

FOOD SCIENCE AND TECHNOLOGY

Lecture11

Lecture 11: Major Chemical and Biochemical Reactions in Foods



Hello everyone, Namaste. Now we are entering in third module of the course and in this third module, the next five lectures will be devoted on major chemical processes in food. And the first lecture of this module, overall lecture 11, we will devote today on major chemical and biochemical reactions in foods.



We will discuss about what are the chemical interactions among major food constituents briefly. Then we will talk about major chemical processes like Maillard reaction, caramelization, fermentation, curing, polymerization. Towards the end, we will also talk about a little bit of chemical reaction kinetics, that is, the Arrhenius relationship. So, let us

start with the chemical interactions among major food constituents. In the earlier classes also, we briefly touched upon this topic.

Chemical interactions among major food constituents

- An ultimate objective of study of food chemistry is to determine cause-and-effect and structure-function relationships among different classes of chemical components.
- The facts derived from the study of one food or model system can be applied to our understanding of other food products.

Four components of analytical approach to food chemistry

- Determining properties that are important characteristics of safe, high-quality foods.
- Determining chemical and biochemical reactions that have important influences on loss of quality and/or wholesomeness of foods.
- Integrating the first two points so that one understands how the key chemical and biochemical reactions influence quality and safety.
- Applying this understanding to various situations encountered during formulation, processing, and storage of food.

You know that the ultimate objective of the study of food is to find out what are the causes and effects and structural function relationships among different classes of chemical components. And in earlier modules, we discussed the structure-function relationship and what are the various quality attributes, etcetera. And you know that the food contains various chemical biochemical etcetera; it is also susceptible to microbes; so, during the value chain, it undergoes different changes, that is, chemical changes, biochemical changes, microbiological changes, and so on. So it becomes imperative to understand these changes, what these reactions are, and how these reactions are happening so that we can take care of these reactions, such as the undesirable reaction rates to be controlled and the desirable reaction rates to be accelerated. So, there is a completely analytical approach followed to the study of food chemistry, and in this analytical approach, the facts derived from the study of one food or model food system can be applied to our understanding of other food products, and then it can be multiplied, So, there are four components to this or you can say four-way we approach to understand the processes that are happening into the food. Number one is determining the properties that are the most important characteristics of safe, high-quality food. We say that yes, this food is good. This food is safe. So what is that? Whether it is color, whether it is flavor, whether it is texture, whatever it is, so find out. That is the particular quality attribute on the basis of which that food is safe. judged as safe and good quality. Then, we find out what the chemical and biochemical reactions that have important influences on the loss of quality and wholesomeness of food.

Then, whatever information is derived in these two points is integrated, and with the integration, we develop models, mathematical models, etc. And find out and derive our

understanding of how the key chemical and biochemical reactions are influencing the quality and safety of that particular food. And then apply this understanding to various situations encountered during the formulation, processing and storage of foods.

Chemical alterations during handling, processing, or storage

- These changes, with exception of those involving nutritive value & safety, are readily evident to consumer.

| Attribute | Alteration | Attribute | Alteration |
|----------------|--|------------------------|---|
| Texture | <ul style="list-style-type: none"> Loss of solubility Loss of water-holding capacity Toughening Softening | Nutritive value | <ul style="list-style-type: none"> Loss, degradation, or altered bioavailability of <ul style="list-style-type: none"> ✓ Proteins ✓ Lipids ✓ Vitamins ✓ Minerals ✓ Other health-promoting components |
| Flavor | Development of <ul style="list-style-type: none"> Rancidity (hydrolytic or oxidative) Cooked or caramel flavors Other off-flavors Desirable flavors | | |
| Color | <ul style="list-style-type: none"> Darkening Bleaching Development of desirable colors (e.g. Browning of baked goods) | Safety | <ul style="list-style-type: none"> Generation of toxic substances Development of substances that are protective to health Inactivation of toxic substances |



So, the various chemical alterations during handling, processing and storage of foods in the various quality attributes are there. Many changes do take place during handling, processing and doing the food value chain. Alright. These changes take place in the texture, flavour, colour and other quality attributes of nutrition value, as well as safety. So, most of these changes they are the many a time become visible to the consumers. So, in the texture there may be loss of solubility, there may be loss of water holding capacity, it may become hard, it may become soft. Similarly, the changes in the flavour might include the development of rancidity, it may be hydrolytic rancidity or oxidative rancidity; it may be cooked or caramel flavour development, other off-flavour development or the development of desirable flavour.

In colour, it may be darkening; it may be bleaching of the colour; it may be the development of desirable colours like in the case of browning of the baked goods, etc. Then, in the nutritive value changes, there may be loss, degradation or alteration of the bioavailability of proteins, lipids, vitamins, minerals and other health-promoting components. All these changes may sometimes impair the safety of the food. There may be the generation of toxic substances or the development of substances that are protective of health or that are proactive to health. They do not favor the health components, etc. The food becomes safe or even sometimes the food becomes that is some of these components if they are antioxidant and also so they protect the food as well. Also, there will be inactivation of toxic substances, etc.

□ Chemical & biochemical reactions leading to alteration of food quality or safety

- Each chemical & biochemical reaction class can involve different reactants/substrates depending on the specific food and the particular conditions for handling, processing, or storage.
- They are treated as reaction classes due to similar general nature of substrates/reactants for all foods.

| Types of reaction | Substrate | Examples |
|------------------------|--|---|
| Non-enzymatic browning | Carbonyl compounds from <ul style="list-style-type: none">• Existing reducing sugars• Diverse reactions, such as<ul style="list-style-type: none">✓ Oxidation of ascorbic acid✓ Hydrolysis of starch✓ Oxidation of lipids | <ul style="list-style-type: none">• Baked goods• Dry and intermediate moisture foods |
| Enzymatic browning | <ul style="list-style-type: none">• Phenolic compounds<ul style="list-style-type: none">✓ Catechol✓ Chlorogenic acid✓ Caffeic acid✓ Tyrosine✓ Gallic acid | <ul style="list-style-type: none">• Cut fruits and some vegetables |



