

Food Processing: A Review on Maillard Reaction

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ABSTRACT

Most of the foods consumed in modern society have been processed. Maillard reaction products (MRPs) are consumed everyday by the population through the consumption of foods such as milk, bakery products, breakfast cereals, caramel, honey, coffee, beer, chocolate, meats, dehydrated vegetables and processed fruits. The reaction of reducing carbohydrates with amino compounds was first described in 1912 by Louis-Camille Maillard. It is of essential importance to the food industry since it is usually responsible for processed food's flavour, taste, and colour. This reaction occurs in three different stages (initial, intermediate and final stage). Each stage is characterized by the formation of specific products (markers/indicators) that indicate the severity of the heat treatment and the loss of nutritional value due to the degradation of lysine. The Maillard reaction in some foods is strongly associated with its organoleptic acceptance, the decrease of nutritional values, and the production of advanced glycation end-product (AGE's). It is necessary to understand the different types of MRPs since depending on the cooking methods and conditions, both beneficial and toxic MRPs can be produced. The primary purpose of this review was to summarize how food processing effects MRPs formation in most common types of foods.

Keywords: MRPs, AGE's, Processing, Antioxidant properties, Amino groups.

I. Introduction

To eliminate pathogenic microorganisms and develop sensory properties, appropriate thermal processing of food is vital before their consumption. However, [Gatellier et al. \[1\]](#) described that thermal processing food might negatively influence its organoleptic and nutritional attributes.

The Maillard reaction was firstly described by a French physician and chemist, Louis Camille Maillard (1878–1936), and it is also known as non-enzymatic browning. Maillard reaction is a spontaneous and exceptionally reaction that occurs during cooking, thermal processing and storage of food, that are initiated by nucleophilic attack of a carbonyl-containing of amino groups on protein, peptides, and amino acids with carbonyl groups on reducing sugars, resulting in Schiff base formation and rearrangement to Amadori compounds [2]. Many food industries frequently use this reaction since it is responsible for giving food taste, colour, and aroma.

[Hodge \[3\]](#) first proposed that the Maillard reaction occurs in three different phases (initial, intermediate and final stage), also known as advanced glycation end-products (AGEs) formation. Each stage is characterized by the formation of specific products (markers/indicators) that indicate the severity of the heat treatment and the loss of nutritional value due to the degradation of lysine. The

initial stage occurs the covalent reaction of reducing sugars, such as glucose, fructose, or glucose-6-phosphate, to amino acid residues or epsilon amino groups of proteins, lipids, and nucleic acids, which produces a Schiff base, a reversible, unstable, colourless, without flavour and aroma [4]. Lysine is the most reactive amino acids in the initial stage, and its degradation occurs during the reaction. Lysine loss is considered to be of higher importance in foods that contain lysine as a reducing amino acid. It is possible to evaluate the degradation of lysine by determining the compound furosine (ϵ -N-2-furoylmethyl-L-lysine). This compound is produced during the acid hydrolysis of Amadori products by the ϵ -amino groups' reaction with glucose, lactose, and maltose [5, 6].

As the reaction progresses, many reactive intermediates substances are formed through a series of sequential and parallel reactions such as dehydration, cyclization, fragmentation and oxidation. Via Strecker degradation, amino acids and dicarbonyls can react to produce aldehydes, and aminoketones. The aldehydes generated are responsible for taste and aroma [7]. This stage is also characterized by the development of fluorescence and absorption in the ultraviolet (due to the presence of substances of slightly yellowish colouration). The fluorescence measurement is an indicator to evaluate the thermal damage in processed foods [5]. In the final stage, the compounds from the intermediate stage will react with amino acids to give the melanoidin brown pigments of varying molecular weight. This step is also characterized by the increase in the formation of fluorescent compounds [8]. N- ϵ -carboxymethyl-lysine (CML), produced in the final stage, is an essential indicator of Maillard reaction in food and biological systems [4]. CML can be formed by the oxidative cleavage of fructose-lysine by the reaction between lysine and dicarbonyls or also generated during the oxidation of ascorbic acid [9].

