Novel Technologies for Food Processing and Shelf Life Extension
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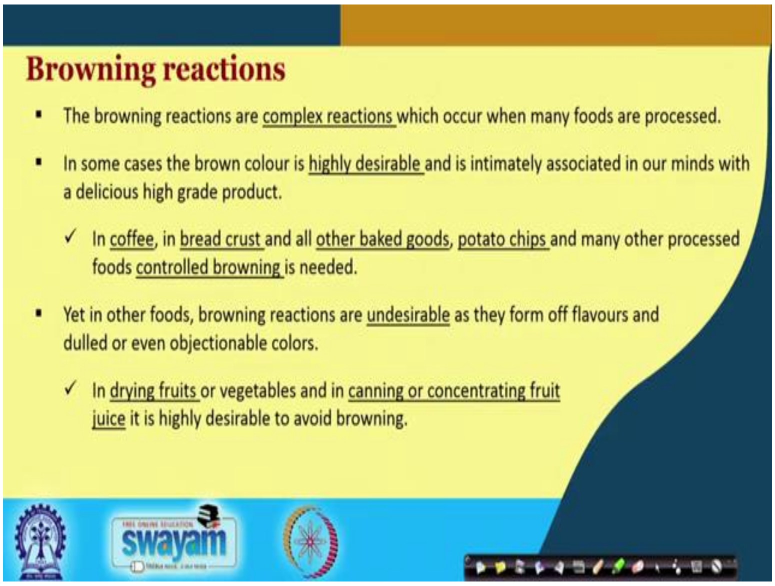
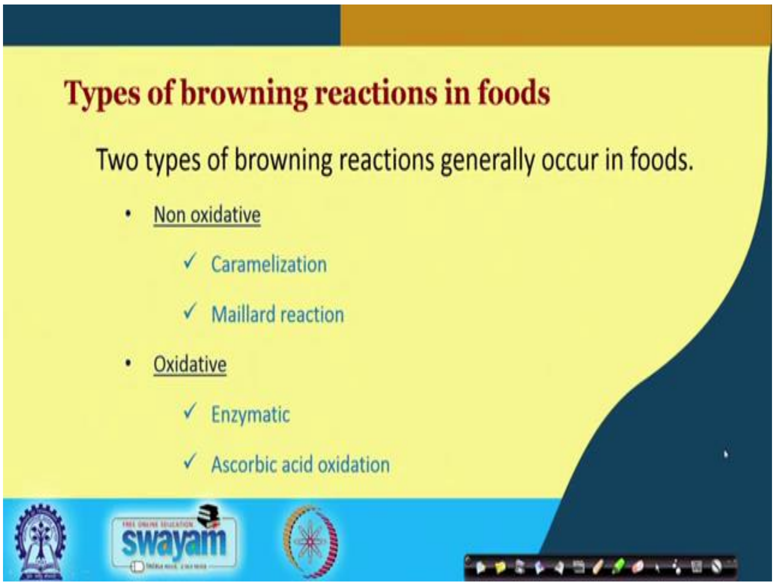
Lecture – 06
Browning Reactions

Browning reactions are important phenomena that occur in many foods when they are exposed to different conditions during processing, handling or storage.



Browning reactions are complex reactions which occur when many foods are processed. In some cases, the brown colour developed becomes highly desirable and are intimately associated with a delicious high grade product. For example, in case of coffee, bread and other baked products. During baking the crust of bread has developed brown colour. In potato chips and many other products, controlled browning is desired. Yet in other foods, browning reactions are undesirable, because, the flavours and colors which are formed in these products as a result of these reactions may sometime produce a foul smell or they may give objectionable colour. In case of drying of fruits or vegetables and in canning or concentrating of fruit juices, it is highly desirable to retard or to avoid browning reactions.



Types of browning reactions in foods

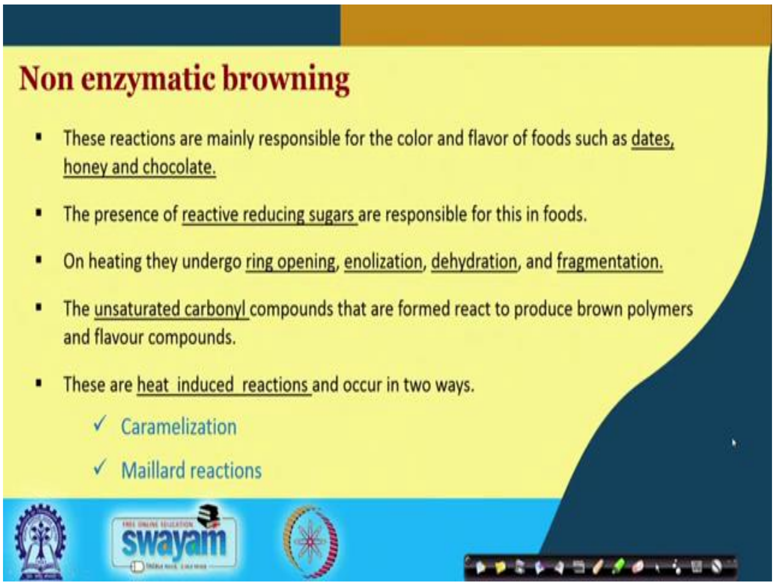
There are two types of browning reactions which generally occur in food.

(i) Non-oxidative browning reaction

- Caramelization
- Maillard reaction

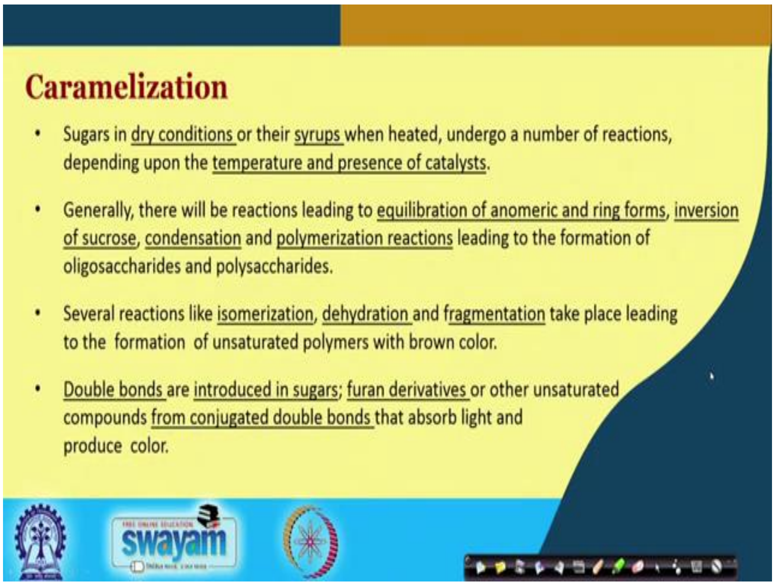
(ii) Oxidative browning reactions.