So, all these chemical interactions or all these changes may be desirable as well as undesirable. Then chemical and biochemical reactions take place, and major reactions which alter the food quality or safety. These are many times they are non-enzymatic browning, enzymatic browning and many other classes. All these reactions are treated as a reaction class due to the similar nature of substrates or reactants for all the foods. Like for example, non-enzymatic browning. This may always be the reaction between either sugars or sugar and amines. So, their sugars may be many polysaccharides, monosaccharides, etcetera there are many sugars reducing sugars. So, the nature general nature of the reaction will be the same in the case of whether the sugar is glucose or it is fructose or any other sugar-reducing sugar or any other amino acid. So, these. Non-enzymatic browning that is the substrate that is the carbonyl compounds from existing reducing sugar or diverse reactions such as oxidation of ascorbic acid, hydrolysis of starch or oxidation of lipids etc., may result in the non-enzymatic browning and these reactions are invariably being seen in the various baked goods or dry and intermediate moisture foods; these reactions may develop during processing etcetera. Then enzymatic browning is these are mainly because of the changes in the phenolic compounds, that is, the polyphenol oxidase enzyme that acts on the phenolases, etcetera or polyphenolic compounds like catechol, chlorogenic acid, caffeic acid, tyrosine, gallic acid etcetera. These reactions are visible many times in cut fruits and vegetable sources. When you cut an apple, you see its surface become dark; when you peel a vegetable or a leaf, in the open atmosphere, its surface becomes dark; in the potato, similar things happen. So, these are basically enzymatic browning reactions.

□ **Chemical & biochemical reactions leading to alteration of food quality or safety**

- Each chemical & biochemical reaction class can involve different reactants/substrates depending on the specific food and the particular conditions for handling, processing, or storage.
- They are treated as reaction classes due to similar general nature of substrates/reactants for all foods.

| Types of reaction | Substrate | Examples |
|-------------------|---|---|
| Oxidation | <ul style="list-style-type: none">• Lipids<ul style="list-style-type: none">✓ Triacylglycerols✓ Phospholipids• Proteins• Vitamins• Pigments | <ul style="list-style-type: none">• Lipids (off-flavors)• Vitamin degradation• Pigment discoloration• Proteins (loss of nutritive value) |
| Hydrolysis | <ul style="list-style-type: none">• Carbohydrates (starches, disaccharides, polysaccharides)• Proteins• Lipids (triglycerides) | <ul style="list-style-type: none">• Invert sugar from sucrose hydrolysis• Casein hydrolysis by rennet in cheese making |



Then, chemical and biochemical reactions will lead to the alteration of food quality and safety. Other reactions may be oxidation or even hydrolysis. The oxidation may be the oxidation of lipids involving either triacylglycerols or phospholipids, or it may also be the oxidation of proteins, vitamins and pigments. Examples of all this that is the development of rancidity or off-flavour in the lipids, fats and oils, or it results in vitamin degradation in fruits and vegetables, pigment discoloration, or protein changes, and oxidation of protein, which results in the loss of nutritional value of the food. Then hydrolysis and hydrolytic reactions are again very important reactions. It takes place in the carbohydrate like starches, disaccharides, etc. They are hydrolyzed or polysaccharides are hydrolyzed to monosaccharides; like the starches, finally amylose and amylopectin, they will be completely hydrolyzed to glucose or maltose and so on. Similarly, proteins may be hydrolyzed. Lipid triglyceride may be hydrolyzed into diglyceride, monoglyceride and so on. These reactions are like inverse sugar; when the carbohydrate hydrolyzes, it may lead to the rise of inverse sugar ok; or casein hydrolysis by rennet enzyme in cheese making. So, that is, the larger polymers are converted into smaller units, rather more reactive units, and then this leads to again several processes and results in the loss of quality, safety, etcetera.

❑ **Chemical & biochemical reactions leading to alteration of food quality or safety**

| Types of reaction | Examples |
|--|--|
| ○ Metal interactions | <ul style="list-style-type: none"> • Complexation (anthocyanins) • Loss of Mg from chlorophyll • Catalysis of oxidation |
| ○ Lipid isomerization | <ul style="list-style-type: none"> • Cis → trans isomerization, Non-conjugated → conjugated |
| ○ Lipid cyclization | <ul style="list-style-type: none"> • Monocyclic fatty acids |
| ○ Lipid oxidation-polymerization | <ul style="list-style-type: none"> • Foaming during deep-fat frying |
| ○ Protein denaturation | <ul style="list-style-type: none"> • Egg white coagulation, enzyme inactivation |
| ○ Protein crosslinking | <ul style="list-style-type: none"> • Loss of nutritive value during alkali processing |
| ○ Polysaccharide synthesis and degradation | <ul style="list-style-type: none"> • In plants postharvest |
| ○ Glycolytic changes | <ul style="list-style-type: none"> • Animal postmortem, plant tissue postharvest |



And again, as I told you, these reactions also are those which result in good changes. These different major reactions of chemical and biochemicals which lead to the alteration in food quality and safety may be broadly categorized as metal interactions like the complexation of metals like in the case of anthocyanins, or there may be loss of magnesium for chlorophyll or catalysis of oxidation, etcetera. So, these are the different reactions where it is changes are because of the interactions of the metal. The other major category may be lipid isomerization like cis to trans isomerization, conversion of non-conjugated to conjugated and therefore, changing the geometry of the material. The lipid crystallization is like in the monocyclic fatty acid development. or lipid oxidation or polymerization, which are the various polymers formed during deep fat frying or other operations. There may be protein denaturation, protein cross-linking or polysaccharide synthesis and degradation, glycolytic changes, etc., in many plant and animal tissues animal materials and, which ultimately may result in the impairment of the food quality or safety.

❑ **Examples of cause-and-effects relationships pertaining to food alteration during handling, storage, and processing**

- Deterioration of food usually consists of a series of primary events followed by secondary events, which, in turn, become evident as altered quality attributes.



- Operating from left to right, one can consider a particular primary event, the associated secondary events, and the effect on a quality attribute.
- Alternatively, one can determine the probable cause(s) of an observed quality change by considering all primary events that could be involved and then isolating, by appropriate chemical tests, the key primary event.
- The utility of constructing such sequences is that they encourage one to approach problems of food alteration in an analytical manner.



