Maillard reaction in food technologies

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Abstract

Introduction. The Maillard reaction is a common reaction that occurs in bakery, confectionary, dairy, meat products, breakfast cereals, and processed fruits as well as in various drinks including wine and beer during cooking, heat treatment, and storage. This reaction determines the sensory properties of food including the taste, colour, and aroma, and consumer preferences largely depend on its intensity.

Materials and methods. The research materials for the present study were scientific publications about the Louis Maillard reaction found in the PubMed, ScienceDirect and Google Scholar databases.

Results and discussion. Information on the chemistry of the Maillard reaction is systematized. The reaction stages leading to the formation of certain compounds, as well as the food products in which these reactions occur, are described. This information will further help to establish in more detail the patterns of the reaction and find out exactly what chemical compounds accumulate in the processed food products.

The Maillard reaction affects the quality of many foods. It has been shown that the Maillard reaction can help create a taste, appearance and aroma that are attractive to consumers, but can, on the contrary, lead to the formation of reaction products with an unpleasant color, taste or even potentially dangerous substances to be consumed.

Meanwhile, for a variety of foods, such as baked bread, grilled meat, or roasted coffee beans, the melanoidin formation is the reaction that will provide the basis for color, taste and odor.

The Maillard reaction is important in the manufacturing of dairy products. It is this reaction that allows the formation of the specific color, smell and taste of baked milk, fermented baked milk or condensed milk, which are valued by consumers.

The Maillard reaction is no less important in food safety. The melanoidin formation can be used to inhibit the growth and development of microorganisms, and has a positive effect on prolonging the shelf life of food products.

Assessing the influence of Maillard reaction products on the formation of the quality and safety of food products involves establishing criteria for its control and management to achieve the specified requirements.

Different Maillard reaction products may have antioxidant, bactericidal, antiallergenic or carcinogenic properties. The formation of certain reaction products depends on the method and duration of food processing. High-temperature processing allows to increase the nutritional value of some food products, while others lose their nutritional value under the same processing conditions.

The Maillard reaction can be used in assessing the quality of food items, namely to identify possible falsification, based on the level of color characteristic of the products formed during this reaction.

Conclusions. The Maillard reaction is of great importance for food production, affecting both the nutritional value and sensory qualities of food. It provides a variety of possibilities for food control, ranging from quality assessment and flavor analysis to nutritional evaluation and adulteration detection.

Introduction

Maillard reaction is one of the most important reactions in the food industry. The first description of the reaction between sugar and an amino acid, which was later called the Maillard reaction, was published more than 100 years ago by Louis Camille Maillard Maillard (1912). This reaction is largely responsible for the color, taste, aroma, and texture of the final product in such traditional production processes as baking bread or biscuits, thermal treatment of coffee, cacao beans, meat, and many others. Louis Maillard's discovery became the cornerstone for understanding non-enzymatic reactions that cause the browning of foodstuff during the technological process, mandatory conditions of which are the presence of free amino acids and reducing sugar, as well as high-temperature treatment of the product (Jaeger et al., 2010). Maillard reaction is still under-researched despite the specifics of its course, and usage has been studied for over a hundred years.

Today, the Maillard reaction, its chemistry, impact on the quality and safety of food products and human health are the object of comprehensive studies (Hodge, 1953; Li et al., 2022; Nursten, 2007; Oliver et al., 2006).

The aim of the present study is to determine the prospect of Maillard reaction usage in expertise of foodstuff, namely for identification and detection of falsification of foodstuff.

Materials and methods

The materials for this study were scientific publications about Louis Maillard's reaction. Several questions were examined, specifically: what impact reaction has on the quality and safety of foodstuff and its effect on physiological aspects in the human body.

Separate consideration was given to the questions regarding Maillard reaction usage in the foodstuff falsification identification and detection.

Chemistry of Maillard reaction

Maillard reaction is believed to be hard to control. This is especially noticeable in food technology since the factors tied to the processing methods of raw materials and semi-finished products impact the reaction course. Hodge in 1953 proposed the first constitutive scheme of the Maillard reaction course (Hodge, 1953) (Figure 1).

The reaction course is split into three main stages: early, intermediate, and advanced. At the first stage, a carbonyl group of the reducing sugar (for example, glucose) condenses with the compound with an available amino group (usually with the epsilon-amino group in the lysine residue in the proteins). This glycation reaction leads to aldimine formation – an unstable Schiff base that regroups spontaneously into more stable 1-amino-1-deoxy-2-ketose (ketoamine), also known as the Amadori product.

Acidic hydrolysis of the intermediate product (lactulose-lysine) with HCl leads to the formation of furosine and pyridoxine – compounds that are indicators of the Maillard reaction (Li, 2005; Li et al., 2014; Töpel, 2004).

The subsequent destruction of the Amadori product depends on the activity of hydrogen ions in the solution (pH). Thus, for example, at pH less than 7, the Amadori products primarily undergo 1,2-enolization with the creation of furfural (involving pentoses) or hydroxymethylfurfural – HMF (involving hexoses). At a pH more than 7, Amadori products degrade. This process is argued to include primarily 2,3-enolization that leads to the formation of reductones (such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one) and various products like acetal, pyruvaldehyde, and diacetyl. These compounds have high reactivity essential in later reactions.

Carbonyl groups can condense with free amino groups, resulting in Nitrogen incorporation into the reaction product. Dicarbonyl compounds react with amino acids, forming aldehydes and α-aminoketones. This reaction is known as Strecker degradation. Next, a series of reactions happen in the intermediate stage that includes cyclization, dehydration, retroaldolization, rearrangement, isomerization, and subsequent condensation, which in the advanced stage result in the formation of brown nitrogenous polymers and copolymers more known as melanoidins (Martins et al., 2000).

