

Maillard Reaction Products in Processed Food: Pros and Cons

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1. Introduction

The Maillard reaction was first reported in 1912 by Louis-Camille Maillard, who described that upon gently heating sugars and amino acids in water, a yellow-brown color developed. The reaction that leads to these colorful compounds, firstly described from a simple observation, is actually the result of a complicated pathway of chemical reactions. The Maillard reaction is often described in food systems but it also occurs in living organisms, and in this case, it is called glycation. In biological systems, the ramifications of the Maillard reaction have been observed and analyzed, as this reaction has become important in the field of food science and medicine (Finot, 2005; Gerrard, 2002a).

The consumption of Maillard Reaction Products (MRPs) has increased in recent decades and there are evidences that these substances are absorbed and may participate in pathological processes such as, cataract, diabetes, degenerative diseases, atherosclerosis and chronic renal failure. On the other hand, these compounds are responsible for essential sensory attributes of thermally processed food products, contributing to their appearance, flavor, aroma and texture.

This chapter will cover the chemistry of Maillard reaction products generation, the role of these products in food acceptability, the analysis of these compounds both in food products and in the human body and the biological activities attributed to these compounds, since this is a contemporary and controversy subject in food science and nutrition field.

2. The chemistry of Maillard reaction products generation

Since the first description of a browning reaction of glycine with glucose by Louis Maillard, the knowledge on chemical structures derived from the reaction of carbonylic and amino compounds has considerably increase (Nass *et al.*, 2007).

Amino-carbonyl and related interactions of food constituents comprise those changes commonly termed as "non-enzymatic browning reactions". Specifically, reactions of amines, amino acids, peptides, and proteins with reducing sugars and vitamin C (Maillard reaction, caramelization, ascorbic acid degradation) and quinones (enzymatic browning) cause deterioration of food during storage and processing (Friedman, 1996).

Non-enzymatic browning reactions depend on many parameters (Table 1), such as, temperature, water activity (a_w), pH, moisture content and chemical composition. In general, maximum browning occurs at a_w between 0.60 and 0.85 and the browning rate increases with increasing pH, up to a pH of around 10 (Gerrard, 2002a; Morales & Van Boekel, 1997).

| Mechanism | Oxygen requirement | NH ₂ requirement | pH optimum | Temperature | a_w |
|---------------------------|--------------------|-----------------------------|---------------|-------------|-------------|
| Maillard reaction | No | Yes | Basic/acid | Medium | Medium/high |
| Caramelization | No | No | Basic/acid | High | Low |
| Ascorbic acid degradation | Yes/No | No | Slightly acid | Medium | Medium/high |

Table 1. Main differences between non-enzymatic browning reactions (based on Finot, 2005)

From 1940, amino-carbonyl reactions and the resulting browning pigments have been investigated by many chemists. In 1953 Hodge proposed a three stages (initial, advanced and final) scheme for the Maillard reaction (Figure 1) (Nursten, 2005). The initial stage starts from the sugar amine systems leading to browning pigments generation. Amadori colorless compounds are formed in this stage, and an increased content of unsaturated carbonyl compounds is observed. During the intermediate stage, both fluorescence and radiation absorbing properties of the system increase due to the formation of small molecules with chromophores. Aldehydes formed by the Strecker degradation of amino acids can condense either with themselves, sugar fragments, furfurals, or with other dehydration product forming brown pigments. Although Strecker's pathway is not the major color-producing reaction, it is responsible for the origin of off-flavours usually associated with Maillard browning. The final stage is characterized by the formation of unsaturated, brown nitrogenous polymers (melanoidins) which may also be generated from the condensation reaction of furfurals or dehydro reductones (Finot, 2005; Hodge, 1953; Morales & Van Boekel, 1997).

Browning development occurs after an induction period, characterized by the production of fluorescent uncolored intermediates. Fluorophores are considered precursors of brown pigments and allow detecting the progress of the reaction before any visual change occurs. Fluorescence from the Maillard reaction is attributed to molecular structures with complex bonds between carbon and nitrogen, and the contribution of sugar caramelization to global fluorescence is insignificant in amino-acid containing systems (Matiacevich & Buera, 2006; Rozycki *et al.*, 2010).

Maillard reaction ratio is proportional to the heat-treatment severity during food processing, when temperatures range from 100 to 250 °C (baking, grilling, frying, extruding and roasting) and/or during storage for long periods at room temperature. This reaction is of most importance for roasted products such as coffee, chocolate and peanuts. In the medical arena, several authors describe the role of the Maillard reaction during ageing and chronic diseases, as diabetes and renal failure (Gerrard, 2002a; Nguyen, 2006; Nursten, 2005).

Maillard reaction occurs in biological systems and the final products are referred as Advanced Glycation End Products (AGEs). AGEs are a heterogeneous group of compounds that arise non-enzymatically by the reaction of reducing sugar and other α -carbonylic compounds with amino groups on proteins, lipids and nucleic acids. Actually, glycation in

living organisms have other pathways that are linked to glucose metabolism and lipid peroxidation, whose products are termed Advanced Lipoxidation End Products (ALEs) (Goldberg *et al.*, 2004; Nass *et al.*, 2007).

