MAILLARD AND CARAMELIZATION REACTIONS IN CONFECTIONERY PRODUCTS

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Abstract: *The Maillard reaction and caramelization are two major non-enzymatic browning reactions that play a vital role in shaping the organoleptic characteristics of sugar-based confectionery. These thermal-induced reactions are responsible for the formation of brown pigments, flavor compounds, and aroma volatiles that define the sensory identity of products such as caramel, toffee, and fudge. This review aims to explore the fundamental mechanisms of both reactions, their dependency on ingredient composition and process conditions, and their contribution to color, flavor, and texture development in confectionery systems. Understanding these reactions is essential for optimizing quality while minimizing risks.*

INTRODUCTION

Confectionery products, especially those based on sugar, are a major part of the processed food industry and are widely consumed for their sweet taste, appealing color, and unique textures. These sensory characteristics are largely influenced by thermal processing, during which chemical changes occur. Among the most important of these changes are the Maillard reaction and caramelization, both of which are responsible for developing the desirable flavor, aroma, and color that define many confectionery products [1,2]. These reactions, however, do not only affect sensory quality. When uncontrolled, they may lead to the formation of unwanted flavors or even compounds that pose health concerns, such as acrylamide, hydroxymethylfurfural (HMF), and advanced glycation end-products (AGEs)[3,4]. With increasing public awareness of food safety and health, it is essential to understand how these reactions contribute both positively and negatively to the final quality of sugar-based confectionery.

A number of previous studies have addressed the chemistry of browning reactions in different food systems such as baked goods [5], roasted nuts [6], and dairy products [7]. However, the application of these findings specifically in sugar-rich confectionery systems especially those involving diverse ingredient compositions has not been comprehensively reviewed.

Therefore, this review aims to provide an analysis of Maillard and caramelization reactions in sugar-based confectionery. The objectives are to explain the basic mechanisms and influencing factors of these reactions, and explore their role in forming color, flavor, and texture in confectionery.

LITERATURE REVIEW

The Maillard reaction is a type of non-enzymatic browning that occurs between reducing sugars and amino compounds under heat. It is widely recognized for its ability to produce a variety of flavor and aroma compounds, as well as brown pigments known as melanoidins [2]. In sugar-based confectionery, common sources of reducing sugars include glucose, fructose, maltose, and lactose, while amino groups may come from milk solids, eggs, nuts, gelatin, or even emulsifiers like lecithin.

The mechanism of the Maillard reaction involves multiple stages. It starts with the formation of a Schiff base between the sugar and the amino compound, which rearranges into Amadori or Heyns compounds. These intermediates then undergo fragmentation and polymerization, forming various volatile compounds and colored polymers [8].

Caramelization is another important browning reaction that occurs when sugars are exposed to high temperatures without the presence of amino compounds. Caramelization is purely thermal degradation of sugars, whether it is reducing or non-reducing sugars and leads to colour changes from brown to nearly black [9], all of which contribute to the caramel-like flavor of certain type confectionary products.

Caramelization generally takes place at higher temperatures than the Maillard reaction [10] and is influenced by pH, time of heating, and type of sugar. The temperatures are approximately 110 °C for fructose, 160 °C for galactose, glucose, and sucrose, and 180 °C for maltose. The process occurs in stages. If starting from a sugar solution, water must first evaporate at around 100 °C; alternatively, solid sugar can be melted through direct heating. For sucrose, soft or semisolid candy is formed at about 129 °C, while producing hard candy requires heating to around 165–168 °C. Caramels are categorized by their color: light caramel forms at 180 °C, medium between 180–188 °C, and dark caramel from 188–204 °C. At 210 °C, sugar becomes severely burnt, producing a dark product known as “Black Jack” caramel, characterized by a strong burnt odor [11]

Both the Maillard reaction and caramelization, while essential for creating appealing sensory attributes, are also associated with the formation of undesirable and potentially harmful compounds. Among them, acrylamide is of particular concern due to its classification as a probable human carcinogen [12]. Acrylamide can be formed in the Maillard pathway from asparagine and reducing sugars, particularly in carbohydrate-rich and protein-containing systems. Other compounds such as hydroxymethylfurfural (HMF) and AGEs have been linked to oxidative stress, inflammation, and other chronic diseases when consumed in high quantities [13,14]. Hence, the balance between achieving desired flavor and avoiding toxicants has become a central issue in confectionery formulation and processing.

