Food Oils and Fats: Chemistry and Technology
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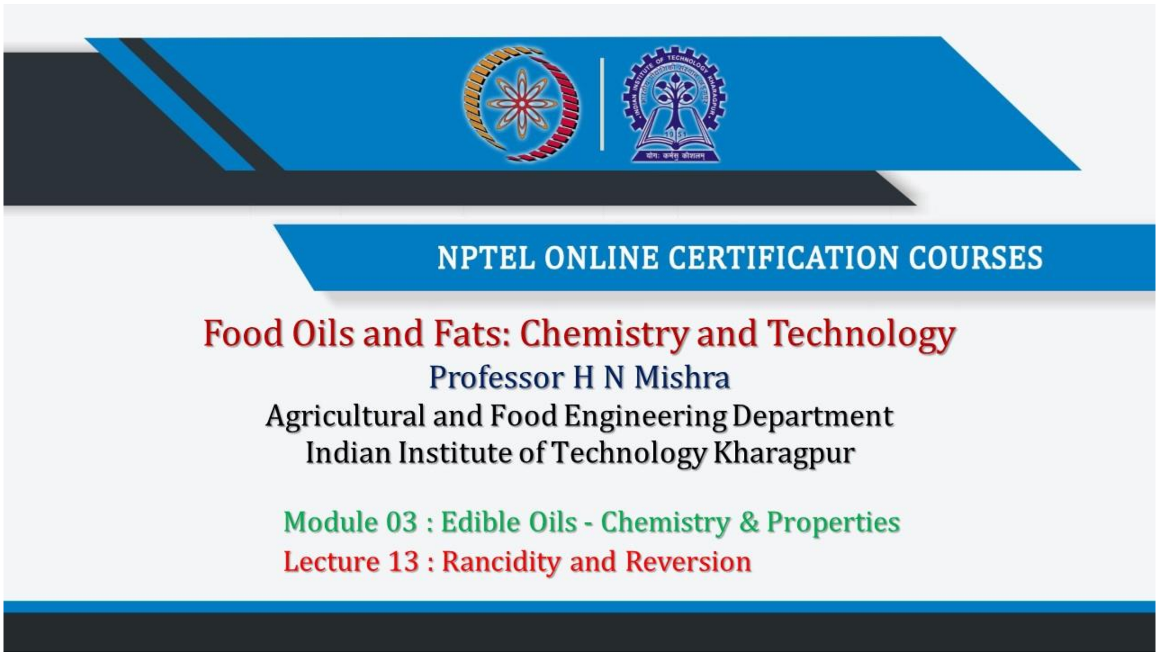
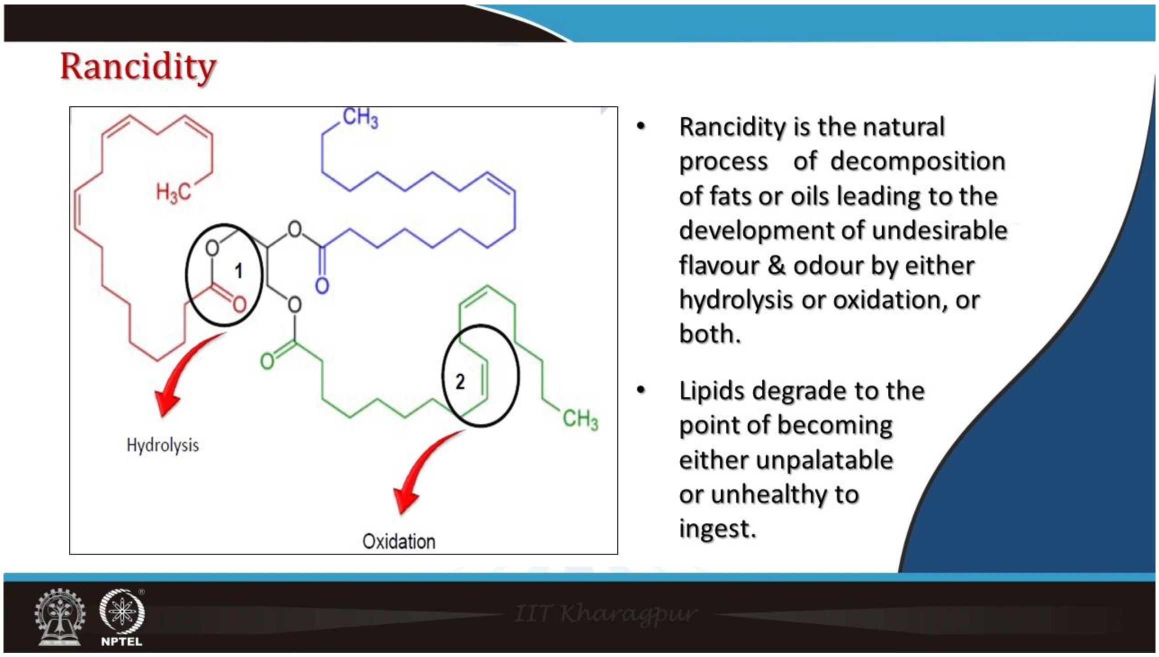
Module 03 : Edible Oils - Chemistry & Properties
Lecture 13 : Rancidity and Reversion

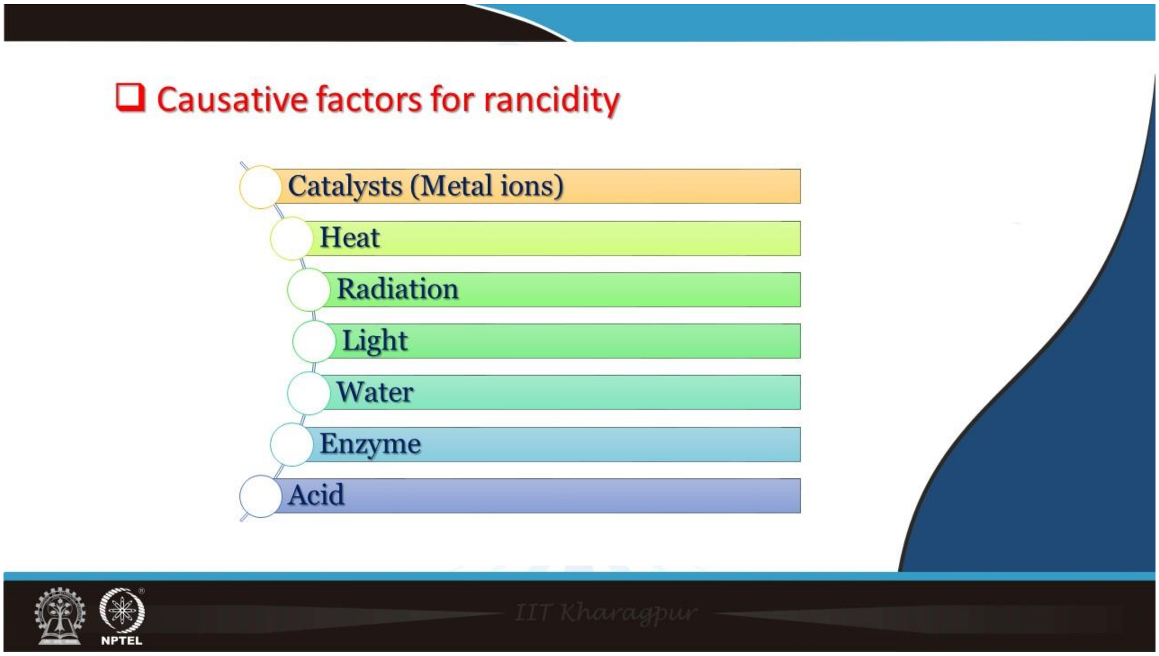


Hello everybody, namaskar. Now, we are in the 13th lecture of this course.