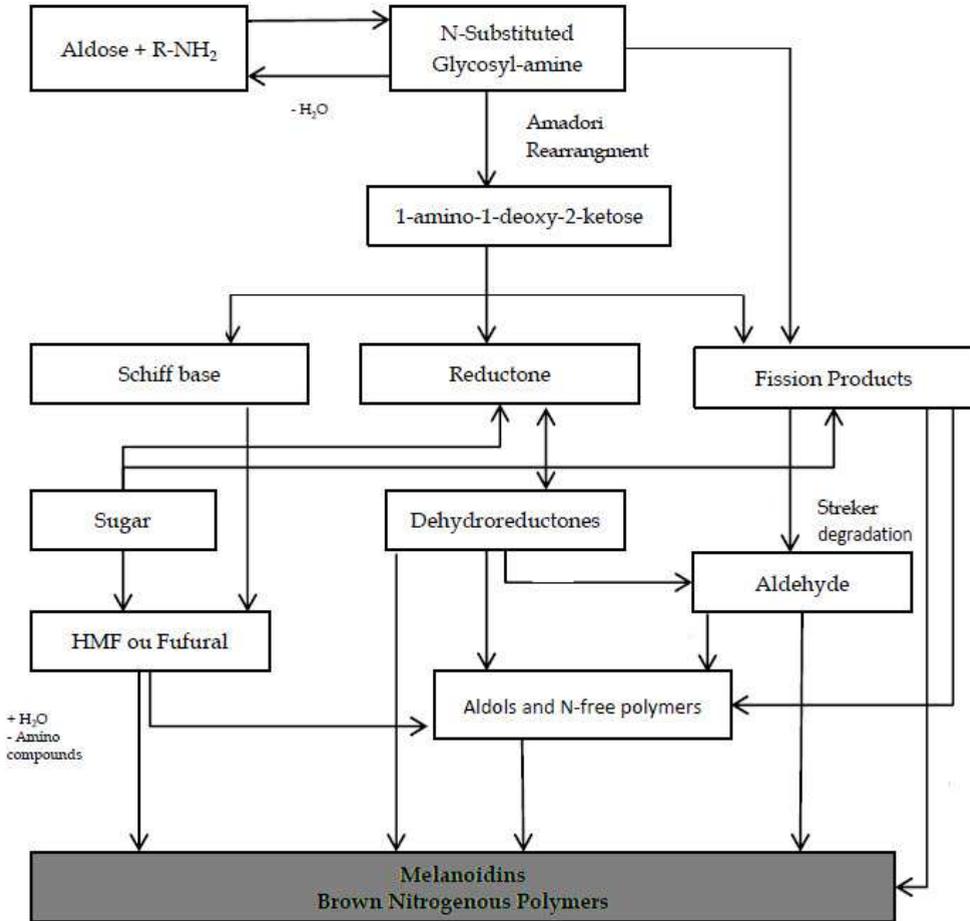


Fig. 1. Main stages in Maillard reaction proposed by Hodge (adapted from Nursten, 2005)

MRPs/AGEs generated in food and biological systems are shown in Figures 2 and 3. Nguyen (2006) describes the MRP/AGE content of selected popular foods, such as roasted almonds (66.5 kU/g), oil (120.0 kU/g), butter (94.0 kU/g), mayonnaise (265.0 kU/g), broiled chicken for 15 minutes (58.0 kU/g), fried chicken for 15 minutes (61.0 kU/g), homemade pancakes (10.0 kU/g), bread (0.5 kU/g). It is noteworthy that temperature and cooking process are more relevant for the formation of MRPs than time of cooking or other parameters (Nguyen, 2006).