METHODE

This review was conducted through a targeted search of textbooks and peer-reviewed journal articles published between 1973 and 2025, using databases such as ScienceDirect, PubMed, and Google Scholar. Keywords included “Maillard reaction,” “caramelization,” “sugar-based confectionery,” “non-enzymatic browning,” and “acrylamide.” Studies were selected based on their relevance to the chemical mechanisms, sensory impacts, and health implications of Maillard and caramelization reactions in confectionery systems.

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RESULT AND DISCUSSION

Maillard reaction is a non-enzymatic reaction that takes place when reducing sugars are reacted with protein in presence of heat and produces a mixture of compounds known as melanoidins [2]. This brown condensation pigment is believed as a contributor to the flavour, aroma, colour and texture. In confectionery, many sources of sugar such as dextrose, fructose, high fructose corn syrup, sucrose, corn starches, and maltodextrins can be used and protein can be from milk solids, cream, egg solids, nuts and nut fragments, cocoa solids, butter (small source of nitrogen), free amino acids from fruit and fruit juice, gelatine, whey proteins and emulsifiers such as lecithin. The Maillard reaction was firstly characterized by scientist Louis Camille Maillard and the name of the reaction came from his name [8]. Sugars that categorised as reducing sugars are all carbohydrate compound that contains aldehyde group and can form α and β isomers as it undergoes mutarotation in solution; however, sucrose which is not reducing sugar can be reactant for Maillard reaction under alkaline condition [15].

Although the Maillard reaction is a complex series of reactions, and how it occurs is not fully understood yet, there are three main stages of its reaction path that can give insight into how it may occur [16]. The carbonyl group from reducing sugar condenses with the free amino group of an amine to form Amadori products. These products undergo a series of reactions such as rearrangement, dehydration, and decomposition then form furfural compounds, reductones or dehydroketones, and Strecker degradation products. The formation of high-molecular-weight melanoidins pigments from the intermediate stage products. Conditions of Maillard reaction system in confectionery are likely to be high temperature with low water activity. Figure 1 provides the general summary of the Maillard reaction.

On the other hand, caramelization reaction seems to have a simpler reactant than the Maillard reaction as it is only a sugar-sugar reaction. The simplest definition of caramelisation is burning sugar. When reducing sugar is heated without the presence of protein (N-containing compound), a complex series of reactions occurs, resulting in the final product known as caramel. Although caramelisation is different from the Maillard reaction in terms of the reactant, the intermediate and the final products are similar to the caramel-like products from the Maillard reaction [15].

The contribution of these two reactions on developing color, aroma, and flavor on confectionery products is unarguable, even though the available literature that gives insight about how precisely it occurs is quite limited. Research about these browning reactions especially the Maillard reaction is still developed, but it does not focus on the study of the very detail of the reaction. The underlying reason behind this may be because the nature of the products (both intermediate and final products) that not easy to observe as it may high volatile compound that releases into the air once the reaction finishes.

Color and Flavour Formation as Result of Caramelisation and Maillard Reaction.

Color changes in toffee and fudge making are responsible for the mixture of high-molecular-weight brown or black pigment that developed on the final stage of the Maillard reaction. The intermediate products from the second stage such as reactive carbonyl compounds and N-containing compounds polymerize and convert to a mixture of complex dark-colored compounds collectively known as melanoidins [15]. What compounds are involved in this mixture is dependent on the diversity of the intermediates and where the array of reactions is more dominant which depends on nature of the system, but commonly all compounds contain aromatic rings and conjugated double bonds. To quantify color in a single Maillard reaction, developed the color activity concept to address the lack of knowledge to understand the key chromophores in the final stages of Maillard reaction. Through this concept, Hofman was successfully analysed a significant chromophore (2-[(2-FuryI) methylidene]- 4-hydroxy-5-methyl-2H-furan-3-one) which has high color activity [17]. However, its absolute contribution to the total colour of the melanoidins mixture was still not fully described [18].

Color formation in caramelisation also is pretty similar to color development in the Maillard reaction. Even though caramelisation does not involve protein or any N-containing compound, a series of complex reaction of sugar (enolation, dehydration, fragmentation, and polymerization) in high temperature lead to formation of the similar compound in Maillard products such as hydroxymethyl furfural, hydroxyacetyl furan, and furan.

In sugar confectionery, when the ingredient is heated and reaches a certain temperature at a certain time, the appearance of color changes mostly followed by the aroma that can be smelled. This phenomenon is linked with the role of caramelization and the Maillard reaction in the development of flavor and aroma in confectionery . The large brown molecules produced by the reaction namely caramelin, caramelen and caramelan are what give caramel its color, its viscosity and its stickiness.