- Enzymatic
- Ascorbic acid oxidation



Non-enzymatic browning

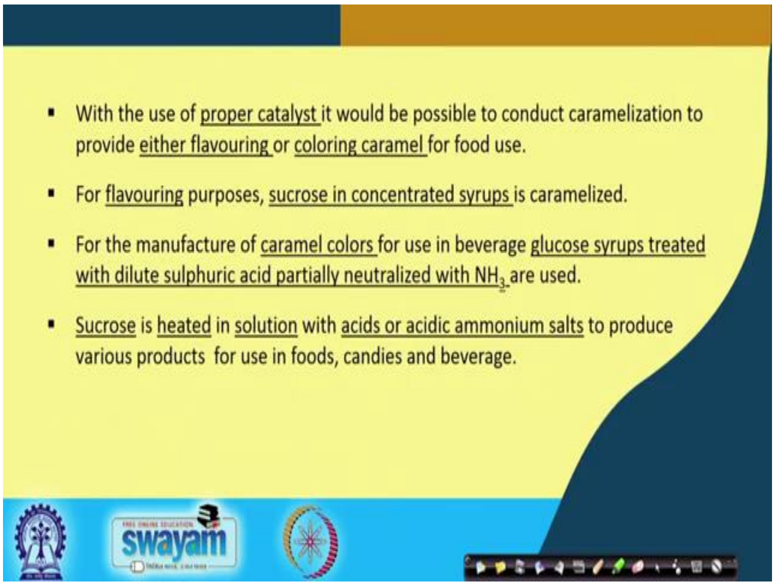
The non-enzymatic browning reactions are mainly responsible for the colour and flavour of many foods like dates, honey, chocolates and so on. In fact, the presence of reactive reducing sugars is responsible for these types of browning reactions in food. When the foods having reactive reducing sugars are heated as in the case of cooking or in such other processes; these sugars undergo ring opening, enolization, dehydration and fragmentation and, as a result of these processes, the unsaturated carbonyl compounds are formed. These unsaturated carbonyl compounds produce brown colour or brown polymer or flavoured compounds in foods. These non-enzymatic browning reactions are generally heat-induced reactions and they can be categorized into two groups; i.e. caramelization and Maillard reaction.



Caramelization

Sugars in dry conditions or in their concentrated syrup form, when heated, undergo a number of reactions depending upon the presence of catalyst or temperature of the heating process. Generally, there are reactions leading to equilibration of anomeric and ring forms. There may be an inversion of sucrose, condensation and polymerization reactions leading to the formation of oligosaccharides and polysaccharides.

Several reactions like isomerization, dehydration, and fragmentation, take place leading to the formation of unsaturated polymers with brown colour. In fact, during these processes conjugated double bonds are introduced in sugars; furan derivatives or other unsaturated compounds that absorb light and produce colour.



However, with the use of proper catalyst, it would be possible to conduct caramelization in a controlled manner to provide either flavouring or colouring caramel for food uses e.g. for flavouring purposes, sucrose in concentrated syrup is caramelized.

For the manufacture of caramel colour for use in beverages, glucose syrup treated with dilute sulphuric acid, partially neutralized with ammonia are used. Sucrose is heated in solution with acids or acidic ammonium salts to produce various products for use in foods, candies and beverages.

Caramel colors

Commercially there are three types of caramel colors are produced.

(i) Acid-fast caramel

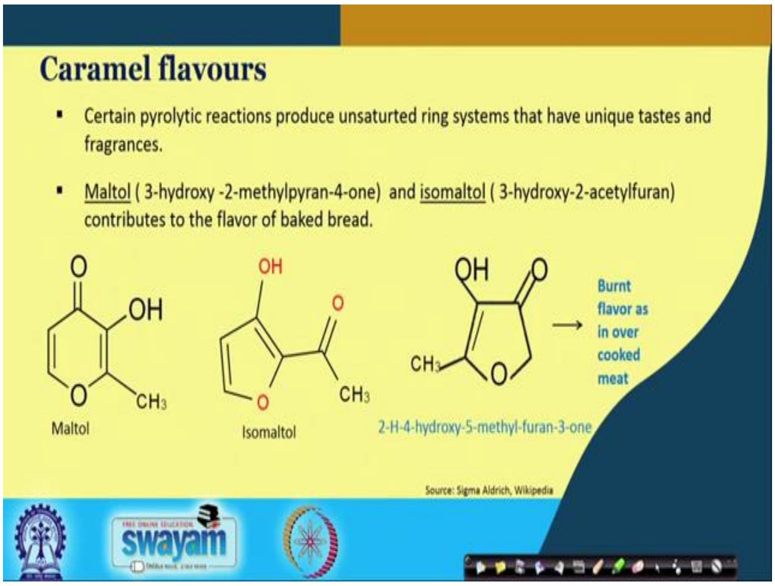
It is the most abundant form of caramel color available in the market and these are made with ammonium bisulphate catalyst to produce the color for cola drinks.

(ii) Brewer colors

These are made by heating sucrose solution with ammonium ion and these colors are used in the brewing industry.