Fluorescence/crosslinked

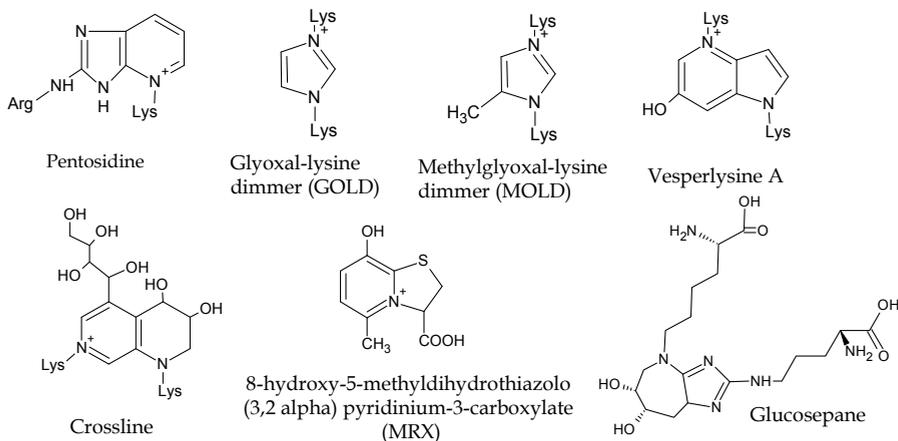


Fig. 2. Main chemical structures of Fluorescence MRPs/AGEs

Non-fluorescence/Non-crosslinked

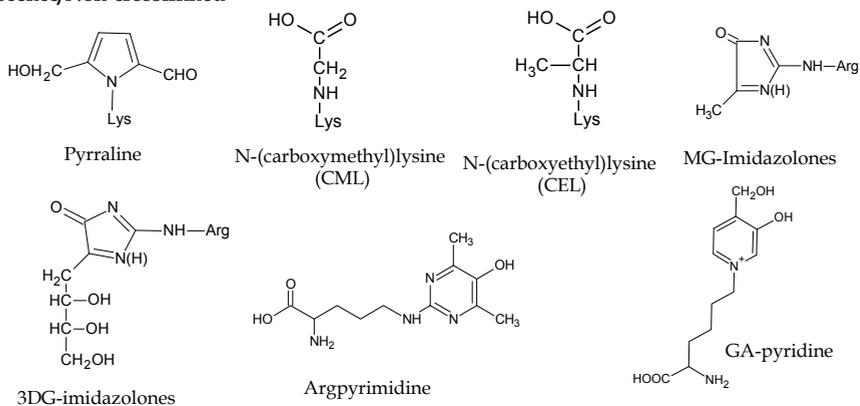


Fig. 3. Main chemical structures of non-fluorescence MRPs/AGEs

Sato *et al.* (2006a) proposed a scheme of formation of six distinct AGEs *in vivo* (AGE-1, AGE-2, AGE-3, AGE-4, AGE-5 and AGE-6). AGE-1 is formed from glucose through Schiff base and Amadori products, AGE-2 from glyceraldehyde, AGE-3 from glycoaldehyde, AGE-4 from methylglyoxal, AGE-5 from glyoxal, and AGE-6 from 3-deoxyglucosone. AGE-2 and AGE-3 are considered toxic AGEs by contributing to the neuronal cell toxicity. They also proposed that pentosidine, Nε-(carboxymethyl)lysine, pyrraline and crossline are nontoxic AGEs, however, other studies are needed to validate these conclusions (Nguyen, 2006).

AGEs formation occurs slowly and naturally in the body of healthy people, however, this process is accelerated under certain conditions, such as hyperglycemia and oxidative stress. MRPs dietary are added to the intra and extracellular AGEs produced, contributing to the

accumulation of these compounds in tissues and, thus favoring the onset and progression of metabolic complications (Barbosa *et al.*, 2008).

Up to 90% of pyrrolidine free and Amadori products excreted by the kidneys are from food source. Free pentosidine, for example, presents about 60 to 80% bioavailability (Forster *et al.*, 2005). Somoza *et al.* (2006) administered casein-linked lysinoalanine (LAL), N ϵ -fructoselysine (FL) and N ϵ -(carboxymethyl)lysine (CML) to rats and revealed that the kidneys are the main organs in which AGEs are accumulated and excreted. In this study, the dietary LAL, FL and CML excreted in the urine was 5.6, 5.2 and 29%, respectively. In other words, the rate of absorption and renal excretion of MRPs depends on dietary intake or the presence of pathologies as well as the amount and type of compound ingested.

3. The role of Maillard reaction products in food acceptability

Maillard reaction is one of the most important reaction which results from food processing. Maillard reaction products (MRPs) greatly influence essential food quality attributes such as flavor, aroma, color and texture. Actually, this reaction can be used to design foods that present sensory attributes demanded by the consumer (Ames, 1990; Yu & Zang, 2010).

3.1 Color

Color formation is the primary characteristic of the Maillard reaction. In the last decade, efforts have been driven to detect Maillard reaction kinetics and the formation ratio of colored compounds, mainly with the use of model systems. Brown color development during processing and storage is desirable for many products such as baked foods, coffee, cookies while undesirable in some kinds of food products orange juice, white chocolate, milk and powder egg. Predicting and controlling food color development are particularly important for companies to satisfy consumer preference, since a complex array of melanoidins produced by the Maillard reaction is strongly dependent on the food matrix composition as well as the technological conditions of the reaction (Wang *et al.*, 2011). Melanoidin can also be formed by sugar caramelization without the participation of amino groups.

The presence of melanoidins, brown nitrogen-containing high molecular weight pigments, responds for the characteristic color of roasted foods such as coffee, cocoa, bread and malt. Although the chemical structures and health effects of these compounds produced both in food and model systems have been investigated for over 30 years, the health effects are not well understood, mainly because their bioavailability depends on several parameters that include gut microbiota metabolism. Despite of the lack of general knowledge, the positive correlation between melanoidins content in food and antioxidant activity is well documented in the literature.

3.2 Flavor and aroma

Flavor and aroma development due to the Maillard reaction depends on the reaction temperature, time, pH, water content and on the type of sugars and amino acids involved (Yu & Zhang, 2010; Van Boekel, 2006). In most cases, the first factor mentioned influences the kinetics parameters, while the second factor determines the type of flavor compounds formed. The intermediate and final stages of the Maillard reaction are the most important to flavor development, especially the so-called Strecker degradation step, in which amino acids are degraded by dicarbonyls formed previously in the reaction, leading to the aminoacids deamination and decarboxylation (Ames, 1990; Rizzi, 2008).

The volatile products of the Maillard reaction can be classified according to the sugar dehydration/fragmentation products as furans, pyrones, cyclopentenones, carbonyls and acids; the amino acid degradation products as aldehydes and sulfur compounds; and the volatiles produced by further interactions as pyrroles, pyridines, imidazoles, pyrazines, oxazoles, thiazoles, and others. Pyrazines and alkylpyrazines are associated with the flavor and aroma of cooked (roasted) and nutty, respectively. Alkylpyridines confer to foods flavor and aroma of green, bitter, astringent and burnt, and furans, furanones and pyranones of sweet, burnt, pungent and caramel-like flavors/aromas.