Formation of desirable and undesirable changes

In sugar-based confectionery, caramelisation and the Maillard reaction are desirable and undesirable changes during processing, depending on the type of product. For instance, in caramel, toffee, and fudge, undoubtedly, they are desirable, but in boiled sweet, avoiding these browning reactions is essential.. Like aforementioned examples on these three types of products, the Maillard and/or caramelisation directly affect the organoleptic parameters of those products. On the other hand, when these changes are undesirable, then some steps may be adopted to control the degree of reaction.

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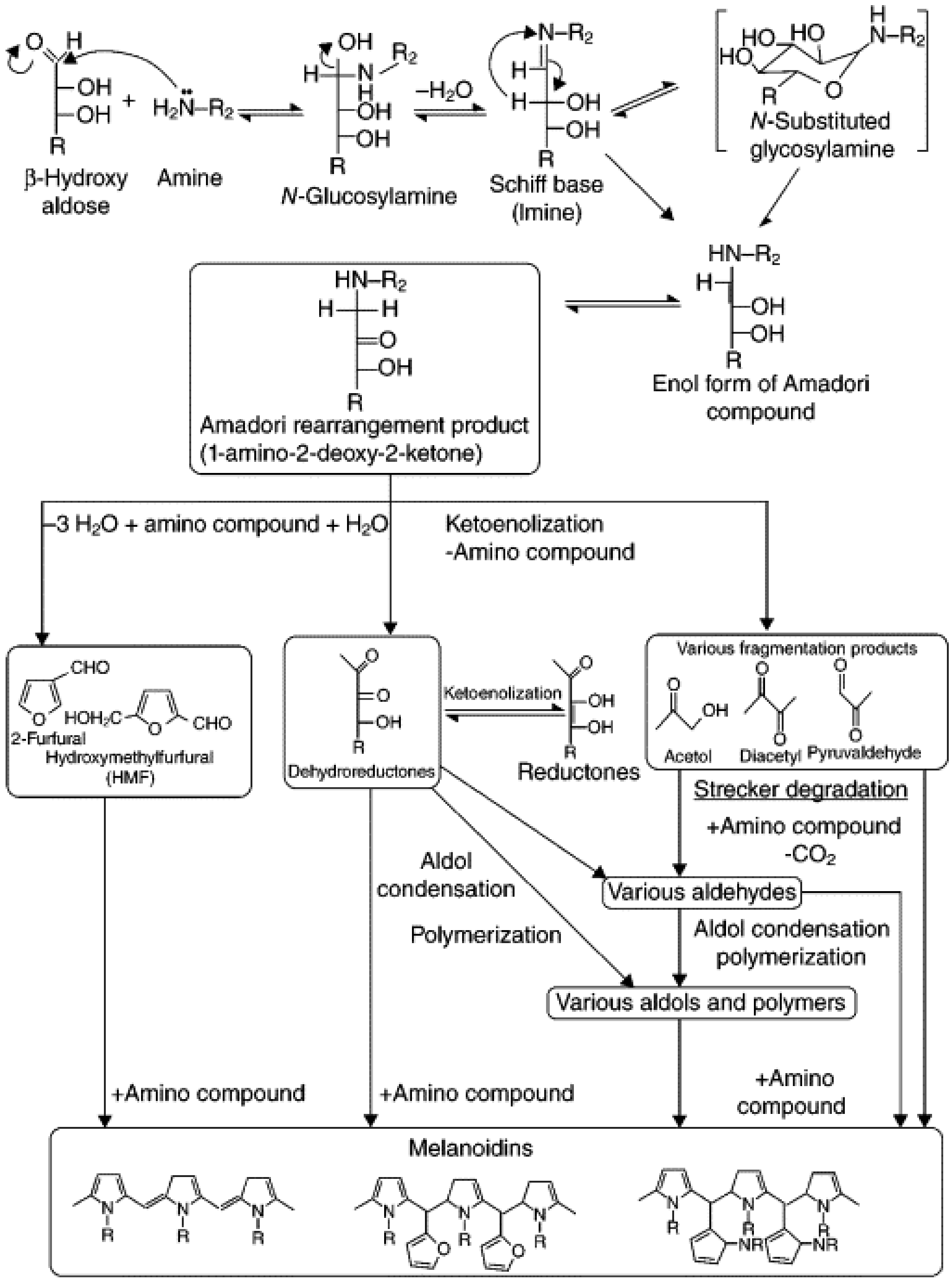

Figure 1. Summary of the Maillard reaction. Source: Perez and Yaylayan (2010).

