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Evaluation of Potentially Food-Borne Beneficial and Toxic Chemical Compounds Formation during Maillard Reaction

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Review Article

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ABSTRACT

Maillard reaction is of utmost important in food technology as it demonstrate the both pros and cons of various thermal treatments on food products. Maillard reaction is mainly heat oriented reaction as higher temperature causes its evaluation attributes towards different thermally treated or processed food products. As, desirable flavoring, taste, coloring properties, melanoidins, N-methylpyridinium; pronyl-lysine formation highlight the significance of maillard reaction in food industry. However, recent studies by many reliable authorities and researchers also identify some potential negative aspects of maillard reaction. Acrylamide, Hydroxymethylfurfural (HMF) are declared as potentially carcinogenic toxicants. These compounds are closely related with heat as high temperature climbed their concentration in food. Besides this, due to excessive heating loss of many vitamins, minerals and other healthy compounds occur. In dairy industry, overall, maillard reaction pose off- flavour and taste along with nutritional loss of many constituents. Mitigation strategies are devised and proposed to overcome these issues. Still, safety concerns pertaining to food needs more structural framework to identify and minimize these toxicants.

INTRODUCTION

With the discovery of Maillard reaction i.e., more than 100 years ago, still it's a key reaction in Food Science discipline that describes the reaction between amino acids and sugars and its resultant products. One of the most important flavour-producing reactions in cooking is the Maillard reaction. Maillard reaction is also referred as the "browning reaction" in cooking process owing to its brown colouring property which is both useful and undesirable in food products. Cooked meats, seafood, coffee, dairy products, confectionary and bakery products and other protein-laden foods change its colour in brown when undergoes heating process. Moreover, caramelization is also a source of brown colour during high temperature processing operations. The Maillard Reaction produce brown colour with characteristic flavour in various food stuff through a series of complex reaction between proteins and carbohydrates and rearranging the amino acid structure. The important thing about the Maillard reaction isn't the colour, it's the flavours and aromas. Indeed, it should be called "The Flavour Reaction" not the "browning reaction". The molecules it produces provide the potent aromas responsible for the characteristic smells of roasting, baking, and frying. This reaction commence with simple indication but in chemistry involve hundreds of complex molecules formation. Most of these new molecules are produced in incredibly minute quantities, but that doesn't mean they're unimportant. Similarly in case of milk during processing various flavouring and aromatic compounds are formed. These compounds are likely undesirable with respect of milk product. Medical science many of the complications caused by the undesired glycation of proteins in the presence of an excess of sugar, i.e., in diabetic conditions, arose from the formation of MR products, medical doctors refer to it as protein glycation, which impaired the functionalities of proteins. The loss of thermal labile compounds such as vitamins as well as essential amino acids (lysine, tryptophan) and/or the formation of undesired tastes and off-flavours are well established phenomena bringing about a loss in the nutritional value and sensorial quality of heated foods. The main issue is release of many hazardous compounds, the so-called food-borne toxicants i.e., compounds that are not naturally present in foods, but that may be developed during heating or preservation and that reveal harmful effects such as mutagenic, carcinogenic and cytotoxic effects. Well known examples of these foodborne toxicants are heterocyclic ammines, nitrosamines and polycyclic aromatic hydrocarbons. However, besides this

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some useful compound are also formed like N-methylpyridinium, pronyl-lysine and melanoidins.

LITERATURE REVIEW

Maillard Reaction

It's a chemical reaction between amino acids and reducing sugars that gives browned food its distinctive flavour. It is named after French chemist Louis-Camille Maillard, who first described it, while attempting to reproduce biological protein synthesis. Hodge [1] elaborated the steps first time involved in Maillard reaction products (MRPs), regarded as advanced Glycation end-products (AGEs). This is non- enzymatic browning reaction that imprint its significance in almost every discipline of thermal food processing. However, important thing to be considered the evaluation of its suitability for health and nutrition in every maillard carrying food product.

Stages of Maillard Reaction

Initial stage

In first stage an unstable Glycosylamine (Imine) formation occur through the condensation reaction between sugar and amino acid. Amadori compound, an aminodeoxyketose is formed through the rearrangement of glycosylamine [2].

Advance stage

In advance stage breakdown of the amadori compound occur through the enol form results in formation of Ketosamine product.