Compounds that are essential to the characteristic flavor and aroma of food products are generally present at trace levels. The oxygen-containing aroma compounds 2,3-butanedione, 2,3-pentanedione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(3H) furanone and 2,5-dimethyl-4-hydroxy-3(2H)-furanone occur in concentration ranging from 1 µg/kg up to 100 mg/kg. The nitrogen-containing aroma compounds 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine and 2-acetyl-1-pyrroline are present in food in an order of magnitude of 0.001–10 mg/kg. On the whole, sulfur containing Maillard odorants constitute the most powerful aroma compounds and often play, although at trace levels, a dominant role in the flavor of cooked meats. These volatile compounds are responsible for the flavor and aroma to stewed beef juice, boiled trout, french fries, bread crust, cooked chicken, roasted chicken, boiled beef, cocoa powder, peanuts, pilsner, roasted beef, popcorn and coffee (Cerny, 2008).

The meat-related flavor compounds are mainly sulphur containing compounds, derived from cysteine and ribose (coming from nucleotides), while the amino acid proline gives rise to typical bread, rice and popcorn flavors. Cysteine-containing mixtures seem to have the most intense meat-like and sulphur smell. The other amino acid-containing sulphur, methionine, generates a highly intense smell of potatoes and it is employed, in the food industry, to enhance the soft flavor of potatoes. Mixtures containing amino acids other than cysteine or methionine in a combination with reducing sugars are characterized mostly by caramel and jammy smell (Stanimirova *et al.*, 2011; Van Boekel, 2006).

The food industry invests great effort trying to create synthetic flavors and aromas by reconstituting combinations of these compounds. The process of creating synthetic flavors is limited since the subtleties of flavor perception are many and varied, and although Electronic Noses may detect these compounds, human sensory perception is considered essential to validate instrumental data, (Gerrard, 2002a; Schaller *et al.*, 1998).

3.3 Texture

Texture definition is complex and a general agreement has been reached which evolved from the efforts of a number of researchers. According to Szczesniak (2002), "texture is the sensory and functional manifestation of the structural, mechanical and surface properties of foods detected through the senses of vision, hearing, touch and kinesthetics".

Maillard reaction influences the texture of food via protein cross-linking. Manipulation of the extent and nature of such protein cross-linking during food processing offers a means by which the food industry can modify the functional properties of food. Despite of this, the extent of how protein cross-linking affects food texture in processed foods and how to control this parameter to maximize food quality is not yet known (Gerrard, 2002b). Protein cross-linking by the Maillard reaction will affect not only texture, but the protein digestibility as well.

Although Maillard reaction effects on food color, flavor and aroma are well understood and used by the food industry, its effects on food texture has attracted less attention from the scientific community. However this is a promising tool for texture development.

4. Analyses of Maillard reaction products

MRPs are present in the diet and many authors have highlighted their health benefits and risks. For that reason, it is of most importance characterizing and quantifying MRPs in common foods, to get the best balance between benefits and potential risks, and then to establish guidelines for food health (Delgado-Andrade *et al.*, 2009).

Development of sophisticated analytical techniques made it possible to isolate, characterize, and quantify several specific non browning reaction compounds formed *in vitro* and *in vivo*, both at the early and advanced stages of Maillard reaction. Among them the most common are: Amadori compounds (indirectly analyzed as furosine), N ϵ -(carboxymethyl)lysine (CML) and some intermediate derivatives of the reaction, such as hydroxymethylfurfural. Measurement of fluorescent compounds formed during the reaction is also a reliable tool to evaluate the extension and ratio of nutritional loss due to thermal processing of foods (Delgado-Andrade *et al.*, 2009; Friedman, 1996).

4.1 Fluorescent compounds

Traditionally, Maillard reaction monitoring in food processing was based on the spectrophotometric evaluation of color development at 420 nm. More recently, the evaluation of fluorescent compounds generated by the Amadori rearrangement product undergoing dehydration and fission has become usual. Besides its use in food systems, fluorescence measurement is also employed to evaluate Maillard reaction at physiological conditions, meaning, AGEs generation, and also to access AGEs correlated pathologies development (Delgado-Andrade *et al.*, 2006).

Fluorescent compounds (FC) are precursors for the brown pigments formed in the Maillard reaction, which present different chemical structures. Evaluation changes in fluorescence intensity helps evaluating the extent of the Maillard reaction in food products (Morales & Van Boekel, 1998; Rufià-Henares & Delgado-Andrade, 2009) and biological systems. Fluorescence was first used to evaluate the formation of MRPs in milk and now it is used to monitor the processing of cereals, cookies, soybeans, infant formula, cooked salmon and bakery products.

Fluorescent compounds may be free in the matrix or linked to the protein fraction. Total FC (free + linked to protein) determination demands a previous enzymatic hydrolysis, which requires the use of a nonspecific protease (pronase) (Delgado-Andrade *et al.*, 2008). Free and total FC have been tested in foods such as milk, breakfast cereals, cooked salmon, roasted soy and enteral formula (Delgado-Andrade *et al.*, 2008; Rufià-Henares *et al.*, 2002).