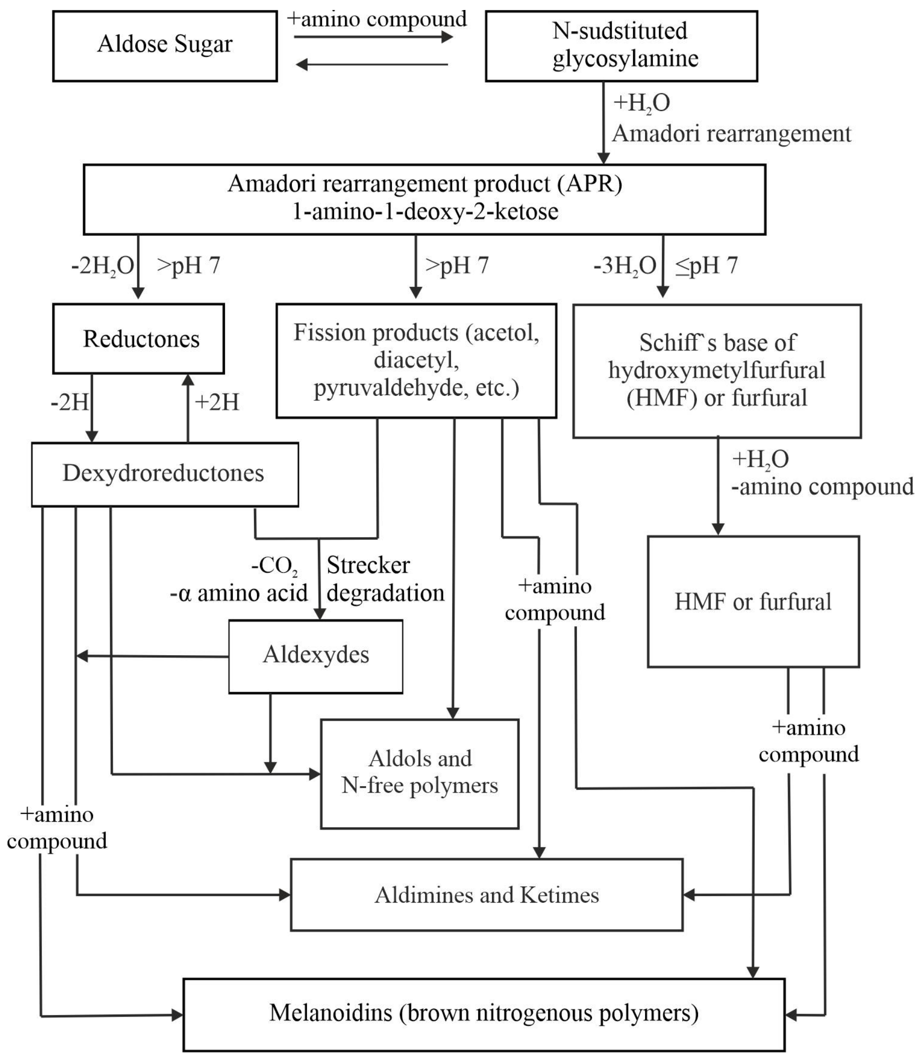

Figure 1. Maillard reaction scheme, adapted from (Hodge, 1953)

Important discoveries took place due to interest in the Maillard reaction. For example, McWeeny and others (McWeeny et al., 1974) discovered that the most important intermediates impacting color are 3-deoxy-2-hexosuloses and 3,4-dideoxyhexosuloses-3-ene. Shortly afterward Ghiron et al. (1988) reported that 3-deoxy-2-hexosuloses, 1-deoxy-2,3-hexodiuloses, and other α-dicarbonyl intermediates can participate in reactions of nucleophilic addition with amino acids in which subsequently decarboxylation takes place resulting in formation Strecker aldehyde.

The Maillard reaction mechanism is described by Hodge and is used to this day, but this hypothesis has some flaws. Firstly, the mechanism describes only the general process of Maillard reaction, while details are not specified. Secondly, some reactions were discovered by other scientists. For example, the work of Japanese scientists Namaki and his colleagues (1975) revealed that carbonyl products of division can also form straight from N-glycosyl amines through an indirect pathway caused by free radicals. This process was named "Namaki Pathway".

1-deoxy- and 3-deoxyglucosones were separated and described from heated Amadori products (Huber et al., 1990). Tressl and others (1995) discovered another perspective on the reaction scheme (Figure 2).

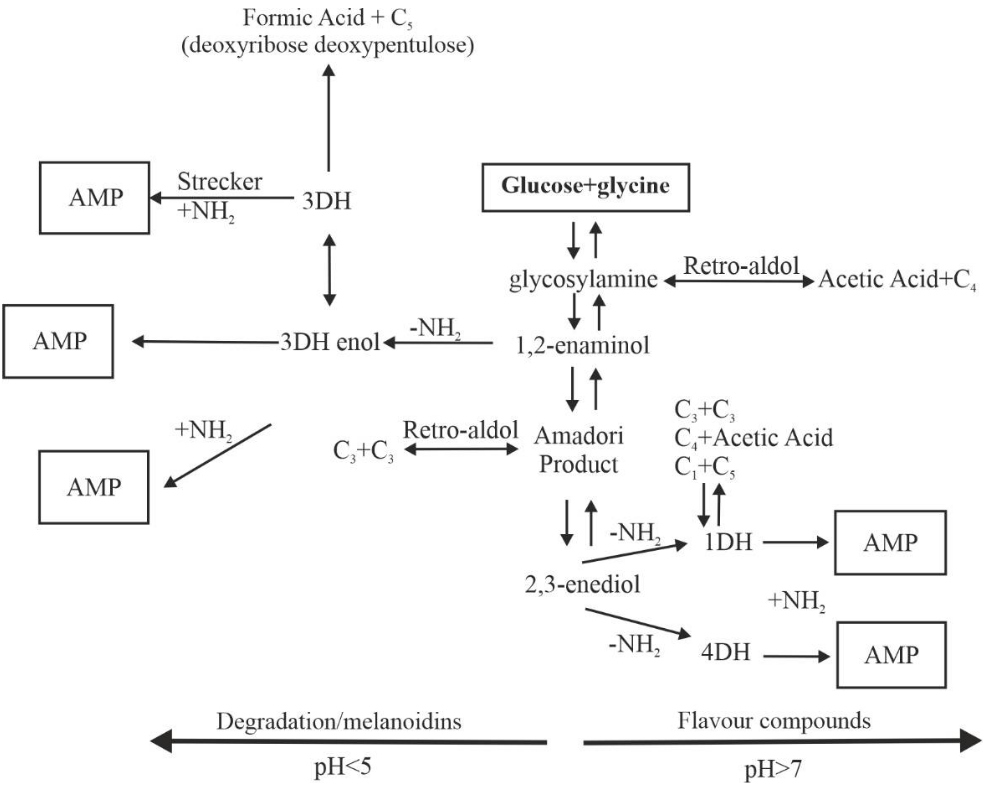

Figure 2. Maillard reaction scheme glucose/glycine
(adapted from Tressl et al., 1995, where AMP (Advanced Maillard Products) are products formed as a result of extended Maillard reaction; 1-DH (1-deoxy-2,3-diketose); 3-DH (3-deoxyaldoketose), 4DH (4-deoxy-2,3-diketose).

At the same time with the enolization reactions, the Amadori product and its dicarbonyl derivatives can be subjected to retro-aldol reactions, resulting in the creation of more reactive sugar fragments C2, C3, C4, and C5, such as derivatives of hydroxyacetone, glyceraldehyde, and diketones. Also, it is worth noting that retro-aldol reactions become more active at higher values of pH.

Huyghues-Despointes and Yaylayan (1996) came to the conclusion that under basic conditions APR (where APR are products of Amadori reaction) can create acetic acid and pyruvaldehyde, as well as lower sugars. The main condition for forming flavor and aroma compounds is the high value of pH in the solution.

Apart from retro-aldol reactions, three redox mechanisms were discovered in which α-hydroxy-carbonyls, α-dicarbonyls, and formic acid are involved. Formic acid as a main product of lactose degradation in the Maillard reaction was reported by Berg and Van Boekel (1994). Van Boekel and Brands (Brands et al., 2000; Van Boekel et al., 2005) indicated that formic and acetic acids are the two main products of glucose and fructose degradation in the Maillard reaction.