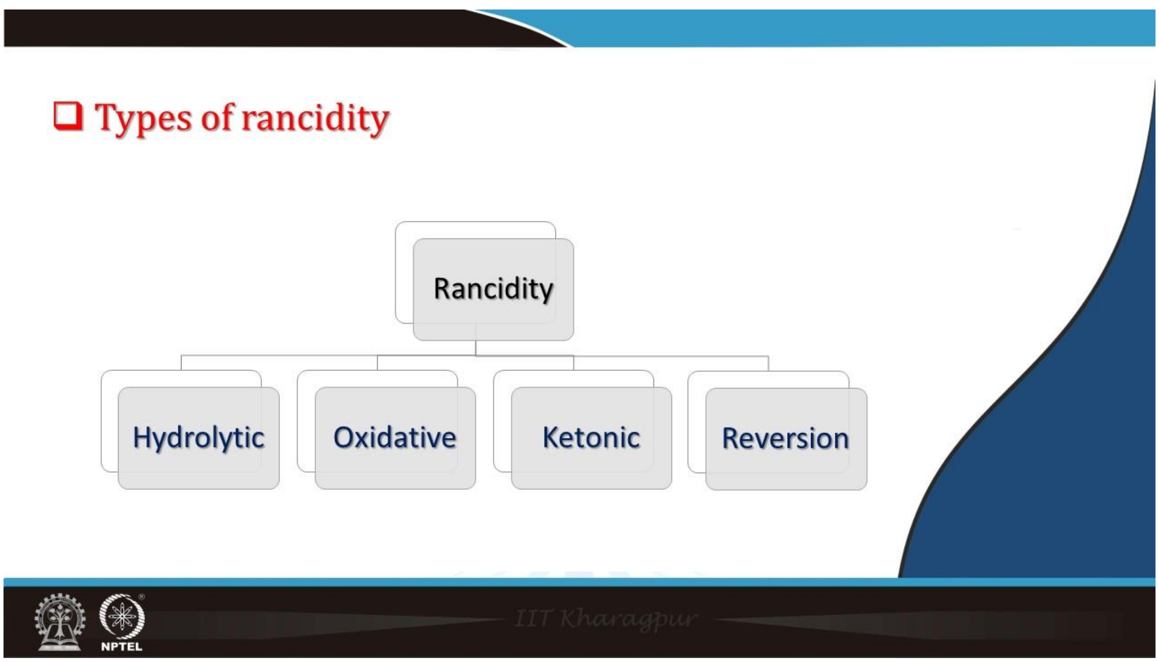
Today in the next half an hour or so, we will discuss a very important phenomenon that takes place in edible oils and that is Rancidity and Reversion. So, we will discuss what is rancidity, its definition, what are the factors that lead to rancidity, and different types of rancidity like hydrolytic rancidity, oxidative rancidity, ketonic rancidity, and then finally, reversion, what reversion is and how it takes place.



Rancidity is the natural process of decomposition of fats or oils leading to the development of undesirable flavor and order by either hydrolysis, oxidation, or both. So, lipids basically in this process degrade to the point of becoming either unpalatable or unhealthy to ingest. You can see here in the fatty acids there is hydrolysis and the fatty acids are released free or when there is an unsaturated bond there may be oxidation. Oxidation of this lipid at the unsaturated position, what is its mechanism, and how it happens will be taken up briefly in this lecture ahead, and in a separate lecture we will be taking up on oxidation that is auto-oxidation.



Then the causative factors for rancidity are normally various catalysts like metal ions, heat, radiation, light particularly UV light, water if there is any and then there are certain enzymes like lipases, lipoxygenases etcetera, and acid. So, these are the various factors or causative factors that lead to the development of or accelerate the rate of development of rancidity in oils and fats.



There may be different types of rancidity that is one is hydrolytic rancidity, other is oxidative rancidity, and ketonic rancidity is another type and reversion although it is directly not the rancidity, it relates to the changes in the flavor and development of undesirable flavor and it might happen in certain oils even before the onset of the rancidity.

Types of rancidity	Main substances producing rancidity	Types of chemical reaction	Materials subject to the type of rancidity
Lipolytic	Low fatty acids, medium chain fatty acids	Enzymic hydrolysis	Milk fat, palm seed oils
Oxidative	Lower aldehydes and ketones	Autoxidation, enzymic oxidation	Polyunsaturated edible oil
Flavor reversion	Oxygen substituted cleavage and rearrangement products	Oxidation cleavage, and rearrangement	Soybean oil
Ketonic	2-Alkanones (methyl ketones)	β-oxidation and enzymic decarboxylation	Milk fat, palm seed oils

