to formation of cross-linked amino acids during thermal treatments of foods. A dehydroalanine residue may be formed. The ε-amino group of lysine may react to give a secondary amine, which is normally indicated with the trivial name of lysinoalanine (LAL).

The nutritional consequences of LAL formation in foods include adverse effects on growth, protein digestibility, protein quality, and mineral bioavailability and utilization. LAL has been shown to provoke lesions in rat kidney cells causing nephrocitomegaly.

There is little (in juice) or no damage to protein content when meat is heated. During higher-temperature roasting, only outer parts get damaged and reduce the availability of some of the amino acids through Maillard-type reactions in case of meat products. Fish proteins are limited by the sulfur amino acids and contain a relative surplus of lysine so that damage to the latter may have no effect on net protein utilization. There is loss of available lysine and tryptophan in the loaf of bread (Bender 1978). Thermal treatment changes the tertiary structure of proteins that may lead to a change in epitopes responsible for allergenicity of certain foods. However, not all allergens can be inactivated by heat treatment (Gerhard et al. 2007).

Changes in Carbohydrates

Carbohydrates account for major energy intake in a balanced diet. Carbohydrates are generally regarded as being stable to processing. However, there is some loss both by leaching into processing water and by breakdown. Losses by leaching will be governed by the factors like particle size, time, and volume of water. During cooking of foods, carbohydrates are lost by breaking. The amount of starch decreases and sugars increase during preliminary soaking of beans (Bender 1978); during wet heat treatment of vegetables and fruits, a more considerable loss of low–molecular weight carbohydrates (i.e., mono- and disaccharides) than that of sucrose into the processing water takes place. The loss of glucose and fructose at boiling was higher than that of sucrose. No leaching of dietary fiber into the processing water has been reported with blanching and boiling. Glycosidic linkages in the dietary fiber polysaccharides may be broken during heat treatment. A decreased association between fiber molecules, and/or a depolymerization of the fiber, results in a solubilization. Heat treatment can also change hydration properties; e.g., boiling increased the water-binding capacity slightly in wheat bran and apple fiber products, whereas autoclaving, steaming, and roasting had no significant effects.

Simple sugars are easily digested in the raw form by digestive enzymes and converted into monosaccharides. However, in certain raw vegetables like potato, starch is encapsulated within the starch granules which cannot be digested by digestive enzymes. Upon cooking of potatoes, the starch granules are gelatinized, and the starch becomes digestible (Burri et al. 2009). Gelatinization refers to the irreversible loss of the crystalline regions in starch granules that occurs upon heating in the presence of water. Gelatinized starch is not in thermodynamic equilibrium and a progressive reassociation of the starch molecules upon aging. This recrystallization (retrogradation) may reduce the digestibility of the starch. The retrogradation of the amylopectin component is a long-term phenomenon occurring gradually upon storage of starchy foods. Amylose, however, reassociates

more quickly. The crystallinity of retrograded amylopectin is lost following reheating to approximately 70 °C, whereas temperatures above 145 °C are required to remove crystallinity of retrograded amylose. This is a temperature well above the range used for processing of starchy foods. This implies that retrograded amylose, once formed, will retain its crystallinity following reheating of the food. The parboiling (i.e., a pretreatment involving heating and drying) of rice reduces the stickiness of the rice, possibly by allowing leached amylose to retrograde and/or form inclusion complexes with polar lipids on the kernel surface which affect the final cooking qualities of the rice. In pasta products, gluten forms a viscoelastic network that surrounds the starch granules, which restricts swelling and leaching during boiling. Nonenzymatic browning reactions occur between reducing sugars and amino groups in foods during heat treatment and storage.

With retrogradation, resistant starches are produced which are poorly degraded by α-amylase and thus generally reach the large intestine, where microbial fermentation takes place. Resistant starches thus may affect the microbial flora composition and the microbial metabolism which may have consequences for gut health by changing, for example, the short-chain fatty acid patterns. Short-chain fatty acids (SCFA) and particularly butyrate are considered to be important substrates for colonic epithelial cells, and relations between butyrate concentration and the risk for colorectal carcinogenesis have been observed. Thus, foods which lead to a higher production of butyrate in the colon may have beneficial effects. Therefore, the generation of resistant starches by thermal treatment of starchy foods may also be associated with beneficial nutritional and health effects. The amount of resistant starches in a food influence the glycemic index (GI). High amounts of resistant starch in a food generally are associated with a low GI, and this property may be nutritionally beneficial. The low-GI diets are responsible to decrease risk of type-2 diabetes and coronary heart disease (CHD) and improve in various metabolic risk factors. Thermal treatment of starchy foods thus favorably changes the nutritional properties of these foods (Gerhard et al. 2007).

Changes in Lipids

Lipids provide 9 kcal/g energy which is highest among other constituents and carriers of fat-soluble vitamins (A, D, E, K) and carotenoids. Lipids undergo various degradative changes which have effects on palatability rather than nutritional value. The nutritional value of fats is limited to the energy content of the triglycerides and to their content of essential fatty acids as well as fat-soluble vitamins. The damage of these vitamins and essential fatty acids is considered as loss of nutritional value. Changes in the fat content of the food itself must be included under nutritional changes – some foods may gain fat and so increase their energy content, and possibly their vitamin and essential fatty acid content; others may lose fat in the process. There is no significant loss of nutritional value of fatty foods such as dairy products, eggs, and meat fat during normal heat processing (Bender 1978). The physicochemical properties of fats are highly affected by

temperature. Unsaturated fatty acids (monounsaturated fatty acids: MUFA; polyunsaturated fatty acids: PUFA) and cholesterol are rapidly oxidized in the presence of oxygen. Furthermore, MUFA and PUFA may undergo isomerization with heat treatment. Fat oxidation compounds in foods are nutritionally undesirable and have not been shown to have any beneficial effects; however, these compounds are of toxicological relevance (Gerhard et al. 2007). At extremes of baking conditions, linoleic acid and possibly other fatty acids may be converted (due to lipoxygenase activity) to unstable hydroperoxides which may affect both the lipid and vitamin (oxidation of fat-soluble vitamins) of the product (Karmas and Harris 1988).

The fats/oils undergo various food preparation techniques, and one of them is deep fat frying. The oils are used as a heat exchange medium to cook the food product that can improve palatability, quality of food product, and provide crispness to, e.g., french fries. But acrylamides are formed in fried products which have toxic effects on living organisms. The frying temperatures range from 135 ° C to 190 ° C depending on the food product (Burri et al. 2009). During frying, fats/oils undergo many desirable and/or detrimental chemical reactions. These reactions include thermal oxidation, polymerization, hydrolysis, flavor changes, and darkening. Excessive heating will cause reaction of carbonyl components resulting from the decomposition of unsaturated fatty acids which may lead to reactions similar to those involved in nonenzymatic browning. During thermal heating of fats/oils, small amounts of *trans*-fatty acid are also produced.

Frying has little or no impact on the protein or mineral content of fried food, whereas the dietary fiber content of potatoes is increased after frying due to the formation of resistant starch. Moreover, the high temperature and short transit time of the frying process cause less loss of heat-labile vitamins than other types of cooking. For example, vitamin C concentrations of French-fried potatoes are **as** high as in raw potatoes, and thiamine is well retained in fried potato products as well as in fried pork meat. Although some unsaturated fatty acids and antioxidants are lost due to oxidation, fried foods are generally good sources of vitamin E. It is true that some fat is inevitably taken up by the food being fried, contributing to an increased energy density (Fillion and Henry 1998). Frying improves the digestibility. Pan frying and deep frying all resulted in an apparent loss of cholesterol in low-fat fish probably due to its leaching out into the frying oil. However, when plant foods are fried in animal fat, cholesterol is taken up by the product. The protein digestibility of foods such **as** hake, beef, pork, swordfish, meatballs, and fish balls is not affected by frying. However, presence of reducing substances (glucose and wheat flour) reduces the nutritive utilization of proteins. The amount of available lysine in white fish dropped from 20 % to 30 % after deep fat frying in various fresh vegetable oils. This is due to the formation of bonds between the amino groups of the protein and oxidation products of the fat. Fish proteins contain a relative surplus of lysine; small damage to this amino acid should not alter the net protein utilization. Deep fat frying significantly increased the percentage of resistant starch due to the formation of amylose-lipid complexes. Although frying decreases the amount of digestible starch in potato, dietary fiber content is increased. Mineral contents are very little affected by deep fat frying in both potatoes and fish.

