Frequently Asked Questions:

1) What is Maillard reaction? Mention the different stages of Maillard reaction.

Ans: Maillard reaction is called the carbonyl-amine reaction, between free amino groups from amino acids, peptides, or proteins and the carbonyl group of a reducing sugar such as ribose, glucose, fructose and galactose. The sugar moiety is a reducing sugar with a free carbonyl group. The end-product is the melanoidins, which are the brown pigments. The different stages of Maillard reaction are sugar-amine condensation, Amadori rearrangement, sugar dehydration, sugar fragmentation, amino acid degradation, aldol condensation, aldehyde-amine polymerization and formation of heterocyclic nitrogenous compounds.

2) What is caramelization? What are the different intermediates formed during the process?

Ans: When sugars are treated under anhydrous conditions with heat, or at high concentration with dilute acid, caramelization occurs, with the formation of anhydro sugars. Glucose forms glucosan or l,2-anhydro-α-D-glucose and levoglucosan or 1,6-anhydro-β-D-glucose with a specific rotation of +69° and -67° respectively. With similar treatment, fructose gives rise to levulosan or 2,3-anhydro-β-D-fructofuranose. Simultaneous hydrolysis and dehydration take place when sucrose is heated at about 200°C, and followed by a rapid dimerization. These compounds are characterized by isosacchrosan, which is a sucrose molecule one molecule of water lesser. Following this, polymerization reactions take place, which in the end form pigments similar to those formed in more concentrated solutions, or at higher temperatures. The intermediates formed during the reaction are caramelan, caramelen and caramelin.

3) Define ascorbic acid browning.

Ans: Browning of ascorbic acid can be briefly defined as the thermal decomposition of ascorbic acid under both aerobic and anaerobic conditions, by oxidative or non-oxidative mechanisms, either in the presence or absence of amino compounds.

4) Explain in detail the process of ascorbic acid browning.

Ans: In the presence of oxygen, ascorbic acid is degraded primarily to dehydro ascorbic acid (DHAA). DHAA is not stable and spontaneously converts to 2,3-diketo-l-gulonic acid. Under anaerobic conditions, ascorbic acid undergoes the generation of diketogulonic acid via its keto tautomer, followed by β elimination at C-4 from this compound and decarboxylation to give rise to 3-deoxypentosone, which is further degraded to furfural. Under aerobic conditions, xylosone is produced by simple decarboxylation of diketogulonic acid and that is later converted to reductones. In the presence of amino acids, ascorbic acid, DHAA, and their oxidation products furfural, reductones, and 3-deoxypentosone may contribute to the browning of foods by means of a Maillard-type reaction.

5) Explain the enzymatic and non-enzymatic lipid browning reactions that occur in food.

Ans: Lipid oxidation is the major reason for browning. It occurs in oils and lard, and also in foods with low amounts of lipids, such as products of vegetable origin. This reaction arises from free radical or reactive oxygen species generated during food processing and storage, hydroperoxides being the initial products. These compounds are quite unstable further leading to many reactions and pathways. The enzymatic oxidation of lipids occurs sequentially. Lipolytic enzymes can act on lipids to produce polyunsaturated fatty acids that are then oxidized by either lipoxygenase or cyclooxygenase to form hydroperoxides or endoperoxides, respectively. Later, these compounds suffer a series of reactions to produce, among other compounds, longchain fatty acids responsible for important characteristics and functions. Via polymerization, brown-colored oxypolymers are produced subsequently from the lipid oxidation derivatives.

6) What are the factors that influence non-enzymatic browning reactions?

Ans: A number of factors can affect non-enzymatic browning. Among these are pH, temperature, moisture content, time, concentration, and nature of the reactants.

Temperature: The rate of browning increases with rising temperature. In model systems the development increases 2 to 3 times for each 10°C rise in temperature. In natural systems, particularly those high in sugar content, the increase may be faster.

pH: Although browning reactions usually slow down as the pH decreases until the optimum stability pH for reducing sugars is passed, this is not so important for food products. Maillard reaction and ascorbic acid degradation is faster at an alkaline pH or a nearly dry state.

Moisture: The moisture content seems to have an important effect on the rate of browning. It is quite likely that for moisture contents above 30% a decrease in reaction is caused by dilution.

Acids: The development of brown color in dried fruits is largely caused by the reaction between amino acids and glucose, a reaction which is speeded by the presence of organic acids.

Fermentation: The formation of ketoseamines in dried whole egg or egg white is avoided by fermentation of the glucose before drying.

Oxygen: Removal of oxygen decreases the rate of browning reactions especially in ascorbic acid oxidation.

Technologies: Modified-atmosphere packages, microwave heating, ultrasound-assisted thermal processing, pulsed electric field processing and carbon dioxide-assisted high-pressure processing are some examples of technological processes that allow ascorbic acid retention and consequently prevent undesirable browning.

7) When is non-enzymatic browning reaction desirable?

Ans: Processing such as baking, frying, and roasting are based on the Maillard reaction for flavor, aroma, and color formation. Maillard browning may be desirable during manufacture of meat, coffee, tea, chocolate, nuts, potato chips, crackers, and beer and in toasting and baking bread. In foods, antioxidant properties of Maillard reaction products have been found in honey and in tomato purees.

8) When is non-enzymatic browning reaction undesirable?