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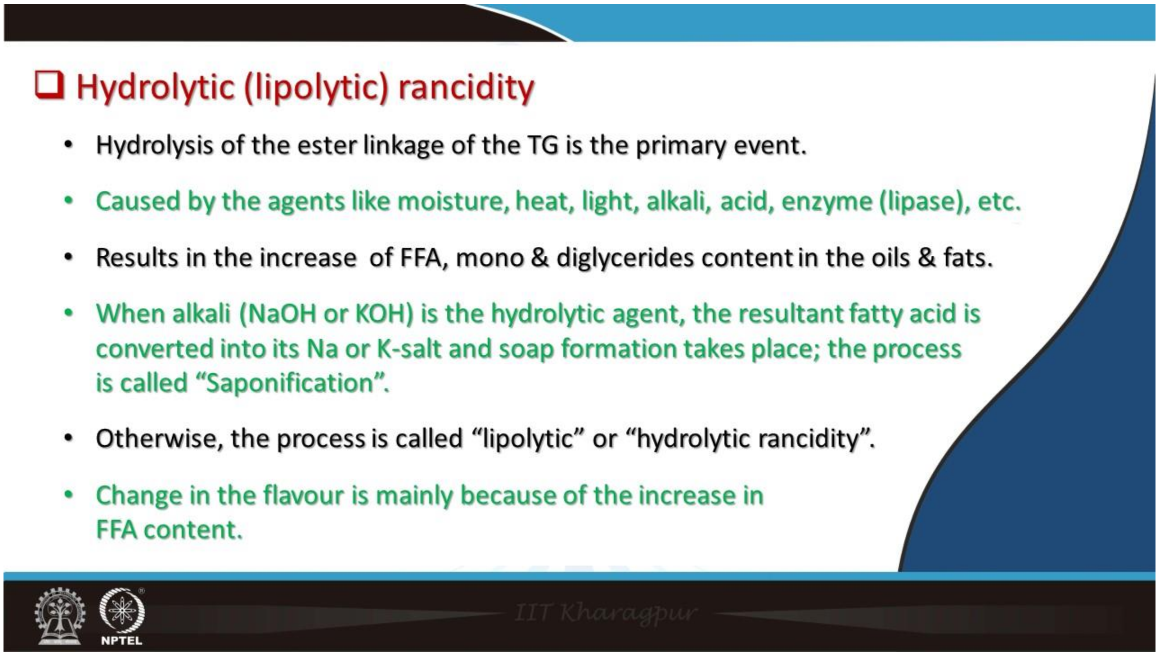
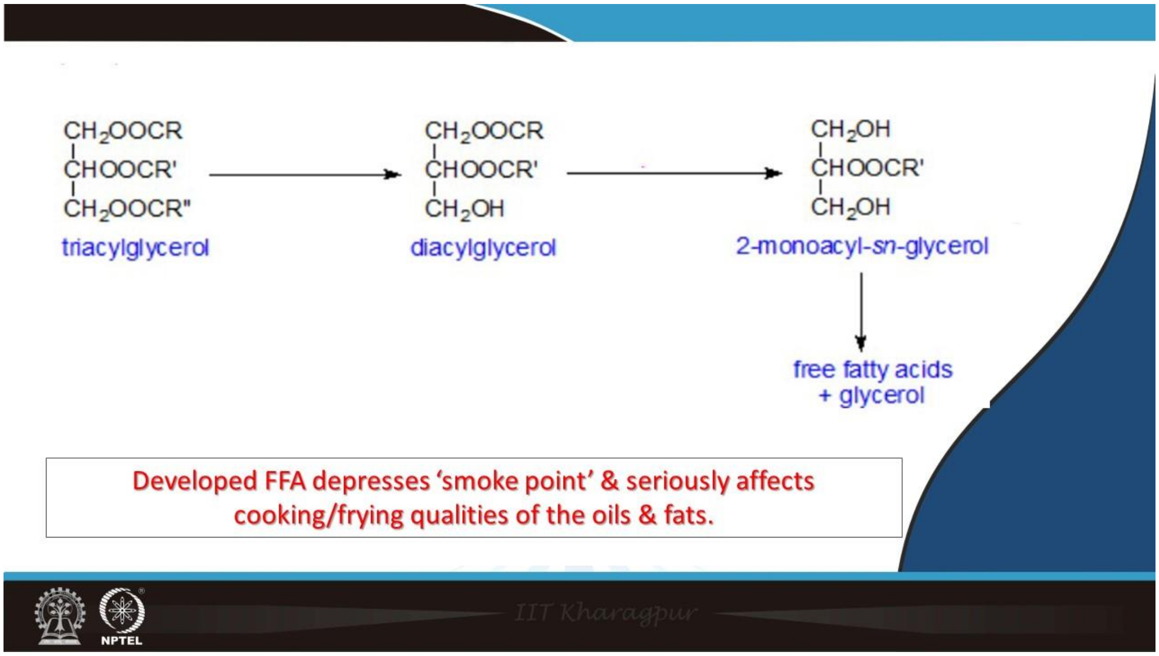
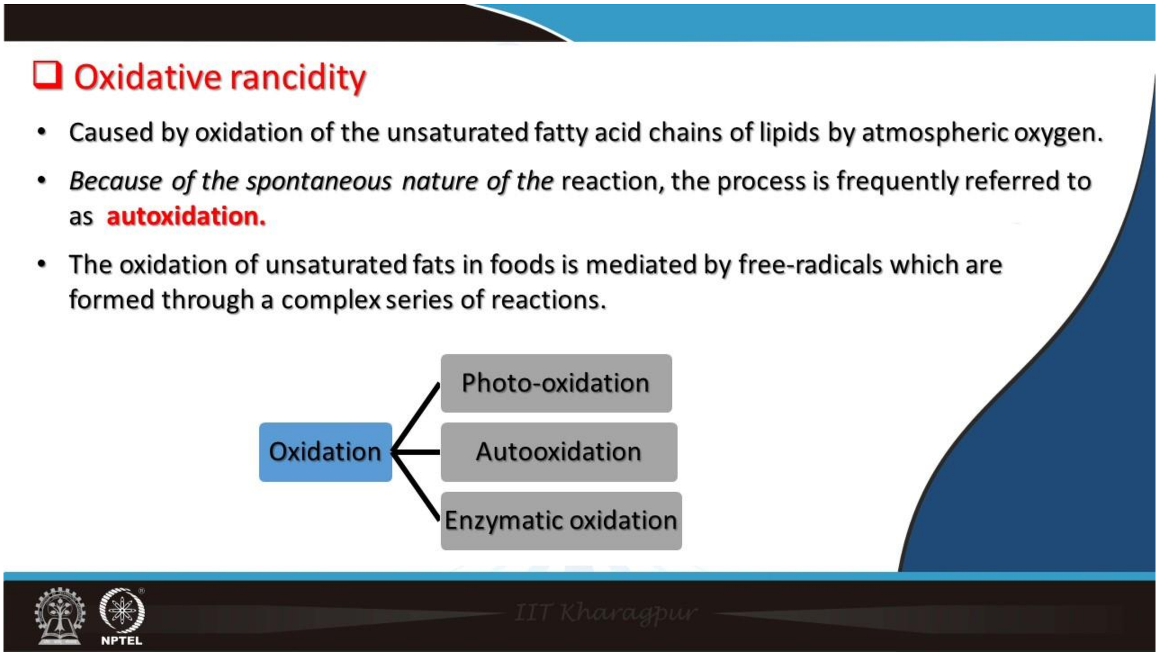
In this table, an overview is provided of the different types of rancidity, what is the main substance producing this particular type of rancidity, the type of chemical reaction that is responsible for this type of rancidity, and materials that subject to this type of rancidity. Let us say first is the lipolytic rancidity. So, involved in the lipolytic rancidity are the low fatty acids, medium chain fatty acids etcetera. This is enzymatic hydrolysis like there is lipase in the enzymes which breaks the ester linkage of the triacylglycerol of the triglycerides. In this process, there is release of free fatty acids in the system and the system will have triglycerides, monoglycerides, diglycerides, and free fatty acids depending upon the extent of the action of the enzymes and hydrolysis reaction. So, basically, saturated fats like milk fat, palm seed oils etcetera are more subject to this type of rancidity. The second is oxidative rancidity and this is here basically the main substrate producing this rancidity is the lower aldehydes and ketones. These lower aldehydes and ketones come from the oxidation of the fatty acids which is there in the triglyceride molecule and ultimately they give various carbonyl compound aldehydes, ketones, acids etcetera which become responsible for the flavor and this type of rancidity. Whereas, in the case of lipolytic rancidity, the flavor is basically the flavor of the free fatty acid, in oxidative rancidity these carbonyl compounds may be the causative agents for the flavor. So, for both the chemical reaction which is also called auto-oxidation, and the enzymatic oxidation, the lipoxygenase is the enzyme responsible. Oxidative rancidity and auto-oxidation are more permanent in oils that have more polyunsaturated fatty acids and more amount of polyunsaturated fatty acids. Then in ketonic rancidity, the main substrate producing the flavor change is 2 alkones that is the methyl ketones. The reactions are beta-oxidation and enzymatic decarboxylation and it is again more prone in palm seed oils or even coconut kernels and milk fat etcetera. Finally, oxygen-substituted change and rearrangement products are responsible for the flavor reversion, and here is the oxidation cleavage and rearrangement of the molecules which is the mechanism of this flavor development. Again this flavor reversion takes place in the oil which has more amount of polyunsaturated fatty acids.