(iii) Baker's color

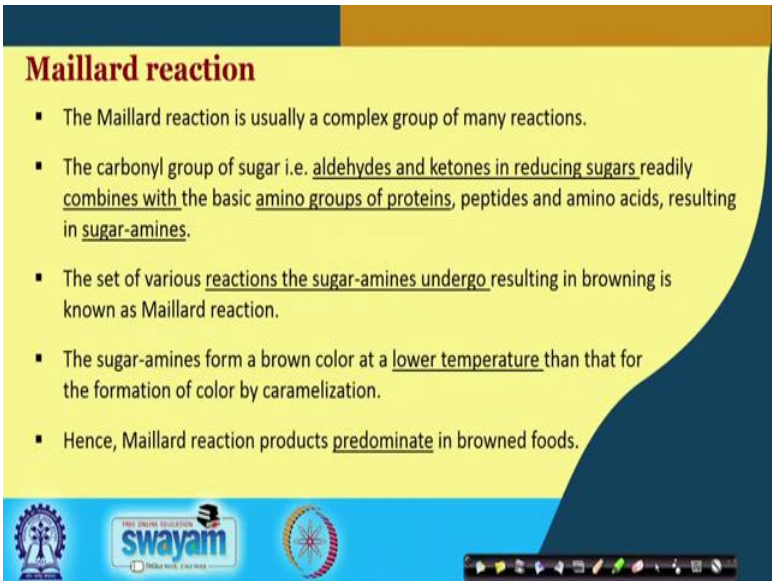
These are produced by direct pyrolysis of sucrose to give a burnt sucrose color. These colors are used in bakery products.



Caramel flavours

Certain pyrolytic reactions produce unsaturated ring systems that have unique taste and fragrances in the materials. For example, maltol and isomaltol contribute to the flavor of many baked products particularly the baked bread.

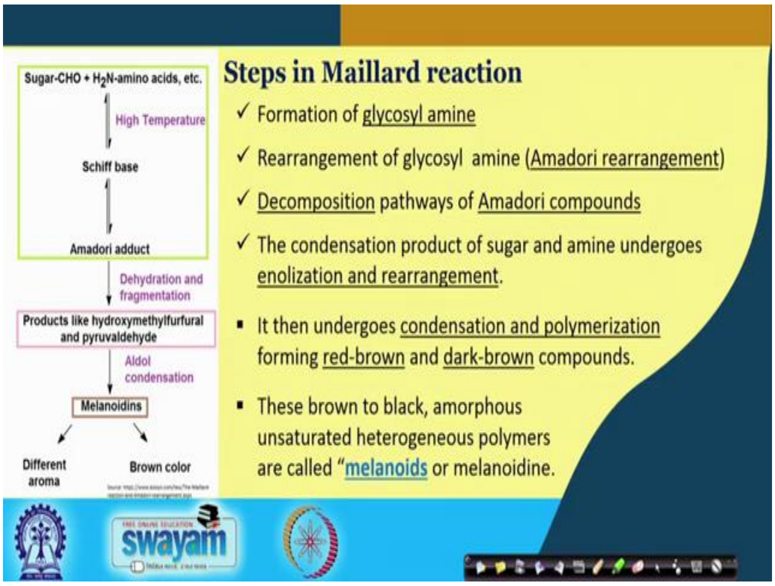
On the other hand, 2-H-4-hydroxy-5-methyl-furan-3-one is a compound which is produced during the process of the browning reactions. This gives the burnt flavor in the overcooked meat or such other materials. The flavor is because of the generation of this compound or related compounds.



Maillard reaction

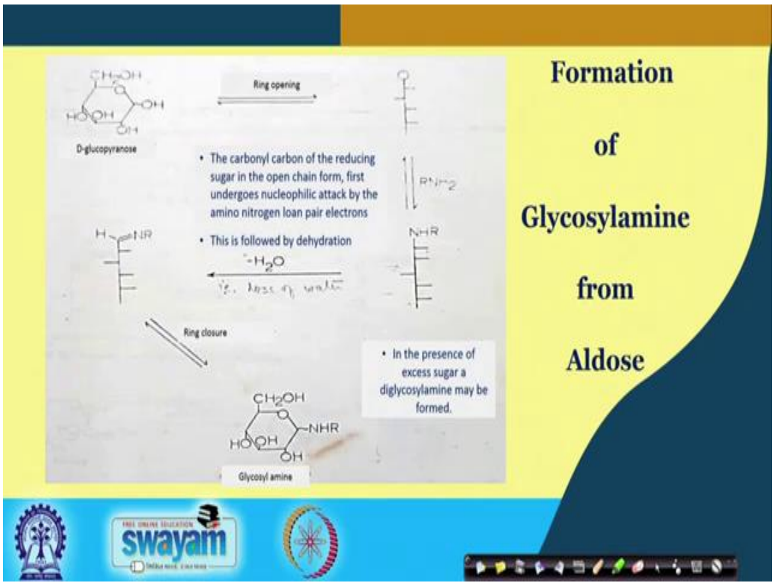
The Maillard reaction is generally a complex group of many reactions. In caramelization reaction, only the free aldehyde group or free ketone group of the reducing sugar is responsible whereas in the Maillard reaction, the interaction between the aldehydes and ketones of the reducing sugar with the free amino groups of the proteins, peptides and amino acids are involved.

The interactions of carbonyl group of the sugar, with the amino group of the protein result in the formation of sugar amines. The set of various reactions that sugar amines undergo resulting in browning is known as Maillard reaction. The sugar amines form a brown color at a lower temperature than that of the formation of the color by caramelization and therefore, Maillard reactions' products generally dominate in brown foods.