In bakery products, coffee, breakfast cereals, cooked meat, cocoa, Maillard reaction is highly desirable due to its contribution to flavour, aroma and colour. The ratio of formation and diversity of MRPs depends on different factors such as cooking time, processing temperature, food composition, water activity, pH, and presence of metal ions [10]. This review aims to summarise the formation of Maillard reaction products (MRPs) during the processing of different types of foods.

II. MRPs in cooked meat and fish

Meat and fish are usually cooked at high temperatures by frying, baking, roasting, and boiling. The MRPs content in cooked meat is related to the cooking method and temperature or industrial preparation and reheating. In general, foods rich in lipids and subjected to dry heat such as grills, roasting, frying and baking have the highest levels of AGEs. Dry heat cooking methods such as frying or roasting promote a formation of MRPs ten times higher than boiling in water [11, 12]. In meat seasoning, the addition of sauces with high content of reducing sugars in their formulation resulted in the most significant development of MRPs in cooked food [11]. Shorter cooking times, lower cooking temperatures and the addition of acidic ingredients such as lemon and vinegar reduce the ratio of MRPs formation [12].

In meat, furosine formation is more precise than CML, and its contents are usually much higher than CML. As expected, the furosine and CML content is strongly influenced by the heat treatment methods; as the heating time increases, the level of these compounds may be higher. Concerning the addition of ingredients rich in sugar, authors [11] observed a 10-fold increase in furosine concentration in cooked beef with soy sauces, bittersweet and barbecue sauce. [Roldan et al. \[13\]](#) observed a 4-fold increase in roasted lamb loins with a flavour enhancement solution. [Yamaguchi et al. \[14\]](#) also reported a higher rate of formation of furosine content in fried and grilled meat with the addition of sodium chloride and sucrose. However, the influence of adding sugars on the cooking of meats in the formation of CML is still not very clear. Higher CML formation in beef, pork, and fish, but in roasted lambs cooked with sous-vide, the addition of reducing sugars did not have higher CML contents [13].

In a preview study, [Tavares et al. \[15\]](#) mentioned that the cooking methods such as frying and baking of fish (hairtail), irrespective of cooking time, generated three- or four-times higher levels of furosine compared to boiling ones. Still, regarding the CML content, almost no difference was observed

between the cooking methods. Trevisan *et al.* [16] also presented a higher range of furosine in breaded-fried and baked beef than the boiled ones, irrespective of cooking temperature. In contrast, CML content was only identified in baked beef. Low level of CML in beef [9] and cooked lamb loins [13]. Low levels of reducing sugar, low lipid content and a low temperature in the geometric centre could explain the low level of MRPs in meat submitted to different domestic cooking methods.

III. Coffee roasting and MRPs

Maillard reaction products can react with amino acids to form the molecules known as melanoidins, which are dark brown compounds that provide colour in coffee and can have roasted, malty, bitter, and burned flavours. In coffee, it can also play an essential role in forming crema by stabilizing the foam [17]. The sugar content in the green beans is critical to the flavour of roasted coffee since the range of flavours generated is crucial to the complexity of the aromas in roasted coffee. Usually, the ratio of Maillard reactions becomes significant in coffee roasting from about 140 °C.

By the roasting process, coffee beans undergo numerous pyrolytic reactions, which lead to the substances responsible for their particular colour and flavour. Besides the Maillard reaction, many others reaction takes place during roasting [18]. In the coffee roasting process, the Maillard reaction is highly desirable due to its contribution to flavour, aroma and colour, which may be a significant factor in choosing this product. MRPs have already been well quantified in granola coffee, and the product submitted to the most severe heat treatment presented a higher concentration of MRPs of the advanced stage (CML) [19].

According to the process, roasting time diverges from 2 and 25min, and temperatures range from 180 to 250 °C. Usually, the internal temperature during this process exceeds 180 °C, which indicates the occurrence of the Maillard reaction [20]. Maillard reaction generates melanoidins upon roasting. Usually, during the advanced stages of the Maillard reaction, coffee melanoidins are produced via polymerization reactions of furans and pyrroles [21]. According to Daglia *et al.* [22], MRPs, caffeine, and some other components of coffee can protect human teeth from *Streptococcus mutans* which is one of the main agents causing dental caries in humans.