Changes in Vitamins

Heat treatment may lead to a decrease in essential nutrients (like various vitamins) and consequently reduce the nutritional value of certain foods. Vitamins are organic components in food that are needed in very small amounts for growth and for maintaining good health. There are mainly two types of vitamins, viz., fat-soluble (e.g., A, D, E, and K) and water-soluble (e.g., folate, vitamin B_{12}, biotin, vitamin B_6, niacin, thiamin, riboflavin, pantothenic acid, and vitamin C). The water-soluble vitamins are heat sensitive whereas fat-soluble vitamins are relatively heat stable. The transformations lead to loss of vitamins and proteins during the Maillard reaction (Burri et al. 2009). Vitamins are unstable in foods. The cooking/heating conditions cause vitamin loss. These losses are varied depending upon severity of temperature and length of exposure, presence of oxygen, light, and moisture. Vitamin A is stable under an inert atmosphere; however, it rapidly loses its activity when heated in the presence of oxygen, especially at higher temperatures. Carotenoids have highly unsaturated structure making them highly susceptible to degradation in presence of heat, oxygen, and light. Vitamin D is vulnerable to alkaline pH range, light, and heat. Retention of vitamin D varied in the range of 60–90 % during culinary treatment of meat and fish. Vitamin E is lost during roasting and broiling and is unstable in presence of reducing agents (light, peroxides, oxygen). During culinary treatments of various types of meat, 44–95 % of vitamin E is retained and 60–93 % in case of legumes. Vitamin K is relatively stable during culinary treatment (Emilla et al. 2006; Mahesh and Uday 2013). Thiamine is highly unstable at alkaline pH, but thermal degradation occurs even under slightly acid conditions. Riboflavin is stable to heat but sensitive to light upon high heat treatment. Folate is lost in food during cooking because it breaks down under heat and leaches into cooking water. Folic acid is one of the heat-labile vitamins and is rapidly destroyed with increasing temperature. Folic acid deficiency is associated with the incidence of neural tube defects and with plasma homocysteine concentrations, an independent risk factor for cardiovascular disease. The bioavailability of folates from natural sources is highly variable and may depend on the food matrix structure and stabilizing factors in the food to reduce folate degradation, for example, by thermal treatment (Gerhard et al. 2007). Pantothenic acid is the most stable vitamin during thermal processing with pH levels of 5–7. Niacin is the most stable water-soluble vitamin. Vitamin B_6 is resistant to heat, acid, and alkalis but sensitive to light in neutral and alkaline solutions. Vitamin B_{12} is generally considered to be stable; it undergoes large losses through leaching into the cooking water. Vitamin B_{12} is normally stable during pasteurization of milk, but sterilization is responsible for 20 % loss of it. Biotin is labile when heated in alkaline solutions (Emilla et al. 2006; Mahesh and Uday 2013).

Thiamin is by far the most heat-labile of the vitamins in meat whereas niacin and riboflavin are relatively stable. Most white fish are relatively poor sources of vitamins, and so losses are of lesser importance. The vitamin D in fatty tissue of fish is relatively more heat stable. High-temperature treatment of cereals leads to destruction of thiamin and loss of available lysine. Baking destroys 15–30 % of the

thiamin of bread with no loss of riboflavin or niacin (Bender 1978). During sterilization of milk, pyridoxal (Vitamin B_6) converts into amine, and on subsequent storage the pyridoxamine complexes with sulfur compounds leading to the formation of bis-4-pyridoxyl disulfide which has much lower biological activity (in rats). The most sensitive nutrients are vitamins C and B whereas vitamins A and D are not affected when milk is subjected to pasteurization. However, there is considerable destruction of vitamins C, B_{12}, B_6, folate, and thiamin, but losses can be reduced by increasing the temperature and decreasing the time (Ultrahigh temperature – UHT) (Bender 1978).

Changes in Minerals

Minerals are the inorganic elements that are essential to the functioning of the human body. The minerals contribute to flavor, texture, and when digested can provide the cofactors for enzymes that influence nutrition. Minerals that retain in food after processing are known as chemically available while minerals which upon consumption become biologically functional to the organism are known as biologically available. Minerals are relatively not affected and lost during food processing, but minerals combine with conutrients or nonfood components during heating. They may become unavailable for digestion due to these interactions. However, destruction of phytates (known as binding ligands) increases the bioavailability of minerals (Mahesh and Uday 2013). The reaction products of depolymerization processes under high temperature might change the chemical form of iron, and it becomes more soluble, which increases its availability. Partially or completely ionized salts of oxalic acid (oxalates) form water-insoluble complexes with Ca^{+2}, Fe^{+2}, and Mg^{+2}. The oxalates are considered as antinutrients by virtue of their disruption of mineral absorption. Foods rich in oxalates potentially can decrease important minerals absorbed into the system. Cooking removes oxalates present in food such as tea leaves, spinach, or cocoa. Blanching and cooking of spinach leaves improves HCl-extractable iron, calcium, and zinc, which is similar to the acidic environment of the stomach. However, calcium, iron, and zinc are lost by heat treatments. During kitchen cooking, minerals are leached out into the hot water. The compounds formed during chemical reaction between proteins and sugars bind minerals. During heating, ascorbic acid is destroyed and in so doing eliminates a key component that facilitates iron absorption.

Baking is not likely to affect the content of minerals in foods. Heat treatment may profoundly affect the absorption and utilization of minerals, through cleavage of complexes, which otherwise renders these minerals less absorbable. Phytate can undergo hydrolysis during the bread-making process that improves the absorption of the phosphorus. During the baking process, some fiber components like hemicelluloses may undergo transformation which may affect mineral absorption. Iron may undergo oxidation or reduction during the baking process, and this might affect its absorbability or biological value (BV) (Karmas and Harris 1988).

Changes in Non-Nutrients and Other Components

Non-nutrients are those bioactive compounds in food that do not seem to be essential for avoiding a specific disease or a clinical condition associated with a deficiency for a specific substance, e.g., a nutrient. However, non-nutrients may have important nutritional and biochemical functions by acting, for example, as antioxidants or having antimicrobial or anticarcinogenic properties, respectively. The bioactive non-nutrients, specifically polyphenols/phytochemicals, are important from a human physiological point of view. Phytochemicals are secondary plant metabolites which are present in small and varying amounts in plants that include carotenoids, flavonoids, isoflavonoids, phenolic acids, glucosinolates, monoterpenes, phytosterins, and saponins. Different polyphenols react differently to thermal treatment. Virgin olive oils contain lignans, hydroxytyrosol, and tyrosol-like substances. The lignans are less affected by heating to 180 °C for 25 h, microwave heating for 10 min, or boiling in a pressure cooker for 30 min than hydroxytyrosol and tyrosol-like substances. Thus, thermal treatment differentially affects bioactive compounds present in the same food and thus very likely changes the nutritional characteristics of that food considerably. Anthocyanins are water-soluble plant pigments present in different fruits and vegetables. The bioavailability of anthocyanins does not seem to be affected by thermal processing. Carotenoids are also a large group of plant pigments, e.g., α- and β-carotene, lycopene, lutein, and zeaxanthin. During thermal processing of tomato, isomerization of lycopene from *all-trans*-lycopene to *cis*-lycopene isomers occurs depending on the temperature and the time of heating. Thermal processing enhances the nutritional value of tomatoes by increasing total antioxidant activity; despite a decrease in vitamin C content with increased duration of processing at 88 °C, lycopene content and total antioxidant activity increased, respectively. The bioavailability of lycopene has been shown to be much higher from processed tomato products (tomato paste) as compared to fresh tomato in a human dietary intervention study (Gerhard et al. 2007).

Food allergies can be defined as adverse, immune-mediated reactions to foods that occur in certain individuals. Food allergy is an abnormal *immunological* response to a food or food component; food allergens are almost always proteins. Food allergic disorders include acute, possibly life-threatening allergic reactions, as well as chronic debilitating diseases. The allergenicity of certain food allergens may be affected by thermal processing. Besides the allergens themselves, however, other modifying factors present in food may play an important role with respect to thermal treatment and heat inactivation of allergens. Heat treatments affect the allergenicity of food, either reducing or increasing it. Processing may destroy existing epitopes on a protein or may generate new ones (neoallergen formation) as a result of changes involving protein conformation. The thermal processing of proteins can form oligomers, become denatured, degraded, aggregated, cross-linked, fragmented, and reassembled, and these changes can alter the overall IgE binding profiles of food allergens. During the Maillard reaction, the interaction with sugars may modify the tertiary structure of the proteins and thus modify their

conformational epitopes, creating novel IgE binding sites, masking the allergenic structure, or exposing previously unavailable sites. The dominating major allergen in codfish is Gad c1, which seems to be extremely stable to thermal treatment. The thermal processing changes the peanut allergens. Roasting of peanuts increased the biological activity 90 times compared to an extract of raw peanuts. The increase in allergenicity may be caused by a Maillard reaction.

Nucleic acids as well as the low molecular weight compounds such as nucleotides, nucleosides, and purine and pyrimidine bases are ubiquitous in food. In fresh unprocessed food, the main part of the nucleo compounds – more than 95 % – is present as RNA and DNA. Heating processes change the distribution of the nucleo compounds in comparison to the raw material. During cooking and frying, the proportions of the low molecular weight nucleo compounds as nucleotides, nucleosides, and free bases expand. Furthermore, it is well known that the individual components increase the content of uric acid in human serum in a different manner which is important for patients suffering from gout. The microwaving heating process reduces the formation of low molecular weight nucleo components in vegetables in comparison to normal cooking and pressure cooking (Isabelle and Alfred 2007).

Toxicological Aspects of the Chemical Changes of Food Components During Heating and Cooking

Heat processing is one of the means to preserve foods and maintain food supplies for longer periods of time than their seasonal availability. The development of various types of thermal processing leads to improvement in palatability of foods, reduction in deterioration of food during storage, as well as improving the quality and safety of food products. The exposure of food to heat can be considered the most used processing step, and hence heating is one of the inevitable steps in a majority of food preparations. The wide range of heat treatments like baking, grilling, frying, toasting, roasting, broiling, microwaving, stoves, pasteurization, and sterilization are applied to various foods depending on their end use that can improve product quality as well as consumer acceptance. However, during processing, various toxic compounds are generated from interactions between various food components as well as added ingredients/additives. The chemical changes in food components, including amino acids, proteins, sugars, carbohydrates, vitamins, and lipids produce some toxic chemical compounds. During thermal processing, the toxic compound produced is generally designated as HEATOX, i.e., heat-generated food toxicants, and considered as carcinogens, genotoxins, neurotoxins, as well as antinutrient effects. Lineback and Stadler (2009) have defined "processing toxicants (process-induced toxicants, process-formed toxicants) as those substances present in food as a result of food processing/preparation that are considered to exert adverse physiological (toxicological) effects in humans, i.e., substances that create a potential or real risk to

human health. Food in this definition also includes beverages and nonalcoholic drinks such as coffee and tea, and thus both parts of the diet are included."