Based on Tressl's conclusions, Yaylayan (1997) developed a conceptual view of the processes that occur during the Maillard reaction. According to this view, the Maillard reaction is described as a reaction in which "chemical pools" are being created and interact with each other. The combination of products formed from a clearly defined precursor's decomposition is called the fragmentation pool, and the group of interconnected chemical reactions and their products is called the interaction pool. Fundamental reactions that are the basis of the interaction pool are classified according to the type of chemical transformation that takes place. The importance of this classification is in its ability to predict the formation of Maillard reaction products in the model systems. Also, according to Yaylayan's theory, it has been established that during the Maillard reaction amino acids and sugars also experience independent degradation in addition to ordinary degradation in which the Amadori product is formed.

Sugar isomerization and degradation during the thermal treatment of the milk are more important than the Maillard reaction from a quantitative point of view (Berg, 1993).

Also, the significance of the Amadori product (which has been considered an intermediate product of the reaction) is questioned in the food industry (Molero-Vilchez et al., 1997).

Table 1 shows brief examples of Maillard reaction stages and the results of their study.

Therefore, the chemistry of the Maillard reaction, its course, specifics, and conditions are still disputed among scientists worldwide, and the study of this reaction continues to this day.

In the context of the food industry, the Maillard reaction and its products form characteristics of quality, safety, and physiological consumption aspects.

Table 1

Examples of Maillard reaction stages

Stage of MR	Foodstuff	Reactions/reaction products	References
Early	Beer	Aldehydes	Hellwig et al., 2014
		Carbonyl compounds: glyoxal, methylglyoxal, aldehydes	Maasen et al., 2021
		3-methylbutanal	Cämmerer et al., 2002; Murata, 2021
Early	Malt, children's cookies	Furosin (~N-2-furoylmethylisin 2-furoylmethyl derivatives such as GABA (γ-aminobutyric acid)	Erbersdobler et al., 1991; Resmini et al., 1991; García-Banos et al., 2004; Cardenas Ruiz 2004; Del Castillo et al., 2000; Sanz et al., 2000, 2001
Early	Cookies, crackers, breakfast cereals, dry milk	Furocin	Rada-Mendoza et al., 2004
Early	Sterilized milk, curdled milk, condensed milk, liquid infant milk	Hydroxymethylfurfural (HMF) as a marker of the intensity of formation of products of the Maillard reaction	Albalá-Hurtado et al., 1999; Olano et al., 1989; Park et al., 1991; Berg, 1993.
Early	Milk, pasta	5-hydroxymethylfurfural, furosine, maltol and pyridoxine	Christie, 1983; Resmini et al., 1994
Early	Black garlic	2-furomethyl-amino acids (2-FM-AA) as indicators of the Maillard reaction	Ríos-Ríos et al., 2018
Early	Black garlic	2-furoylmethyl-γ-aminobutyric acid and 2-FM-arginine	Ríos-Ríos et al., 2018
Early	Orange juice	2-furoylmethyl derivatives of aminobutyric acid (2-FM-GABA) and arginine (2-FM-Arg) as early indicators of non-enzymatic darkening	Del Castillo et al., 2000
Intermediate	Beer	Carbonyl compounds 1-deoxyglucoson, 3-deoxyglucoson and methylglyoxal	Hodge, 1953
Intermediate	Coffee	Carbohydrates and pyrolysis of organic compounds; melanoidins as a result of polymerization and/or pyrolysis of furans.	Tressl et al., 1998; Belitz et al., 2009
Late	Milk	Condensation, polymerization, degradation, cyclization reactions occur; Fluorescent compounds	Hodge, 1953; Birlouez-Aragon et al., 1998
	Fried fish and grilled meat	Acrylamide and heterocyclic aromatic amines	Friedman, 2003; Carthewa et al., 2010

Table 1 *(Continue)*

Stage of MR	Foodstuff	Reactions/reaction products	References
Late	Model system of amino acid and sugar	α-hydroxycarbonyls, α-dicarbonyls and formic acid	Van Boekel et al., 2005
Late	Instant coffee, decaffeinated coffee, tea	Dicarbonyl compounds, methylglyoxal, diacetyl and glyoxal	Nagao et al., 1979
Late	Cereal products	2-fluoromethyl-GABA	Marchenko et al., 1973
Late	Roasted coffee, boiled meat	2,3-butanedione, 2,3-pentadione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(3H)furanone (sotolon) and 2,5-dimethyl-4-hydroxy-3 (2H)-furanone; 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine and 2-acetyl-1-pyrroline, 2-furfurylthiol, 20-methyl-3-furanthiol, 3-mercapto-2-pentanone and methional	Lieske et al., 1994

Maillard reaction and its impact on the quality of food products

The positive significance of this reaction was recognized in 1912 when it was discovered that malty aroma during beer brewing forms due to the reaction between the reducing sugars and leucine (Lintner et al., 1912), which later has been confirmed (Helling et al., 2014; Ruckdeschel and Brauw, 1914). But in this regard, Akabori (1927) discovered that aldehydes form with high yield during the decarboxylation of amino acids in the presence of glucose. Other carbonyl compounds, such as glyoxal, methylglyoxal, or diacetyl, also lead to the formation of aldehydes (Neuberg et al., 1927).

Schçnberg and Moubacher were the first to demonstrate that vic-dicarbonyl compounds (any diols that have two hydroxyl groups connected to adjacent carbons) are always needed for the "Strecker degradation" (1948). They are formed as intermediate products during the Maillard reaction (Schçnberg et al., 1952). This confirms Ruckdeschel's postulate on the formation of 3-methylbutanal – an important aromatic compound formed in malt from leucine during Strecker degradation (Damn et al., 1964).

The Maillard reaction has 3 stages. In the intermediate stage, different carbonyl compounds are formed from Amadori products, including such dicarbonyl compounds as 1-deoxyglucosone, 3-deoxyglucosone, and methylglyoxal. These dicarbonyl compounds are more reactive than source material or reducing sugar. Reactive dicarbonyls interact with each other and with amino groups in amino acids and proteins, creating aroma and color (Ho, 1996).

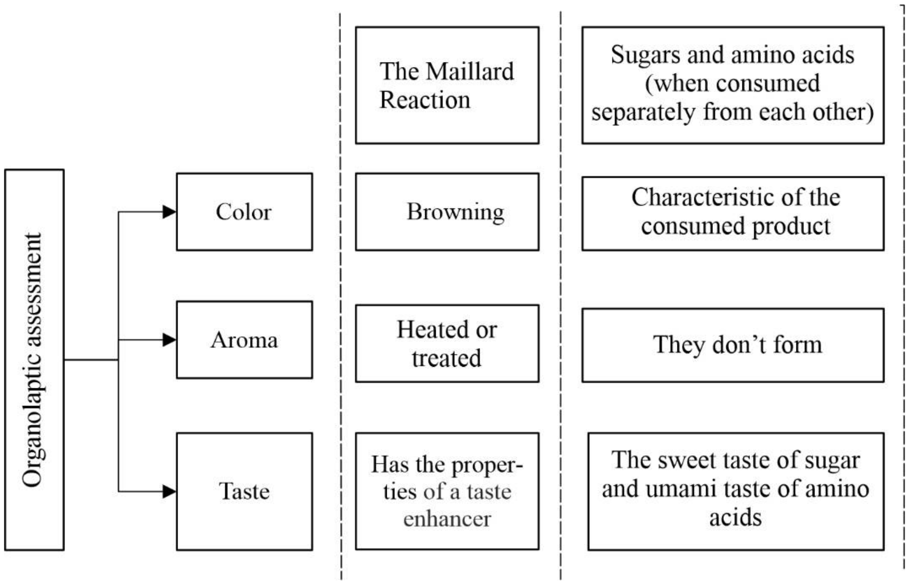

Figure 3. Correlation between Maillard reaction and sensory characteristics of the food product