IV. MRPs in processed fruits and vegetables

In recent years, consumers have been more concerned about food choices, and the consumption of fruits and vegetables has many health benefits. As fruits and vegetables are fundamental in the diet, the consumption of this type of food has been increased worldwide. Therefore, the choice of the type of treatment used is essential, dictating the changes that may occur during processing and thus not causing changes in the beneficial health effects obtained from fruits and vegetables.

According to processing conditions (time and temperature), furoylmethyl derivatives (FM) has been found in processed fruits and vegetables. FM have been found in dehydrated orange juice [23], kiwi, plum, papaya and lemon [24] and dried apricots, prunes, figs [25]. It is shown that processing condition such as time and temperature is essential for FM formation in food. Dehydrated products promote higher level of furoylmethyl derivatives than juices.

Antioxidant properties of several compounds produced by the Maillard reaction have been reported in processed foods. Oxidoreduction reactions act on endogenous polyunsaturated lipids and phenolic compounds leading to the formation of off-flavour due to products that may potentially have toxic effects and reduce shelf-life [26]. Therefore, the search for active molecules and natural inhibitors is essential to prevent oxidative reactions. Maillard reaction products (MRPs) are recognized to exhibit various antioxidant properties, depending on the reaction conditions and type of treatment. Due to the production of MRPs, prooxidants are produced when vegetables are processed at low temperatures, and at higher temperatures decreases the prooxidants and increases antioxidant properties. In many fruits and vegetables, during post-harvest handling and processing, endogenous phenolic compound

oxidation is catalyzed by oxidoreductases, (polyphenoloxidases and tyrosinases) in the presence of O₂. Thiol-derived MRPs were highly prone to originate inhibitory compounds of polyphenoloxidases activity [27].

V. Maillard reaction in milk and dairy products

Milk and its derivatives as raw material play an important role in human nutrition, however, it has a relatively short shelf life. To prevent microbiological hazards, the dairy industry accepted pasteurization, sterilization, UHT, and high-temperature processing as essential steps to extend the shelf life of dairy products [28]. As dairy processing always produces new nutritious or harmful compounds, it is necessary to detail the products and processes applied. These actions induce variable physicochemical changes in milk molecules, depending on the duration/harshness of heating. [Arena et al. \[29\]](#) defend that pasteurization, UHT treatment, sterilization, concentration in vacuo, and formation of milk caramel affect the nutritional quality and alter the sensory attributes of the final products. These treatments generate chemical products not present in the raw material, including those due to enzymatic processes that occur during the heating of combinations of proteins and reducing sugars, in what is known as the Maillard reaction.

Since milk is rich in protein and sugar, processing milk at high temperatures such as pasteurization or sterilization may lead to different MRPs. Maillard reactions in some dairy products are generally detrimental to the product's organoleptic, nutritional, and functional qualities and, therefore, undesirable. However, some dairy processes exploit a controlled Maillard reaction during manufacturing, the browning reactions being Maillard is an integral part of the manufacture of products such as *Dulce de leche* and *khoa*, in which the milk is heated in the presence of sucrose to produce brown products with a taste pleasant [30].

In most dairy products, the carbonyl compound will initially be the reducing sugar lactose (or its hydrolysis products, glucose and galactose) and the amino groups can be derived from casein or whey proteins, which contain amino acid residues that are shown reactive for Maillard chemistry. Other sources of amine groups may include amino phospholipids or free amino acids, while milk fat provides another source of carbonyl compound [28]. Lactose participates in the Maillard reaction as reducing sugar, but it also undergoes degradation via a second pathway [31]. The evaluation of the initial stages of the Maillard reaction can be carried out by the determination of Furosine (ϵ -N-2-furoylmethyl-L-lysine). Furosine is an artificial amino acid formed during the acid hydrolysis of Amadori compounds, originating from the interaction of the amino groups of lysine with glucose, lactose and maltose. It is a helpful indicator of damage in milk, prolonged heating or inadequate storage results in increased levels of Furosine [32].