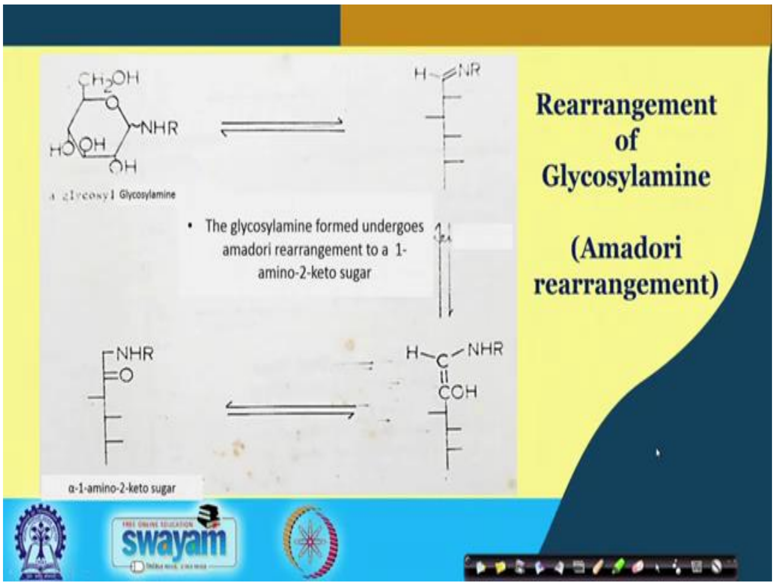
Steps in Maillard reaction

The first step is the formation of glycosyl amine that undergoes rearrangement, generally known as amadori rearrangement or reverse amadori rearrangement depending upon whether aldose sugar or ketose sugar is involved. These amadori compounds then undergo rearrangement or get decomposed. The condensation products of sugar and amine undergo enolization and rearrangement. It then undergoes condensation and polymerization forming red-brown or dark brown compounds. These brown to black compounds, amorphous unsaturated heterogeneous polymers, which are produced as a result of the Maillard reaction, are generally known as melanoids or melanoidins.

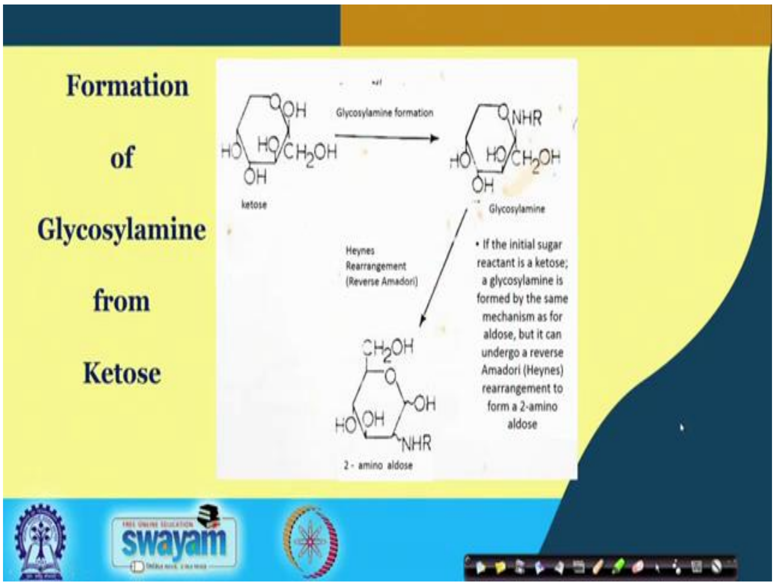


Formation of glycosylamine from aldose

So, as discussed in the earlier slides, the carbonyl carbon of the reducing sugar (see figure) i.e. D-glucopyranose in the open-chain form, first undergoes nucleophilic attack by the amino nitrogen lone pair electron. This is followed by dehydration, ring closure and diglycosylamine is formed in the presence of excess sugar.

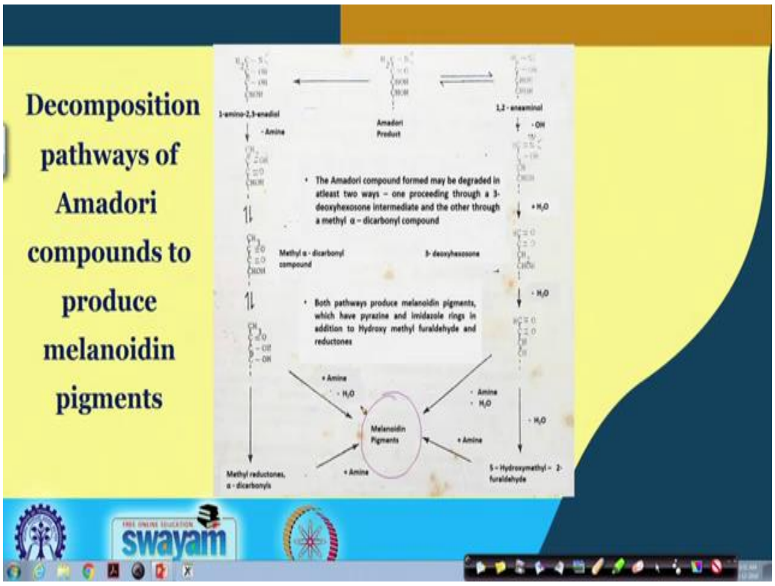


The glycosylamine formed undergoes amadori rearrangement and results in α-1-amino-2-keto sugar.



Formation of glycosylamine from ketose

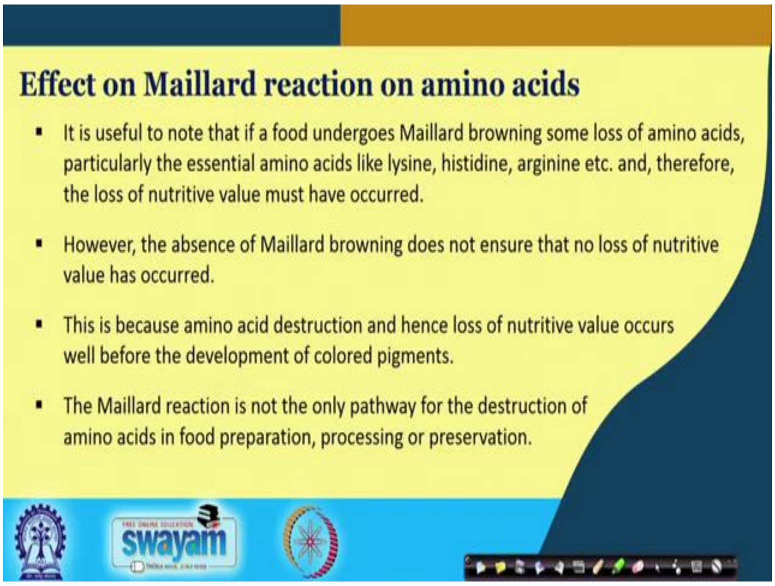
If the initial sugar reactant is a ketose, a glycosylamine is produced in a similar mechanism as it is produced from aldose sugar. However, it can undergo a reverse amadori arrangement which is commonly known as Heyne's rearrangement and it produces 2-amino aldose.