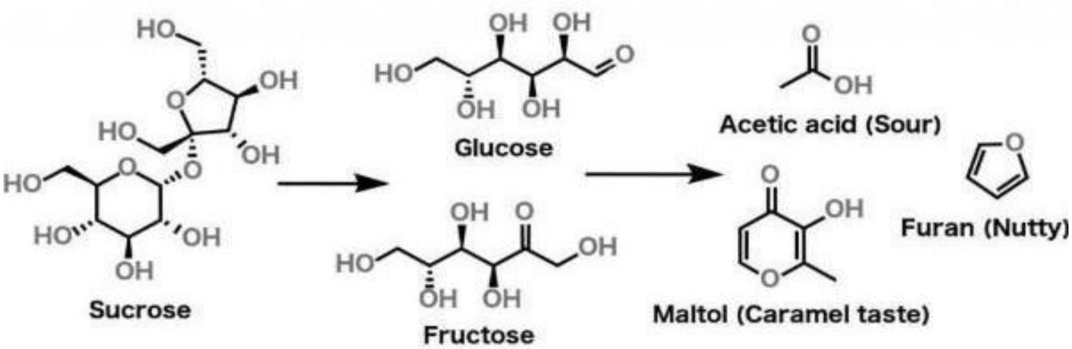

Figure 2. The schematic reaction of caramelization

Apart from its usefulness to introduce new taste, color, and flavor, a mixture of melanoidins also associated with health issues such as the effect of that polymer on human microbiota in the digestive system, diabetes, renal disease, Alzheimer's disease, and cardiovascular disease [19,20]. Excessive intake of food products containing Maillard reaction-derived compounds may accelerate aging and increase the risk of chronic diseases by subtly disrupting physiological functions over time [14].

Controlling the degree of reaction

There are five important variables that can be used to control the degree of Maillard reaction. Since the Maillard reaction occurs in high temperature and the rate of reaction is directly proportional with the increase of temperature. Therefore, temperature is crucial in controlling Maillard reactions. The optimum temperature of Maillard reaction generally is above 100 C and under 120 C [21]. However, in royal jelly this reaction can also occur at much lower temperatures [22] and, in animal protein even below freezing temperature [23]. Secondly, decreasing the pH will decrease the reaction rate due to reactivity of oxygen atom of carbonyl group and reactivity of amine group is inversely proportional toward the protonation reaction. A slightly acidic environment slows the Maillard reaction but can lead to more pronounced browning and flavor development [24], while extreme pH conditions can modify the reaction pathways, altering the final taste and color of cooked foods [25]. Thirdly, this reaction is a function of water activity of the system and the maximum rate of reaction occurs at water activity value 0.6-0.7 or around 30% moisture [15]. At high water activities, the mobility of reactants will also be high, whereas at lower water activities reactants become more concentrated, which will increase the rate until a certain point when the system becomes too concentrated and limits diffusion of reactants [26]. The specific sugar is the fourth variable because each type of sugars has different chemical properties, then controlling the degree of reaction can be easier when the reactant on the reactions is known. Lastly, the presence of transition metal ions affect the formation of the pigment compound on the final stage of Maillard [27].

Example of the Maillard reaction in confectionery products

Caramel, fudge, and toffee are an example of caramelisation and Maillard browning in confectionery. There are no clear boundaries of which products are produced by solo reaction of caramelisation or Maillard reaction since nowadays sugars confectionery are evolving with innovation to meet the demand of customers. The nomenclature of these three products can be quite confusing as each literature has different definitions [16,28].

Deciding which one is caramel in a sugar-based confectionery product is confusing. The word caramel sometimes is used interchangeably with the word toffee, but here caramel will refer to a product with the simplest ingredients, only sugars which are based on the definition of caramelization reaction . The brand for caramel with single ingredients is hard to find, unless for traditional products. Example of caramel with a single ingredient is Ppopgi, a traditional Korean caramel candy or Gula Gait, a traditional Indonesian caramel candy that nowadays hard to find. While Gula Gait is simply produced by heating only sugar, Ppopgi is made by adding baking soda to create texture in the final products. The baking soda reacts with the burnt sugar and release carbon dioxide that is trapped between the caramel, introducing a foam-like consistency on the caramel. As comparison, turning back to the caramel products that available in today modern market, they relatively have the same ingredient with toffee. The distinguish things between caramel and toffee is the amount of moisture left and the amount of fat used [28].