So, let us take one or two examples of the causes and effects relationship pertaining to food alteration during handling, storage and processing. So, you are now clear that the

deterioration of food usually consists of a series of primary events, which are followed by deterioration. Secondary events are the consequences which, in turn, are altered or evident as the quality, change quality or altered quality. So, there is a primary event, then a secondary event, or you can say the consequence of the primary event and finally, which manifested in the changed quality attributes. So, operating from left to right, one can consider a particular primary event all right and then the associated secondary event and its effects on the quality attribute. For example, if there is a fruit, there may be damage in the fruit tissue, then what will be the consequences of the damage in the fruit tissue and then how it will result in the impairment of the quality, etcetera that can be. Alternatively, the reverse of this that is right to left you have a product like you have got a canned food or any other food and you see that yes what is the visible quality change and then depending upon the nature of the product you can go backwards that what was the food and what might have been the possible major reactions for that and then you study and analyze that and then finally you take appropriate measures.

So, the utility of constructing such sequences is that they encourage one to approach problems of food alteration in an analytical matter, in a very systematic manner. You can actually understand what is happening in this food, which is resulting in the development of bad colour flavour, etcetera or poor quality. So, that you can really do the needful and take preventive measures for these reactions.

Examples of cause-and-effects relationships pertaining to food alteration during handling, storage, and processing (Contd...)

| Primary causative event | Secondary event | Attribute influenced |
|---------------------------------|---|--|
| ○ Hydrolysis of lipids | • Free fatty acids react with protein | • Texture, flavor, nutritive value |
| ○ Hydrolysis of polysaccharides | • Sugars react with protein | • Texture, flavor, color, nutritive value |
| ○ Oxidation of lipids | • Oxidation products react with many other constituents | • Texture, flavor, color, nutritive value; Toxic substances can be generated |
| ○ Bruising of fruit | • Cells break, enzymes are released, oxygen accessible | • Texture, flavor, color, nutritive value |



So, let us take some examples like primary events, as I told you, if it is hydrolysis of fat. So, if the fat gets hydrolyzed, what will happen? In the system, there will be free fatty acid development, and then these free fatty acids may interact with the protein or other food components. And it may influence all the properties like texture, flavour, nutritional value, etcetera. The other primary event, if you take hydrolysis of polysaccharides, means that

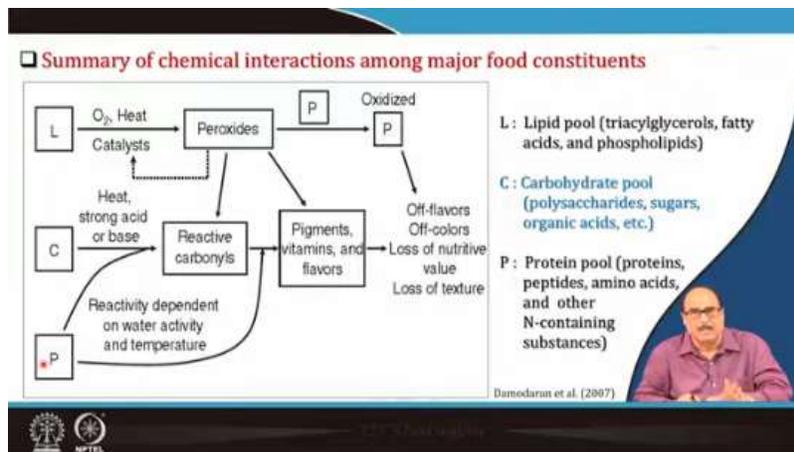
there will be monosaccharides will be generated, sugars, etcetera. They will again be reactive, and they will react to protein, and then this protein and sugar interaction will ultimately result in a change in almost all quality attributes. Another primary event is the oxidation of lipids. The oxidation product will react with many other constituents and take your colour, flavour, and nutritive value, and even this oxidation of lipids may result in the toxic generation of toxic substances. Bruising of fruit, as I told you if there is damage, the primary event is the damage to the fruit tissue, then this may result in the breakage of the cell and the breakage of the cell may result in the release of the enzymes and substrates, etc. Oxygen becomes accessible, and the various reactions follow that again result in the change in the texture, colour, flavour and nutritional value.

Examples of cause-and-effects relationships pertaining to food alteration during handling, storage, and processing (Contd..)

| Primary causative event | Secondary event | Attribute influenced |
|-------------------------------------|--|--|
| ○ Heating of horticultural products | • Cell walls & membranes lose integrity, acids are released, enzymes become inactive | • Texture, flavor, color, nutritive value |
| ○ Heating of muscle tissue | • Proteins denature and aggregate, enzyme become inactive | • Texture, flavor, color, nutritive value |
| ○ Cis → trans conversion in lipids | • Enhanced rate of polymerization during deep-fat frying | • Excessive foaming during deep-fat frying, diminished nutritive value and bioavailability of lipids, solidification of frying oil |



Also, if you can say that heating of the horticultural product, like during cooking, cell walls and membranes lose integrity, acids are released, enzymes become inactive, and these changes, which are attributes which are influenced, may become texture, flavour, colour, nutritional value and so on. Then, similarly, with heating of the muscles like cooking meat, etc., protein denatures and becomes aggregate, enzymes become inactive, and the quality attributes like texture, flavour, colour, and nutritional value get changed. Similarly in the case of lipids like cis to trans isomerization normally happens during the heating or frying of the oils even during the refining process also cis isomers are converted into trans and that results in the enhanced rate of polymerization during deep fat frying and then excessive foaming during deep fat frying, diminished nutritional value bioavailability of lipid or solidification of the frying oil etcetera might be the attribute that is changed.



So, this is the overall summary of the reactions. This figure, earlier also, we discussed. Then what happening is the nature of the major pool shown in this figure is dependent on the physiological state of the product tissue at the time of processing or storage and the constituents which are present are added to the non-tissue foods and each class of compound can undergo its own characteristic types of deterioration and noteworthy here in all these processes is the role that carbonyl compounds may play in many deteriorative processes and they arise mainly from the lipid oxidation, carbohydrate degradation and can lead to the destruction of nutritional value to the development of off flavor and off colours. So, as I told earlier it is the same series of reactions, same type of reaction also that leads to desirable flavors and colors during cooking or frying or baking or many other processes.