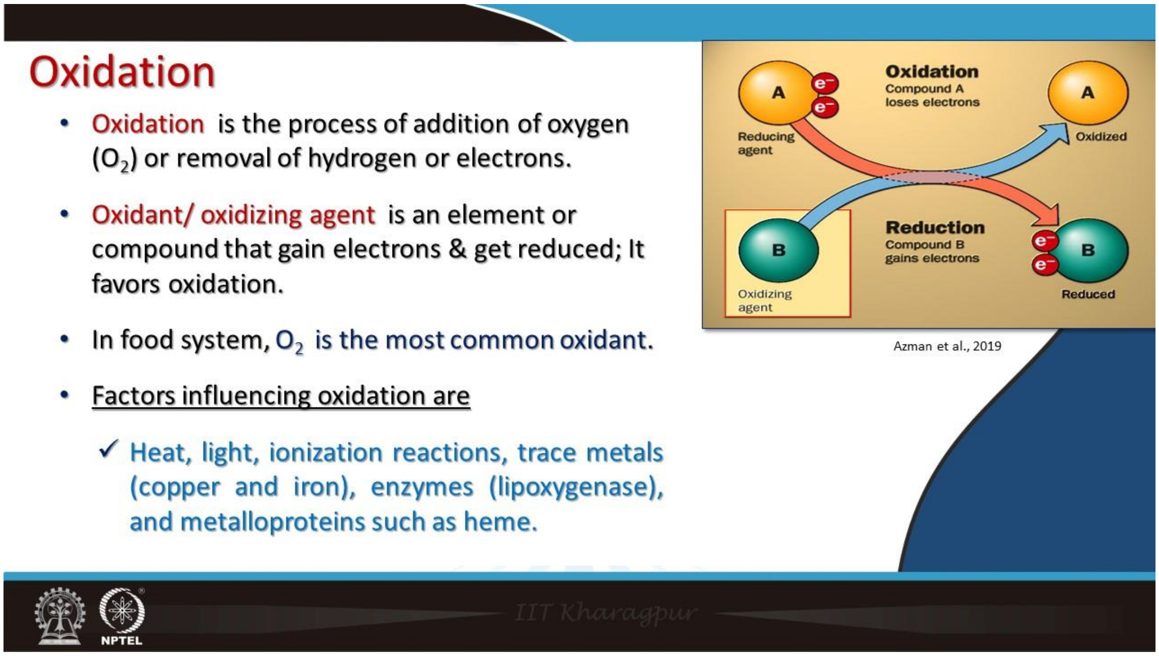
Hydrolysis is the breakage of the ester linkage, that is the breakage of the free fatty acids from the triglyceride is the primary event. It is caused by agents like moisture, light, heat, alkali, acid, enzymes, lipase etcetera. It results in the increase of free fatty acids and mono and diglyceride content in the oils and fats. Particularly when an alkali like sodium hydroxide or potassium hydroxide is the hydrolytic agent the resultant free fatty acid is converted into its sodium or potassium salt, that is sodium or potassium salt of the respective fatty acids. For example, suppose it is a palmitic acid then sodium palmitate or potassium palmitate formation will take place and this process is called saponification and that is how even in the industry soaps are produced. Otherwise, the process is called lipolytic when other agents are there like light, heat, moisture, enzyme, acid, etc., and when these are the causative agents the process is called lipolytic rancidity or hydrolytic rancidity. Here change in the flavor is mainly because of the increase in the free fatty acids content and this free fatty acid content causes several changes in the oil. The oil's smoke point is seriously depressed like cottonseed oil if that is the even 1 percent smoke developed free fatty acids it reduces it’s smoke point by even 100 degrees Celsius. Also, food that is fried in oil containing a high amount of free fatty acids may tend to be darker in color and there may be more fat absorption by the fried food that the surface of the fried material may be cracked it may not be smooth as it should be. As I told you that is in this case of hydrolytic rancidity there is the flavor mainly is because of the flavor of the free fatty acid and this is more pronounced in the short-chain fatty acids like butyric, capric, caprovic etcetera which are generally present in the milk fat or such other products.



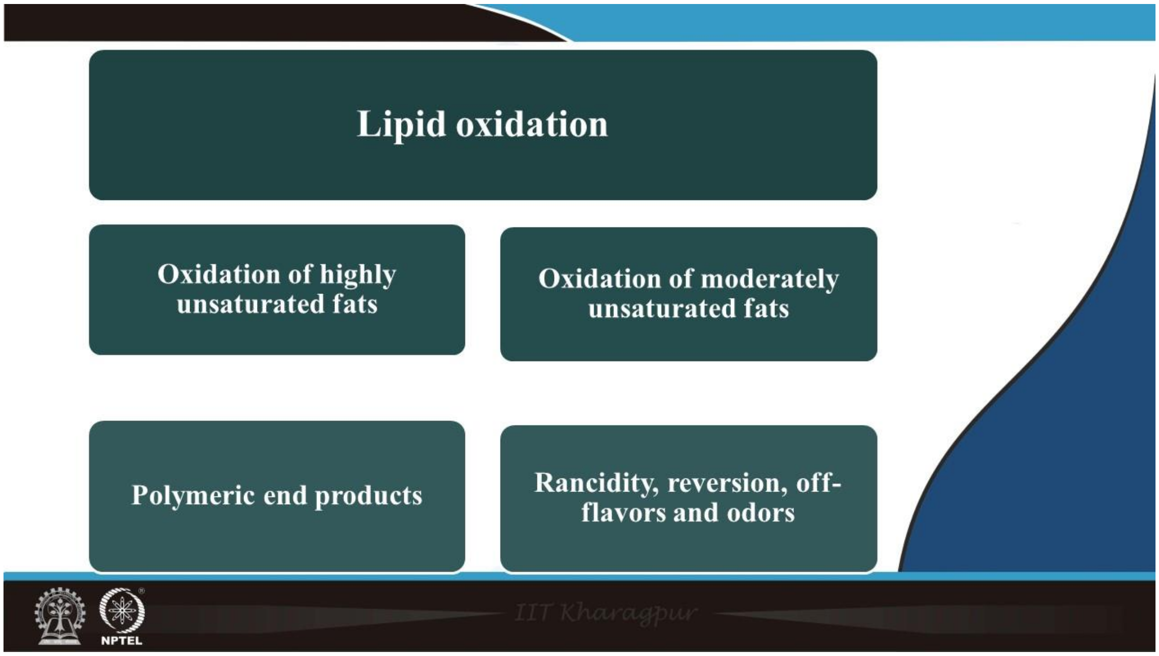
Here is the development of FFA that is it reduces the smoke point and seriously affects the cooking or frying quality of the oil and this is the reaction to how this lipolytic hydro rancidity takes place. Ultimately if there is a complete hydrolysis there will be free fatty acids and glycerol. On partial hydrolysis, diacylglycerol, monoacylglycerol, triacylglycerol, and then a free fatty acid mixture will be formed because of the reaction mechanism.