During heating and cooking, a number of chemical reactions occur simultaneously, and one of the key reactions is the Maillard reaction. It is a very complex reaction involving reducing sugars and amino acids. The Maillard reaction is known to produce more than 550 volatile compounds that contribute to the flavors and aromas while nonvolatile products such as the melanoidins contribute to the browning colors in cooked foods. However, compounds formed during Maillard reactions have adverse physiological effects or potential health risks (Lineback and Stadler 2009). There are various books and papers available on this topic but readers are advice to read one of the excellent book edited by Stadler and Lineback (2009) for further details.

Heterocyclic aromatic amines, acrylamide, acrolein, hydroxymethylfurfural, furans, chloropropanols, and chloroesters, Maillard reaction products, and nitrates as potential toxicants are produced during heating/cooking of foods as well as aspect on *trans*-fatty acids in heat-treated oils that can be discussed in subsequent sections.

Hydroxymethylfurfural (HMF)

Hydroxymethylfurfural (5-hydroxymethyl – 2-furaldehyde, HMF) is formed naturally during heating and is an intermediate in the Maillard reaction (MR). The molecular formula of HMF is $C_6H_6O_3$ having molecular weight 126.11 g/mol, and melting point varies from 32 °C to 34 °C, which is shown in Fig. 1.

HMF is considered as one of the direct indicators for assessing the quality of heat-treated food. When carbohydrate-rich products undergo heat treatment and subsequent storage, HMF is produced.

Formation and Occurrence of HMF in Food

The formation of HMF depends on presence of precursors like glucose, fructose, amino acids, as well as the temperature, pH, and duration of storage. The acidic foods can form high amounts of HMF. The food products which can be stored at longer time contribute to high HMF. Sugars decompose into furfural compounds by the Maillard reaction, caramelization, or pyrolysis of either reducing moieties of disaccharides or free monosaccharides (Morales 2009). The mechanism for formation of HMF is shown in Fig. 2.

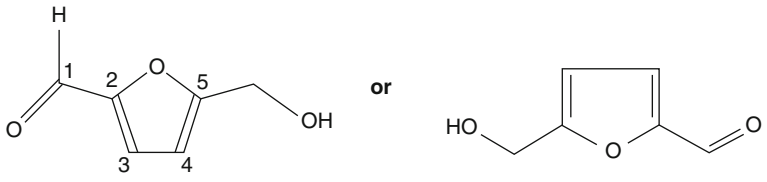


Fig. 1 5-hydroxymethyl – 2-furaldehyde, HMF

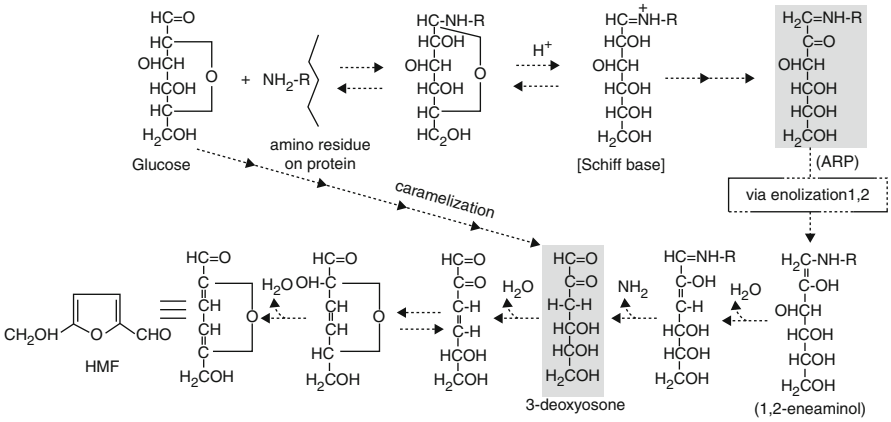


Fig. 2 Formation of HMF during heat treatment of foods (Morales 2009: Copyright © 2009 by John Wiley & Sons, Inc. Reprinted with permission)

The Maillard reaction is a complex reaction that has occurred in heated, dried, or stored foods. This reaction is considered as nonenzymatic browning or amino-sugar browning. During heating of food, the Maillard reaction occurs, which results in formation of characteristic color and flavor in the products. The Maillard reaction can be divided into three (i.e., early, advanced, and final) stages. In the early stage, the condensation of a carbonyl group (e.g., glucose) with a free amino group (ε-amino group of lysine) which forms glycosylamines subsequently undergoes series of reactions producing unstable Schiff bases to more stable amadori rearrangement product (ARP). Under advanced stages of the Maillard reactions, the ARP undergoes several degradation reactions during severe heat treatment or prolonged storage, leading to production of 1,2-dicarbonyls. ARP is degraded to form reductones and furfurals that can react further to produce colored, high molecular mass products and melanoidins in the final stage. Dicarbonyl compounds can lead to the formation of Strecker aldehydes, pyrazines, thiophenes, and furans which contribute to flavor. Moreover, the dicarbonyl fragments can act as precursors of acrylamide (Morales 2009). HMF is formed by degradation of the ARP via 1,2-enolization pathways. The positively charged amino group shifts to enol forms in which a hydroxyl group is eliminated to yield 2,3-enol. The 2,3-enol subsequently hydrolyzed a Schiff base to glycosulose-3-ene, which is an unsaturated dicarbonyl compound and undergoes cyclodehydration to form HMF (Morales 2009).

Caramelization involves the degradation of reducing sugars without the condensation step. When sugars are heated above their melting points under alkaline or acidic conditions, they darken to form brown color polymers. HMF arises from monosaccharides through an acid-catalyzed dehydration and cyclization mechanism. HMF is formed from both the degradation of hexoses and an intermediate in the Maillard reaction. The formation of HMF is dependent on the temperature, water activity, pH, acidity, presence of bivalent metals, organic or inorganic acids,

Table 1 HMF content in selected food products

Food products	HMF content (mg/kg)
Baby food (cereal-based)	0–57.18
Baby food (milk-based)	0.18–0.25
Barley	100–1,200
Bottled tomato puree	3.95–9.94
Bread	3.4–87.7
Breakfast cereals	6.59–240.51
Caramel products	110–9,500
Chicory	200–22,500
Coffee (instant)	400–4,100
Cookies	0.5–74.5
Dried fruits	1 –780
Dried plums	1,100–2,200
Fruit juices	2–22
Jam	5.5–37.7
Malt	100–6,300
Must (*arrope*) syrup	3,500–11,000
Soluble coffee clusters	691–4,023
Sugarcane syrups	100–300

Compiled from Morales (2009) and Kowalski et al. (2013)

or salts. The reducing carbohydrates directly undergo 1, 2 enolization, dehydration, and cyclization reactions during caramelization. Caramelization requires higher temperatures than the Maillard reaction to develop HMF, and different sugars have a different impact on the formation of HMF (Morales 2009). HMF undergoes decarboxylation, oxidation, dehydration, and polycondensation reactions during further processing and storage. The various products like levulinic acids, formic acids, 5-hydroxymethyl-2-furan carboxylic acid, 5-hydroxymethylfuroic acid, furan-2,5-dicarboxylic acid, 2-(2′-hydroxyacetyl)-furan, and pyranone are degraded products from HMF.

The various thermal treatments like baking, roasting, and sterilization applied in preparation of food products like breakfast cereals, coffee, bread, as well as pasteurized juices or pulps is responsible for formation of HMF. In roasted products like coffee and roasted chicory are found appreciable amounts of HMF. In fresh and untreated fruit juices, HMF is not present. However, when the fruit juices undergo heat treatment and prolonged storage, HMF is produced. HMF is formed in milk upon treatment at temperatures above 120 °C. Infant formulas are fortified with ascorbic acid, lactose, and iron, which are relatively more susceptible to the formation of HMF. The HMF contents found in selected food products are shown in Table 1.

Toxicity of HMF

There are possibilities of colon cancer, tumors in kidney, skin papillomas, induction of chromosomal aberrations, as well as an irritant to the eyes, upper respiratory

tract, skin, and mucous membranes by HMF and related substances that have been reported in the literature. However, it is not confirmed whether human exposure to HMF represents a potential health risk, and the data from epidemiological studies or case reports on potential association of HMF with cancer risk in humans are not available. The in vitro and in vivo data available raise some concern with respect to genotoxicity (Morales 2009; Kowalski et al. 2013). Studies on rat and mice, however, have indicated potential carcinogenic properties of HMF. HMF can initiate and promote the growth of aberrant crypt foci in rat colons. Furfural and 5-hydroxymethyl-2-furfural induced a significant number of chromosome aberrations. The oral acute toxicity for HMF by oral or gavage administration to rodents is reported as LD50 ranging between 2.5 and 5.0 g/kg bw. Human diet contains abundant amounts of HMF, and humans may ingest up to 150 mg HMF/day, equating to 2.5 mg bw/day for a 60 kg person (Ulbricht et al. 1984).

Maillard Reaction Products

The Maillard reaction is also known as the "nonenzymatic browning reaction." A French scientist, Louis Camille Maillard, studied the reaction in the period 1912–1917. As mentioned earlier, the Maillard reaction is aminosugar type of browning in which reactions between a free amino group of amino acids, peptides, and proteins and a carbonyl group of reducing sugars occur during the preparation or the subsequent storage of foods. The Maillard reaction also takes place in vivo, and hence, to differentiate nonenzymatic glycosylation (in food) with the enzymatic glycosylation of proteins (in living cells); the word "glycation" is used. Proteins get modified in vivo during diabetes and aging that produces various products known as advanced glycation end products (AGEs) through various chemical pathways as described for heated foods. The AGEs are involved in several diseases (i.e., pathophysiological processes). The glycotoxins are also used for dietary glycation compounds in heated foods (Henle 2009).