Decomposition pathways of amadori compounds to produce melanoidin pigments

The amadori products or reverse amadori may be decomposed or degraded at least in two ways (see Fig.). One way is proceeding through a pathway leading to the formation of 3 deoxyhexosone intermediate and the other is through the formation of methyl α-dicarbonyl compounds.

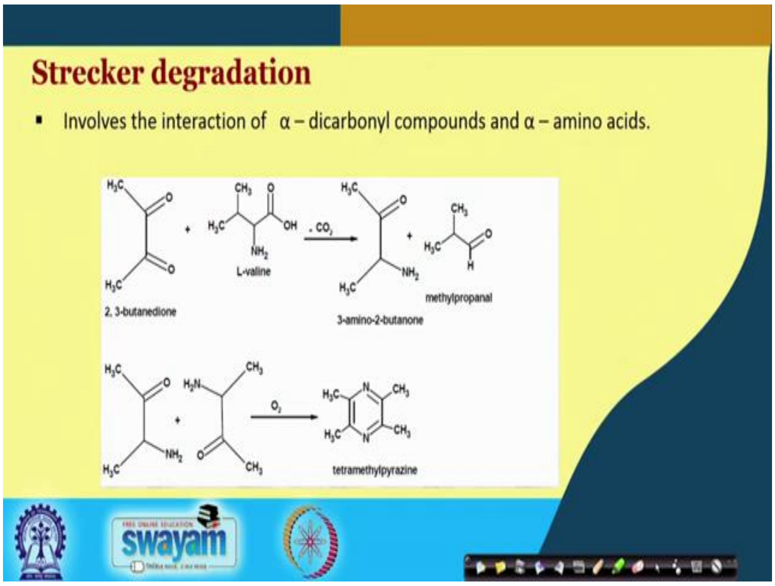
Both the pathways at the end undergo amino dehydration reaction and ultimately produce melanoidin pigments which have pyrazine and imidazole rings in addition to hydroxyl methyl furaldehyde and reductones. These melanoidins usually give the undesirable color or flavor in the materials.



Effect on Maillard reaction on amino acids

In the Maillard reaction, it has been seen that the reaction takes place between the free amino group of the amino acids or proteins and an aldehydic and ketonic group of the reducing sugars in free form. It is obvious that if the amino acid involved in the Maillard reaction is an essential amino acids like lysine, histidine, arginine, etc. then definitely there will be some loss of nutritive value of the food.

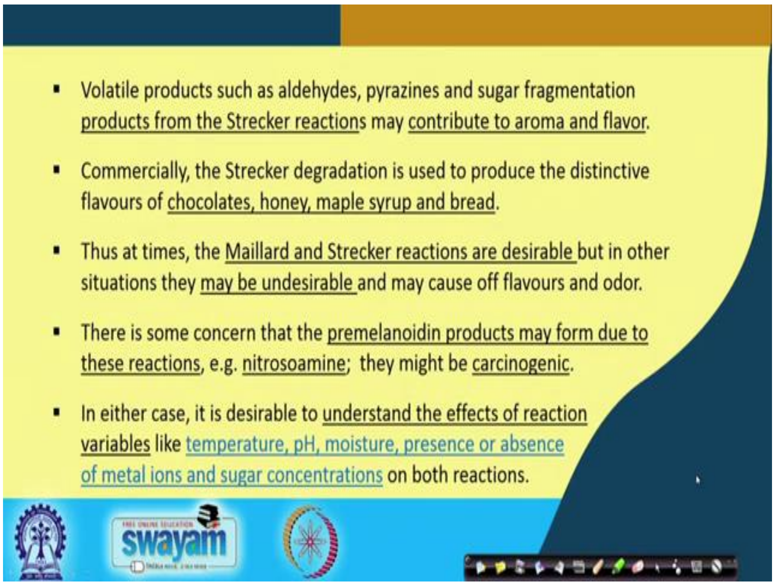
However, the absence of Maillard browning does not ensure that there is no loss of nutritive value has occurred. This is because the amino acid destruction even occurs well before the development of colored pigment. The colored pigment development actually is the last step of the Maillard browning reaction wherein the amino acid interacts in the very beginning of the process and sugar amines are formed. So, the Maillard reaction is not the only pathway for the destruction of amino acids in food processing or food preparation.



Strecker degradation

There are some other pathways through which the nutritive value of a protein is degraded. One very prominent among these is the Strecker degradation which involves the interactions of α-dicarbonyl compound to α-amino acids. It can be seen in this reaction (figure) that the amino acid, L-valine interacts with the α-dicarbonyl compound i.e. 2, 3-butanedione undergoes the decarboxylation reaction and produces methylpropanal and 3-amino-2-butanones.

Two molecules of 3-amino-2-butanone compounds, in the presence of oxygen, condense and give tetramethylpyrazine which results in the loss of amino acid properties. Therefore, it is indicated that the Strecker degradation might result in the loss of nutritive value of the food.

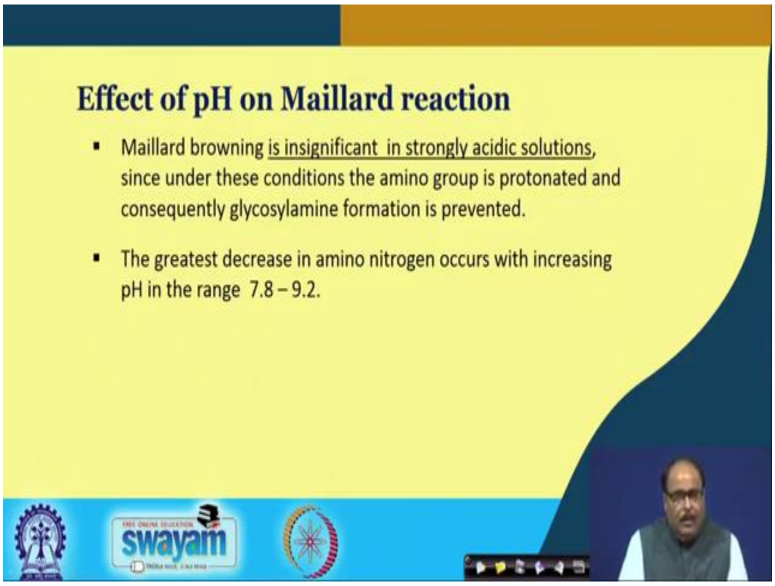


Similarly, there might be other complex reactions depending upon the nature of the dicarbonyl compounds and the nature of the amino acid involved. Volatile products such as aldehydes, pyrazines and sugar fragmentation products from the Strecker reactions may contribute to aroma and flavor.