Figure 3 depicts the correlation between the Maillard reaction and the color, aroma, and taste of food products. It is known that Maillard reaction products are formed due to the heating of sugars, amino acids, or proteins. Thus, it can be said with complete confidence that the brown color and caramelization aroma (typical for this reaction) indicate that the product contains sugar and amino acid or a protein, which is important for consumers, especially for whom sugar is contraindicated. Also, apart from having an impact on browning and aroma, recent studies have shown that different products of the Maillard reaction can act as sweeteners or taste modifiers (Festring et al., 2010; Ho, 1996; Kaneko et al., 2011; Ottinger et al., 2003; Perestrelo et al., 2019; Shima et al., 1998).

A short generalized characteristic of the impact the Maillard reaction has on the quality and safety of food products is shown in Table 2.

Impact of the Maillard reaction on the sensory properties of food products

The origin of the volatile organic compounds responsible for the formation of aroma in food products is hard to identify to this day because of their varied origination and structure. Scientists show great interest in studying this question, especially with the aim of controlling the generation of distinctive aromas and colors of food products.

The development of gas chromatography-mass spectrometry in the last decade significantly intensified the analysis of compounds with a specific odor, including aroma created during the Maillard reaction (Buckholz, 1988; Chuyen, 1998; Ho, 1996; Taylor et al., 1996). Thus, for example, Lane and Nursten (1983) identified 12 amino acids, 5-7 of which, in their opinion, together with glucose participate in the creation of aromas of bread, crunchy cookies, biscuits, and toasts at studied temperatures from 100 to 220°C at selected time intervals up to thirty minutes.

Table 2

Effect of the Maillard reaction on food quality and safety

Quality and safety of food	Food example or explanation	References
Darkening or pigmentation	The color of beer, soy sauce, bread crust and roasted coffee	Murata, 2021; Hayase et al., 2006; Kanzler et.al, 2020
Formation of aroma	Toasted bread, grilled meat and roasted coffee	Lane et al., 1983
Formation of taste enhancer	Boiling beef broth and ripening soy sauce	Shima et al, 1998; Ottinger et al., 2003; Fetring et al., 2010; Kaneko et al., 2011
Antioxidant and antimutagenic activity	Individual structures of enediol and enaminol molecules in melanoidins and various compounds formed by the Maillard reaction; The antimutagenicity of pyrazines contained in Maillard's products correlates with the inhibition of the cytochrome P-450 IA2-linked ethoxycoumarin deethylase mutagen-activating enzyme in microsomes.	Griffith et al., 1957; Chuyen et al., 1998; Eric et al., 2013; Jenq et al., 1994
Loss of lysine	Long-term storage of dry milk	Plakas et al., 1985; Chuyen et al., 1991; Pellegrino et al., 1999
Formation of mutagens	Acrylamide and heterocyclic aromatic amine	Arvidsson, et al., 2005; Nagao et al., 1979; Sugimura et al., 1990; Kovtun et al., 2022

Coffee is one of the most popular drinks among consumers around the world. The desired smell of coffee drinks occurs during the roasting of coffee beans. The typical temperature range for this process is from 180 to 250°C, and the duration of the roasting is from 2 to 25 minutes, depending on the procedure used (Belitz et al., 2009). This results in the Maillard reaction and caramelization, formation of carbohydrates, and pyrolysis of organic compounds. Melanoidins are formed as a result of the Maillard reaction during the roasting as the product of polymerization and/or pyrolysis of furans. They combine among themselves via a poorly understood reaction of condensation polymerization during the intermediate stage of the reaction (Tressl et al., 1998).

In turn, Fors (1983) published a literary review on the sensory properties of the volatile Maillard products and related compounds. This review is centered on the quality of the aroma and description of the taste, color, and sensory threshold values for different compounds classified by their chemical structureors.

As for the color, it is known that the brown color typical for the Maillard reaction is caused by the melanoidins. During the last stage of the Maillard reaction, several chemical reactions take place: condensation, polymerization, degradation, cyclization, and so on – which is accompanied by melanoidin formation (which are heterogeneous polymers). The structure of these polymers is not known for certain, and several theories exist on their chemical structure and formation (Wang et al., 2011). Thus, according to one of these theories, the main skeleton of melanoidin contains saturated aliphatic carbon atoms formed from the products of sugar decomposition and branched by amino compounds (Murata, 2021). Hayase and others (1986), with the use of nuclear magnetic resonance spectroscopy, suggested another polymer. It is known that in the Maillard model reaction system with only a monosaccharide and an amino acid the main skeleton of the melanoidin with high molecular mass is considered a polymer product of the sugar decomposition because dicarbonyl compounds such as 1-deoxyglucosone, 3-deoxyglucosone, and methylglyoxal can be condensed with the help of the aldol reaction (Cammer et al., 2002; Maasen et al., 2021; Murata, 2021). But by themselves these basic structures are colorless. Therefore, according to this theory, it can be assumed that melanoidins should have partial structures of different chromophores.

According to the second theory, melanoidins are polymers of low molecular weight pigments formed from sugars and amino acids (Murata, 2021). Hayase and others assumed that melanoidins are formed from heterocyclic intermediate products of the Maillard reaction through the aldol reaction and the Michael 1,4 addition (this is a reaction between Michael donor (an enolate or other nucleophile) and Michael acceptor (usually α,β-unsaturated carbonyl) with the creation of the Michael adduct with the carbon-carbon bond at the acceptor's β-carbon), i.e. they are formed by the aldol condensation and Michael reaction.

Hoffman speculated that melanoidins in food are created by protein crosslinking (Hofmann, 1998, 1999). It was also reported that melanoidins are not characterized by a specific absorption maximum of visible light (380–780 nm), which clearly indicates that melanoidins have mixed chromophores.

Various low molecular weight pigments created as a result of the Maillard reaction were discovered and identified. In some cases, these pigments greatly enhance coloration (Murata, 2021).

On the final stage of the Maillard reaction, colored intermediate products and other reactive precursors (products of enaminol, low molecular weight analogs of sugar, unsaturated carbonyl products) are condensed and polymerized with the amino catalyst creating brown polymers that have furan ring with different functional groups, including carbonyl, carboxyl, amino, amide, ether methyl or/and hydroxyl groups (Ames et al., 1993; Ledl et al., 1990; Tressl et al., 1998).

It should be noted that the discovery and identification of colored Maillard reaction products were being carried out only using model systems, usually for products with low molecular mass (less than 500 Da). Thus, Hashiba (Hashiba, 1982) compared the reactivity of different reducing sugars with a singular amino acid (glycine) and concluded that browning is directly proportional to the reducing ability of sugar and the amount of glycine.