Formation and Occurrence of Maillard Reaction Products in Food

Maillard reactions occur in mainly early, intermediate, and final (or advanced) stages, which is described in Fig. 3.

During early stages of the Maillard reaction, the major reaction products are the lysine derivatives such as *N*-ε-lactulosyllysine, *N*-ε-fructosyllysine, or *N*-ε-maltulosyllysine. Moreover, in infant formula, the Amadori products are *N*-α-lactulosylvaline, or *N*-α-lactulosylleucine is also formed. The 1,2-dicarbonyl compounds (glyoxal, methylglyoxal, 3-deoxyglucosulose) are produced during intermediate stage. The dicarbonyl compounds represent the direct precursors for the formation of AGE as it is produced in advanced stages of the Maillard reaction (Henle 2009). The various AGEs are quantified in foods, viz., *N*-ε-carboxymethyllysine (CML), pyrraline, pronyl-lysine, pentosidine, gyloxal-lysine-dimer, methylglyoxal-lysine-dimer, and 3-deoxyglucosulose-lysine-dimer. The chemical structures of CML and pyrraline are shown in Fig. 4.

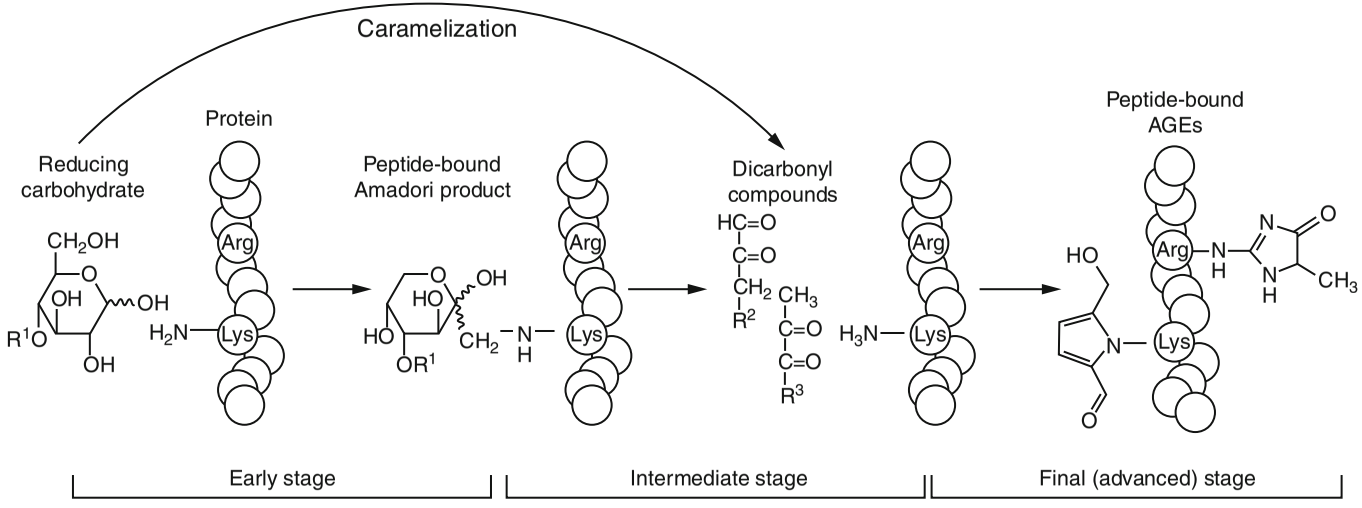


Fig. 3 Stages of Maillard reactions in food. R^1: H in case of glucose, a β-galactosyl or α-glucosyl moiety in the case of maltose or lactose respectively; R^2: 3-deoxyglucosulose R^3: 1-deoxyglucodiulose (Henle 2009: Copyright © 2009 by John Wiley & Sons, Inc. Reprinted with permission)

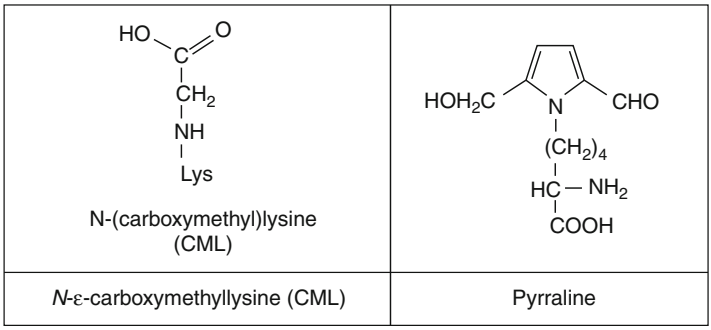


Fig. 4 Chemical structure of CML and pyrraline

The pyrraline is heterocyclic AGEs formed by reaction of the ε-amino group of lysine with 3-desoxyglucosulose. Pyrraline is a suitable indicator for "advanced stages" of the Maillard reaction. The *N*-ε-carboxymethyllysine (CML) was the first amino acid derivative of the advanced Maillard reaction formed from oxidative cleavage of Amadori products. It accounts for 3–10 % of the Amadori products (Büser and Erbersdobler 1986). The Maillard reaction products in foods are shown in Table 2.

The heat treatment of milk and subsequent storage leads to 10–20 % modification in lysine which can extend up to 70 % in case of lactose-hydrolyzed whey. The lysine derivatives like *N*-ε-fructoselysine and *N*-ε- maltuloselysine are found in bakery products. Pyrraline is also found in milk products, enteral formula, pasta, and bakery products. The pyrraline concentrations found ranged from 150 mg/kg protein in sterilized milk up to 3,700 mg/kg protein in bread crusts. The concentration of pentosidine was up to 35 mg/kg protein found in roasted coffee and some bakery products.

Toxicity of Maillard Reaction Products

Protein-containing foods that undergo early Maillard reactions contain Amadori compounds which represent the major form of glycation compounds. However, the concentration of advanced glycation compounds is significantly lower and divided up in several individual compounds of varying concentrations. The glycation reaction occurring in vivo was linked to the pathophysiology of diabetes and corresponding biological disorders such as cataract, joint stiffening, or diabetic nephropathy. AGEs represent an important class of uremic toxins because uremic patients were found to accumulate glycation compounds such as pentosidine or CML in the plasma and tissues. However, debate is going on about the toxicological effect of a dietary glycation compound. Food rich in excess AGE may contribute to oxidation and inflammation which cause health effects. The formation of AGEs in the bodies of healthy people is a slow process, but progression of this process is favorable in presence of dietary Maillard reaction products. We usually consume a large quantity of food having AGEs in our dietary life. Therefore, the safety of food AGEs is a problem of concern (Chuyen et al. 2005; Sebekova and Somoza 2007).

Table 2 Maillard reaction products in foods

Foods	Amadori compounds mmol/mol lysine	CML mmol/mol lysine	Pyrraline mmol/mol lysine	Pronyllysine mmol/mol lysine	Pentosidine mmol/mol arginine	Foods	1,2-dicarbonyl compounds	
							Glyoxal	Methylglyoxal
							ppm	ppm
Milk products	–	nd–10	nd–25	–	–	Cheese	4–6	4–11
Pastured milk	1–2	–	–	–	–	Yogurt	0.6–0.9	0.6–1.3
UHT	2–5	–	–	–	nd–0.01	Wine, sherry	0.6–0.9	0.7–1.8
Sterilized milk	up to 50	–	–	–	–	Cocoa	0.9–3.4	0.02
Milk/whey powder	50–200	–	–	–	–	Roasted beans (Coffee)	20–130	20–220
Lactose-hydrolyzed Whey powder	up to 700	–	–	–	–	Brew (Coffee)	–	23–47
Bakery products		nd–20	1–10	–	nd–0.4	–	–	–
Bread crumb	up to 200	–	–	0.01	–	–	–	–
Bread crust	up to 800	–	up to 180	0.1	–	–	–	–
Pasta	up to 400	–	nd–13	–	–	–	–	–
Roasted meat	1–10	up to 0.1	nd	–	–	–	–	–

Adopted from Henle (2009) with modification
nd not detected

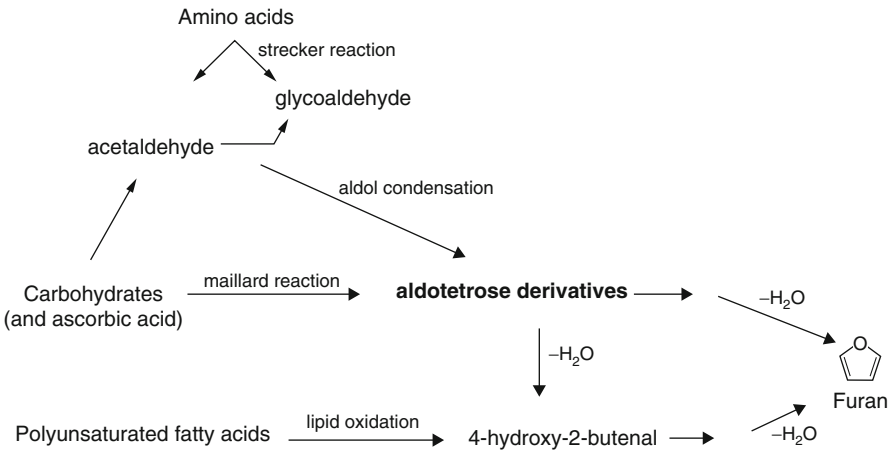


Fig. 5 Formation of furan from amino acids, carbohydrates and polyunsaturated fatty acids

Hazards of Furan

Furan is a colorless chemical (C_4H_4O) having a low molecular weight of 68, a high volatility with boiling point of 31 °C, and water insoluble. Furans are a major class of compounds forming during the Maillard reactions in foods (Maga 1979). The metabolite of furan, *cis*-2- butane-1,4- dial, plays an important role in furan-induced toxicity, including carcinogenesis, probably attributable to a genotoxic mechanism.