Fluorescence of Advanced Maillard products and Soluble Tryptophan (FAST) is a well established method used to evaluate the nutritional and lysine damages. FAST is based on the quantification of protein denaturation using fluorescence: (1) fluorescent of the advanced Maillard products (FAMP), such as pyrrole and imidazole derivatives, at excitation/emission 330/420 nm; and (2) tryptophan fluorescence (FTrp) at excitation/emission 290/340 nm at pH 4.6. The FAST index is calculated as follows: $(100 \cdot \text{FAMP} / \text{FTrp})$ (Birlouez-Aragon *et al.*, 2002).

4.2 Hydroxymethylfurfural

Hydroxymethylfurfural (HMF) is an intermediate compound formed during the Maillard reaction and by the degradation of hexoses at high temperatures at acid conditions (Figure 4) (Arribas-Lorenzo & Morales, 2010).

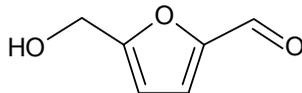


Fig. 4. Chemical structure of HMF

Spectrophotometric (colorimetric) methods, which are the most usual methods for HMF determination in food, are of limited accuracy since other chromophores in foods may absorb radiation in the same wavelength region, interfering with the results. In addition, colorimetric methods have low sensitivity. Chromatographic methods (liquid or gas high resolution chromatography) are more accurate and sensitive for this purpose, and one of the major advantage of the use of chromatographic methods is the individual determination of HMF and furfural, what can not be achieved by spectrophotometric methods (Erbersdobler & Somoza, 2007; Morales *et al.*, 1997; Rufià-Henares *et al.*, 2001).

HMF formation is directly linked to the heat intensity applied to food, and because is not usually present in raw and fresh foods, it is considered a thermal damage marker for products containing high carbohydrate concentrations. Moreover, it can be used to monitor the thermal process applied to several different food products such as: breakfast cereals containing dried fruits; caramel and honey; pasta and bakery products (Rufià-Henares & Delgado-Andrade, 2009; Rufià-Henares *et al.*, 2006).

4.3 Furosine

Amadori compounds are measured as furosine (ϵ -N-2-furoylmethyl-L-lysine) (Figure 5). The content of furosine present in foods is influenced by the kind of heat treatment and/or the storage time. Levels of furosine tend to decline after prolonged storage or after overheating to give rise to other compounds such as CML (Delgado-Andrade *et al.*, 2005; Friedman, 1996; Rufià-Henares *et al.*, 2009).

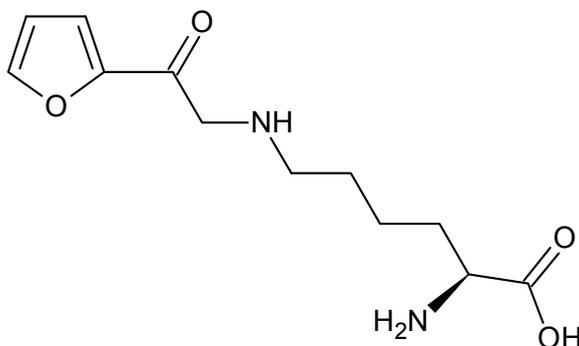


Fig. 5. Chemical structure of furosine

Furosine is the most specific and important indicator of the initial phase of the Maillard reaction. It is widely used in the analysis of cereal products, since lysine is the limiting amino acid of this product and, thus the presence of furosine is an important marker of protein biological value loss. Monitoring furosine formation and contents helps tailor the processing conditions in order to guarantee the maintenance of the nutritional value of food products (Rufián-Henares *et al.*, 2004, 2006; Resmini *et al.*, 1990).

Regarding analytical procedures, in 1992, an ion pairing HPLC based methodology was proposed and successfully applied in a series of studies. In 1996, when furosine became commercially available, Reverse Phase-HPLC became the method of choice for furosine analysis. Due to the possible transformation of CML into furosine during heating it is necessary for the acid hydrolysis to be performed in an inert atmosphere, which impairs furosine degradation (Erbersdobler & Somoza, 2007).

4.4 N ϵ -(carboxymethyl)lysine

N ϵ -(carboxymethyl)lysine (CML) is a stable, low reactivity advanced Maillard product (Figure 6). CML can be produced by Amadori compound degradation, such as N ϵ -(fructosyl)lysine (FL). FL undergoes oxidation to form, N ϵ -(carboxymethyl)lysine (CML). R-dicarbonyls such as glyoxal (GO), formed during the oxidation of the sugar or the Amadori rearrangement products are immediate precursors of CML. Lipid peroxidation is another route to CML, and GO has been suggested as an intermediate. CML is one of the more important markers of bioactive Maillard products and its content is usually correlated to the health risk of ingestion of heat-treated foods (Charissou *et al.*, 2007).

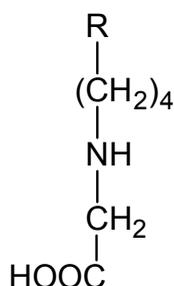


Fig. 6. Chemical structure of CML

The three main methodologies proposed to evaluate CML in foods are: a) RP-HPLC (Reverse Phase/ High Performance Liquid Chromatography), b) GC/MS (Gas Chromatography connected to Mass Spectrometry) following methylation of the carboxylic group and acylation of the amine group and c) enzyme-linked immunosorbent assay based on a monoclonal anti-CML antibody (Charissou *et al.*, 2007).