Major chemical processes

Non-enzymatic browning reactions

- **Non-enzymatic browning reactions** are responsible for
 - Colour & flavour of foods, like dates, honey, & chocolate
 - Distinctive flavor upon roasting coffee beans, groundnuts, cashewnuts & breakfast cereals
- **Presence of reactive reducing sugars** is responsible for browning in foods
 - On heating, reducing sugars undergo ring opening, enolization, dehydration & fragmentation to form unsaturated carbonyl compounds
 - These compounds react forming brown polymers & flavour compounds.
- **The heat-induced browning reactions** occur in two ways
 - Caramelization
 - Maillard reaction

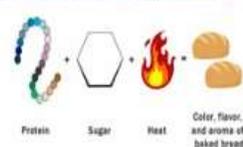
If we look at the major chemical process like non-enzymatic browning, non-enzymatic browning reactions are responsible for color and flavor of foods like dates, honey and chocolate. They are also responsible for distinctive flavours upon roasting coffee beans, groundnuts, and cashew nuts and in many breakfast bowls of cereal, the flavour develops because of the non-enzymatic browning reactions. There, it is the presence of reactive

reducing sugar that is responsible for browning in foods. So, what happens to foods which have reactive reducing sugar or also the amino groups, etcetera? Then, on heating, these reducing sugars undergo ring opening, enolization, dehydration and fragmentation to form unsaturated carbonyl compounds, and these carbonyl compounds react, forming brown polymers and flavour compounds. So, these are the heat-induced reactions that are non-enzymatic browning reactions, and they can be of two types like caramelization and Maillard reaction.

Non-enzymatic browning reactions (Contd..)

▪ **Maillard reaction**

- The Maillard reaction is actually a complex group of many reactions.
- The carbonyl group of acyclic sugars readily combines with the basic amino groups of proteins, peptides, and amino acids, resulting in sugar-amines.
- The set of various reactions sugar-amines undergo, resulting in browning, is known as the Maillard reaction.
- The condensation product of sugar and amines undergoes enolization and rearrangement and then undergoes condensation & polymerization forming red-brown and dark-brown compounds.
- The sugar-amines form a brown colour at a lower temperature than the formation of the colour by caramelization. Hence, Maillard-reaction products predominate in browned foods.



The diagram illustrates the Maillard reaction process. It shows a protein chain (represented by a blue and green ribbon) reacting with a sugar molecule (represented by a hexagonal ring). This reaction is triggered by heat, indicated by a flame icon. The final products are color, flavor, and aroma, represented by a slice of baked bread.



A small inset image shows a man in a purple shirt speaking, likely providing a lecture or explanation related to the content.

 The bottom left corner of the slide features two logos: one for the Indian Institute of Technology (IIT) and another for NPTEL (National Programme on Technology Enhanced Learning).

So, the Maillard reaction is actually a complex group of many reactions. These are that the carbonyl group of the acyclic sugars are reducing sugar readily combined with the basic amino group of proteins or peptides and or amino acids and results in the formation of sugar amine ok. Sugar amines then undergo a set of reactions like Amadori rearrangement, reverse Amadori rearrangement, etc. And they follow these Amadori products. They follow different specific pathways, metabolic pathways and, in the process, various reactions. Carbonyl compound, new carbonyl compounds are formed, all right, and which result into, that is, they form compounds known as melanoidin's, and these melanoidin's are responsible for the dark brown colour of the product.

The Maillard reaction occurs in three main steps

- Formation N glycoside**

$$\begin{array}{c} \text{H}-\text{C}=\text{O} \\ | \\ \text{R} \end{array} + \text{H}_2\text{N}-\text{R}' \rightarrow \begin{array}{c} \text{OH} \\ | \\ \text{H}-\text{C}-\text{NH}-\text{R}' \\ | \\ \text{R} \end{array} \rightleftharpoons \begin{array}{c} \text{H}-\text{C}=\text{N}-\text{R}' \\ | \\ \text{R} \end{array} \rightleftharpoons \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{OH}-\text{C}-\text{NH}-\text{R}' \\ | \\ \text{OH} \end{array}$$

D-Glucose D-Glucosylamine
- After formation of N glycoside the immonium ion is formed and then isomerize, this reaction is called Amadori rearrangement and forms a compound called ketosamine.**

$$\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{N}^+-\text{R}' \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H} \end{array} \rightleftharpoons \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{NH}-\text{R}' \\ | \\ \text{C}=\text{O} \end{array}$$

1-amino-1-deoxyketose

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So, this is here that it is shown the reaction, how this Maillard reaction can happen. First is the formation of N-glycosides, and then after the N-glycosides are formed, the ammonium ion is formed and then isomerizes, and this reaction is called, as I told you, Amadori rearrangement. The compound forms either glucosamine or ketosamine by Amadori or reverse Amadori rearrangement. There is one amino one deoxy ketose that is formed.

- The ketosamine products then either dehydrates into reductones and dehydro-reductones, which are caramel, or produces short chain hydrolytic fission products such as diacetyl, acetol or pyruvaldehyde which then undergo the Strecker degradation.**

$$\begin{array}{c} \text{R}-\text{CH}-\text{COOH} \\ | \\ \text{NH}_2 \end{array} \xrightarrow{-\text{H}_2\text{O}} \begin{array}{c} \text{R} \\ | \\ \text{C}=\text{N} \\ | \\ \text{C}=\text{O} \\ | \\ \text{OH} \end{array} \rightarrow \begin{array}{c} \text{R} \\ | \\ \text{C}=\text{N} \\ | \\ \text{C}=\text{O} \\ | \\ \text{OH} \end{array} \xrightarrow{-\text{H}_2\text{O}} \begin{array}{c} \text{R}-\text{CHO} \\ | \\ \text{C}=\text{O} \end{array}$$

Strecker Aldehyde
- The brown to black, amorphous unsaturated heterogeneous polymers are called "melanoids."**

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And then these ketamine products then either dehydrate into reductase or dehydrodelectrons, which are caramels. They produce short-chain hydrolytic fission products such as diacetyl, acetol or pyruvaldehyde, which can go under Strecker degradation and many other reactions. These group of complex groups of new polymers are formed, which have conjugated double bonds, and these conjugated double bonds absorb light of different intensities and look of various colors. So, these brown-to-black amorphous unsaturated heterogeneous polymers are known as melanoids or melanoidins, which is the end product of the Maillard browning reactions. So, these Maillard Browning reactions are very important they may take. place during processing, etc. So sometimes they are undesirable. So they need to be checked.