In fact, sometimes these Strecker degradation products are highly desirable and used commercially to produce the distinctive flavors of chocolate, honey, maple syrup, bread, etc. But at times, Maillard reaction products, as well as Strecker reaction products are not desirable.

In short it can be said that, the Maillard reaction products or Strecker reaction products may be desirable in some cases or may be undesirable in other cases. So, it needs to be properly understood that in which product these reactions are required or in which they are not required and accordingly the processing parameters should be properly controlled. One important thing needs to be considered here is that some time premelanoidin products may be formed due to these reactions like nitrosoamines and such products might be carcinogenic or mutagenic. They may have certain health concerns, so care should be taken about these products.

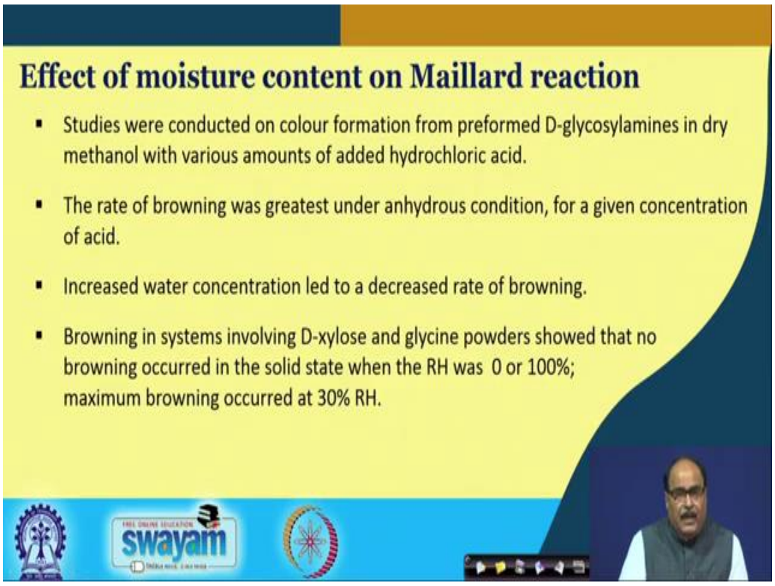
In either case, it is desirable to understand the effect of reaction variables like temperature, pH, moisture, presence or absence of metal ions and the sugar concentration on both the reaction. That will be helpful to control these reactions to get the desired end product.



Effect of pH on Maillard reaction

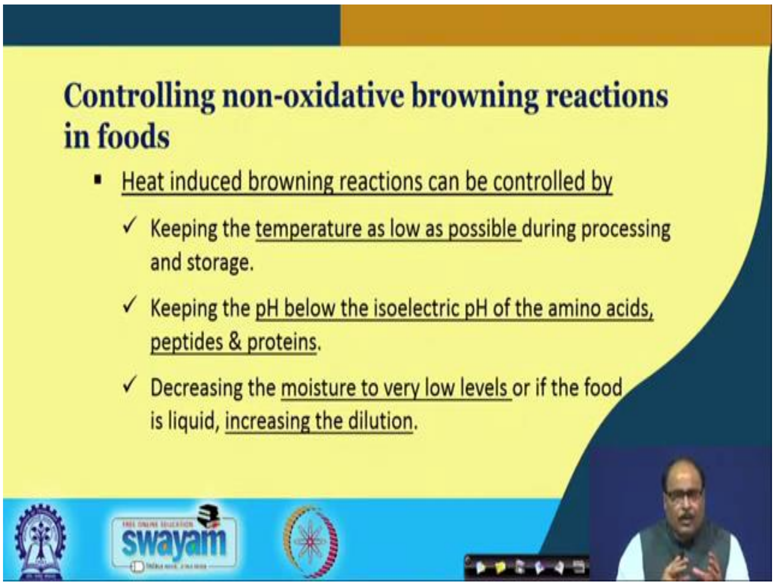
The pH has a significant effect on the Maillard browning reaction rate. In strongly acidic solution, it becomes insignificant because under strongly acidic conditions the amino group of the protein is protonated and consequently the glycosylamine formation is prevented.

The alkaline conditions in the food favor the Maillard reaction and therefore, the pH in the range of 7.8 to 9.2 is the most optimum for the Maillard reaction to occur.



Effect of moisture content on Maillard reaction

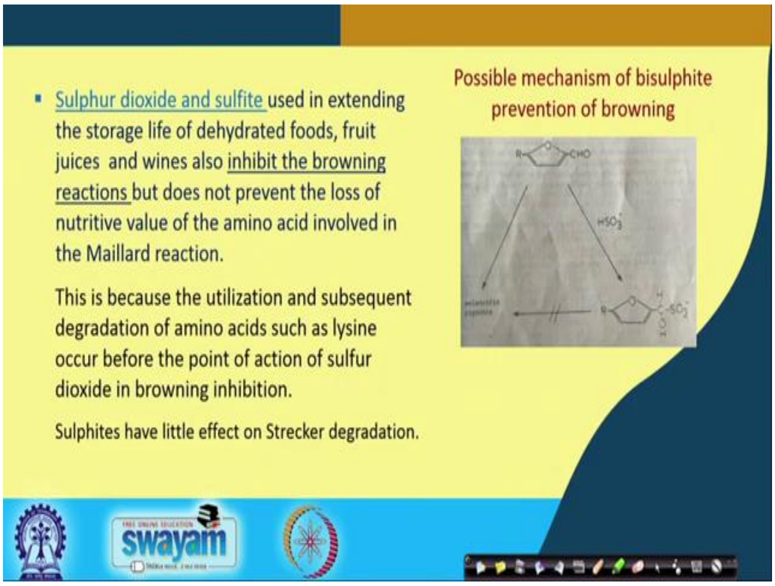
The moisture content of the food also has a significant effect on the Maillard reaction rate. Various experiments have been conducted by researchers and a lot of data is available in this regard in the literature. In general, it shows that the intermediate moisture favours the browning reactions. Maillard browning reactions can be avoided in completely dried food or completely diluted food. So, 30 % relative humidity was reported to be maximum or optimum where the browning reactions occur at the fastest rate.