Formation and Occurrence of Furan in Foods

Furan is formed from multiple sources, viz., thermal degradation of reducing sugar (glucose, lactose, and fructose) alone or in the presence of amino acids (Maillard reaction); thermal degradation of certain amino acids; thermal oxidation of ascorbic acid, polyunsaturated fatty acids, and carotenoids (Maga 1979; Perez and Yaylayan 2004; Vranová and Ciesarová 2009). According to the US FDA (2004b), a variety of carbohydrate/amino acid mixtures or protein model systems (e.g., alanine, cysteine, casein) and vitamins (ascorbic acid, dehydroascorbic acid, thiamin) have been used to generate furan in food. Becalski and Seaman (2005) reported that furan can be formed through the oxidation of polyunsaturated fatty acids (PUFAs) at elevated temperatures while the addition of commercially available antioxidants (such as tocopherol acetate) reduced the formation of furan up to 70 %. The formation of furan (Vranová and Ciesarová 2009) is mentioned in Fig. 5.

US Food and Drug Administration (US FDA) published a report on the occurrence of furan in a number of foods that undergo thermal treatment, especially canned and jarred foods (US FDA 2004a). Parent furan was identified in a small number of heat-treated foods, such as coffee, canned meat, bread, cooked chicken, sodium caseinate, hazelnuts, soy protein isolate, hydrolyzed soy protein, rapeseed protein, fish protein concentrate, and caramel back in the 1960s and 1970s (Maga 1979). The levels of furan in foods are mentioned in Table 3.

Table 3 Furan content in selected foods

Foods	Furan (μg/kg)
Infant foods	1.3–87.3
Coffee beans/powder	239–5,050
Baby foods	1–112
Fruit preserves	0.9–37
Coffee brewed	3–125
Bread, toasted	18–30
Crisp breads/crackers	4.2–18.6
Fish	1.5–8
Meats	1.7–39
Sauces	3.3–46
Soups	3–125
Vegetables (in cans and jars)	0.8–48
Candy and chocolate	0.5–10.3
Baked beans	23.3–122

Source: EFSA (2004a, b) and FDA (2004)

The analytical method used had a limit of quantification of about 5 μg/kg for most foods and 2 μg/kg for most liquids including coffee. The FDA (2004) found that many heat-treated foods contained detectable furan, including almost the entire baby foods sold in jars and many of those sold in cans. The highest levels were for vegetables, particularly beans, squash, and sweet potatoes, packed in jars or cans (Crews and Castle 2007). Substantial levels of furan (20–200 μg/kg) have been reported in foods not cooked in closed containers, including potato crisps, crackers and crisp breads, and toasted bread (Hoenicke et al. 2004). High levels of furan are found in roasted coffee beans, probably on account of the roasting process where the high temperatures exceed most other food-processing procedures (Crews and Castle 2007).

Toxicity of Furan

Furan induces tumors in animal assays; the most remarkable is the induction of hepatic cholangiocarcinomas in rats and mice (Vranová and Ciesarová 2009). IARC (1994) has classified furan as possibly carcinogenic to humans (Group 2B). The European Food Safety Authority (EFSA) has expressed the opinion that "furan is clearly carcinogenic in rats and mice" and that "the weight of evidence indicates that furan-induced carcinogenicity is probably attributable to a genotoxic mechanism" (EFSA 2004a). Furan is absorbed quickly into the body but is also excreted with high efficiency. Furan administered to 50 mice at 8 or 15 mg/kg bw 5 days per week for 2 years causes loss of body weight at 15 mg/kg bw and significantly increases in hepatocellular adenomas and carcinomas (Crews and Castle 2007). It is likely that furan or *cis*-2-butene-1,4-dial reacts with DNA in target cells and can play a role in furan-induced tumors (Peterson et al. 2000). EFSA (2004a) estimated exposure to furan based on the limited data available. Baby food was of particular interest as a high proportion of samples sold in jars and cans contained furan and such foods may form the sole diet of many babies. The estimated intake based on

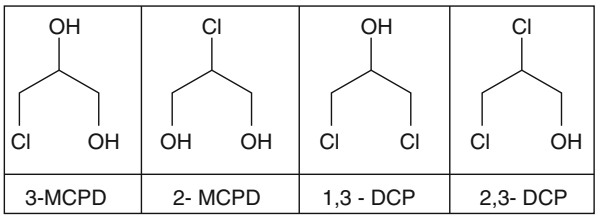


Fig. 6 Major substances of chloropropanol

consumption of baby food from glass jars was <0.2–26 μg furan per day or <0.03–3.5 μg/kg bw per day for a 6-month-old baby weighing 7.5 kg. The daily intake from coffee based on data from 45 samples was 2.4–116 μg/person, making coffee the major dietary source for adults (Crews and Castle 2007).

Chloropropanols and Chloroesters

Chloropropanols and their fatty acid esters (chloroesters) are formed during the processing and manufacture of certain foods and ingredients (Colin and Peter 2009). The chloropropanols and chloroesters could be formed in hydrolyzed vegetable proteins (HVP) produced by hydrolysis of proteinaceous by-products from edible oil extraction (such as soybean meal, rapeseed meal, and maize gluten) by hydrochloric acid (Velíšek et al. 1979). The main chloropropanol found in HVP was 3-chloropropane-1,2-diol (3-MCPD) together with lesser amounts of 2-chloropropane-1,3-diol (2- MCPD), 1,3-dichloropropanol (1,3- DCP),2,3-dichloropropanol (2,3- DCP), and 3-chloropropan-1-ol (Colin and Peter 2009), which are shown in Fig. 6. The chloroesters were intermediates in the formation of dichloropropanols (DCPs) and monochloropropanediols (MCPDs) which formed from lipids (Collier et al. 1991).

Formation and Occurrence of Chloropropanols and Chloroesters in Food

The free glycerol was shown to be the major precursor of MCPDs in leavened dough in preparation of bread (Hamlet 2004; Hamlet et al. 2004). During proving, yeast produced the glycerol that reacted with added chloride during baking accounting for approximately 70 % of the MCPDs formed. Addition of glucose promoted MCPD in dough due to removal of potential amino inhibitors (e.g., amino acids) via the Maillard reaction (Breitling-Utzmann et al. 2003; Hamlet and Sadd 2005). The formation of MCPDs from glycerol via the intermediate glycidol (Hamlet et al. 2004) is shown in Fig. 7.

Minor precursors of MCPDs (together with chloride) in dough were found to be monoacylglycerols, lysophospholipids, and phosphatidylglycerols present in white flour used in bread making. These compounds could account quantitatively for the remaining contribution (30 %) to MCPD in bread (Hamlet et al. 2004; Colin and Peter 2009).

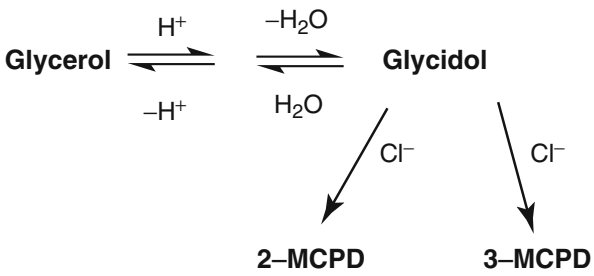


Fig. 7 Formation of MCPDs from glycerol via the intermediate glycidol (Hamlet et al. 2004)

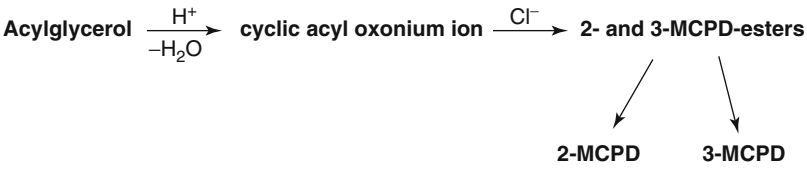


Fig. 8 Proposed mechanism of formation of MCPD-ester from partial acylglycerols

The chloroester formation was correlated with MCPD generation which was increased on heating (Hamlet et al. 2004; Hamlet and Sadd 2004). The presence of low levels of chloroesters in bread crumb due to <100 ° C temperature indicates that partial acylglycerols (i.e., mono- and diacylglycerols) may form these compounds. The cyclic acyl oxonium ion formed during this temperature and subsequently the ring structure is opened by chloride ion that can generate chloroesters as intermediate product of MCPD (Colin and Peter 2009), which is shown in Fig. 8.

The chloropropanol (3-MCPD) has been found in cereal, coffee, cheese, licorice, fish, and meat. Thermally processed products (e.g., cereals) account for the greatest incidence of 3-MCPD with some of the highest amounts found in products attaining high temperatures (e.g., bread crust and toasted bread). Processed garlic accounted for the highest incidence and concentration of 3-MCPD which varies from 5 to 690 μg/kg (Colin and Peter 2009). The 3-MCPD present in various foods is mentioned in Table 4.

The formation of 3-MCPD-esters (monoesters and diesters with higher fatty acids) may be widespread in processed foods derived from cereals, potatoes, meat, fish, nuts, and oils (Hamlet et al. 2004; Hamlet and Sadd 2004; Svejkovská et al. 2004). Hamlet *et al*. (2004) and Hamlet and Sadd (2004) measured 3-MCPD-esters in bread and toast. The highest amounts were found in regions of the bread that attained the highest temperature (i.e., the crust), and concentrations increased from 60 to 160 μg/kg when the bread was toasted over 40–120 s. The highest level of 3-MCPD-esters (6,100 μg/kg) was found in a sample of French fries (Svejkovská et al. 2004). The 3-MCPD-esters present in various foods are mentioned in Table 5.