The Advanced Maillard Reaction begins when the Amadori compound breaks down into a range of different products according to the pH of the system. Hydroxymethyl furfural (HMF) can be used to assess the progression of MRPs formation, however, UHT milk may have different levels of HMF. In systems with a pH below 7, the main molecules formed due to degradation of HMF, furfuryl alcohol and pyrrolin. This pathway is called the 1,2 enolization route or sometimes 3-deoxyolone-pathway. Therefore, for milk and dairy products 1, 2 enolization is not the main pathway. For the second group of foods with neutral and alkaline pH, there is another way called the 2,3 enolization route or the 1-deoxyosone-pathway, leading to the formation of β -pyranone, 3-furanone, reductones, α -dicarbonyls, cyclopentenone, galactosilisomaltol and acetylpyrrole. It should be mentioned here that under normal conditions, the stability of the Amadori compound in milk (lactulosilysin) is relatively high unless the product is exposed to high temperature or stored for a significant period of time [33].

Most of the compounds responsible for the taste and odor of heat-treated foods are produced in the Maillard reaction and during the Strecker degradation of amino acids. Briefly, amino acids are decarboxylated and converted to Strecker aldehydes and, consequently, carbon dioxide is released [34]. These compounds have been identified in different dairy products; 3-methylbutanal in pasteurized and sterilized milk, 2-methylbutanal and isobutanal in UHT milk and 2-methylbutanal and isobutanal in

powdered milk. Finally, the Maillard reaction pathway approaches its end when the Amadori Compound degradation molecules begin to polymerize and generate the brown pigments known as melanoidins that have high molecular weight. It has been shown that the proportion of sugars and amino acids has a significant influence on the formation of brown pigments; while sugars have a promoting effect, amino acids seem to have a preventive role in this regard [30].

VI. MRPs in bakery products

Bakery products can be defined as transformed products, essentially made of flour and water (added other ingredients such as sugars, fat, egg, leavening agent, and other additives) in food with specific sensory attributes. In this way, the attributes such as aspect and colour of food surface are generally the first quality parameter evaluated by consumers and are critical in the product's acceptance [35]. Maillard reaction produces desirable colour and flavour in baked products, however, it can produce undesirable compounds such as acrylamide and furfurals, which may have negative health concerns.

Bread enriched with natural antioxidants from fruits or plant extracts promotes human health benefits [36]. Melanoidin is a new antioxidant source formed as MRPs during a prolonged heating process. Recently, some studies have investigated the MRPs and their antioxidant activity in model systems. The antioxidant capacity of white pan bread is moderately linked with browning intensity [37]. According to [Hwang et al. \[38\]](#), fructose-alanine MRPs presented the highest browning intensity in comparison with other amino acids with glucose or fructose, while glucose-arginine MRPs and glucose-proline MRPs presented the lowest browning intensity. [Shen et al. \[37\]](#) mentioned in their study that the melanoidin content was lower for bread with arginine compared with other amino acids (proline, glycine, threonine, lysine, alanine). Usually, the type of amino acid plays an essential role in the final antiradical activity of the MRPs, and lysine had high antioxidant activity.

The development of MRPs is essential to the appreciation and acceptance of bread by consumers. However, some MRPs formed during baking is associated with potential health risks. Acrylamide, whose main precursor is asparagine, is formed during the Maillard reaction at temperatures above 120 °C. Some studies on acrylamide content in bread have indicated that dough fermentation, the level of damaged starch in flour and the baking conditions influenced the content of acrylamide formed in the crust [39, 40]. According to [Forstova et al. \[41\]](#) the acrylamide content in a common type of Czech bread baked in various bakeries was low, ranging from 7 to 22 µg/kg. The level of acrylamide was higher in bread prepared using a commercial starter (*Lactobacilli*) and yeasts than in bread prepared using natural sourdough. In general, that yeast fermentation contributes to low the formation of acrylamide.