Controlling non-oxidative browning reactions in foods

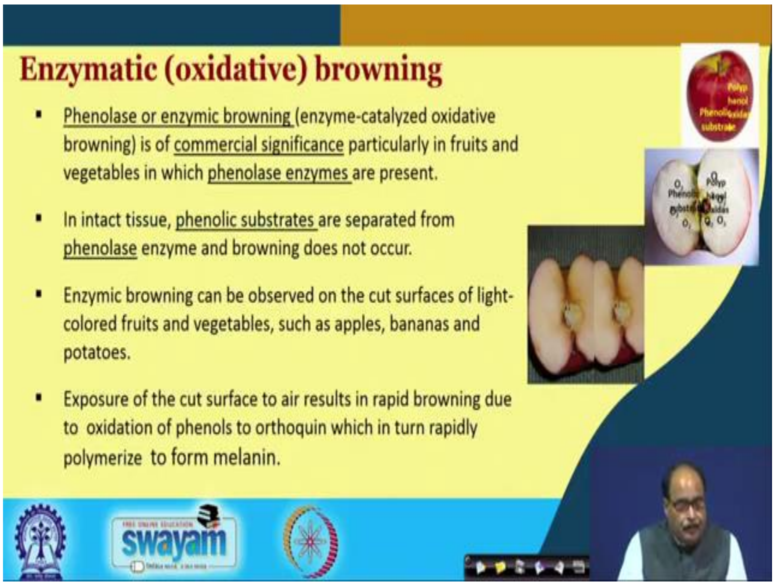
At times, it becomes necessary to control non oxidative browning reactions in the food. Obviously, this can be done by controlling the process variables or the factors which accelerate these reactions. As discussed earlier, temperature is the important parameter which influences these reactions. If the temperature in the system during processing is kept as low as possible then the browning reaction can be avoided.

Similarly, these heat-induced browning reactions can be controlled by keeping the pH below the isoelectric pH of the amino acid, peptide and proteins and by decreasing the moisture to a very low level near dehydrating conditions or to the critical moisture content level. If the food is a liquid, then it would be diluted as much as possible which retard the Maillard reactions.



Many times, sulphur dioxide and sulfites are added in the food, particularly in dehydrated foods, fruits, vegetables, etc. to extend their shelf life. These sulphur dioxide and sulfites also inhibit browning reactions. However, they do not prevent the loss of nutritive value of the amino acid involved in the Maillard reaction. This is mainly because of the utilization and subsequent degradation of an amino acid such as lysine which occurs well before the point of action of sulphur dioxide in browning inhibition.

Sulfites have their little effect on Strecker degradation. The possible mechanism of the use of sulphur dioxide or sulfites in the prevention of browning is that it interacts with the free aldehydic group or free ketonic group and blocks the formation of sugar amine and ultimately the chain reaction is stopped.

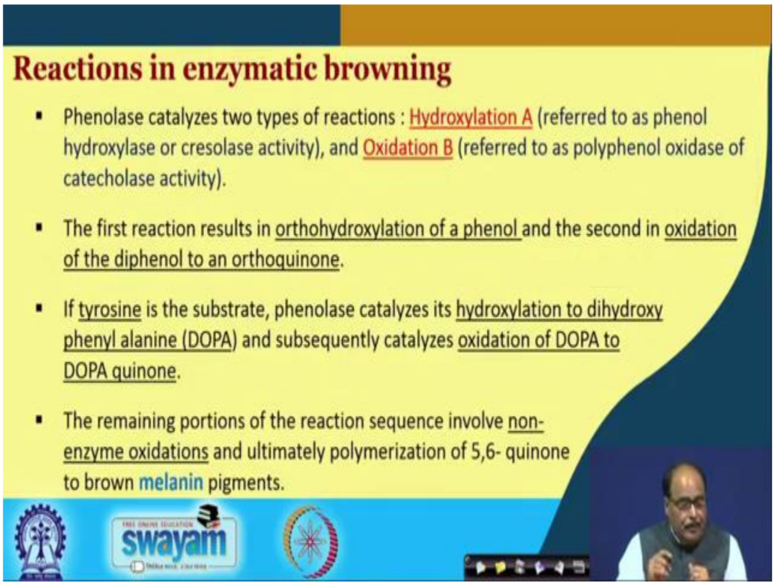


Enzymatic (oxidative) browning

Another set of the browning reaction is the enzymatic or oxidative browning reactions. These are also known as phenolase browning reaction or enzyme-catalyzed oxidative browning reactions. These are of commercial significance, particularly in the fruits and vegetables in which phenolase enzymes are common.

The fruits and vegetables like apple, banana, potato, etc. they contain the enzyme phenolase and also contain the substrate phenolic compounds, but, in the intact tissue phenolic substrates are separated from the phenolases or polyphenolase. So, they cannot come in contact and do not interact. Therefore, the enzymatic oxidation reaction does not take place. But, when the tissue of these vegetables or fruits are damaged for example, when apples or potatoes are peeled, these substrate phenols and the enzymes phenolases, get released from their cells, come in contact with each other and in the presence of atmospheric oxygen, an instant or very fast oxidative reaction takes place.

A series of complex processes are followed which produce brown coloured compounds which are generally known as melanins.