Maillard reaction (Contd..)

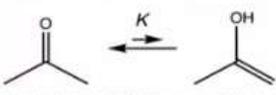
- **Inhibition of the Maillard-browning reaction can be accomplished by**
 - ✓ Keeping the pH below the isoelectric pH of the amino acids, peptides, and proteins
 - ✓ Keeping the temperature as low as possible during processing and storage
 - ✓ Use of non-reducing sugars, like sucrose, under conditions not favouring inversion
 - ✓ Sulphur dioxide and sulphites inhibit browning
- **Importance**
 - ✓ Maillard reaction is responsible for many of the specific tastes, aromas, and colour of foods
 - ✓ It results in a decrease in the nutritive value of proteins as in this reaction, the alpha-amino group of the essential amino acid like lysine reacts with carbonyl groups of sugar and fatty-acid oxidation compounds.
- **Application**
 - ✓ The brown colour of the crust of bread is due to the Maillard reaction between the protein and sugars, which occurs during baking.




Alright. Like, so, to control the Maillard Browning reactions, one should keep the pH of the food below the isoelectric pH of the amino acid peptide and proteins. Also, keeping the temperature of processing as low as possible during the processing and storage. And also, one can use non-reducing sugars like sucrose, etc. Because it is the Maillard reaction is only a reaction between reducing sugar and amino acids. And also, sulfur dioxide or sulfites, the potassium metabisulfite and all those, inhibit the Maillard reaction. So Maillard reaction is responsible for many of the specific taste, aroma and color of the foods. It results in a decrease in the nutritional value of proteins. In this reaction, it is particularly the amino acid which is involved in the Maillard reaction is an essential amino acid. So, it means that there will be a loss of nutritive value. So, this brown colour of the crust bread during the baking process; in many bakery products, the development of brown colour, is desired in the crust of bread and all those things, they are mainly because of the Maillard reaction. That is the reaction between protein and sugars, which occurs during the baking process.

Non-enzymatic browning reactions (Contd..)

- **Caramelization**
 - Sugars in dry condition or their syrups, when heated, undergo a number of reactions, depending upon the temperature and presence of catalysts.
 - Generally, there will be reactions leading to equilibration of anomeric and ring forms, inversion of sucrose, condensation reactions leading to the formation of oligosaccharides and polysaccharides, isomerization, dehydration and fragmentation, leading to the formation of unsaturated polymers with brown colour.
 - With the use of proper catalysts it would be possible to conduct caramelization to provide either flavouring or colouring caramel for food use.



The molecule on the left is a 'keto' the one on the right an 'enol'.
The reaction going from left to right is an enolization.




Then, the other non-enzymatic browning reaction is caramelization. This is mainly because of the exclusive reaction of the sugars. That is, these sugars, when they are heated either in

their dry form or in their concentrated solution form or weak solution form, undergo a number of reactions depending upon the temperature and presence of catalysts. Generally, there will be a reaction leading to equilibration of anomeric forms and ring forms, inversion of sucrose, condensation reaction leading to the formation of oligosaccharides and polysaccharides, isomerization, dehydration and fragmentation which ultimately leads to the formation of again unsaturated polymers with brown color. And with the use of a proper catalyst, it would be possible to conduct caramelization to provide either flavouring compound or colouring compounds like caramel colours, etc., for food use or even both. So, you can see here that the figure that the molecule is left with the ketone and on the other side, it is enol.

Caramelization (Contd.)

- For the manufacture of caramel colours for use in beverages, glucose syrups treated with dilute sulphuric acid partially neutralized with ammonia are used.
- As dry sugar is heated, it melts to a colourless liquid and it soon develops a brown colour, giving a pleasing characteristic caramel aroma.
- Caramelization can be halted by the addition of water when the desired colour and flavour have developed.
- Sugar breaks down during caramelization and various organic acids are formed.
- Caramelization of sugar is useful in the preparation of confections.



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So, for the manufacture of caramel colour for use in beverages. Industrially, and commercially, these huge caramel colours for the beverage industry, cola colours and all those things. So, this glucose syrup is treated with dilute sulfuric acid, and it is partially neutralized with ammonia. So, as dry sugar is heated, it melts into a colourless liquid, and it soon develops a brown colour giving the pleasing characteristic caramel aroma. Caramelization can be halted by the addition of water when the desired color and flavor have been developed. Sugars break down during caramelization and various organic acids are formed. This caramelization of sugar is very useful in the preparation of confectionery, bakery and other confectionery products. Depending upon the various temperatures, different caramel colours, etcetera can be formed.

□ Examples of caramelization reaction and related colour development in processed foods

| Product | Applications |
|--------------------|---|
| ○ Black tea leaves | <ul style="list-style-type: none"> • Firing used for halting fermentation causes caramelization resulting in characteristic colour |
| ○ Beverages | <ul style="list-style-type: none"> • Caramel use gives them dark to light brown colour |
| ○ Ghee | <ul style="list-style-type: none"> • Butter begins to boil at 90 °C and at 120 °C, the curd particles begin to brown & pleasant aroma of caramelization emanates • This is also used as an indication of end of clarification process |
| ○ Khoa | <ul style="list-style-type: none"> • Slight brown color if caramelization occurs during heating |
| ○ Chikki | <ul style="list-style-type: none"> • Cooking jaggery solution on medium flame after reaching 130°C imparts brittleness and a mild caramel flavour to the product |



So, I give here some of the products that are examples of caramelization and related colour development; in the black tea leaves, you can see that in the processing, like during frying or drying, it is used to halt fermentation. It also causes caramelization resulting in the characteristic color of the black tea processed tea. In the beverages, caramel is used to give a dark to light brown colour. In the ghee, when the butter begins to boil at 90 degrees Celsius, and at 120 degrees Celsius, the curd particles begin to brown, and a pleasant aroma of caramelization emanates. This is also used as an indication of the end of the clarification process. Khoa, in khoa preparation, a slight brown color of caramelization occurs during the heating process. In chikki manufacture, cooking jaggery solution on medium flame after reaching 130 degrees Celsius imparts brittleness and mild caramel flavour to the product.