Toffee is fat emulsified in an aqueous system that was originally made by highly boiled brown sugar, invert sugar, fat (butter) and did not contain milk. Although toffee did not boil in a low water content condition, somehow it was similar to butterscotch. Later adding milk to toffee increases the moisture up to around 8 or 9% from around 5% (without milk) ([28]. The texture of toffee is a combination between chewiness and toughness which is highly affected by process and ingredients. The example of product bellow has basic ingredient mentioned before and some additional ingredients to meet the desired quality properties. The basic ingredients (sugars, glucose syrup and protein sources) are the reactant for caramelisation and the Maillard reaction which create color, aroma and falvour while the additional ingredients is required to retain the quality of final product (e.g. changes during storage) [29].

Ingredients of Werther's Original Chewy Toffees
Glucose Syrup (from Wheat)
Sweetened Condensed Skimmed Milk (21.6%)
Sugar
Vegetable Oil
Humectant
Whey Powder
Cream (3.9%) (from Milk)
Condensed Whey
Butter (2.5%)
Salt
Cane Sugar Syrup
Emulsifier (Soy Lecithin 322)
Flavour.

Figure 3. Example of Toffees Product that Available at Modern Market.

As it provides in the list of ingredients (Fig. 3), various sources of protein are used. Milk protein, apart from its function as the reactant for Maillard reaction and introducing flavour and color on toffee, also plays an essential role in the texture. The low water content of protein sources is widely used with the consideration that it does not require much time for evaporation can lead to denaturation of the protein then affect the texture. The combination of the type of protein's sources here may be to get a unique flavour and taste which is the characteristically of the brand and makes it different with same products from different brands.

Other ingredients are fat and butter which play the role in texture, flavor, and aroma even though it does not undergo caramelisation and the Maillard reaction. The fat globule and sugar solution build a complex blend, introduce a characteristic of the texture, and high-fat content will give a chewier and less sticky texture. Furthermore, the presence and emulsifier become essential to improve the dispersion of the fat then prevent the migration of oil to the surface [30]. The last ingredients are humectant, salt, and flavour. The function of humectant may be for controlling the water content of the products while salt and the flavour are for taste and odour properties (salt rounds out the flavour) [16]. The ratio of the ingredients depends on what type of toffee, it is creamy toffee or regular one, and whether wrapped or unwrapped because each type has different handling, storage, and quality requirement.

According to Lees and Jackso [28], fudge is a cross between a caramel and a fondant while Edwards [16] said in the book the science of sugar confectionery, fudge is made by adding fondant to toffee. In general, fudge basically is a toffee formulation but contains higher concentration of milk and fat than the original toffee and sugar crystal also developed during the processing. The texture of the finished product highly depends on the treatment during processing instead of the formulation. Three parameters that are required for a good quality of fudge are it should have a firm and uniform texture and microbiologically stable.

Figure 4 is assorted fudge, an example of commercial fudge. Its ingredients are the same as standard fudge with the addition of preservatives. Its higher water content than other similar products means it is more prone to spoilage either by bacteria or fungi or to any kind of deterioration during storage. However, it seems that its high sugar content makes spoilage by bacteria rarely to be the case.

Ingredients of Assorted Fudge
Sugar
Condensed Milk
Glucose Syrup
Butter (4.5%)
Vegetable Fat
Fructose
Emulsifier (322 from Soy)
Preservative (202).\

Figure 4: Example of Fudge Products at Modern Market

The type of sugar used here as the ingredients consider the nature of sugar that can affect the texture or physical properties of the fudge during the processing and handling (e.g. the cold flow). For instance, disaccharide is less liable to give chewiness or toughness than glucose syrup and to create stickiness compared to monosaccharides. Therefore in bulk handling production, sugars that give sticky structure is avoided to use unless for other purposes such as the use of brown sugar in toffee for flavour and colour [28].

CONCLUSION

The Maillard reaction and caramelization are critical chemical processes in the production of sugar-based confectionery, contributing significantly to the development of color, aroma, and flavor. Although the mechanisms involved are complex and not yet fully understood, these reactions are highly dependent on factors such as ingredient composition, temperature, pH, and moisture content. While they enhance the sensory quality of products like caramel, toffee, and fudge, they can also lead to the formation of harmful compounds such as acrylamide, HMF and AGEs when not properly controlled. Therefore, understanding the reaction pathways and processing variables is essential for optimizing product quality while minimizing potential health risks.

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