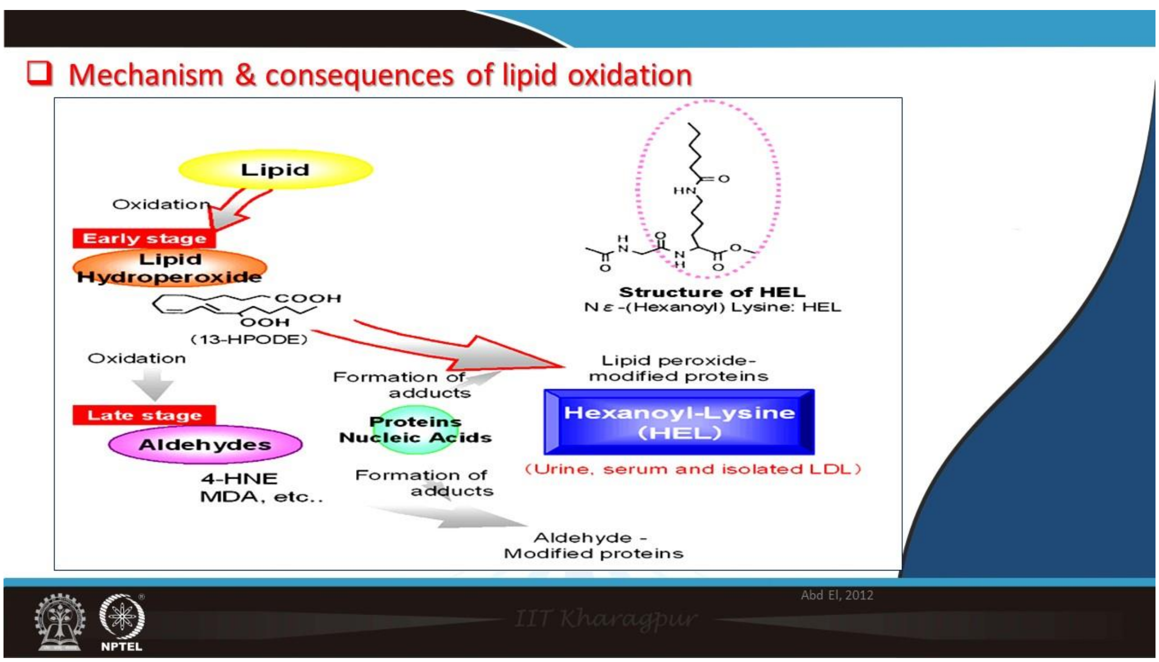
Then let us discuss oxidative rancidity. This obviously, as the name indicates it is caused by oxidation of the unsaturated fatty acid chains of lipids by atmospheric oxygen. Because of the spontaneous nature of the reaction that is once the reaction has started it will continue, it will propagate, it will go further its rate will increase if it is not controlled. So, if once it is initiated it spontaneously takes care and it follows it goes on and that is why this process is frequently referred to as auto-oxidation. So, the oxidation of unsaturated fats in food is mediated by free radicals which are formed through a complex series of reactions and these may be photo-oxidation, auto-oxidation, or enzymatic oxidation. Details of all these processes particularly what is photo-oxidation, auto-oxidation, and enzyme oxidation, their mechanism, and their various adverse effect will be taken up separately in the next class.



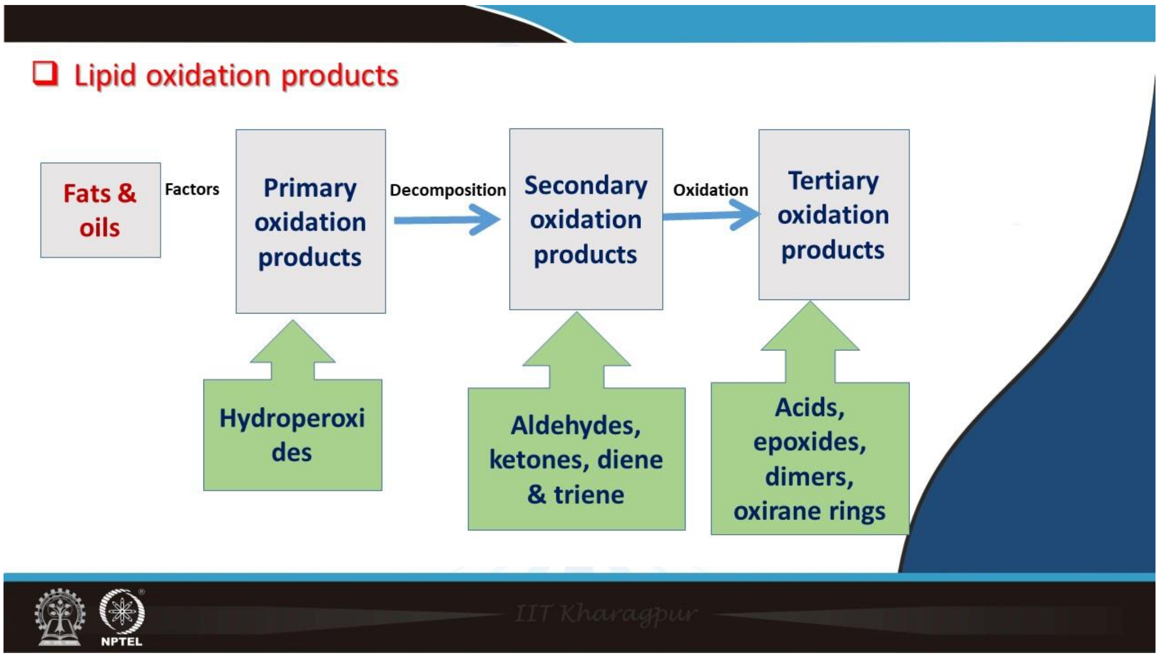
Oxidation is the process of the addition of oxygen or removal of hydrogen or electrons. An oxidant or oxidizing agent is an element or compound that gains electrons as you can see here in the picture and it gets reduced and this favors oxidation. In the food system, oxygen is the most common oxidant. The factors influencing oxidation are heat, light, ionizing reactions, trace metals like copper and iron, and enzymes like lipoxygenases and metalloproteins such as heme, etcetera. You can see here there is oxidation of compound A, compound A loses the electrons, becomes a reducing agent, and gets oxidized whereas, the B compound gains electrons and gets reduced this is shown. So, that is how the oxidation-redox reaction takes place.