Major chemical processes

□ Fermentation

- Fermentation is a food preservation technique and major bio-chemical process based on multiplication of select groups of microorganisms whose metabolic products help food preservation.
- Natural fermentations have played a vital role in the preservation of foods from early times. e.g.
 - Fruit juices exposed to air underwent natural fermentation and acquired an alcoholic flavour
 - Milk on standing became slightly acidic
 - These changes used as means of preservation of otherwise perishable foods
 - Changes in the texture and taste of fermented foods were found desirable
- The list of foods produced by fermentation includes
Cheese, curd, butter, all alcoholic beverages, pickles, sauerkraut, vinegar, bread, idli, soya sauce, coffee, tea, and cocoa.



Then the other chemical process is the major chemical process. One of them is the fermentation and it is also sometimes used as a food preservation technique. It is a basically major biochemical reaction process based on the multiplication of select groups of microorganisms whose metabolic products help food preservation and even also this

fermentation it occurs naturally and natural when it is there are basically microbiological reactions and when it is controlled becomes fermentation desirable reaction when it is uncontrolled it becomes spoilage reactions like, for example, that is in the fruit juices which are exposed to air, they undergo natural fermentation and they acquire alcoholic flavor. Milk, if you leave as such, it becomes slightly acidic. These changes used as means of preservation of otherwise perishable foods, fermentation reactions, and changes in the texture and taste of fermented foods are also found, many times, desirable. Many a time these microbial reactions, the microorganism they lead to the undesirable reaction, but there are many microorganism desirable microorganisms which is used in the fermentation process to develop various products like cheese, curd, butter, all alcoholic beverages, pickles, sauerkraut, vinegar, even bread, idli, soya sauce, coffee, tea, cocoa, all these are the fermented products.

Control of fermentation in foods

The factors that influence the growth and metabolic activities of micro-organisms in food fermentation are

| Controlling factor | Action | Example |
|--------------------|--|--|
| Acid | Inhibitory effect on harmful micro-organisms | <ul style="list-style-type: none"> Raw milk <ul style="list-style-type: none"> Streptococcus produce lactic acid but is inhibited when acid concentration rises Lactobacillus (more acid resistant) still grows but inhibited later Milk is clotted and curdled Acid-resistant yeasts and moulds activated & moulds oxidise acids Yeasts produce alkaline end products thus acidity decreases Growth of proteolytic and lipolytic spoilage bacteria results in off-odour and gassy condition in curd |
| Alcohol levels | Preservative depending on concentration | <ul style="list-style-type: none"> Yeasts convert sugar to alcohol but cannot tolerate alcohol concentration >12% When alcohol content is below 12%, as in beer, pasteurization of food is necessary to prevent spoilage |

So, sometimes we need to control the fermentation reactions in order to preserve the food or to get the desirable changes. So, it is the controlling factor sometimes becomes acid. Here acid, it has an inhibitory effect and harmful microorganism. And good example here is the milk. If you keep the raw milk as such without heating, so what will happen? First the streptococcus will grow in the milk, it will produce lactic acid. But when the acidity of the milk goes beyond a certain level, it becomes inhibitory to the streptococcus bacteria. And then lactobacillus comes into force. The lactobacillus, which is more resistant to acid, grows, but again, when the acidity further increases, lactobacillus also stops growing in the milk, and then milk is clotted and curdled, and the acid-resistant yeast and moulds now get activated and mould oxidize acid. Yeast produces alkaline in the products, and that acidity decreases, and the growth of proteolytic bacteria and lipolytic spoilage bacteria results in the off-flavor and gassy conditions in the curd. Similarly, alcohol levels. Preservative depends upon the concentration. Yeast converts sugar to alcohol, but it cannot tolerate

alcohol concentrations of more than 12 or 14%. So, if in a material, the alcohol concentration is more than 12 or 14 per cent, it the bacteria, the spoilage bacteria will not grow. So, when alcohol content is below 12 per cent, as in the case of beer etcetera, pasteurization of food becomes necessary to prevent spoilage.

Control of fermentation in foods (Contd...)

| Controlling factor | Action | Example |
|--------------------|--|---|
| Use of starters | Growth of particular types of microorganisms prevents growth of others | • Curd making or wine making: part of previous batch of curd or wine is added to fresh milk or grape juice |
| Oxygen levels * | Can encourage or inhibit microorganisms | • Vinegar production has two steps <ul style="list-style-type: none"> ✓ Conversion of sugary substances to alcohol in anaerobic environment ✓ Conversion of alcohol to acetic acid in aerobic conditions |
| Salt levels | Inhibitory effect | • Salt added to cheese curd controls proteolytic organisms during the long ripening periods. |
| Temperature | Affects microbial reactions | • In sauerkraut fermentation, three types of microorganisms which grow at different temperatures involved. • Fermentation started at initial low temperature (about 21°C) and then increased in later stages. |



Similarly, the use of starter culture, like the growth of particular types of microorganisms prevents the growth of others. Like in curd making or wine making, part of the previous batch of the curd or wine is added to fresh milk or grape juice to have a new. Similarly, oxygen levels can encourage or inhibit microorganisms. This happens during vinegar production like there is a first conversion of a sugary substance to alcohol in an anaerobic environment and then a conversion of alcohol to acetic acid in aerobic conditions. So, both oxygen-aerobic and anaerobic conditions are required there. Similarly, salt levels and temperature. The salt level has an inhibitory effect. Temperature affects the microbial reactions, etc. Like in the case of sauerkraut fermentation and many other fermentative processes.