Table 4 3-MCPD in selected foodstuff

Foodstuff	3-MCPD (μg/kg)
Breads	<10–76
Crust on bread	24–275
Cake, fruit	<10–210
Crackers/toasts	<10–134
Doughnuts	11–24
Cheese	<10–95
Smoked fish	<10–191
Licorice	20–23
Bacon	<5–22
Beef burger/hamburger	7–71
Smoked meats (Bacon)	<10–47

Compiled from Food Standards Agency (2001), Crews et al. (2001), EC (2004), Colin and Peter (2009)

Table 5 3-MCPD-esters in selected foodstuff

Foodstuff	3-MCPD-esters (μg/kg)
Breads (toast)	60–160
Coffee	100–390
Nuts, roasted	433–500
Virgin seed oils	100–300
Virgin germ oils	100–300
Refined seed oils	300–1,234
Refined olive oils	300–2,462

Compiled from Hamlet et al. (2004), Hamlet and Sadd (2004), Colin and Peter (2009)

Toxicity of Chloropropanols and Chloroesters

The EU Scientific Committee concluded that the 3-MCPD should be regarded as a genotoxic carcinogen and since a safe threshold dose could not be determined, residues in foods should be undetectable by the most sensitive analytical method (EC 1997). In rats and mice, the kidney was the main target organ for toxicity with effects also observed on male fertility. The 1,3-DCP was hepatotoxic, induced a variety of tumors in various organs in the rat, and was genotoxic in vitro (Schlatter et al. 2002a, b). JECFA (2006) concluded that a representative mean intake of 1,3- DCP for the general population was of 0.051 μg/kg body weight per day and an estimated high-level intake (young children included) was 0.136 μg/kg body weight per day.

Heterocyclic Aromatic Amines

Sugimura, a Japanese scientist, first discovered carcinogenic and/or mutagenic heterocyclic aromatic amines (HCAs/HAAs) in fish and meat cooked at temperatures over 150 °C in 1977, and more than 25 HCAs have been isolated and identified in cooked meat products (Nagao et al. 1977; Sanz et al. 2008). Heterocyclic

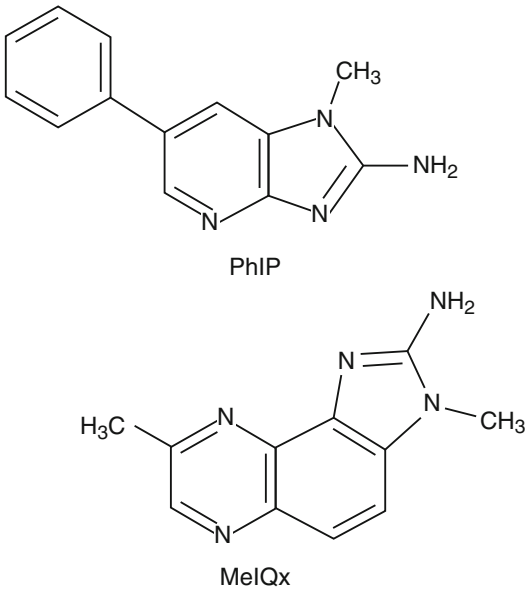


Fig. 9 Heterocyclic aromatic amines

aromatic amines are potent mutagens at ng/g levels in cooked foods (Sugimura 2002). Some of the HAAs like 2-amino-3,8-dimethyl-imidazo[4,5-f]quinoxaline (MeIQx), 2-amino-3,4-dimethyl-imidazo[4,5-f]quinoline (MeIQ) and 2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP) reported as possible human carcinogens follow in class 2B as well as probable human carcinogens (2-amino-3-methylimidazo[4,5-*f*] quinoline (IQ), class 2A) by International Agency for Research on Cancer (IARC 1993; Kizil et al. 2011). Some of the chemical structures of HAAs are shown in Fig. 9.

Formation and Occurrence of Heterocyclic Aromatic Amines in Food

HCAs can be classified into two major groups called as aminoimidazoazoarenes (AIAs) [or imidazoquinoline (IQ)-type compounds or thermic HCAs] and aminocarbolines [or non-IQ-type HCAs]. The AIAs are the most important class in cooked foods formed by heat-induced nonenzymatic browning known as Maillard reaction which involves the reaction of free amino acids creatine, creatinine, and hexoses during cooking of foods at conventional cooking temperatures (150–300 °C). They have an imidazo group linked to a quinoline, a quinoxaline, or a pyridine. The aminocarbolines are mainly formed by pyrolysis of amino acids and proteins at higher temperatures above 300 °C (Jagerstad et al. 1983; Sugimura and Adamson 2000; Busquets et al. 2004; Kizil et al. 2011). Some of these carbolines contain a 2-aminopyridine moiety as a common structure. The formation of them highly depends on method, time, temperature of cooking; type of meat, fat, and moisture content (Minako and Sugimura 1995; Sugimura and Adamson 2000); pH, sugar, free amino acid, and creatinine content of meat; lipid oxidation; and

Table 6 The HCAs levels in some of the cooked foods

Processed foods	PhIP (ng/g)	MeIQx (ng/g)
Chicken, fried	0–70	0–3
Meat extract	0–4	0–80
Beef burger, fried	0–32	0–7
Beef burger, pan residue	0–13	0–6
Beef stock cube	0–0.3	0–0.6
Salmon, fried	0–23	0–5
Fish	0–10	0–2
Poultry	0–330	0–3
Red meat	0–35	0–10

Compiled from Skog et al. (1998) and Busquets et al. (2004)

presence of antioxidants (Pais et al. 1999; Kizil et al. 2011). The HCA levels in some of the cooked foods are shown in Table 6.

Toxicity of Heterocyclic Aromatic Amines in Food

The mutagenicity in Salmonella varied more than 160,000 times between the strongest and the weakest HCAs, affected by number and positions of exocyclic substituents, especially the 2-amino-group of the imidazo part of the molecular structure present in most HCAs (Nagao et al. 1977). HCAs have been found to be potent carcinogens, which induce a variety of histological types of tumors in multiple organs following long-term oral administration (Eisenbrand and Tang 1993; Sugimura et al. 1993). It is notable that some HCAs induced tumors of the colon (PhIP, IQ, MeIQ), mammary gland (PhIP, MeIQ), and prostate (PhIP), which are common cancers in Western countries and have been associated with Western life style, i.e., high fat/meat consumption. There is also good epidemiological evidence correlating a high intake of HCAs with colon cancer although this correlation is not consistent (Margaretha and Kerstin 2005). Human exposure to HCAs has been estimated to range from a few ng/day to some μg/day. The major source of human exposure to HAAs is through consumption of household-cooked meats and fish. The range of HAAs detected in foods is highly variable and dependent on cooking preferences, i.e., pan-frying or barbecuing of meats at high temperature produces the greatest amounts of HAAs (Robert 2009).

Acrylamide

Chemically, acrylamide ($CH_2 = CH\text{-}CO\text{-}NH_2$; 2-propenamide) is a water-soluble low-molecular-weight compound (molecular weight 71.08) built up of a reactive ethylenic double bond linked with a carboxamide group (IARC 1994) which is shown in Fig. 10. It is white crystalline solid with melting point 84.5 ± 0.3 °C and a high boiling point (136 °C at 3.3 kPa/25 mmHg). Acrylamide is a difunctional monomer, containing a reactive electrophilic double bond and an amide group (Habermann, 1991).

Fig. 10 Chemical structure of acrylamide

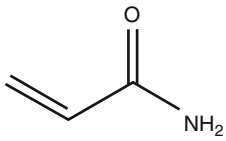
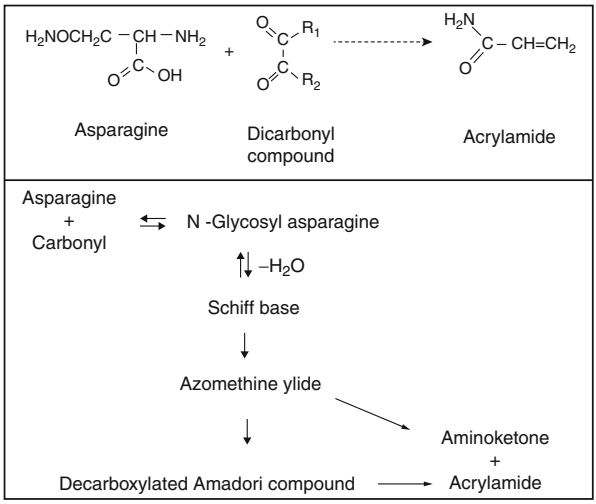


Fig. 11 Mechanisms for formation of acrylamide in foods



Formation and Occurrence of Acrylamide in Food

Acrylamide has been found in foods that have been cooked or processed at high temperatures and levels that can increase with the time of heating. Acrylamide appears to be formed as a by-product of the Maillard reaction. The Maillard reaction can occur during baking or frying when there is a proper combination of carbohydrates, lipids, and proteins in foods (Tareke et al. 2000). Acrylamide in food is largely derived from heat-induced reactions between the carbonyl group of reducing sugars as glucose and the amino group of the free amino acid asparagine during baking and frying (Margaretha and Kerstin 2005). The mechanisms for formation of acrylamide in foods is illustrated in Fig. 11.