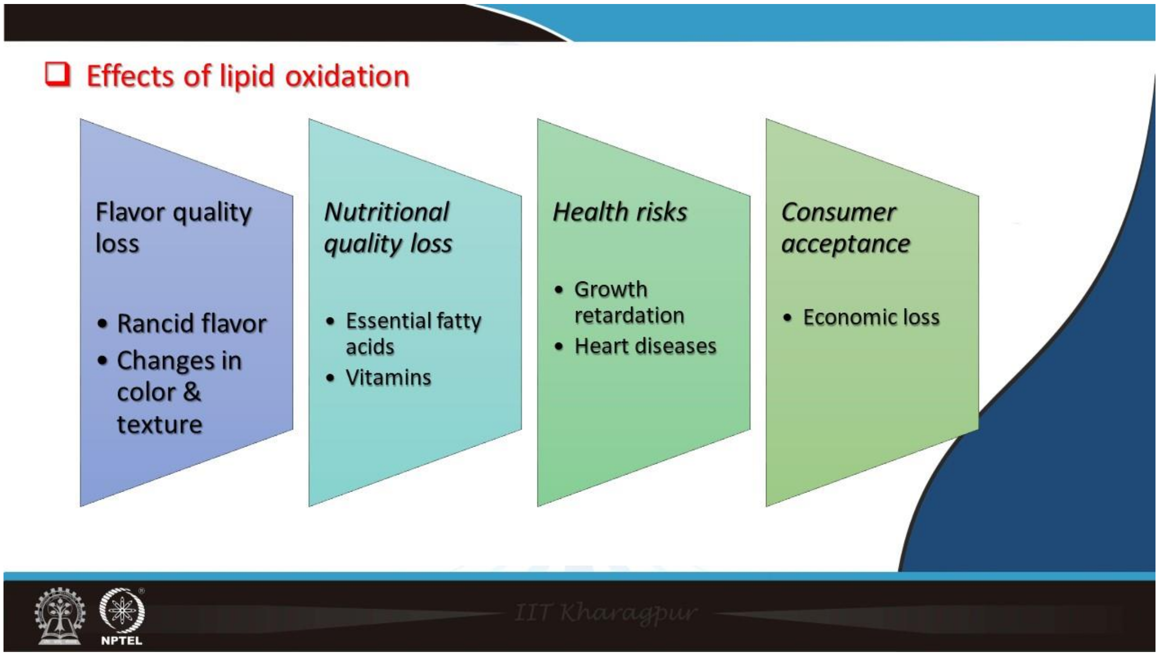
Lipid oxidation is the oxidation of highly unsaturated fatty acids. It may be also because of the oxidation of moderately unsaturated fatty acids. Oxidation of highly unsaturated fatty acids leads to the polymeric end products and ultimately it leads to rancidity reversion, off flavors, and odors development.



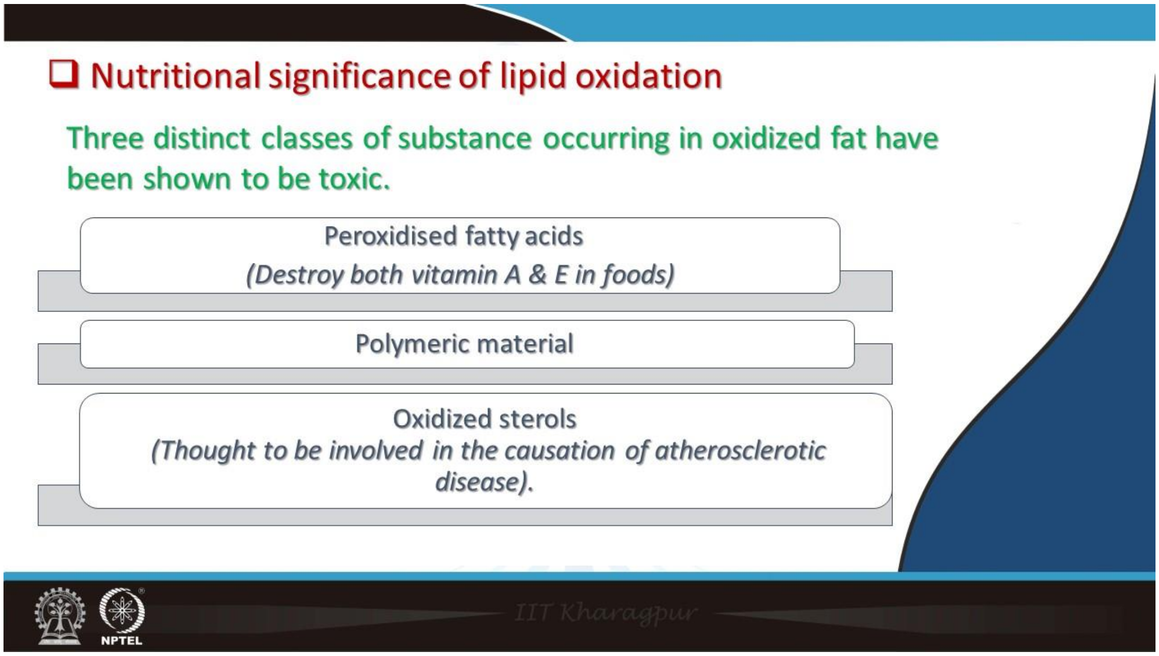
Let us see the mechanism and consequences of lipid oxidation that is when the lipid is in the early stage it oxidizes the lipid into lipid hydroperoxides and then these lipid hydroperoxide at a later stage may further oxidize into aldehydes etcetera or there may be formation of adducts like hexanol lysine, ok. This is the structure of hexanol lysine that may from the aldehydes, etcetera. There is the formation of adducts like aldehydes or modified proteins. In the end, various unsaturated carbonyl compounds like aldehyde ketones etcetera are formed which give the undesirable flavor. This oxidation product even may be the cause of toxicity in the food.