□ **Curing**

- **Curing of meat**
- Curing brings modification of meat affecting preservation, flavour, colour & tenderness.
- Originally, curing was practiced as a means of preservation before the days of refrigeration.
- When modern methods of preservation are available, the prime purpose of curing is to produce uniquely flavoured meat products & another special purpose is to preserve red colour of meat.

| Curing ingredient | Function |
|-------------------|---|
| • Common salt | • Retards microbial growth • Gives flavour to the meat |
| Nitrite | • Fixes the red colour of myoglobin • Beneficial effect on the flavour of cured meats • Inhibitory effect on <i>Clostridium botulinum</i> |
| Sugar | • Helps stabilize colour • Counteract saltiness • Adds flavour |
| Spices | • Added mainly for flavour |



Then, curing meat is basically another type of reaction. It is the modification of meat affecting the preservation, flavor, color and toughness etcetera. Originally the curing was practiced as a means of preservation before the days of refrigeration. When the modern method of preservation is available now, the prime purpose of curing is to produce uniquely flavoured meat products, and another special purpose is to preserve the red colour of the meat. So, in the curing, actually, basically some sort of curing mixture is developed, and then it is smeared on the meat pieces, etcetera and then either it is lightly smoked or dried. So, various common salts, nitrites, sugars, spices, etc. are used, and they have various specific purpose function roles to play. Like common salt, it retards microbial growth. It gives flavour to the meat.

The nitrite fixes the red color of myoglobin. It has a beneficial effect on the flavour of the cured meat, and also it is inhibitory to *Clostridium botulinum*, which is a toxicogenic bacteria. Sugars help stabilize the colour. It counteracts saltiness and adds flavour. And spices, are added mainly for the flavour.

□ Polymerization

- The stability of a fat or fatty food is important to maintain a fresh taste or odour during storage & use.
- The stability is related to the composition of the lipid moiety and the changes it is subjected to.
- Fats with substantial unsaturation in the fatty acids are usually unstable.
- The presence of agents causing oxidation (pro-oxidants) or preventing oxidation (anti-oxidants) and the methods of storage determine their stability.
- Vegetable fats are usually more stable than some of the animal fats, such as lard even though the total unsaturation of the vegetable oils may be greater, because of the natural antioxidants usually present in them.

The slide also features a small video inset of a man in a purple shirt speaking, and logos for institutions at the bottom left.

Then polymerization is again very important. Like many sugars, they polymerise into polysaccharides, amino acids, and fatty acids. The polymers are big molecules. They are formed. And many times, this happens naturally also, but sometimes, these polymerization reactions are dangerous reactions, particularly in the case of fats and oils. The polymers, various polymers which are formed during processing, may be undesirable stability of the fat or fatty foods is important to maintain a fresh taste or colour and odour during storage and use and the stability is related to the composition of lipid moiety and the changes it is subject to. So, when these fats and oils or triglycerides are heated owing to the temperature of heating, they are broken down, and the presence of agents causing oxidation, like pro-oxidants or preventing antioxidants and other methods of storage, determine their stability.

So, vegetable fats are usually more stable than animal fats such as lard, etc. Total unsaturation of the vegetable oil may be greater because of the natural antioxidants usually present in them.

Polymerization (Contd..)

- Unsaturated fatty acids in lipids undergo polymerization owing to heat and oxidation, presence of free radicals or polar catalysts.
- Heating of fats and oils, as in frying operations, can produce changes due to polymerization in molecular weight, colour, viscosity, and refractive index.
- **Polymers effects on oil include**
 - ✓ Decrease the heat transfer efficiency of oil
 - ✓ Affect quality of products fried in oil
 - ✓ Adversely affect oil's nutritional quality & wholesomeness under extreme conditions

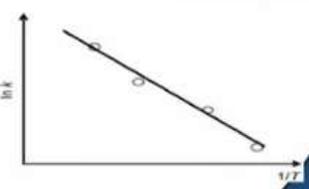


So, this being apart, the main thing polymerization, when such oils are heated, then depending upon their saturation and unsaturated polyunsaturated fatty acid they undergo at a high degree of polymerization and these polymers are formed and the oil becomes that is you see that during heating oil it becomes very dark in color. So, this unsaturated fatty acid undergoes polymerization owing to heat, oxidation, and the presence of free radicals or even polar catalysts, and these polymers, which are then during the heating of the fats and oils as in frying operation, can produce changes due to the polymerization in molecular weight, color, viscosity, refractive index, etc. These polymers, which are present in the oil, may many times be toxic. Also, they decrease the heat transfer efficiency of the oil. They affect the quality of the product fried in such oils. Also, they adversely affect the oil's nutritional quality and wholesomeness under extreme conditions.

Chemical reaction kinetics

□ Arrhenius relationship

- The effect of temperature on an individual reaction can be estimated from the Arrhenius equation, $k = A \cdot e^{-E_a/RT}$
- Data conforming to the Arrhenius equation yield a straight line when $\log k$ is plotted vs. $1/T$.
- Parameter E is activation energy that represents the free energy change required to elevate a chemical entity from a ground state to transition state, whereupon reaction can occur.

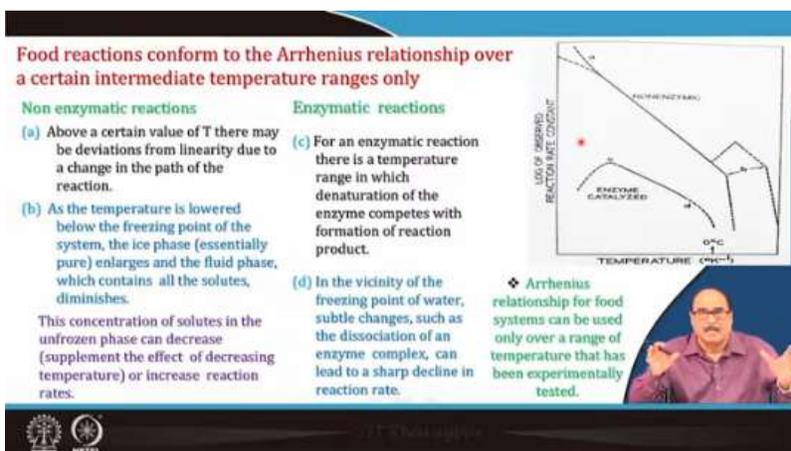


Arrhenius diagram displaying the linear dependence of the rate coefficient with respect to the inverse temperature