Final stage

The ketosamine products then either dehydrates into reductones and dehydro reductones, which are caramel, or products short chain hydrolytic fission products such as diacetyl, acetol or pyruvaldehyde which then undergo the Strecker degradation. Finally result in very complex mixtures, including flavour compounds and brown high molecular weight pigments melanoidins.

DISCUSSION

Chemical Compounds Associated with Maillard Reaction

During various stages of Maillard reaction various chemical compound formation occur with complex nature. These compounds are vary in their chemistry as well as effects on consumers. Researchers have found various compounds with their various organoleptic properties.

Beneficial aspects

Melanoidins formation occurs in Maillard Reaction [3]. N-methylpyridinium; pronyl-lysine formation may oocur. Flavouring compounds especially compounds with low molecular fission energy during Amadori's degradation process. During Advance Maillard reaction antioxidents formation occurs [4] which stated that antibacterial compounds formation may occur.

Melanoidins

Melanoidins are polymeric higher molecular weight compound that commonly exist in thermally processed food products. It comprised of nitrogen with brown in color [5]. The main proportion of melanoidins found in coffee and bakery products. In bakery and cereal products melanoidins is mainly present in crust. Borrelli and Fogliano [6] reported that in bread melanoidins proportion is directly proportional to the thermal input potency and bread melanoidins can be extracted by using the enzymatic digestion method. Apart from color impartment, melanoidins plays important role in quality and nutrition through it various useful properities to improve food products and human health. Melanoidins act as antioxidant [7]. This antioxidant activity has been observed in coffee, Bread crust, vinegar, honey [8], meat flavoring, particular components responsible for antioxidant activity in melanoidins are not yet explored, but its protecting role in food quality is significant. Melanoidins depicts the antimicrobial activity which is more affective against Gram-positive bacteria than Gram-negative bacteria [9]. Melanoidin's higher antioxidant activity against gram positive bacteria is owing to lack of protective outer membrane [10]. Melanoidins pose no genotoxic threat to human health as its low dose is safe for health [11]. Melanoidins also identified as potential anti-hypersenstive [9], prebiotic activity as to facilitate the growth of *Bifidobacteria*, *Lactobacilli*, *Bacteroides*, *Clostridia* in gastrointestinal tract (GIT) tract [6,12].

Characteristic flavor formation

Maillard reaction especially in milk and dairy products besides off- flavor activity also provide many desirable and characteristic flavors or precursor in flavor compounds. As this is heat oriented process, so dairy products usually goes through maillard reaction under industry by pasteurization or UHT treatment and also in household cooking. Chemistry of flavoring compound in maillard rection is very complex as hundreds of compounds are involved in specific products. These include Oxygen-Containing Compounds (Furans and pyrans), Nitrogen-Containing Compounds (Pyrazines, Oxazoles and Oxazolines, Pyrroles, Pyrrolines), Sulphur-Containing Compounds (thiols, sulphides, disulphides, Furanthiols). However, in general, sulfur compounds considered

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as active constituent in flavor formation and yet no exact chemical reaction series identified mostly researcher's support their ideas by using various modelling systems. Jousse et al. [13] identified that flavour formation during maillard reaction depends upon the temperature, time, pH, water content, and amino acid or sugar type. In dairy industry butter, cheese, ghee, chocolate are good illustration of flavour rich products as when applied in different food products through various processing and cooking techniques, flourish the flavour by imparting more intense and durable thermal operations.

Harmful aspects

Swedish National Food Administration [14] has declared Acrylamide and Hydroxymethylfurfural (HMF) a Food- Borne toxicants, carcinogens formed during Maillard Reaction. Development of off-color and off-flavor during maillard reaction. Loss of heat sensitive minerals and essential amino-acids especially Lysine and Tryptophan [15].