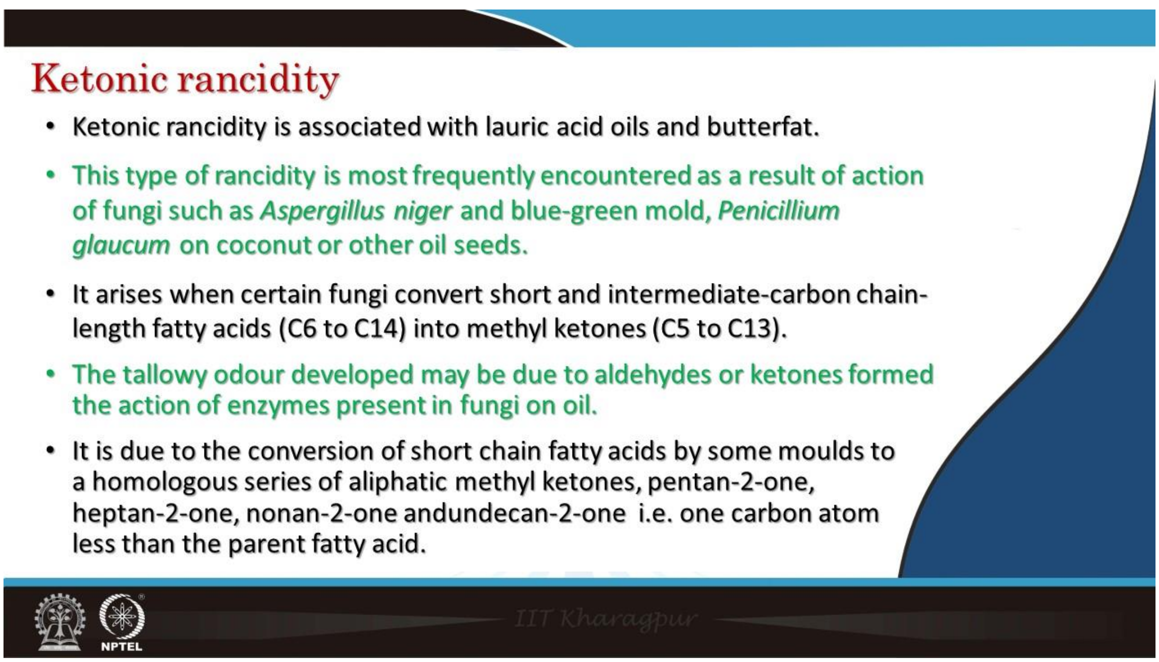
The hydroperoxides are the primary oxidation products and then these hydroperoxides decompose into secondary oxidation products like aldehydes, ketones, dines, and trines. And then, there is the oxidation of secondary oxidation products they get oxidized and result in tertiary oxidation products like acid, epoxides, dimers, oxirane rings etcetera. So, lipid oxidation primary products are hydroperoxide, secondary products are aldehydes, ketones etcetera and tertiary products are acids, epoxides, dimers, and oxirane rings. These tertiary and secondary products may sometimes be the source of toxicity.



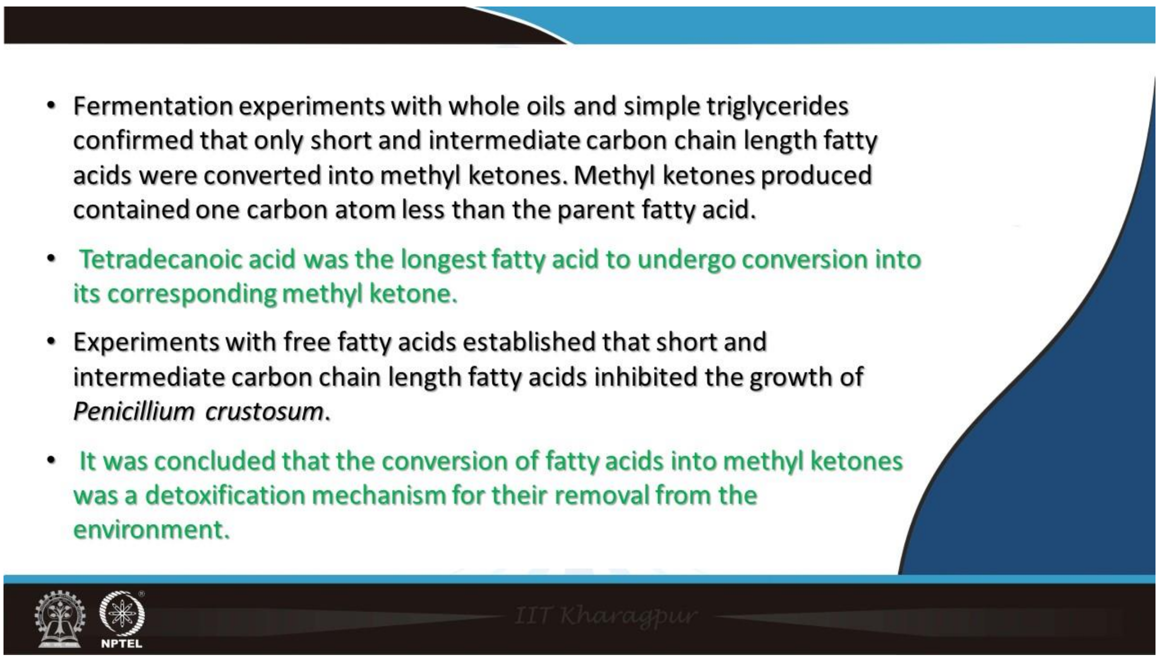
All these lipid oxidation products which are formed influence the various properties of the oils and fat such as flavor quality loss, there is development of rancid flavor, and also changes in the color and texture of the food which are fried in this or even in which these oxidized oil is used. There is a nutritional quality loss in the essential fatty acids particularly if they are oxidized then there is a loss of the essential fatty acids, and there is also if there are vitamins that may get adversely affected. The health risks as I told you there may be growth retardation or heart diseases because of various secondary and tertiary products which are formed. Finally, there is a loss of consumer acceptance, there is economic loss because the consumers might not like to buy these oxidized products, oxidized oils, or lipids.



In the nutritional significance of lipid oxidation, if you see, there are three distinct classes of substances occurring in oxidized fat that have been shown to be toxic. Those are the peroxidized fatty acids that destroy both vitamin A and E in the foods, then polymeric material, and finally, the oxidized sterols which are thought to be involved in the causation of the atherosclerotic disease.



Ketonic rancidity is associated with lauric acid oils and butter fat. This type of rancidity is more frequently encountered as a result of the action of fungi such as *Aspergillus niger* and the blue-green mold that is *Penicillium glaucoma* on coconut oil or other oil seeds. It arises when certain fungi convert short and intermediate carbon chain length fatty acids like C6 to C14 carbon-containing fatty acids into methyl ketones like C5 and C13, which means one carbon atom is reduced by the action of enzymes present in fungi. It is due to the conversion of short-chain fatty acids by some molds to a homologous series of aliphatic methyl ketones, pentan-2-one, heptan-2-one, nonan-2-one andundecan-2-one i.e. one carbon atom less than the parent fatty acid.



Fermentation experiments with whole oils and simple triglycerides confirmed that only short and intermediate-carbon chain-length fatty acids were converted into methyl ketones. Methyl ketones produced contained one carbon atom less than the parent fatty acid. Tetradecanoic acid was the longest fatty acid to undergo conversion into its corresponding methyl ketone. Experiments with free fatty acids established that short and intermediate-carbon chain-length fatty acids inhibited the growth of Penicillium crustosum. It was concluded that the conversion of fatty acids into methyl ketones was a detoxification mechanism for their removal from the environment.