Rizzi (1997) concluded that plenty of colored products are products of (retro) aldolization/dehydration of sugars, which can or can not be connected to the proteins or other sources of amino nitrogen.

Hoffman (1999), using a series of model experiments and chemical, instrumental, and sensory methods, identified some products of carbohydrate decomposition as a precursor of browning (deoxysones, glyoxal, methylglyoxal, hydroxy-2-propanone, 3-hydroxy-2-

butanone, and glycolaldehyde), which fit in with Figure 2, and proved that their reactivity in producing substances that determine color of the product change with thermal treatment.

The degree of browning is often determined similarly to the evaluation of the intensity of the Maillard reaction and generally is measured using absorption at 420 nm (Baisier et al., 1992).

The formation of a golden crunchy crust on the food surface is one of the most obvious signs of fried food. This layer (known as browning) is created as a result of the chemical and structural changes in the product several minutes after the contact with oil. The golden color of the crust is formed due to the Maillard reaction, which causes chemical changes in sugars on the product's surface. In this particular case, the Maillard reaction occurs when high temperatures combine with low moisture content (Skjoeldebrand et al., 1980). In other words, the crust is a dry layer that acts as a barrier between the inner part of the food product and the oil outside. The crust also limits heat transfer.

However, melanoidin creation in food products is not always desirable. For example, during the analysis of various colorants in technological processes of sugar production. Pearson came to the conclusion that melanoidins are the most dangerous colorants from the perspective of final products (Reva et al., 1978).

Utilization of different compounds with amino groups results in the creation of various flavor profiles due to the created compounds. Table 3 shows a possible range of flavors created by heating various amino acids with glucose. Milk proteins usually are rich in amino acids, some of which have residues that can participate in the Maillard reaction without destroying the protein.

Table 3

Creation of possible flavors that occur due to heating of various amino acids with glucose in different conditions (adopted from Van Boekel et al., 2006)

Amino acid	**The smell of the product when heated with glucose**
Alanine	Fruity, floral, sweet
Arginine	Bitter, sour, fruity
Aspartic acid	Fruity, sweet
Cysteine	Sulphurous, meaty
Glutamic acid	Sour
Glycine	Caramel, sweet, floral
Histidine	Sour
Isoleucine	Burnt, caramel
Leucine	Burnt, caramel
Lysine	Pleasant/sweet, caramel, cardboard, herbal
Methionine	Potato, shrimp
Threonine	Sweet, fruity, tart
Serin	Fruity, sweet
Proline	Fruity, bitter
Phenylalanine	Floral, almond, bitter
Tyrosine	Fruity, floral, tea
Valin	Caramel, biscuit, malt, chocolate, bitter

The hydrolysis process leads to the increase in available amino groups for the Maillard reaction. As can be seen in Table 5, present and available amino acids can cause a number of taste properties (Wong et al., 2008).

Effect of Maillard reaction products on sensory characteristic of milk products

The taste of milk products is one of the most considerable sensory characteristics that consumers take into account. It is well known that fresh and high-quality milk usually has a characteristic mild taste. Therefore, any deviation in taste can be very notable. The main source of the taste components is the milk itself, but lowering the quality of components during processing also has a major impact on the overall taste (Ames, 1998; Nursten et al., 1997).

The Maillard reaction affects the sensory characteristic of numerous food products, especially milk products. Its effect becomes more prominent during heat treatment. This reaction's course can create favorable flavors, appearance, and aromas (Van Boekel et al., 2006). An example of a desirable Maillard reaction in milk can be observed in baked milk (Figure 4) (Mandiuk et al., 2024).

a b

Figure 4. Example of the Maillard reaction in baked milk:
a, pasteurized milk
b, baked milk

This reaction can also cause a reduction in the product quality, undesirable colors, unpleasant tastes and aromas, and potentially create harmful compounds in food products, as well as harmful substances (Keramat et al., 2011; Töpel et al., 2022).

But in the case of milk products, unwanted flavors can be concerning both during the manufacturing and during storage of the milk, especially powdered milk. Thus, reducing the Maillard reaction in dairy products is a priority.

But there are a number of milk products, aromas of baked milk, or pasteurization for which are desirable. Such products are baked milk (Sserunjogi et al., 1998; Yadav et al., 1992), butter, kefir, barbecue cheese, condensed milk, ryazhanka (fermented product typical for Ukraine), taffy, fudge, dulce de leche (Pauletti et al., 1999), and milk chocolate crumb (Muresan et al., 2000).

It is known that the Maillard reaction is a reaction between amino groups and reducing sugars that occurs during the heating process. The main sugar in the milk is lactose, which not only participates in the Maillard reaction but also takes part in the caramelization process.

Maillard reaction and its effect on safety of food products

Mutagenic and carcinogenic products are found in foods that contain significant amounts of proteins. Such mutagenic and carcinogenic products are formed by several mechanisms: caramelisation of sugars, thermal degradation of proteins, amino acid/creatinine reactions and amino carbonyl reactions (Maillard reaction). Available amino groups during the amino acid/creatinine reaction and the aminocarbonyl reaction (Maillard reaction) condense with reducing sugars to form brown melanoid, furanine, carbonylin and other products (Friedman, 1996, 2005).

The Maillard reaction is important for food product safety. Some genotoxic compounds, such as acrylamide and heterocyclic aromatic amines, are produced during this reaction (Friedman, 2003; Carthewa et al., 2010; Bartkiene et al., 2016). Meanwhile, acrylamide is known as a bioavailable neurotoxin (Losso et al., 2016).

In 1994, the International Agency for Research on Cancer classified acrylamide as a probable carcinogenic compound for humans (Huff et al., 2002). Already in 2002, Swedish food researchers at Stockholm University identified significant concentrations of acrylamide in some thermally processed foods, such as bread, coffee and French fries.

The reaction mechanism has a significant impact on the mutagenicity of the reaction products. For example, it was proved that ketose sugars have higher mutagenic reactivity than aldose sugars (Alink et al., 2000). However, because of the complexity of non-fermentative browning reactions and the low stability of the intermediate products, only several well-researched toxic compounds exist, among which the most studied is acrylamide. Acrylamide, also known as prop-2-enamide, is a carcinogen and can cause neurological damage. Acrylamide has been discovered in almost all food products, but fried and baked food treated at high temperatures contain far more acrylamide (Table 4) (Fogliano, 2015).

Table 4

Acrylamide content in some food products

Food product	N*	Acrylamide content (µg/kg)		
		Median	Mean	Maximum
Potato chips	216	490	628	4180
French fries	529	253	350	2668
Cookies	227	169	317	4200
Bread	272	50	136	2430
Breakfast cereal	128	100	156	1600
Coffee	208	188	253	1158
Other products	854	169	313	4700

N* – number of individual data analyzed for each food category.

It has been established that acrylamide is a hazardous chemical compound in foods that are thermally processed at temperatures over 120 °C. A number of studies have been conducted on acrylamide toxicity, mechanism of generation, measurement, reduction and correlation of risk assessment among different foods (Tareke et al., 2002).