Acrylamide associated with Maillard reaction

Acrylamide first declared to be a foodborne carcinogen by Swedish National Food Administration [14] as it reported in many carbohydrates- based food products like potato chips, bread, coffee beans. According to European Food Safety Authority Acrylamide, does not exist in the raw materials of food products. But, when heating these materials under certain critical temperature i.e., above 120°C especially carbohydrates containing foods produce acrylamide through the maillard reaction between reducing sugars and free amino acid especially asparagine [16,17]. Granvogl and Schiberle stated that during maillard reaction upon enzymatic decarboxylation of free asparagine an intermediate is formed i.e., 3-APA and produce acrylamide with heating even without carbonyl source. Enzymatic decarboxylation of asparagine may also result in acrylamide [18]. Stadler and Scholz [19] described the acrylamide formation through acrolein and acrylic acid. Casado et al. [20] declared through their findings that in sterilized olives peptides/proteins are precursor for acrylamide formation. European Food Safety Authority [21,22] (efsa) in June issued a report in which mentioned the overall sources, causes, and effects of acrylamide on the human health. According to WHO potential risk assessment strategies must be improved to explore the nutritional and biological linkages of acrylamide. Acrylamide is mainly formed in food i.e., Baked, Grilled, Roasted, usually absent in boiled and microwaved food. In March, the United States Environmental Protection Agency (US-EPA) [23] reported about the risk and hazard dose-response assessment to lethal activity of acrylamide through conducting tests on animals to obtain references values of carcinogenic activity for humans in multiple tissues and degenerative peripheral nerve damage. Federal Institute for Risk Assessment (BfR) [24] revealed through the series of testing process that acrylamide intake relation with cancer development is inconsistent [24]. Health Canada presented a detailed acrylamide dietary exposure and its assessment to cause chronic cancer through series of observations showed that acrylamide is a potential health concern [25]. The Danish National Food Institute (DTU) reported that depicts about contaminants of food observed for the period 2004–2011. In this period Danish population's dietary intake especially for those products that are potential source of acrylamide was observed with the conclusion that acrylamide is significant for food safety [26]. The Food Standards Australia New Zealand (FSANZ) revealed through a comprehensive report on 24th Australian Total Diet Study (TDS), in which acrylamide also considered through research and experiment's by observing the behavior of various food and beverages as dietary intake source of acrylamide and declared that acrylamide is a genotoxic and carcinogenic for human health [27]. The National Toxicology Program (NTP) explored that AA is human carcinogen through logical anticipation [28]. The International Agency for Research on Cancer (IARC) categorized acrylamide as Group 2A carcinogen i.e., may be carcinogen to human health [29]. Acrylamide when ingested it is absorbed in Gastrointestinal Tract (GIT) and metabolized. These metabolites moves to all major body organs and parts especially Glycidamide. Glycidamide reacts with DNA to form DNA adducts and is more reactive to DNA than acrylamide. Characterization of glycidamide-DNA adducts to check its reactivity. Several mitigation strategies for acrylamide are proposed and tested by various researchers as it mainly evident in potato and cereal based products but less in dairy products. Capuano and Fogliano [30] described the feasible mitigation approaches like varietal improvement, recipe modification, and addition of certain proteins, amino acids, acidulants, enzymes, cyclodextrin, natural antioxidants or antioxidant extracts etc. Replacement of reducing sugars with sucrose and of ammonium bicarbonate with sodium bicarbonate). Alteration in process like change in baking and frying time and temperature as well as pH level of various ingredients of the products. Up to now, most beneficial and authentic tool to control acrylamide is addition of an enzyme asparaginase [30]. Its main activity is to catalyze the hydrolysis of asparagine in aspartic acid and ammonia hence reducing the precursor asparagine concentration.

Hydroxymethylfurfural (HMF) associated with Maillard reaction

The hydroxymethylfurfural (HMF) or 5- Hydroxymethylfurfural gained attention since 19th century as many renowned group of scientist paid special attention to this chemical compound. In 1895 two scientists worked independently and explored the synthesis method and chemical behaviour by Dull and Kiermeyer and introduced term ''oxymethylfurfurol". Middendorp published a detailed sketch about the synthesis, physical, chemical behaviours and other important concepts about HMF. More than thousand research paper has been published that shows the worth of HMF. There are different HMF formation pathways i.e., under acidic condition, high temperature [3], low temperature, dry and pyrolytic condition [31]. HMF can be formed through the glucose and fructose reaction with dicarbonyl intermediate 3-deoxyglucosone (3-DG) by Maillard and Caramelization reactions [31]. Pasteurization, cooking and storage mainly source of hydroxymethylfurfural (HMF) in foods. Although, HMF is also present in small quantities in sugar-containing foods including Milk, honey, fruit juices, spirits, and bread. Storage conditions with high acidic conditions also produce HMF in food. The compound hydroxymethylfurfural (HMF) or 5 - Hydroxymethylfurfural is an organic