Reactions in enzymatic browning

The enzymatic browning reactions occur in two ways i.e. phenolase catalyzes two types of reactions –

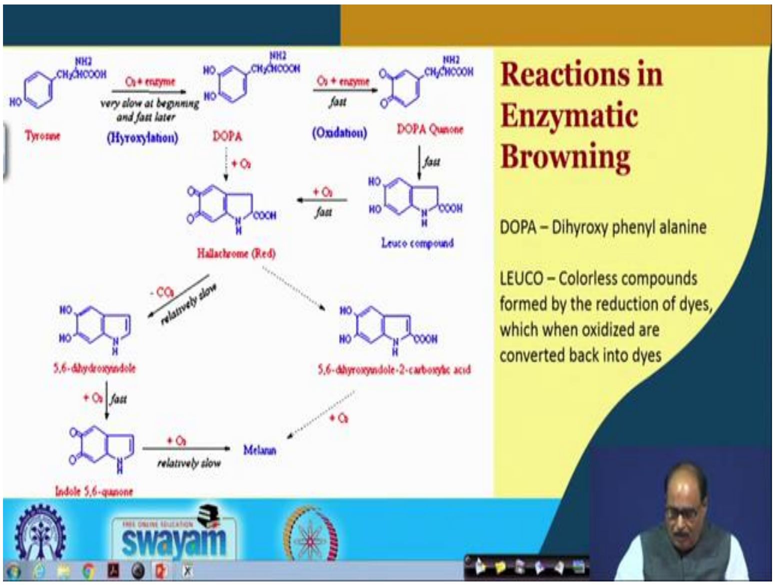
(i) Hydroxylation A

It is referred to as phenol hydroxylase of cresolase activity. This reaction results in orthohydroxylation of a phenol.

(ii) Oxidation B

It is referred to as polyphenol oxidase of catecholase activity. This reaction results in the oxidation of diphenol to an orthoquinone.

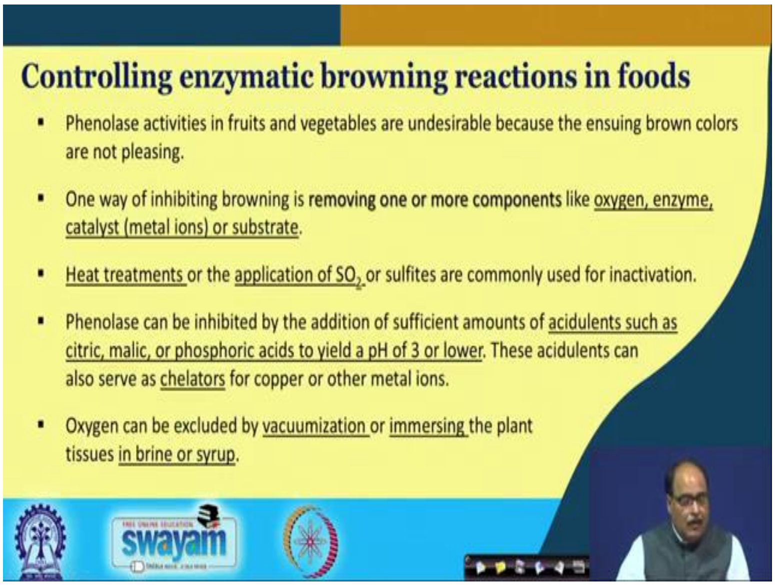
If tyrosine is a substrate, phenolase catalyzes its hydroxylation to dihydroxy phenyl alanine that is called DOPA and, subsequently DOPA is converted into or oxidized into DOPA quinone. The remaining portions of the reaction sequence involve non-enzymatic oxidations and ultimately polymerization of 5, 6-quinone to brown melanin pigments.



Reactions in enzymatic browning

The reaction pathway of the tyrosine is shown in Fig. The substrate, tyrosine in the presence of oxygen and phenolase enzyme undergoes hydroxylation reaction that forms DOPA. Further, the DOPA is converted into DOPA quinone through oxidation in presence of the enzyme. In absence of enzyme, the oxidation of DOPA results into hallachrome. DOPA quinone is converted into LEUCO compounds which is then oxidized into hallachrome.

This hallachrome may go decarboxylation reaction and get changed into 5, 6-dihyroxyindole and 5, 6-dihyroxyindole-2-carboxylic acid and ultimately both are converted into various unsaturated carbonyl compounds which are collectively known as melanins. These are responsible for the brown color of the food materials or such fruits and vegetables.



Controlling enzymatic browning reactions in foods

These enzymatic browning reactions may be undesirable in the fruits because it might influence the marketability of these products. Sometime if it is not controlled, these may become unhealthy. So, it is needed to control the factors which accelerate these reactions e.g. phenolases activities may be inhibited or may be controlled by removing one or more components in the food like oxygen. Similarly, these enzymatic oxidation reactions are catalyzed by certain agents like metal, ions, etc. So, if these metal ions are removed from the system or even the substrate like phenolases that can inhibit the browning reaction. Heat treatment or the application of sulphur dioxide or sulfite is commonly used for the inactivation of polyphenolase, polyphenol oxidase enzymes. Also at a certain temperature, these enzymes get inactivated, therefore, many of these fruits and vegetables are given mild heat treatment which is called blanching. The purpose of blanching is to inactivate the enzyme; so, as to control these browning reactions during their subsequent drying and dehydration processes.

Phenolases can also be inhibited by the addition of sufficient amounts of acidulants in the system such as citric acid, malic acid, phosphoric acid or such other acid and by bringing down the pH 3 or lower; under the extreme pH conditions, these enzymes become inactive. However, this should be done with caution because lowering down the pH might increase the acidity and affect the sensory characteristics of the food.

These acidulants like citric acid, phosphoric acid, etc. also act as chelating agent. They bind metal ion making them unavailable for the oxidation reaction. Oxygen can be excluded from the system by either vacuum or nitrogen flushing or immersing the plant tissue in a brine solution or in syrup solution. In fact, during the preparation of potato chips or even during peeling operations, it is commonly used to avoid these enzymatic browning.

However, the same set of enzymatic browning reactions like phenolases and polyphenol oxidase and the substrate like phenols, catechol, catechins, etc. are highly desirable in products like tea as they are involved in the formation of coloring or flavoring compounds. During the tea processing, particularly in black tea processing, enzymatic oxidation by phenolases are very important. In black tea manufacturing, during fermentation or oxidation, tea leaves are exposed to suitable conditions to encourage the enzymatic oxidation reaction in a controlled way so that the desirable coloring and flavoring compounds are produced.

In the nutshell, it can be said that browning reactions are the very important reactions in food. They may be desirable in some foods or may be undesirable in the other foods. Therefore, a clear understanding of the desirability or undesirability of the reaction in food is needed. Accordingly, the proper control of the processing conditions or the parameters should be taken to get the desired results.