The tolerable average dietary intake of acrylamide is 0.3-0.6 µg/kg daily, but it can lead to its accumulation in the body (Claus et al., 2008). According to modern data on acrylamide, it is possible to argue that:

1. Amino acids split at high temperatures, and products of this split react with reducing sugars and form acrylamide;
2. The first maillard reaction product – n-glycoside – plays a major role in the creation of acrylamide;
3. ɑ-dicarbonyl compounds react with amino acids and form acrylamide;
4. Strecker degradation contributes to acrylamide generation due to the creation of aldehydes during the degradation;
5. Free radicals also promote acrylamide formation;
6. Acrylamide can be created in several ways. It shouldn't be forgotten that acrylamide is both formed during food processing and can migrate from packaging materials made from polyacrylamide or flocculants (Wang et al., 2012).

In the literature, there isn't much data on the possible role the Maillard reaction can have on the inhibition of microorganisms' growth in food products. Thus, was identified Maillard reaction products through dephlegmation of solutions containing asparagine and xylose and then studied their reactivity on the pathogenic microorganisms and spoilage microorganisms that usually are present in food products. Some inhibition effects on *Staphylococcus aureus* have been noted. But at the same time, an opposite effect could be seen for *Bacillus subtilis* and *Esherichia coli*, and *Candida tropicalis* was found to be practically unresponsive to the Maillard reaction products (Einarsson et al., 1983, 1988; Rufián-Henares et al., 2008).

Table 5 shows data of the impact Maillard reaction products on microorganisms (adopted from ALjahdali et al., 2017).

It is interesting that Maillard reaction products are effective against yeast, which have a positive effect on the safety of food products and their shelf life (Tauer et al., 2004). The negative effect of the Maillard reaction products on the viability of yeasts in alcohol production was first proven by Sattler in 1949 (Sattler et al., 1949; Finot 2005). Ten years later, Krug and others determined LD50 for various products of the reaction between free amino acids and glucose and identified that a mix of lysine and sugar is one of the most toxic ones (Krug et al., 1959).

The most obvious negative effect is the toxic effect of mutagens and carcinogens formed during the thermal treatment of meat and fish (Sugimura et al., 1990). Also, several cyclic amines, obtained as a product of the Maillard reaction in the presence of creatinine, were identified. They belong to the imidazoquinoline and imidazoquinoxaline classes. Others were discovered as a result of heating tryptophan, glutamic acid, or phenylalanine. Thanks to this identification, sensitive detection methods of some heterocyclic amines were created, which made it possible to avoid their creation in the meat industry (Gross et al., 1990).

The loss of the food products' nutritional value is associated with the formation of mutagenic compounds. Nagao and others identified mutagenic substances in instant coffee and decaf coffee (Nagao et al., 1979). They were composed of dicarbonyl compounds, methylglyoxal, diacetyl, and glyoxal, from which methylglyoxal is the most mutagenic. However, there was no quantity correlation with carcinogens.

Mutagenic compounds derived from heterocyclic amines were found in fried meat and fish, especially the grilled ones (Arvidsson et al., 2005). Flavones and flavonoids inhibit the formation of heterocyclic mutagens like amines (Lee et al., 1992). The antimutagenic effect of the Maillard reaction products also has been reported (Lee et al., 1994; Yen et al., 1992).

Table 5

Impact of Maillard reaction products on microorganisms

Product of the Maillard reaction	Microorganisms	Research result	Reference
Acrylamide	*Lactobacillus plantarum*	Reduction of acrylamide level	Baardseth et al., 2006
	Lactobacillus sakei Pediococcus pentosaceus Pediococcus acidilactici	Reduction of acrylamide level	Chalova et al., 2012
Melanoidins	*Salmonella typhimurium*	Use of 15% melanoidins as a source of carbon and energy	Chalova et al., 2012
	Escherichia coli	Suppression of growth rates	Rufian-Henares et al., 2008; Yen et al., 1992
	Listeria monocytogenes Salmonella enterica Bacillus cereus Brevibacillus brevis	Inhibition of growth	Kukuminato et al., 2021
Aminoreductone	*Pseudomonas aeruginosa Escherichia coli Staphylococcus aureus*	Inhibition of growth	Trang et al., 2013
Hydroxymethylfurfural	*Salmonella typhimurium*	Mutagenicity	Sommer et al., 2003

Regarding the safety of food products, the role of the Maillard reaction in the formation and elimination of mutagens is still a question in need of an answer. There are no data on the correlation of these compounds with cancer.

The Maillard reaction produces antioxidant components as well. Griffith and Johnson were one of the first scientists to report that adding 5% glucose to sugar cookies led to a noticeable browning of the cookies and increased resistance toward oxidative rancidification (Griffith et al., 1957). Since this discovery, Maillard reaction products have been studied in light of their antioxidant properties and ability to protect food from lipid oxidation (Chuyen et al., 1998).

Table 5 shows a short generalized characteristic of the Maillard reaction's impact on the quality and safety of some food products.

Maillard reaction and its impact on physiological aspects

Some studies (Finot et al., 1981, 1990) describe such physiological effects of consuming fried and thermally treated food products or the reaction between sugars and free amino acids or proteins as a decrease in protein-digesting levels and amino acids intake, organ hypertrophy, cellular changes and decrease in activity in intestinal and pancreas enzymes, as well as in liver enzymes responsible for metabolizing medication, serum transaminase and alkaline phosphatase, chelation of metals. All of these effects are connected to premelanoidins (Adrian, 1974).

Also, negative effects of the Maillard reaction in food products can include loss of the nutritional value of proteins that participate in the reaction, which causes a decrease in quality and potentially leads to a decrease in the safety of food products. A number of studies focused on this loss. The loss was explained as a decrease in absorption, destruction, and/or biological inactivation of amino acids including such essential amino acids as lysine and tryptophan, inhibition of proteolytic and glycolytic enzymes, and interaction with metal ions (Ericksson, 1981; Friedman, 1996; Namiki, 1988).

Lysine is the most susceptible to loss during non-enzymatic browning, followed by alkaline amino acids, including L-amino acids like L-arginine and L-histidine. In addition to the reaction between sugars and amino acids, Strecker degradation also results in the loss of amino acids. The formation of complex molecules decreases the solubility of proteins and lowers their nutritional value.

The impact the Maillard reaction has on the availability of amino acids was studied on the rainbow trout (Salmo gairdneri). Results showed that in the mix of isolated fish protein and glucose stored at 37 °C for 40 days, arginine and lysine suffered the biggest loss, and notable absorption of particular acids (especially lysine) was lower in trout fed fried protein than trout fed control protein (Plakas et al., 1985).

Additionally, protein molecules can be crosslinked by the Maillard reaction products (Chuyen et al., 1991; Pellegrino et al., 1999).

Also connection was found between the Maillard reaction and lysine loss during the storage of biscuits. Noguchi et al. (1982) discovered that lysine loss increases if biscuit samples are stored at room temperature during long-term storage. Storage effect on the lysine loss in biscuits enriched with protein was studied (Hozova et al., 1997) and assessed by measuring lysine levels and nutritional value of amaranth biscuits and amaranth crackers stored for 4 months in lab conditions (20°C and 62% of relative humidity). Despite the experiment resulting in a slight loss of lysine authors speculated that lysine degradation might continue during prolonged storage and it should be accounted for in relation to the consumers and extension of shelf life.

