Maillard Browning: Pros and Cons in Dairy and Food Industries

Harish Kumar*, Neha Choudhary, Varsha Garg, Naveen Kumar Swami, Hitesh Kumar, Raman Seth
National Dairy Research Institute, Karnal, Haryana, India

Abstract
The Maillard reaction, also known as non-enzymatic browning reaction between reducing sugars and amino groups. This reaction is responsible for the formation of several compounds, called MRP (Maillard Reaction Products) for food products. The Maillard reaction produces undesirable effects during the processing and storage of different liquid foods such as milk or fruit juices whereas for other solid foods the changes are favorable (in the case of bread, breakfast cereals, candies, coffee, chocolate, etc.). The Maillard reaction is a complex reaction, since it is influenced by many factors such as temperature, pH, time, water activity, type and concentration of reactant source and sugar involved. In heated food products, two carcinogenic compounds are produced during maillard reactions, acrylamide and imidazoquinoline. Furosine and HMF are two compounds that indicate the extent of the maillard reaction related to the type and intensity of the food processing conditions.

Keywords: Maillard reaction, melanoidin, furfural, amadori rearrangement

Abbreviations: HMF - Hydroxy-methylfurfural; MRP – Maillard Reaction Products; AGEs - Advanced glycation end products

*Author for Correspondence: E-mail harishkanwar3@gmail.com

INTRODUCTION
The Maillard reaction is of most importance for quality of foods, in particular for heated foods. It induces browning of foods, has an effect on nutritive value, can have toxicological implications (suchas the formation of acrylamide), can produce ant oxidative components and it has also a large effect on flavor. Browning of food and food products is one of the major problems in food industry. Browning in a food occurs by oxidation and non oxidation reaction. Oxidative reactions involve enzymes (polyphenols oxidases) and oxygen; it is also called enzymatic browning, while non-oxidative reactions are called maillard reaction [1]. The Maillard reaction is named for L.C. Maillard, who conducted pioneering work on sugar-amino acid condensations from 1912 to 1917. He reported that upon gently heating sugars and amino acids in water, a yellow-brown color developed, called it a maillard reaction. The Maillard reaction (MR) or non-enzymatic glycation is there action of reducing sugars with amino acids and amino groups of peptides or proteins. This reaction produces a variety of early, intermediate and advanced compounds. The advanced compounds of protein–sugar reactions are referred to as advanced glycationend products or AGEs and melanoidins (more concrete, melanoproteins) [2]. This reaction has become important in the field of food science and medicine [3]. 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 [4]. Dairy powders are sensitive to the maillard reactions they contain high concentration of lactose and proteins with high lysine level [5]. 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 [6].
Chemistry of the reaction

The Maillard reaction has been named after the French chemist Louis Maillard (1912) who first described it but it was only in 1953 that the first coherent scheme was put forward by Hodge. In essence, it states that in an early stage a reducing sugar, like glucose, condenses with a compound possessing a free amino group (of an amino acid or in proteins mainly the ε- amino group of lysine, but also the α-amino groups of terminal amino acids) to give a condensation product N-substituted glycosilamine, which rearranges to form the Amadori rearrangement product (ARP). The subsequent degradation of the Amadori product is dependent on the pH of the system. At pH 7 or below, it undergoes mainly 1,2-enolisation with the formation of furfural (when pentoses are involved) or hydroxymethylfurfural (HMF) (when hexoses are involved). At pH >7 the degradation of the Amadori compound is thought to involve mainly 2,3 enolisation, where reductones, such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one (HMFOne), and a variety of fission products, including acetal, pyruvaldehyde and diacetyl are formed. All these compounds are highly reactive and take part in further reactions. Carbonyl groups can condense with free amino groups, which results in the incorporation of nitrogen into the reaction products. Dicarbonyl compounds will react with amino acids with the formation of aldehydes and α-aminoketones. This reaction is known as the Strecker degradation. Subsequently, in an advanced stage, a range of reactions takes place, including cyclisations, dehydrations, retroaldolisations, rearrangements, isomerisations and further condensations, which ultimately, in a final stage, lead to the formation of brown nitrogenous polymers and copolymers, known as melanoidins. The complexity and the variety of the maillard reaction products have, throughout the years, raised the interest of scientists in different fields of research [7]. New important pathways, not accounted for by Hodge, have been established. In maillard browning most important intermediates in color formation are 3-deoxyosuloses and 3,4-dideoxyosulos-3-enes, which in the case of glucose is 3-deoxyhexosulose (DH) and 3,4-dideoxyhexosulos-3-ene (DDH) [8]. 3-deoxy-2-hexosuloses, 1-deoxy-2, 3-hexodiuloses and other -dicarbonyl intermediates can undergo nucleophilic addition reactions with amino acids with subsequent decarboxylation to produce the so called Strecker aldehyde (RHC=O). In [9] Huber and Ledl isolated and characterized 1-deoxy- and 3-deoxyglucosones from heated Amadori products. More recently, in agreement with the previous reports, Tressl, Nittka and Kersten [10] using 13C-labeled sugars, have given a new perspective to the reaction mechanism. It involves different reaction pathways, in which the key intermediates are the 1-, 3- and 4-deoxyhexosuloses. Moreover, a major influence of the pH is expressed. Along with enolization reactions, the Amadori product and its dicarbonyl derivatives can undergo concurrently retro-aldol reactions producing more reactive C2, C3, C4 and C5 sugar fragments, such as hydroxyacetone derivatives, glyceraldehyde and diketones. Retroaldol reactions become more important at higher pH values. Also, Yaylayan and Huyghues [11] stated that under basic conditions, ARP could generate acetic acid and pyruvaldehyde and other lower sugars in addition to free amino acid. As a result, high pH is suggested to be the main pathway to flavor formation. In addition to retroaldol reactions, three redox mechanisms have been identified, in which hydroxycarbonyls; dicarbonyls and formic acid are involved. Berg and Van Boekel [12] reported formic acid as a main degradation reaction product for the maillard reaction of lactose. Also, Boekel [13] reported formic acid and acetic acid as two main degradation products for the maillard reaction of glucose and fructose. Berg [14] concluded that isomerization and degradation reactions of the sugar are, from a quantitative point of view, more important than the maillard reaction, for conditions as in heated milk. Finally, the central importance of the Amadori product, formerly supposed to be the main intermediate of the reaction, has been questioned in both food [15] and medical fields [16]. The Maillard reaction is influenced by many factors, including temperature, time, initial pH, water activity (aw), physical state of the matrix, reactant concentration and type of carbohydrate involved [17]. In spite of all the work that has been done, the mechanism of the Maillard reaction is still a controversial issue. Mechanism of maillard reaction is shown in Figure 1.
Pros of Maillard Reaction in Foods