The asparagine is mainly responsible for acrylamide formation in heated foods after condensation with reducing sugars or a carbonyl source (Gokmen and Palakzaglu 2008). Moreover, the sugar asparaginase adduct, *N*-glycosylasparagine, generates high amounts of acrylamide, suggesting the early Maillard reaction as a major source of acrylamide (Stadler et al. 2005). Becalski et al. (2003) reported that acrylamide could be produced from oils and nitrogen-containing compounds present in foods in which acrolein is formed from the thermal degradation of glycerol (Umano and Shibamoto 1987). Subsequently, oxidation of acrolein to acrylic acid and ultimately reaction of acrylic acid with ammonia, which potentially could be generated by pyrolysis of nitrogen-containing compounds, leads to the formation of acrylamide. The asparagines content within a certain category of foods

Table 7 Acrylamide levels in different processed foods

Food	Acrylamide (ppb)
Baked products: bagels, breads, cakes, cookies, pretzels	70–430
Beer, malt, and whey drinks	30–70
Biscuits, crackers, Bakery products and biscuits	18–3,200
Bottled prune juice	53–267
Breakfast cereals	30–1,649
Canned baby foods	10–121
Chips/French fries	59–5,200
Chocolate powder	10–909
Chocolate products	2–826
Coffee powder	170–1,188
Crisp bread	800–1,200
Fish products	30–39
Gingerbread	90–7,834
Infant biscuits	10–1,060
Potato crisps	117–4,215
Potato fritters	42–2,779

(e.g., potatoes) varies greatly; there is very wide variability of acrylamide levels even within one food category. Acrylamide is formed when carbohydrate-rich foods are fried, baked, or roasted at high temperatures above 120 ° C (INFOSAN 2005). The acrylamide concentrations in different foods are listed in Table 7.

High levels of acrylamide are found in processed foods like bread crust, crisp bread, potato chips, French fries, tortilla chips, different baked goods, coffee, and cereal formulations. However, due to variations in processing, parameters like temperature, time, nature of frying oil, and nature of food matrix are responsible for wide variations in levels of acrylamide in the foods (Margaretha and Kerstin 2005).

Toxicity of Acrylamide

FAO/WHO (2002) estimated an intake of acrylamide to be in the range of 0.3–0.8 μg/kg bodyweight per day for an adult corresponding to 21–56 μg/day for a person weighing 70 kg. Rice (2005) has reviewed the carcinogenicity of acrylamide. The mutagenic and carcinogenic properties of acrylamide are assumed to depend on the epoxy metabolite, glycidamide. Glycidamide induces mutation in bacteria. Acrylamide has a potential to cause a spectrum of toxic effects (IARC, 1994; European Union Risk Assessment Report 2002), including neurotoxic effects as has been observed in humans. IARC (1994) reported that acrylamide and its metabolite glycidamide form covalent adducts with DNA and hemoglobin in mice and rats; acrylamide induces gene mutations, chromosomal aberrations, and cell transformation in mice and rodents, which makes an overall evaluation that acrylamide is probably carcinogenic to humans.

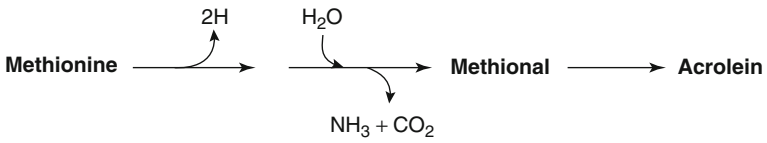


Fig. 12 Formation of acrolein from methionine

Acrolein

In 1839, Berzelius had characterized aldehydes from a thermal degradation product of glycerin, who named it acrolein (2-propenal). Acrolein is ubiquitously present in (cooked) foods and in the environment. The presence of acrolein was reported, in early 1960s, in samples obtained from pyrolysis of fats. Acrolein was reported as a volatile aroma constituent in various foods. It is formed from carbohydrates, vegetable oils and animal fats, and amino acids during heating of foods. Chemical reactions responsible for release of acrolein include heat-induced dehydration of glycerol, retroaldol cleavage of dehydrated carbohydrates, lipid peroxidation of polyunsaturated fatty acids, and Strecker degradation of methionine and threonine.

Formation and Occurrence of Acrolein in Food

Esterbauer et al. (1991) stated that frying of foods in oils produces acrolein. Acrolein reported to form during food processing (neutral pH and 100 ° C) from various amino acids and polyamines. The 3-substituted propanals produced from decarboxylation and deamination of amino acids (e.g., methionine, cystathionine, homocysteine, and homoserine) can readily decompose to yield acrolein (Shibamoto 2009). It was hypothesized that via Strecker degradation, methional formed from methionine and further oxidation of the methional formed acrolein, which is shown in Fig. 12.

Maillard reactions are responsible for generation of cooked flavor in various heated food products as a result of reaction between amino acids and carbonyls. The cooking or dietary oils, as a source of carbonyl reactant, contributed to formation of volatile acrolein. Moreover, processing of lipid-rich foods as well as cooking practices like deep-fat frying are responsible for generation of acrolein (Beauchamp et al. 1985; Shibamoto 2009), especially in the air. The concentrations of acrolein in the air 15 cm above the surface of heated oil were found in the range of 2.5–30 mg/m^3 (Shibamoto 2009). The heated lipids are the major source of acrolein in foods. Upon high temperature, acrolein was proposed to form from the dehydration of glycerol (Izard and Libermann 1978); it may also form from oxidative degradation of various fatty acids via radical chain mechanism involving hemolytic fission of R-O bonds more likely to occur at high temperature (Frankel 1982). The formation of acrolein from triglycerides in food is illustrated in Fig. 13.

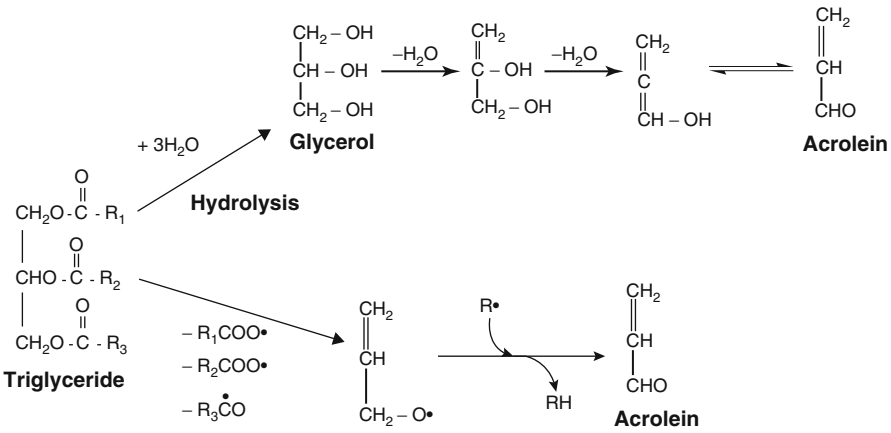


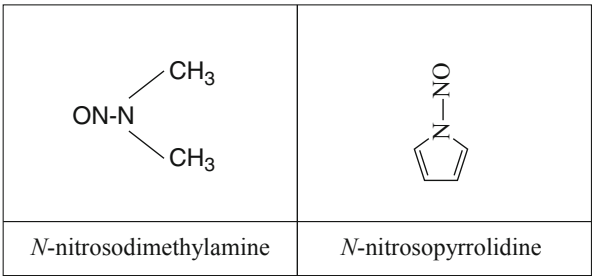
Fig. 13 Formation of Acrolein from triglyceride

Toxicity of Acrolein

There have been many reports on the toxicity of acrolein. Acrolein is commonly present in the outdoor air as well as indoor air pollution as it forms from lipids such as cooking oils, lipid-rich foods such as beef and pork which undergo at high-temperature processing, and acrolein is mainly concerned with inhalation toxicity. A clinical study was carried out on human volunteers and found that the average threshold of sensation ranged from 0.09 (eye irritation) to 0.30 mg/kg (respiration rate, throat irritation), and nasal irritation occurred at 0.15 mg/kg (0.35 mg/m^3) (Weber-Tschopp et al. 1977). A typical acute oral LD_{50} ranging from 10.3 to 33 mg/kg in Sprague–Dawley rats has been reported (Bioassay Systems Corporation 1981). The ocular and nasal irritation, growth depression, histopathological changes of the respiratory tract, (Feron et al. 1978), as well as Alzheimer's disease (Calingasan et al. 1999) were also found.

Nitrates, Nitrites, and Nitrosamines

Nitrates and nitrites, used as food additives in preserved meats, prevent the growth of botulinum toxin-producing organism. However, nitrates and nitrites have been shown to have adverse effects, responsible for formation of nitrosamines. Nitrites react with secondary amines to form a variety of nitrosamines. Sodium nitrite is used to preserve herring meal which was found to be a source of nitrosamines in food. Methylamines in the fish meal reacted with sodium nitrite to form dimethyl-nitrosamine. Nitrosamines are detected in cured meats, smoked fish, and soy protein foods dried by direct flame. The secondary amines reacting with nitrous acid is considered as principal chemical reaction for formation of *N*-nitrosamines. The former are present at low concentrations in proteinaceous foods. The nitrous acid can be formed from enzymatic reduction of nitrate, which is commonly present in



N-nitrosodimethylamine | *N*-nitrosopyrrolidine

Fig. 14 Common nitrosamines produced in cooked and heat-processed food

small quantities in water and foods or from sodium nitrite used as a preservative (James and Kenneth, 1975; Richard and Phillip 1975).

Formation and Occurrence of Nitrosamines in Foods

N-nitroso compounds are divided into *N*-nitrosamines, which are stable, and *N*-nitrosamides, which are unstable groups. In acidic conditions, nitrous acid is generated from nitrite and can be reacted with amine which undergoes nitrosation reactions. All nitrosamines have N–N = O as functional group. Nitrosation reaction can occur during the frying of nitrite-cured bacon. The amines necessary for the nitrosation reaction occur widely in many foods. The *N*-nitrosodimethylamine (NDMA) and *N*-nitrosopyrrolidine (NPYR) are two nitrosamines commonly reported in cooked foods, which are shown in Fig. 14.