Currently, CML analyses in foods are performed by specific immunosorbent (AGE-ELISA-Enzyme Linked Immuno Sorbent Assay). This test is suitable for quantitative CML analysis both in biological samples and food (Goldberg, 2004).

Among the Maillard reaction products, CML is the best characterized end product. It is employed as an advanced glycation end products/advanced lipoxidation end products (AGEs/ALEs) markers in research (Goldberg, 2004).

5. Biological activity of the Maillard Reaction Products (MRPs)

The Maillard reaction is of outstanding importance for the formation of flavor and color of heated foods. Despite the unquestionable beneficial effects on the sensory quality of food products, the Maillard reaction products may be harmful for human health.

Protein nutritional impairment, consequence of the destruction of essential amino acids or the decrease in their bioavailability, is one of the oldest known nutritional implication of this reaction (Delgado-Andrade *et al.*, 2007a; Seiquer *et al.*, 2006). The decrease in the availability of several amino acids, mainly lysine, which may correspond to 50%, is noticeable (Rerat *et al.*, 2002). Total lysine contents in breakfast cereal products can decrease from 20-54% as a result of processing (Rutherford *et al.*, 2007; Torbatinejad *et al.*, 2005). Comparing the effects of diets with different MRPs contents on dietary protein utilization in male adolescents indicated that the consumption of a diet rich in MRPs resulted in 47% higher nitrogen fecal excretion, 12% lower apparent nitrogen and 6% lower nitrogen digestibility. Therefore, the protein apparent absorption and digestibility were significantly lower (Seiquer *et al.*, 2006).

The bioavailability of minerals can also be affected by MRPs, since these compounds are able to chelate minerals interfering, therefore, with their solubility (Delgado-Andrade *et al.*, 2011). The effects of diets with different Maillard reaction products contents on iron biological utilization showed that significant decrease on dietary iron availability occurred when diets rich in MRP were consumed (García *et al.*, 2009a). It was also observed a negative influence on dietary phosphorus absorption in male adolescents exposed to a rich-MRPs diet, as a result of an increased phosphorus fecal excretion concomitant to a decrease in its apparent absorption (Delgado-Andrade *et al.*, 2011). Magnesium and calcium bioavailability can also be affected by the presence of Maillard reaction products in the diet (Delgado-Andrade *et al.*, 2007b; García *et al.*, 2009b).

The results of studies on the genotoxic and mutagenic potential of the MRPs are controversial. While there are studies indicating that the MRPs can cause mutations, no association between MRPs and genotoxicity was found by Wagner *et al.* (2007). In *in vitro* systems, melanoidins mixtures have negligible mutagenic effects (Somoza, 2005), while 5-hydroxymethylfurfural (HMF) is considered a potentially carcinogenic to humans and some epidemiological studies have found an association between acrylamide intake and the occurrence of tumors the occurrence of tumors (Capuano & Fogliano, 2011).

The formation of advanced glycation end products (AGEs) is observed during normal ageing and occurs inside as well as outside of cells (Nass *et al.*, 2007). These compounds, when cross linking with proteins profoundly affect protein functionality and irreversibly modify chemical properties and functions of diverse biological structures (Barbosa *et al.*, 2008), which seems to be implicated in inflammatory processes and diabetic complications, such as nephropathy and vascular disease (Jakus & Rietbrock, 2004; Linden *et al.*, 2008; Mostafa *et al.*, 2007).

AGEs accumulate in various tissues during aging, including skin, neural, vascular, renal and cardiac tissues, collagens and crystalline lens. In the skin, glycation is involved in many metabolic processes and, along with aging, affects the functionality of certain cells, such as the synthesis of fibroblasts, enzyme activation of matrix degradation (metalloproteinases) and the organization of the matrix (Hartog *et al.*, 2007; Pigeon, 2010; Pawlak *et al.*, 2008). It is proposed that the accumulation of the advanced glycation end products (AGEs) and the

activation of the receptor for AGEs in the retina could play a significant role in the initiation and progression of age-related macular degeneration and cataracts (Pawlak *et al.*, 2008).

Kalousová *et al.* (2002) and most recently, Mostafa *et al.* (2007) showed that AGEs level in plasma proteins are elevated in patients with diabetes. The high blood glucose levels favor the occurrence of spontaneous reactions (glycation) between glucose and proteins, resulting in the formation and excessive deposition of AGEs (Magalhães *et al.*, 2008). In patients with renal failure AGEs accumulation occurs due to the decrease in the extent of degradation and elimination from the body and, also, to increased exposure to oxidative stress. On the other hand, the AGEs and products derived from the process of oxidation promote damage in the renal tissue, leading to greater accumulation of AGEs, creating a vicious cycle (Hartog *et al.*, 2007). The increase in consumption of heated, cooked or roasted food of AGEs accumulation.