Ans: In processes such as pasteurization, sterilization, drying, and storage, the Maillard reaction often causes detrimental nutritional and organoleptic changes such as lysine damage. Other type of undesirable effects produced in processed foods by Maillard reaction may include the formation of mutagenic and carcinogenic compounds such as acrylamide while frying or grilling of meat and fish. The formation of these compounds depends on cooking temperature and time, cooking technique and equipment, heat mass transport, and/or chemical parameters. The Maillard reaction is one of the main reactions causing deterioration of proteins during processing and storage of foods. This reaction can promote nutritional changes such as loss of nutritional quality, attributed to the destruction of essential amino acids or reduction of protein digestibility and amino acid availability.

9) Explain in detail carbonyl-amine condensation in Maillard reaction.

Ans: The carbonyl-amine condensation occurs between free amino groups from amino acids, peptides, or proteins and the carbonyl group of a reducing sugar such as ribose, glucose, fructose and galactose. Among the most reactive carbonyl compounds are α,β-unsaturated aldehydes such as furaldehyde, and α-dicarbonyl compounds such as diacetal and pyruvaldehyde. The reaction which is reversible starts between an aldose or ketose sugar and a primary or secondary amine, the product of which is a glycosylamine.

10) How is Amadori rearrangement different from Heyns rearrangement?

Ans: When glucose reacts with ammonia, glycosylamine is formed. The rearrangement of glycosylamine to form 1-amino-1-deoxy-D-fructose in the presence of an acid catalyst is called Amadori rearrangement whereas in Heyns rearrangement, the reaction is between fructose and ammonia. However the end product of both the reactions is 2-amino-2-deoxy-α-D-glucopyranose.

11) What is Strecker's reaction? Explain in detail the degradation steps involved in the formation of non-enzymatic brown pigments.

Ans: The intermediate stage of Maillard reaction leads to breakdown of Amadori compounds and the formation of degradation products, reactive intermediates such as 3-deoxyglucosone or formation of osones by Strecker's reaction and volatile compounds that lead to the formation of flavor. The 3-deoxyglucosone participates in cross-linking of proteins at much faster rates than glucose itself, and further degradation leads to two known advanced products: 5-hydroxymethyl-2-furaldehyde (HMF) and pyraline. The main pathway for the formation of brown color in foods appears to be degradation and condensation by way of the 1,2-enol forms of the aldose or ketose amines. The amino group of the amino acid at the alpha position to the carbonyl group and the CO_2 release from the carboxyl group of the amino acid moiety produces carbonyl compounds and amines. These dicarbonyl compounds are osones and are active agents for Strecker degradation. Pyrazine compounds with different amounts of substitution are formed in carbonyl-amine reactions and can cause Strecker degradation of the amino acid to form 2,5-dimethylpyrazine from a glucose and glycine reaction. The final stage is characterized by the production of nitrogen-containing brown polymers and copolymers known as melanoidins that are able to cross-link proteins via ε-amino groups of lysine or arginine to produce high molecular weight colored melanoidins.

12) Explain in detail the formation of caramels from isosacchrosan in the caramelization process.

Ans: The formation of isosacchrosan is followed by the formation of various anhydrides of sugar with loss of water molecules. Two molecules of sucrose lose 9% of water to form caramelan, a pigment with the molecular formula of $C_{24}H_{36}0_{18}$.

$$2\ C_{12}H_{22}0_{11} - 4\ H_{2}0 = C_{24}H_{36}0_{18}$$

On further heating, three molecules of sucrose lose eight molecules of water to form caramelen.

$$3\ C_{12}H_{22}0_{11} - 8H_{2}0 = C_{36}H_{50}0_{25}$$

This is followed by the formation of humin, which is an infusible, dark mass with a high molecular weight, and is called caramelin. The molecular formula of caramelin is $C_{125}H_{188}0_{80}$.

13) How is acrylamide formed? How can its formation be controlled in foods?

Ans: Acrylamide is a chemical formed by the reaction of sugar with an amino acid during high temperature cooking methods such as baking, roasting and frying. The formation of carcinogen acrylamide is observed in a range of cooked foods. Moderate levels of acrylamide (5–50 μg/kg) is found in heated protein-rich foods, and higher levels (150–4000 μg/kg) in carbohydrate rich food, such as potato, beet root, certain heated commercial potato products, and crisp bread. It is present at significant levels in fried, grilled, baked, and toasted foods. On the basis of the large number of existing studies, the International Agency for Research on Cancer has classified acrylamide as probably carcinogenic to humans. Raw or boiled foods do not form acrylamide hence, these methods can be employed during cooking.

14) What modern technologies can be employed to prevent non-enzymatic ascorbic acid browning in fruits?

Ans: Modified-atmosphere packages using different concentrations of oxygen, nitrogen and carbon-di-oxide; microwave heating, ultrasound-assisted thermal processing, pulsed electric field processing and carbon dioxide-assisted high-pressure processing have been employed to prevent non-enzymatic ascorbic acid browning in fruits.

15) Explain the different browning reactions that take place within a food matrix.

Ans: Browning reactions that occur in food is mainly classified as enzymatic and non-enzymatic browning. Enzymatic browning involves enzymes oxidize substrates such as phenols and cresols to form undesirable melanins. The non-enzymatic browning of foods include browning which occurs due to the interaction of sugars, proteins and lipids in combination or alone to form brown pigments.