Then we see that finally, let us talk about chemical reaction kinetics, you know that the Arrhenius relationship is a well-established reaction kinetics which gives the effect heat or temperature has on the rate of reaction or rate of a chemical reaction. So, this can be described by an equation that is Arrhenius equation is basically $K = A \cdot e^{-\frac{E_a}{RT}}$,

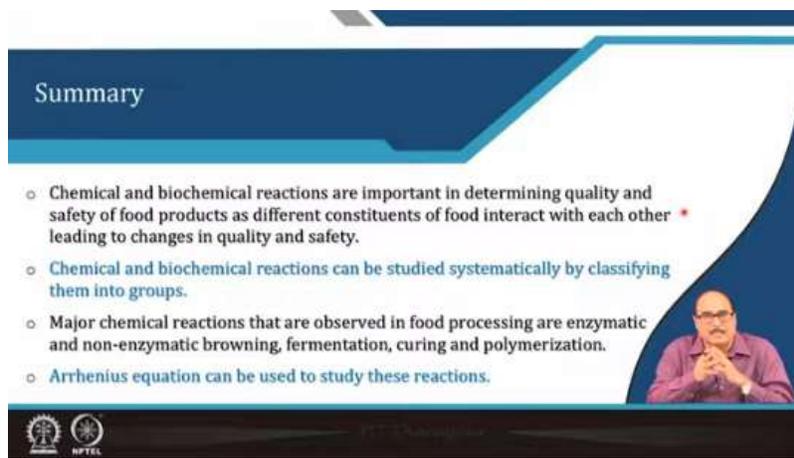
where E_a is the activation energy, R is a gas constant and T is the temperature. So, you can see that data confirms the Arrhenius relationship; that is when the $\ln k$ is plotted versus $1/T$, a linear relationship, a straight line is obtained. So, this parameter E is the energy of activation E_a , it represents the free energy change that is required to elevate a chemical entity from a ground state to a transition state whereupon the reaction can occur (after that the reaction occurs), that is, you have to give that minimum activation energy for the reaction to process. So, this is a general relationship in the chemical reaction kinetics.



But what is more important here that I would like to emphasize is that these, our food, the biochemical, although they contain chemicals, do not confirm the Arrhenius relationship over a long range of temperature. So, food reactions confirm the Arrhenius relationship over a certain intermediate temperature range only. I give here in the form of two examples, we have taken one. The non-enzymatic process as well as the enzymatic process. In the case of a non-enzymatic process, you can see either an increase in the temperature or a decrease in the temperature. That is, these two points, A and B, that is, A, were above a certain temperature value. There may be a deviation from the linearity due to a change in the path of the reaction. For example, if you are concentrating, evaporating. So, when the evaporation takes place, it is concentrates, water goes on in the concentrate, and the solutes, their concentration is decreased and therefore, the concentration increases in the concentrate and therefore, it may result in the deviation from the reaction path. On the other side, on the lower side, you see as the temperature is lowered below the freezing point of

the system, the ice phase is essentially pure. It enlarges the fluid phase, which is when you can say that it was earlier it was evaporation.

Now, we see the freezing; when water is freezing, or any in the food material, food juice, let us say fruit juice you are freezing. So, the water becomes that ice. But as the freezing progresses, the concentration of solutes in the unfrozen water increases. This increase in the concentration of solutes results in changes in almost all colligative properties, physical properties, heat transfer and all those characteristics, etc. And that results in the deviation of the path of the reaction. That is, the concentration of solutes in the unfrozen phase can decrease like supplement the effect of decreasing temperature or increase the reaction rate, as the case may be. If we take the example of an enzymatic reaction, enzyme-catalyzed reaction, consider point C here that is above the enzymatic reaction, there is a temperature range which denatures the protein. The enzyme completes, and the formation of reaction products seizes, and the enzyme is basically inactivated. So, the reaction rate decreases or stops in the vicinity towards the lower temperature side in the vicinity of the freezing point of water changes such as dissociation of an enzyme complex can lead to a sharp decline in the reaction rate. So, in both of these, the reaction path can change, or some of the reactants can get depleted, or the concentration of the material gets changed. So, either of these changes, even in the enzyme reaction, that is, the active functional group on the functional group on active site of the enzyme some may get changes, and various things might happen depending upon the various other components which are there in the food. So, it is very important that the Arrhenius relationship for the food system can be used only over a range of temperatures and that has been experimentally tested. There are methods for testing it. So, one should go with the proper testing procedure and then use the Arrhenius relationship.



Summary

- Chemical and biochemical reactions are important in determining quality and safety of food products as different constituents of food interact with each other leading to changes in quality and safety.
- Chemical and biochemical reactions can be studied systematically by classifying them into groups.
- Major chemical reactions that are observed in food processing are enzymatic and non-enzymatic browning, fermentation, curing and polymerization.
- Arrhenius equation can be used to study these reactions.



So, finally, I would like to summarize these reactions, but that these chemical or biochemical processes and microbiological processes are very important in food. There are several reactions, and even these processes are undertaken naturally also when the food is harvested, when it is kept in a room, as I gave you the example of milk, etc. So, these changes will take place. Alright. Sometimes, these changes also are aggravated depending upon the environmental conditions. Some even say that if the heat is a little bit more like, for example, microbiological reaction, if you give them up to 35-37 degrees Celsius, they may act. So, each reaction has optimum requirements, etc., of the conditions: temperature, pH, or environment (oxygen) and all those things. So, we need to understand this. Once we have understood properly, whether it is an enzymatic reaction or non-enzymatic reaction, during processing, that is what we do. That is, in chemistry, we study all these things, details, and the nitty-gritty of the process. And then finally, we apply this either during storage or during processing or during handling. Our aim becomes that these undesirable reactions should be stopped. Desirable reaction rates should be accelerated and allowed to continue. In this way, we make sure that our processed food or even unprocessed food after storage, handling, etc., is good in quality and safe to consume.



These are the references that were taken in this lecture.



Thank you very much for the patience hearing. Thank you.