VII. Maillard reaction in cocoa and derivatives

Cocoa beans are used in various food products, both raw and after alkaline treatment. It is processed to obtain chocolate liquor, cocoa powder, cocoa butter and a wide range of products [42]. The ideal conditions to occur Maillard reaction are high temperatures and low moisture content by the roasting process. By cocoa roasting, about 600 volatile identified compounds are produced, including alcohols, phenols, esters, pyrroles, furans, furanones, pyranes, pyrones and pyrazines, such as 2-methylpyrazine, 2,5-dimethylpyrazine, 2,3,5-trimethylpyrazine, 2,3,5,6-tetramethylpyrazine (TMP) and others [43].

Maillard reactions are initiated by interactions between carbonyl groups (mainly of reducing sugars) and the nucleophilic amino groups of amino acids, peptides or proteins, resulting in sugar-amine condensation and rearrangement into Amadori products. These reactions are complex and lead to the simultaneous or consecutive formation of highly reactive low molecular weight (LMW) compounds, such as α -dicarbonyl and α -hydroxycarbonyl compounds, furfurals, and Strecker aldehydes [2]. Furthermore, [Oracz & Nebesny \[44\]](#) argued that at higher roasting temperatures (135 and 150°C), Maillard reactions advance to produce melanoidins, high-molecular-weight (HMW) compounds that produce the specific brown colour and texture to cocoa beans. These macromolecules

are responsible for the characteristic brown colour and texture of roasted cocoa beans and exhibit a binding affinity for the LMW aromatic compounds released in the roasting process.

The carbonyl derivative produced from the Maillard reaction reacts with the free amino acids due to the degradation of amino acids into aldehydes, ammonia and carbon dioxide. These aldehydes and their derivatives, produced during roasting, contribute to the aroma [45]. During roasting, the flavour produced is the result of combinations of 400–500 compounds, including pyrazines, aldehydes, ethers, thiazoles, phenols, ketones, alcohols, furans and esters. Aldehydes and pyrazines are among the main compounds formed during roasting. The roasting process generates new volatile compounds for specific flavours through the pyrolysis of sugars and loss of minor compounds that influence the final flavour of chocolate [46].

VIII. MRPs in Soybean Processing

Soybean is one of the richest and cheapest sources of protein and is essential in the diets of people and animals. The seed contains 17% of oil and 63% meal, 50% of which is protein. Soybean protein is strongly recommended as healthy food and play an important role in cardiovascular health based primarily on its favourable effect on cholesterol and blood pressure [47]. Soybean must be processed before consumption, so its processing is an important factor for preserving its nutritional quality and these operations should be appropriately done to reduce the risk of altering negatively the product.

According to Yu *et al.* [48], the darker coloured compounds were formed through the Maillard reaction and enhanced desirable sensory characteristics. Results demonstrated that peptides showed a high increase of antioxidant activity through Maillard reactions. Žilić *et al.* [49] reported that soybean proteins were susceptible to the Maillard reaction. Furosine was formed under slight heating conditions during extrusion and infrared heating. Still, microwave heating at lower temperatures for a longer time yielded lower acrylamide levels in the final soybean products due to its partial degradation. During infrared heating, acrylamide formation increased with decreasing moisture content. Relatively to HMF level, it increased in all three processes with the increase of time and temperature, and it was significantly higher in microwave treatment. The results showed that microwave heating improved the antioxidant properties of soybean compared to raw soybean. Huang *et al.* [50] mentioned that cysteine and thiamine could contribute to the colour formation and the overall acceptance of soybean peptide MRPs. MRPs with added cysteine and thiamine had improved antioxidant activity.

IX. Conclusion

The Maillard reaction is a sequence of consecutive, parallel and complex reactions that is extremely important to control its extension. During the processing of the different types of foods, Maillard reaction products have both positive and negative impacts on human health. Maillard reaction contributes to the formation of desirable sensory attributes, and different MRPs can act as antioxidants, antiallergenic, antibrowning, prooxidants, and carcinogens. By processing food at high temperatures, it might have a negative impact on its organoleptic and nutritional attributes. Toxic MRPs such as acrylamide has been reported as a carcinogen to humans. Processing at high temperatures promoted the formation of acrylamide via Maillard reaction in different types of food. Overall, this review may help better understand the formation of MRPs during the processing of several food groups.

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