It is interesting that the physiological effects Maillard reaction products have are not only negative. For example, antimutagenic effects were shown in some Maillard reaction products which somewhat evens out their negative effect.

Therefore, there are a lot of aspects of the quality and safety of food products that are related to the Maillard reaction. The technologist's objective is to balance beneficial and inauspicious effects in the technological process – optimization of nutrition value loss during the heat-moisture treatment, change in taste and color during the milk drying process, maximization of antioxidant generation, etc.

Understanding the Maillard reaction is an additional condition not only for the traditional process of frying, baking, and boiling but also for the development of new technology like microwave ovens and high-pressure processing (Ames, 1998; Shahidi et al., 1998).

Maillard reaction in expertise of foodstuff

Usage of the Maillard reaction in the expertise of foodstuff is prospective.

In the sensory evaluation of the quality of the milk product dulce de leche, popular in the Rio de la Plata region, color is a critical factor that defines a customer's choice. For this, a method of receiving a preliminary structural characteristic of chromophores created by the Maillard reaction was developed (Rodríguez et al., 2019). With its help, it was determined that melanoidins formed during the reaction have molecular mass from 300 to 2000 Da, but the compounds with the bigger molecular mass contribute to the color of the milk product the most.

Identification of furosine – one of the Maillard reaction products and an indirect indicator of the protein-bound lactulose-lysine – is widely used for the evaluation of the quality of pasta (García-Baños et al., 2004) and dry dairy products (Rutherfurd et al., 2006).

Thus, the identification of furosine (~N-2-furoyl-methyl-lysine) formed as a result of an acidic hydrolysis of the Amadori product created in the early stages of the Maillard reaction (Erbersdobler et al., 1991) is used for malt (Molnar-Perl et al., 1986), pasta (Resmini et al., 1991, Garcia Banos et al, 2001, Cardenas Ruiz 2004), and baby biscuits (Carratu et al., 1993). Other 2-furoyl-methyl derivatives, such as GABA (γ-aminobutyric acid), also were used in the Maillard reaction and suggested as indicators for its early stages (Del Castillo et al., 2000; Sanz et al., 2000, 2001).

The early stage of the Maillard reaction in biscuits, crackers, and breakfast cereals was also evaluated via quantitative analysis of furosine (Rada-Mendoza et al., 2004). Furosine was found in all analyzed samples, but variability was high. Taking into account that a significant amount of furosine was found in powdered milk (Corzo et al., 1994; Guerra-Hernandez et al.,1996, 1999), it is probable that part of the furosine detected in cereal products with powdered milk comes from powdered milk (Rada-Mendoza et al., 2004) that had furosine added. The 2-fluoromethyl derivative – equivalent to GABA – was found in the cracker and breakfast cereal samples but not in most biscuit samples. This compound's presence in breakfast cereals and crackers can be linked to the significant amount of free GABA found in rice and corn used for their production. A considerable amount of free GABA in corn chips has been reported before (Marchenko et al., 1973). Different amounts of powdered milk used in the manufacturing of cereal products, and different levels of free GABA in the untreated grain are the main disadvantages in furosine and 2-fluoromethyl GABA usage as corresponding indicators for differentiation in grain-based commercial products. However, in the grain industry, where the exact composition of raw material is known, measurement of 2-fluoromethyl GABA and formed furosine can be used as an indicator for monitoring processing conditions during the manufacturing of grain products.

Olano and others (Olano et al., 1989) reported differences in the chemical composition of sterilized milk treated at ultra-high temperatures. Levels of HMF created during heat treatment can be used as a marker for the intensity of the Maillard reaction product creation in the manufacturing process of baked or condensed milk. However, the amount of HMF accumulated in milk during ultra-high temperature treatment depends on such factors as the presence of vitamin A, casein, or iron (Albala-Hurtado et al., 1999). The color of the product can be an indicator of Maillard reaction completion (Park et al., 1991)

As noted before, the reaction speed of the Maillard reaction can be controlled using quantitative detection of 5-hydroxymethylfurfural, furosine, maltol, and pyridoxine.

Such Maillard reaction products as 5-hydroxymethylfurfural, furosine, and lactulose are used as "heat load indicators" for the estimation and control of the heat treatment severity. Unlike lactulose, both compounds are already present in raw milk, but the concentration of

5-hydroxymethylfurfural might vary significantly (Table 6). Therefore, for the estimation of heat treatment severity, it is necessary to determine the amount of 5-hydroxymethylfurfural in the raw material.

Table 6

Indicator substances (derivatives of lactose) for the estimation of heat treatment severity of milk (adopted from Christie, 1983; Resmini et al., 1994; Töpel, 2004)

Product	Lactose, mg/kg	5-hydroxymethidfurfural, µmol/l	Furosin, mg/100 g of milk protein
Raw milk	0	2–9	3–5
Pasteurized milk	<50	6–8	–
UHT-milk	100–500	5–20	45–150
Sterilized milk	600–1400	20–100	110–450

UHT milk is milk that has been processed at ultra high temperature (UHT).

Also, created heterocyclic compounds absorb UV light and fluoresce. Fluorescent products are formed through the Maillard reaction when storing food products and biological systems together with brown pigments. These products can be used as early indicators for this reaction. Matiacevich and Buera (2006) demonstrated that under unfavorable conditions (low pH, presence of salts) fluorescent products can be used as adequate markers, including for the early stages of the reaction.

Fluorescent compounds also are formed at the later stages of non-enzymatic browning. Several methods based on measuring fluorescence were used for the estimation of the reaction stage. For example, method FAST (fluorescence of advanced Maillard products and soluble tryptophan) proposed by Birlouez-Aragon with coauthors (1998) corresponds to the molecular structures formed by the reaction between reducing sugars and lysine remnants in proteins. The method is based on the measuring fluoresce emission maximum in an excited state and at the wavelength 330-350 nm. In this case, fluoresce depends on the thermal treatment and is connected to the loss of nutrients in proteins. This method was first validated on milk samples and then was studied on breakfast cereals. Birlouez-Aragon and others (1998) studied the FAST index in manufactured and commercial samples of extruded cereals, as well as the correlation between lysine loss and hydroxymethylfurfural creation. Therefore, the fluorescent method FAST is an interesting alternative for the nutritional value evaluation of grain products subjected to different types of temperature treatment.

The method of molecular fluoresce allows the identification of falsification of milk (Ischenko, 2018) due to changes in absorption specters and fluoresce at 330-420 nm.

In their study, Ríos-Ríos and others (2018) reported the formation of 2-furoymethyl amino acids (2-FM-AA) that indicate the occurrence of the Maillard reaction during the black garlic production. They also determined the content of furosine with the help of ion pair RP–HPLC–UV. Analysis was carried out on samples produced via traditional methods – convective drying (CDP), and ohmic heating (OHP). Besides furosine (2-FM-lysine) 2-furoymethyl-γ-aminobutyric acid and 2-FM-arginine were identified. Furosine levels were higher in the samples created via convective drying (46.6-110.1 mg/100 g of protein) than in ohmic heating samples (13.7–42.0 mg/100 g of protein), probably because of harsher treatment conditions used in the first case. These results highlight the suitability of 2-FM-AA as chemical indicators in the monitoring of the garlic treatment process for the purpose of obtaining high-quality products.