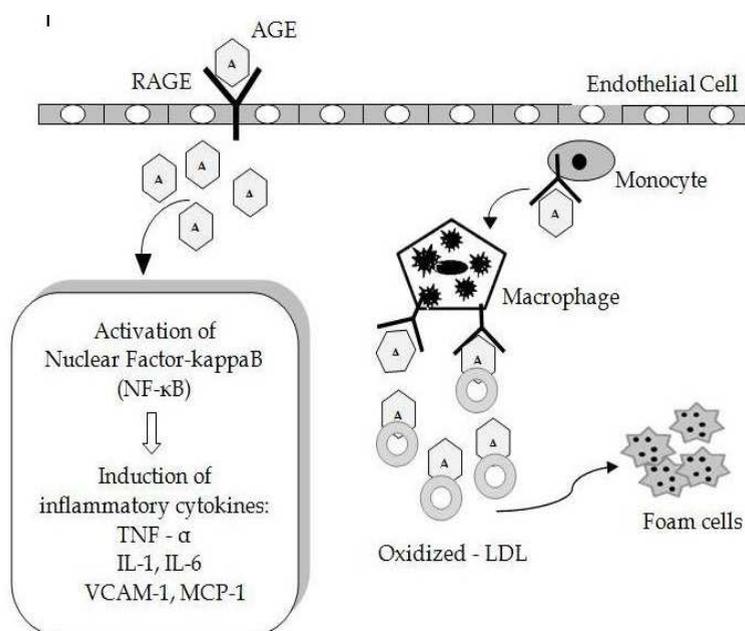


Fig. 7. AGE-RAGE interaction and its association with atherosclerosis (Based on Hartog *et al.*, 2007).

Among the mechanisms by which AGEs may contribute to the development and progression of vascular complications of diabetes, is the interaction of these compounds with receptors on the surface of various cell types, such as RAGEs (Receptors for Advanced Glycation End Products) (Marchetti, 2009). The AGE-RAGE interaction in the endothelial cells activates the transcription of nuclear factor-kappaB (NF-κB), with the induction of proinflammatory cytokines, such as the tumor necrosis factor (TNF), interleukin-1 (IL-1), interleukin-6 (IL-6), monocyte chemoattractant protein-1 (MCP-1) and enhances the expression of the vascular cell adhesion molecule-1 (VCAM-1) (Basta, 2008; Magalhães *et al.*, 2008; Méndez *et al.*, 2010; Muscat *et al.*, 2007). In addition, this interaction in monocytes induces their activation to macrophages and promotes monocyte chemotaxis, and in smooth muscle

cells, is associated with increased cellular proliferation (Marchetti, 2009). Besides, some studies demonstrate that AGEs may promote atherogenesis by oxidizing low density lipoproteins (LDL) (Basta *et al.*, 2004). Indeed, AGE form crosslinks with low-density lipoprotein (LDL), which become more atherogenic and less susceptible to absorption and subsequent clearance. In addition, LDL modified by AGEs is more easily captured by receptors located on macrophages, generating foam cells (cells with fat droplets and cholesterol) (Hartog *et al.*, 2007; Vasdev *et al.*, 2007) (Figure 7).

It has also been suggested that AGEs are involved in neurodegenerative diseases, such as Alzheimer and Parkinson (Grillo & Colombato, 2008; Sato *et al.*, 2006b), arthritis (Vytásek *et al.*, 2010), loss of bone mass (Ding *et al.*, 2006) and promotion of changes in the function and/or structure of DNA and RNA molecules (Li *et al.*, 2008).

Considering AGEs as important mediators of pathological processes, investigations aiming to verify the action of chemical compounds against the synthesis of AGEs and its possible use in therapy of patients with several metabolic complications are in course of development. Substances present in foods, such as pyridoxamine, allyl cysteine (component of garlic extract), phenolic compounds, taurine and carnosine, showed significant anti-AGE effects, but, at present, there is no indication of food components able of reducing AGEs generation *in vivo* (Barbosa *et al.*, 2008). Despite of this, dietary therapies also appear to be an effective alternative in the control of diseases associated with accumulation of AGEs.

Restricting the consumption of fried, grilled or baked foods seems to be the most effective way of decreasing AGEs endogenous pool. Dietary AGEs restriction seems to be a successful strategy in suppression of inflammatory molecules in diabetes, implying eventual prevention or delay of atherosclerosis (Vlassara *et al.*, 2002). Several studies indicate that Maillard reaction products from the diet increase the endogenous AGEs pool and, whether this might become a health problem is yet controversial. There are many gaps that must be evaluated before conclusions can be drawn as, for example, the fate of MRPs in the organism. Notwithstanding, several researchers advocate towards the decrease of MRPs ingestion and, therefore, food industry has an important role by considering processes towards the production of foods with lower contents of MRPs.

On the other hand, there are authors who advocate for MRPs as substances that may promote benefits, such as increases in immunity and decreases in the toxicity of some nitrosamines. Figure 8 is a summary of the main biological effects attributed to Maillard Reaction Products (MRPs) / Advanced Glycation End Products (AGEs).

Some studies suggest the MRPs exert positive influence on the gut microbiota (Tuohy *et al.*, 2006). It has been shown that anaerobic bacteria, particularly *Bifidobacteria* strains, are able to use bread melanoidins as carbon source (Borrelli & Fogliano, 2005). Maillard Reaction products in roasted cocoa beans, for example, were able to inhibit the growth of *E. coli* spp. and *Enterobacteriaceae* (Summa *et al.*, 2008).