Maillard reaction occurs during many industrial and domestic thermal treatments of foods. It is widely used because of its role in creating colors, flavors, textures and other functional properties in foodstuffs. Proteins glycated without the use of conventional chemical reagents have demonstrated to improve techno-functional properties as heat stability, emulsifying and foaming properties. It has been a central and major challenge in food industry, since the maillard reaction is related to aroma, taste and color, in particularly in traditional processes such as the roasting of coffee and cocoa beans, the baking of bread and cakes, the toasting of cereals and the cooking of meat [18].

Now-a-days maillard reactions products are proved to have antioxidant properties as well. These products also use to improve the properties of protein as polyssaccride - protein conjugate formed during the maillard reaction have better property than the native one [19].

Color Formation

Color formation is the primary characteristic of the Maillard reaction. 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 [20]. Color occurs due to the formation of high molecular weight (>12, 000 Daltons) polymeric compounds also known as melanoidins. These are generally formed by the reaction of the Amadori product and with other dicarbonyls, i.e., the deoxyosuloses, with amino acids [21]. 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 [22]. Melanoind compound formed by the reaction of amadori product and with other dicarbonyl that is deoxyosuloses with amino acid is a reason for characteristic color of roasted foods such as coffee, cocoa, bread and malt. Color development depends on the reactant, structure of melanoidin, structure of chromatographic moiety and method of isolation of melanoidins [23]. It is very hard to separate the individual compound and structure of melanoidin, due to its complex nature. The composition of melanoidin depends on the binding of amino groups of lysine that bound to proteins. In the food products there are heterogenous mixtures of food products, which have a different maximum absorbance due to which color formation takes places. In general sugar to amino acid is 1:1 for pentoses and 1.5:1 for glucose [24]. Although the chemical structures and health effects of these compounds produced both in food and model systems have been investigated.

**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 [25]. Mostly reaction temperature influences the kinetics parameters, and time determines the type of flavor compounds formed. The intermediate and final stages of the maillard reaction are the most important in flavor development [26]. Maillard reaction between different carbohydrate and proteins gives different end products that produce versatile flavors. The volatile products of the maillard reaction depend on kind of sugar that undergoing dehydration/fragmentation and produces furans, pyrones, cyclopentenes, carbonyls and acids. The amino acid degradation during maillard reaction produces aldehydes and sulfur compounds; and upon further interactions they creates pyrroles, pyridines, imidazoles, pyrazines, oxazoles, thiazoles, and others. All of these compounds are volatiles and associated with flavor production. The amino acid proline gives rise to typical bread, rice and popcorn flavors while other sulfur containing amino acids (methionine), generates a highly intense smell of potatoes (Gu) Cysteine and glucose generally produces sulfur compounds, but in oxidized condition they synthesize pyrane and furan, while cysteine when react with ribose gives 2-methyl-3furathioin, an important flavor contributor in meat. Glutathione and glucose produces thiophene, thiozole and cyclic polysulfites at pH 6 and 8 while furan at acidic pH. Pyrazines and alkyl pyrazines are associated with the flavor and aroma of cooked (roasted) and nutty, respectively. Alkyl pyridines adds green, bitter, astringent and burnt flavor, while furans, furanones and pyranones imparts sweet, burnt, pungent and caramel-like flavors [27]. Maillard reaction mechanism is to develop a sweet, caramel-type flavor in the final whipped cream product [28]. The flavor compounds developed in the advanced stage of the maillard reaction likely contribute to the characteristic flavor of UHT processed milk [29]. 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 [30]. 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 amino acids deamination and decarboxylation [31]. The oxygen-containing aroma compounds 2,3-butanedione, 2,3-pentanedione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5- dimethyl-
(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-3,5dimethylpyrazine, 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. Mixtures containing amino acids other than cysteine or methionine in combination with reducing sugars are characterized mostly by caramel and jammy smell [32]. 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 [33].