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compound that is produced by acid-catalyzed dehydration of sugars primarily fructose. Sucrose undergoes decomposition process with the release of glucose or fructose. But most critical is the release of reactive intermediate, fructofura-nosyl cations. These positive ions readily converted into HMF as temperature climbed to 250°C or more in the presence of dry pyrolytic conditions [31]. HMF is evident by many researcher findings in carbohydrates based food products processing like frying, baking and roasting. Occurrence of HMF in processed food especially in fried food products and is frying material is critical in safety and health concerns as it can move directly into frying material. HMF production mainly depends upon type of sugar and amino acid. Moreover, they revealed that amino acids glutamine, aspartic and glutamine acids lead to higher production rate of HMF while lysine, arginine, and histamine are reduced indicator of HMF synthesis. Besides amino acid and sugar type, Temperature, water activity, pH, time, leavening agents [32] plays a worth mentioning role in HMF production. HMF concentration is varies in different food products but, domestic storage and cooking conditions may strongly affect the actual exposure to HMF. Dried fruits, plums, grapes and roasted coffee are main source of HMF. Although, fresh fruits depicts relatively low level of HMF concentration. Estimated intakes range between 4 and 30mg per person and day. HMF daily intake level is not significant but several investigations has declared it as potentially carcinogenic and mutagenic. Removal of HMF from different food products is difficult task as its desirable colour, taste and aroma production in maillard and caramelization reactions. But suitable techniques are used to stop the contents of HMF in foods through the reconstruction of product recipe reducing the cooking and frying temperature and time high hydrostatic pressure, fermentation, ionization radiation, vacuum technology and ingredients addition like poly unsaturated fatty acids, carotenoids, ascorbic acid [26].

Development of off-flavour and off-colour

Flavor and color of various food products has prime value as it directly influence the consumer acceptance level. McSweeny, Nursten, and Urbach find out that milk flavor is a combination of more than 200 volatile compounds. Milk and dairy products are main areas where maillard reaction and lipid oxidation not only cause the negative flavor but also poor color development. Sederstrom and Peterson [33] identified that maillard reaction produce three off-flavour compounds that are responsible for ''cooked'' flavor in UHT milk denoting that maillard reaction is vital in off-flavor formation during thermal treatment of milk and to demonstrate the effective and feasible pathway to overcome this issue. Pasteurized and heat treated milk possesses an odor different from raw milk, probably from formation of such volatile substances as ammonia, hydrogen sulfide, mercaptans, and volatile phosphorus compounds that occur from protein breakdown. UHT treatment deals with intense temperature at about 135-140°C. this thermal treatment induces severe changes in the milk chemistry trough maillard reaction. Kokkinidou and Peterson identified that phenolic compounds are considerably effective to control the maillard reaction off-flavor formation in UHT milk during heat treatments and storage activity thus increasing the consumer acceptance rates. Milk color is also change when it goes through thermal treatments as thorough heating induce brown color in milk products. Brown color in dairy products is undesirable and deviate from consumer preference.

CONCLUSION

Maillard reaction is considered undeniable phenomena especially in products that undergoes intensive temperature. This reaction has variable chemistry in each heated or processed food and resulting food borne molecules are also vary. However, acrylamide is mostly noticed food-borne toxicant by several global research organizations and it considered hazardous for human being as its genotoxic and carcinogenic properties. Besides, HMF is also a threat having nearly similar effect on human community. These food borne toxicant's concentration fluctuate in different food items. Although, many factors contribute in these compounds formation, but most critical factor is temperature as higher temperature pronounce these toxicants amount in processed food. Temperature modification along with other measures can reduce its quantity. Loss of nutritional components like minerals, vitamins due to high processing heat especially in dairy products is reported. Brown color that is recognition of maillard reaction is good for some products but it at the same time problematic in other food combinations. Flavoring molecules produced in large number during this reaction, but due to various intermediates and processing factors, off-flavor synthesis occur that result in product damage in sensory evaluation.

CONFLICT OF INTEREST

There is no conflict of interest regarding this article.

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