Furthermore, MRPs exhibit antioxidant activity (Açar *et al.*, 2009; Chang *et al.*, 2011; Chawla *et al.*, 2009; Rao *et al.*, 2011; Summa *et al.*, 2008). Melanoidins from roasted coffee and biscuits exerted protective effects against oxidative stress on human hepatoma HepG2 cells (Goya *et al.*, 2007; Martín *et al.*, 2009). Regarding coffee antioxidant activity, more than 50% of the observed antioxidant activity is due to the low molecular weight compounds linked to the melanoidin skeleton, promoting a chelating ability that is also involved in the shelf life of the product (Delgado-Andrade & Morales, 2005). *In vivo*, a MRPs rich diet was able to suppress lipid peroxidation and to increase antioxidant activity of plasma, although it has

not modified the antioxidant enzymes activity (superoxide dismutase, glutathione peroxidase and catalase) (Seiquer *et al.*, 2008).

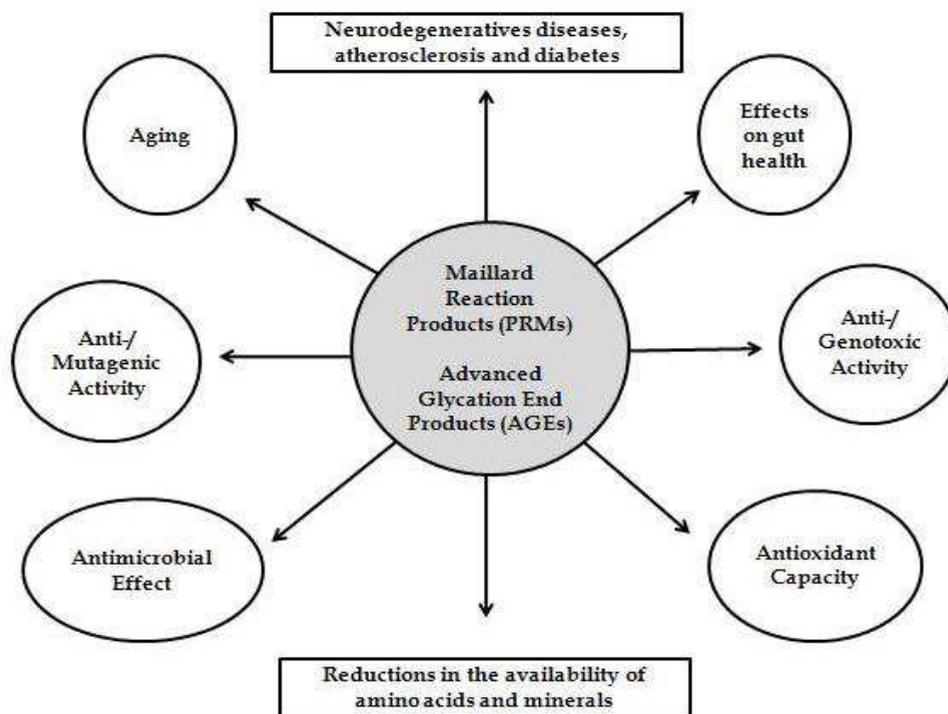


Fig. 8. Possible biological effects of the Maillard Reaction Products (MRPs) and Advanced Glycation End Products (AGEs) (Based on Somoza 2005).

6. Conclusion

For food industry, coping with the Maillard reaction and the effects of the reaction products in food and in health is important to the improvement and development of food products. This chapter discussed the positive and negative aspects of the Maillard reaction in food products. The positive contributions of the Maillard reaction are sensory attributes generation, such as color, flavor, aroma and texture. The negative aspects are off-flavor development, flavor loss, discoloration, and loss of protein nutritional value. In the food industry, the role of flavor and color either desirable or undesirable is the key in the manufacture of products of consistent sensory quality. Contradictory knowledge about the effects of Maillard Reaction Products on health indicates that studies are needed to further expand the AGEs and MRPs database as well as development of methods for reducing MRPs generation during home cooking and food processing. Understanding the chemical, nutritional and toxicological consequences of browning reactions and related transformations, *in vitro* and *in vivo*, can lead to better and safer foods and improved human health.

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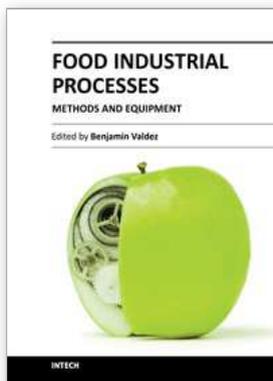
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The global food industry has the largest number of demanding and knowledgeable consumers: the world population of seven billion inhabitants, since every person eats! This population requires food products that fulfill the high quality standards established by the food industry organizations. Food shortages threaten human health and are aggravated by the disastrous, extreme climatic events such as floods, droughts, fires, storms connected to climate change, global warming and greenhouse gas emissions that modify the environment and, consequently, the production of foods in the agriculture and husbandry sectors. This collection of articles is a timely contribution to issues relating to the food industry. They were selected for use as a primer, an investigation guide and documentation based on modern, scientific and technical references. This volume is therefore appropriate for use by university researchers and practicing food developers and producers. The control of food processing and production is not only discussed in scientific terms; engineering, economic and financial aspects are also considered for the advantage of food industry managers.

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