In the study of different types of orange juice del Castillo and others (2000) showed the formation of 2-furoymethyl derivatives of aminobutyric acid (2-FM-GABA) and arginine (2-FM-Arg) as early indicators of non-enzymatic browning. Thus, in the dehydrated orange juice presence of 2-FM-GABA and 2-FM-Arg was determined after the very first day of storage at 30 °C. In this type of juice, the amount of these two compounds increased with the increase in temperature (30, 50 °C) and storage time (1-7 days). Formation of 2-FM-GABA and 2-FM-Arg in the liquid orange juice heated to manufacturing conditions was not detected. According to the received results, the content of 2-FM-GABA and 2-FM-Arg can be used as an indicator for the evaluation of the main changes caused by the Maillard reaction during the manufacturing process and/or storage of concentrated orange juice.

Aside from the creation of color and taste, Maillard reaction impacts the aroma. However, the key aromatic compounds often are present only in residual concentrations from 1 mcg/kg to 1 mg/kg. Nevertheless, they contribute to the creation of appropriate taste due to the low threshold of smell perception. Even though intermediate Maillard reaction products such as Amadori products and deoxyosones are formed in decent quantities during the model reactions, the yield of the aromatic compounds, especially ones containing nitrogen and sulfur, is often low (0.001-0.01%), which indicates their formation via adverse reactions. Thus, Cerny (2008) claims that volatile Maillard reaction compounds that determine food taste are typically present in small quantities. Oxygen-containing aromatic compounds such as 2,3-butanedione, 2,3-pentanedione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(3H)-furanone (sotolon), and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furaneol; Firmenich, Switzerland) occur in concentrations from 1 mcg/kg for soloton to 100 mg/kg for 3-methylbutanal and furaneol. At the same time, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, and 2-acetyl-1-pyrroline are examples of nitrogen-containing aromatic compounds. They are present in food in concentrations 0,001-10 mg/kg. Overall, sulfur-containing aromatic compounds of the Maillard reaction are the most powerful aromatic compounds, and despite their small quantities, they often play a dominant role in the taste of boiled meat and roasted coffee. For example, it can be 2-furfurylthiol, 2-methyl-3-furanthiol, 3-mercapto-2-penthanone and methional.

Xu et al. (2019) came to the conclusion that the Maillard reaction in the temperature-influenced water environment combined with vacuum dehydration is a new and perspective way for obtaining intermediate Maillard reaction products (MRIs), such as products of Amadori rearrangement or Heyns rearrangement that are deemed important non-volatile precursors of aroma with stable physicochemical properties compared to the Maillard reaction products (MRP). MRIs obtained from glutamic acid and xylose are a potential replacement for MRP in the manufacturing of artificial flavors.

Fermented hydrolysates are used as reagents for artificial meat flavors (Cheserek et al., 2013; Lieske, 1994; Liu et al., 2012; Song et al., 2008). Lieske and others (1994) reported that peptide fraction 2000-5000 Da in chicken fermented hydrolysate is responsible for the intense aroma of fried chicken. Meanwhile, Liu and others (2015) showed that in the MRP of chicken fermented hydrolysate peptide fraction with less than 500 Da facilitated the fried chicken aroma, peptide fraction with more than 1000 Da, formed by crosslinking peptide fraction with less than 500 Da, added kokumi taste, while peptide fraction with more than 3000 Da contributed to the bitter taste. A study by Kang et al. (2019) demonstrated the possibility of using RP-HPLC (F-3-F-8) fractions as peptide flavor precursors for artificial flavor creation. However, the amount of literary sources regarding structural properties and action mechanisms of peptides that participate in the meat compound formation via the Maillard reaction is not yet sufficient. Further research in the formation mechanisms of meat aroma and flavor-active compounds from MRP and MRIs is prospective for the identification of flavor compounds.

Paresto's research (2019) refers to the profiling of volatile compounds in Madeira wines and their connection to odor descriptors. A connection between varietal, enzymatic, and aging aromatic compounds and their odor descriptors was established via sensory analysis of Madeira wine. It can be seen that, based on aroma composition, the grape variety is an important parameter that affects the sensory properties of young Madeira wines, while aged wines are greatly impacted by the aging process. The Maillard reaction and oak diffusion were the most influential factors connected to these descriptors. A detailed database of volatile compounds found in Madeira wines and corresponding odor descriptors can be a prospective instrument for winemakers to use for the identification of wine odor, its age, and the grape variety it was made from.

Therefore, Maillard reaction products can be utilized as markers for falsification identification and detection in a wide range of food products. However, the number of developed methods is insufficient, and their use in practical foodstuff expertise remains limited.

It is known that controlling the baking process by color is a key factor for the research of the milk baking process, which is vital for manufacturing such products as baked milk, ryazhanka, and condensed milk.

The Maillard reaction can be used to monitor acrylamide levels in food products (acrylamide content is strictly controlled).

Conclusion

1. The Maillard reaction is important for the food technology reaction based on the interaction between sugars and amino acids. Despite the fact that the Maillard reaction is traditionally associated with cooking and taste development, it has several prospective uses in the study of food products.
2. The Maillard reaction plays an important role in food product quality. For example, this reaction greatly impacts the taste and odor of different food products. Knowing specific compounds that are formed during the browning process via the Maillard reaction, flavor profiles of various products can be better analyzed and evaluated, which is very useful for the development and optimization of recipes for new types of products.
3. The Maillard reaction is responsible for the development of desired color in food products, such as golden-brown crust on bread or saturated brown color of roasted coffee beans. Methods of measuring color can be used for the quantitative identification of browning degree by Maillard, at the same time gaining important information about the quality and texture of the product.
4. The Maillard reaction is widely used in researching safety parameters. It was established that the Maillard reaction products suppresses the growth and development of such microorganisms as *Escherichia coli, Listeria innocua*, *Listeria monocytogenes, Salmonella enterica, Bacillus cereus, Brevibacillus brevis, Pseudomonas aeruginosa,* and *Staphylococcus aureus*.
5. Simultaneously, the Maillard reaction requires control over the heat treatment process at 120 ºC since it can lead to the formation of acrylamide, which has mutagenic and carcinogenic properties.

6. Evaluation of nutritional value: the Maillard reaction can impact nutritional composition by changing the availability of specific nutrients and creating new compounds with potential health effects. A more detailed and thorough study of the Maillard reaction in food products can help scientists understand its impact on the bioavailability of certain nutrients, protein absorption, etc.
7. Falsification identification and detection in food products: unique chemical fingerprints created via the Maillard reaction can be used to identify fraud, falsification, and forgery of food products. By analyzing the Maillard reaction products in food samples, researchers can compare them to the established profiles to verify their authenticity and quality.
8. Evaluation of shelf life: monitoring of the Maillard reaction progression during storage can provide an understanding of the shelf life stability of food products. Changes in browning by Maillard with time can indicate the development of off-flavors, texture deterioration, and other quality problems tied to food spoilage.

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