**Texture**

Texture is complex sensory attribute of structure, mechanical and surface properties of food that is judged through the senses of vision, hearing, and touch, acceptability of food mainly bakery products depends on texture. According to Szczesniak [34] 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 kinesthetic. Maillard reaction influences the texture of food via protein cross-linking and its extent and nature. Functional properties of foods can be manipulated by altering the extent and nature of these cross-linking. This protein cross-linking by maillard reaction also improves their digestibility [35]. 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 [36].

But the extent of how much protein cross-linking affects food texture in processed foods and how to control this parameter to maximize food quality is not yet known [37]. 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.

**Antioxidant Property**

In the literature antioxidant activity of maillard reaction products have been noticed. Maillard reactions products like amino reductone, heterocyclic compounds, or high molecular melanoid have antioxidant properties. MRPs prepared from aqueous ribose-lysine and fructose lysine show antioxidant activity, they have radical chain breaking activity, metal chelation, and decomposition of hydrogen peroxide and scavenging of oxygen species [38]. Due to different reaction conditions and reactant reactivity MRPs exhibit varying antioxidant activity [39]. Whey protein isolates and sugar react to form maillard reaction products have good antioxidant activity. This antioxidant property can be used to protect the lipid oxidation in food products. Maillard reaction products prepared by heating mixture with higher initial pH showed higher antioxidant activity [40].

**Improve Functional Properties of Protein**

Proteins have wide application in food industry because of their functional properties. Their functional properties depend on physicochemical and intrinsic structure. Maillard reaction was used to improve the functional properties like heat stability, emulsifying foaming stability of β-lactoglobulin glyced with several sugars (arabinose, galactose, glucose, lactose). The functional properties of proteins can be modified by chemical, physical and enzymatic treatments. But these treatments also modify the ability of proteins to form gel, water
Cons of Maillard Browning Reaction
Maillard reaction products not only have beneficial effect but some of maillard reaction products also have harmful effect on human health. The most common harmful effect of maillard reaction products are:
1. Protein nutritional impairment [44].
2. Stale or “cardboard” flavors have also been reported in different types of dried dairy ingredients, including milk powders due to the maillard reaction [45].
3. Nutritional damage in lactose-hydrolysed milk by maillard reaction was reported in liquid milk [46].
4. Loss of nutritive value due to blockage of lysine residues which are no longer available for digestion (early, advanced and final maillard reaction reduced digestibility and inhibition of enzymes [47].
5. Destruction of essential amino acids and reduction in bioavailability: - Amino acid lysine is more prone to destruction during maillard reaction especially in breakfast cereals near about 20–54% lysine undergoes destruction during processing [48].
6. Exhibit mutagenic activity: - Maillard reaction product exhibit mutagenic activity. Cysteamine a decarboxylated compound of cysteine that is formed during maillard reaction exhibit mutagenic activity, also sometime it is further degrades to thiazolidine which also have mutagenic activity. Various products form during maillard reactions like 1,2 carbonyl compound (diacetyl, maltol), dihydroxyacetone, glyceraldehydes, glyoxal, methyl glyoxal and glyoxylic acid as proved to have mutagenic activity [50] caramelized sugar can induce high frequency chromosomal breakage. Maillard products from ketose sugar exhibit higher mutagenic activity as compared to aldose isomer due to difference in reaction mechanism [51].
7. Produces off flavor: - Maillard browning reaction products like furfural, furane, pyrole, pyrazine produces off flavor. These compounds also responsible for altering the milk flavor [52].
8. Other harmful effects: - Maillard reaction product, 5- hydroxymethylfurfural (HMF) is considered a potentially carcinogenic to human [53]. The formation of advanced glycation end products (AGEs) is observed during normal ageing and occurs inside as well as outside of cells [54]. These compounds, when cross linking with proteins profoundly affect protein functionality and irreversibly modify chemical properties and functions of diverse biological structures [55], which seems to be implicated in inflammatory processes and diabetic complications, such as nephropathy and vascular disease [56, 57]. 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 [58]. It is proposed that the accumulation of the advanced glycation end products (AGEs). The receptor for AGEs in the retina could play a significant role in the initiation and progression of age-related macular degeneration and
Coping with the maillard reaction food and the effects of the reaction products on health is important to the improvement and development of food products. The maillard reaction has positive as well as negative aspects in food industry. 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.

REFERENCES


35. Gerrard J. A. Protein-Protein Crosslinking in Food: Methods, Consequences,