Formation of nitrosamines through various processes during manufacture, cooking, and/or storage leads to their presence in food. Major significance for nitrosamine formation in the food is the presence of *N*-nitrosatable amines and of nitrosating agents. A large group of *N*-nitrosoamines, viz., NDMA (*N*-nitrosodimethylamine), NDEA (*N*-nitrosodiethylamine), NPYR (*N*-nitrosopyrrolidine), and NPIP (*N*-nitrosopiperidine) present in food are volatile carcinogenic. However, the main forms of *N*-nitroso compounds in food are nonvolatile (e.g., proteins containing *N*-nitrosated peptide linkages, such as *N*-nitrosoproline) which are noncarcinogenic or nonmutagenic but might act as precursors to volatile carcinogenic nitrosamines (Margaretha and Kerstin 2005). When bacon or smoked belly of pork is fried in which nitrite is added as preservative, *N*-nitrosoproline (NPRO) is produced through nitrosation of the proline, which subsequently decarboxylates to NPYR. High temperature and long frying time increase the amounts of NPYR formed (Margaretha and Kerstin 2005). However, as much as 90 % of the volatile nitrosamines produced during cooking are vaporized (Walker 1990; Tricker and Preussmann 1991; Tricker and Kubachi 1992).

The smoking of fish or meat and direct-fired drying of milk can be accompanied by the formation of oxides of nitrogen leading to the deposition of nitrate in the foods. The formation of *N*-nitrosamines in meat and meat products can occur as a result of various processing techniques such as smoking, salting, and/or curing. NPYR in cured meat is mainly formed by heat-induced decarboxylation of nitrosoproline. In addition to the generation of NPYR by thermal decarboxylation

Table 8 Different *N*-nitrosamines in heat treated food

Foods	Concentration, μg/kg	Types of *N*-nitrosamine
Meat products	nd-14	NDMA, NPYR, NDEA
Fish products	nd–131	NDEA, NPYR
Beer	<0.2–68	NDMA
Malt beverages	up to 1,080	NDMA
Milk powder	0.07–1.05	NDMA
Instant coffee, infant formula, cocoa, powdered egg and instant soup	<1	NDMA
Dried chilies, dried chili powder	6.1–16	NPYR, NDMA

of NPRO, *N*-terminal NPRO-containing peptides might also act as progenitors. The different *N*-nitrosamines in heat-treated food are shown in Table 8.

Toxicity of Nitrates, Nitrites, and Nitrosamines

NDMA is the most common *N*-nitrosamine found in food that contributes primarily to the total human exposure with volatile *N*-nitrosamines. For most industrialized countries, the estimated average present-day intake of volatile *N*-nitrosamines is approximately 0.2–0.3 μ g/person, respectively 3.3–5 ng/kg body weight. Beer, meat products, and fish are considered the main sources of exposure (Michael and Gerhard 2009). Barnes and Magee (1954) reported liver damage and liver tumors in rats after the administration of dimethylnitrosamine. Since then, many researchers worked on biological effects of *N*-nitroso compounds and found them to be carcinogenic, mutagenic, and teratogenic. *N*-nitrosamines, potent carcinogens, found mainly in protein-rich foods include *N*-nitroso-piperidine, *N*-nitroso-diethylamine, *N*-nitroso-pyrrolidine, *N*-nitroso-dimethylamine. These compounds are likely to increase the risk of rectum, bladder, colon, pancreas, and stomach cancers. Preformed and endogenously formed *N*-nitrosamines are well absorbed from the gastrointestinal tract. The rate of absorption varies for different *N*-nitrosamines. *N*-nitrosamines are distributed by the bloodstream and are rapidly metabolized in the liver, particularly at low concentrations. Most of the *N*-nitrosamines are precarcinogens and subject to metabolic activation. The DNA-damaging effect is generally accepted to be the causative factor for the carcinogenicity of *N*-nitrosamines (Michael and Gerhard 2009).

General Aspect on *Trans* Fatty Acids

Saturated and unsaturated fatty acids are present in lipid-containing foods. Most naturally occurring unsaturated fatty acids are found in the *cis* form. *Trans* fatty acids are the *trans* isomers of unsaturated fatty acids. The *cis* and *trans* forms refer to the position of the hydrogen around the double bonds on the fatty acid chain.

When the atoms are on the same geometric side of the chain, they are referred to as being in the *cis* position; those on opposite sides of the chain are in the *trans* position. A high level of *trans* acids will pack together to form hard or crystal fats. The *trans* fatty acids (TFAs) are generally defined as unsaturated fatty acids that contain nonconjugated carbon–carbon double bonds in the *trans* configuration.

Foods containing partially hydrogenated edible oils are major sources of *trans* fatty acids in the diet. A small amount of TFAs in edible oils is produced during the cooking and frying processes. Thermal treatments of fats and oils such as deodorization, cooking, and frying generate TFA isomers. Heating mainly induces *trans*-18:2 and *trans*-18:3 formations. The degrees of TFA formation during frying depends on the frying condition and on the frying materials. When partially hydrogenated fats are used, the formation of TFA is generally lower, but high initial contents of these acids result in a larger concentration of *trans* isomers in fried food. The quantity of *trans* isomers formed at elevated temperature indicates that a specific amount of energy is required to transfer double bonds from *cis* to *trans* configuration. Activation energy for isomerization decreases when the number of *cis* double bonds increases. TFA accumulation in edible oils by heating has been associated with the thermal oxidative deterioration of unsaturated FAs.

Singlet oxygen–induced *trans* fat formation and free radical–induced isomerization are the two mechanisms leading to formation of *trans* fat during heat treatment. Singlet oxygen reacts with *cis* double bonds and alters *cis* double bonds into *trans* configuration. In addition, a free radical can be added reversibly to a double bond to form a radical adduct. When a double bond is reconstructed, *trans* configuration is favored because a *trans* double bond is more thermodynamically stable. Singlet oxygen and free radicals are known as the key initiators in lipid oxidations. During thermal treatment, both lipid oxidation and *trans* fat formation occur simultaneously; however, *trans* fat formation has never been reported along with the lipid oxidation (Tsuzuki 2011; Vu and Siwarutt 2013).

A number of substances like free fatty acids, phospholipids, carbohydrates, proteins, water, chlorophyll, carotenoids, and fatty acid oxidation products that can be present in natural vegetable oils may contribute to changes in color, taste, and aroma, restrict their application, and reduce their shelf life time. Oils are refined to remove these substances. Refining generally includes degumming, neutralization, bleaching, and deodorization steps. In refining, vegetable oils are commonly heated between 60 °C and 100 °C before deodorization. Tasan and Demirci (2003) observed that the TFA 18:2 content increased 13.8-fold at the end of a refining process. Refined edible oils contain a small amount of *trans* fatty acids (0–2 %). Various foods like fast foods, packaged snacks, bakery products, and margarines contain *trans* fat. Fast food contains very high levels of *trans* fat, and it is possible to consume 10–25 g *trans* fat in 1 day. Customers who have a habit of consuming fast food every day have a daily intake of *trans* fat of about 5 g. This level of *trans* fat daily intake is associated with 25 % increase in the risk of ischemic heart disease (Stender et al. 2006).

TFAs are associated with cardiovascular disease, sudden death, and possibly diabetes mellitus. TFAs have hazardous effects on plasma lipoproteins that increase low-density lipoprotein (LDL) levels and decrease high-density lipoprotein (HDL) levels. This condition responsible to increase the LDL/HDL ratio is an important indicator of the risk of development of cardiovascular diseases. High consumption of TFA during pregnancy has been associated to effects on intrauterine development. A rise in allergic diseases has also been observed upon the high ingestion of these fatty acids. The association between TFAs in adipose tissue and the incidence of cancers of the breast, prostate, and colon is still equivocal.

Conclusions and Future Directions

Thermal processing of foods is necessary to make food digestible and palatable, to ensure microbial safety, and to produce a distinct taste, aroma, and texture. This may lead to extensive changes in the foods. The processes occurring during thermal treatment of foods are by far not completely understood and a multitude of compounds formed by thermal reactions not characterized. The nutritional effects of thermal treatment of foods are very diverse. The effects of thermal treatment can be nutritionally beneficial, for example, by increasing the bioavailability of bioactive components from an altered food matrix; however, also some of these bioactive components, particularly water-soluble vitamins and some heat-sensitive phytochemicals, will be lost during heat treatment of foods. The knowledge about the nutritional consequences of chemical and physical changes in food induced by thermal processing is scarce. It has been debated for many years whether thermal processing may create neoallergens. Even though sporadic reports on the formation of quite new allergens have occurred, there is still no good evidence that qualitatively new epitopes are formed during thermal processing of foods. For the influence of thermal processing on food allergenicity, an intelligent combination of biochemical, immunochemical, and clinical techniques must be applied for future research. There are number of toxic compounds formed during heating/cooking, but the question remains which toxicants are of greatest concern in foods from a dietary health perspective? Various compounds have been identified in foods having mutagenic, carcinogenic, or neurotoxic properties at high doses in animal studies. Such toxicants can be classified by structural characteristics or by the processing methods in which they occur. However, chemical changes during thermal processing are a very complex phenomenon. To understand the effect on various nutrients as well as formation of numerous chemical toxic compounds and their health effect requires interdisciplinary knowledge. The involvement of various disciplines and areas of expertise like agronomy, analytical chemistry, food chemistry, food technology, toxicology, epidemiology, nutrition, and consumer research is a very crucial step. Hence, there is need of a strong systematic interdisciplinary research project and effort to shed further light on these complex thermal processing issues.

Cross-Reference

- ▶ Chemical Composition of Bakery Products
- ▶ Contamination from Industrial Toxicants
- ▶ General Properties of Major Food Components

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