The essential prerequisites for the formation of ketonic rancidity appear to be

- the presence of moulds,
- a low water activity,
- a low partial pressure of oxygen, and
- the presence of short chain fatty acids in the medium.

Fatty acid (3 μmoles)	Methyl ketones (μmoles) 4 hr		8 hr	
	+KOH	−KOH	+KOH	−KOH
C_6	Nil	0·08	Nil	0·09
C_8	0·70	0·85	1·46	1·70
C_{10}	0·24	0·83	0·33	0·63
C_{12}	0·09	0·26	0·12	0·27

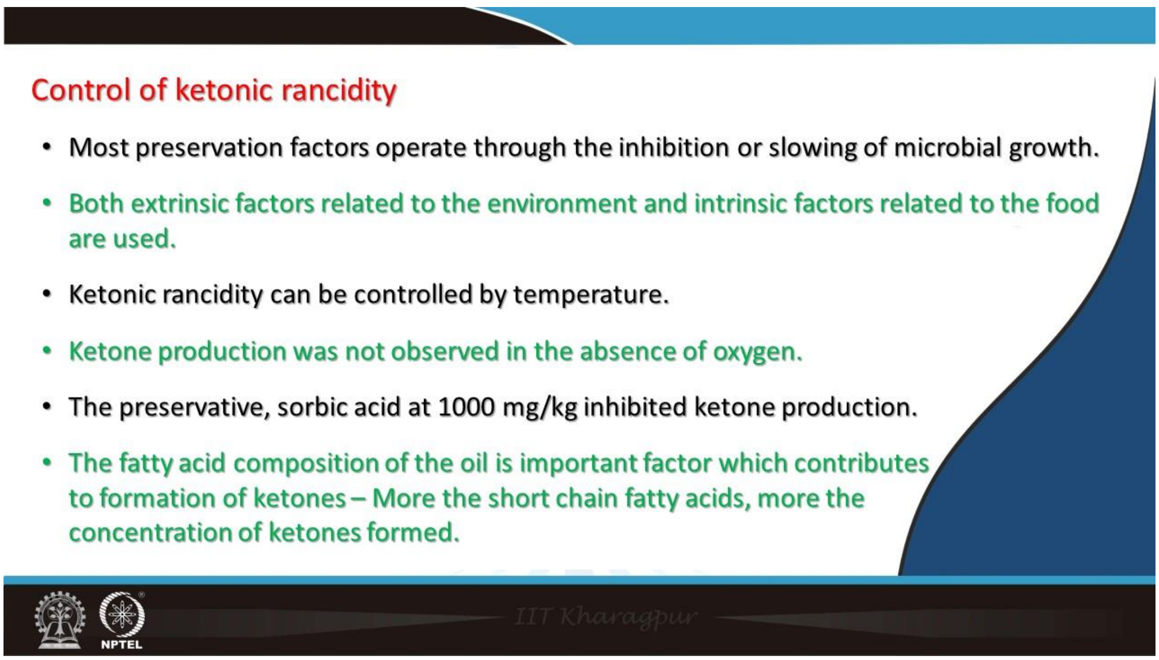
Lawrence, 1966

The essential prerequisites for the formation of ketonic rancidity appear to be the presence of molds, low water activity, and low partial pressure of oxygen because low water activity and low partial pressure are the requirements that favor the growth of molds and the presence of short-chain fatty acids in the medium. The mold enzymes convert these short-chain fatty acids shown here into methyl ketone molecules and the quantity produced after 4 hours and 8 hours is shown.

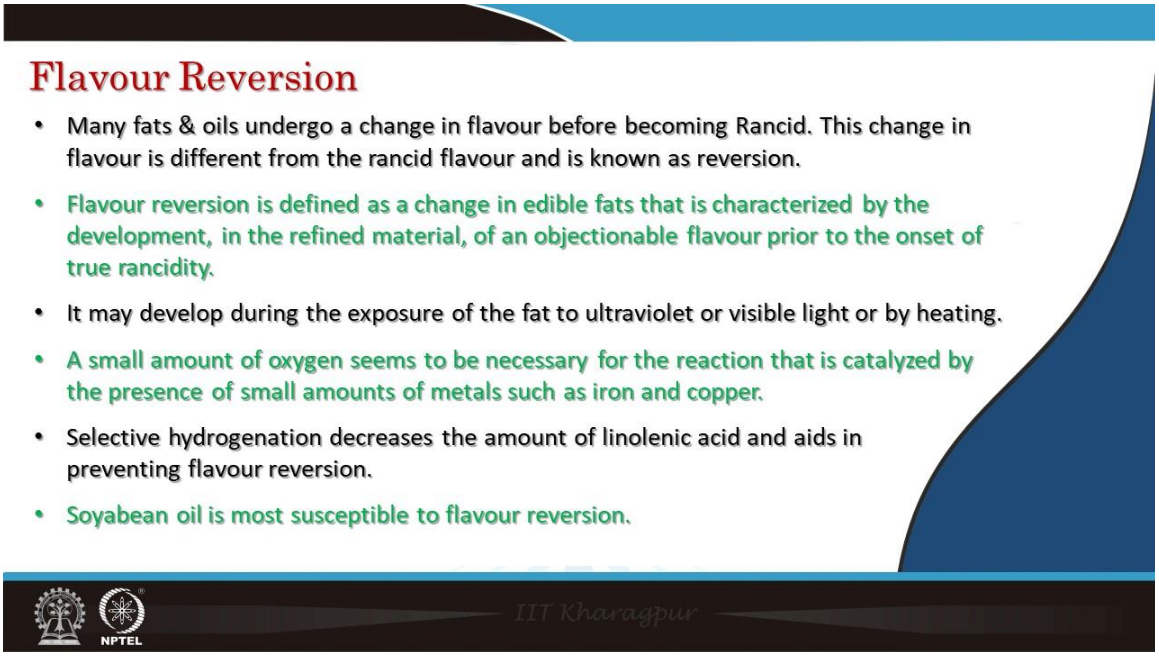
Ketonic rancidity in coconut oil

- Coconut oil has a higher concentration of medium chain fatty acids (C6:0 - C12:0)
- The triacylglycerols of coconut oil has a high concentration of lauric acid (C12:0) and myristic acid (C14:0).
- Ketonic rancidity involves the fungal conversion of medium chain fatty acids (C6-C~2) to the methyl ketone one carbon atom less.
- Conversion of triacylglycerols to methyl ketones involves two reactions.
- The first reaction involves lipolysis of triacylglycerols containing medium chain length fatty acids to release free fatty acids
- The second reaction involves the conversion of free medium chain fatty acids to the methyl ketone one carbon atom less.
- Thus lauric acid (C12:0) is converted to 2-undecanone (C11:0), capric acid (C10:0) is converted to 2-nonanone (C,~) and caprylic acid (C8:0) is converted to 2-heptanone (Cv).

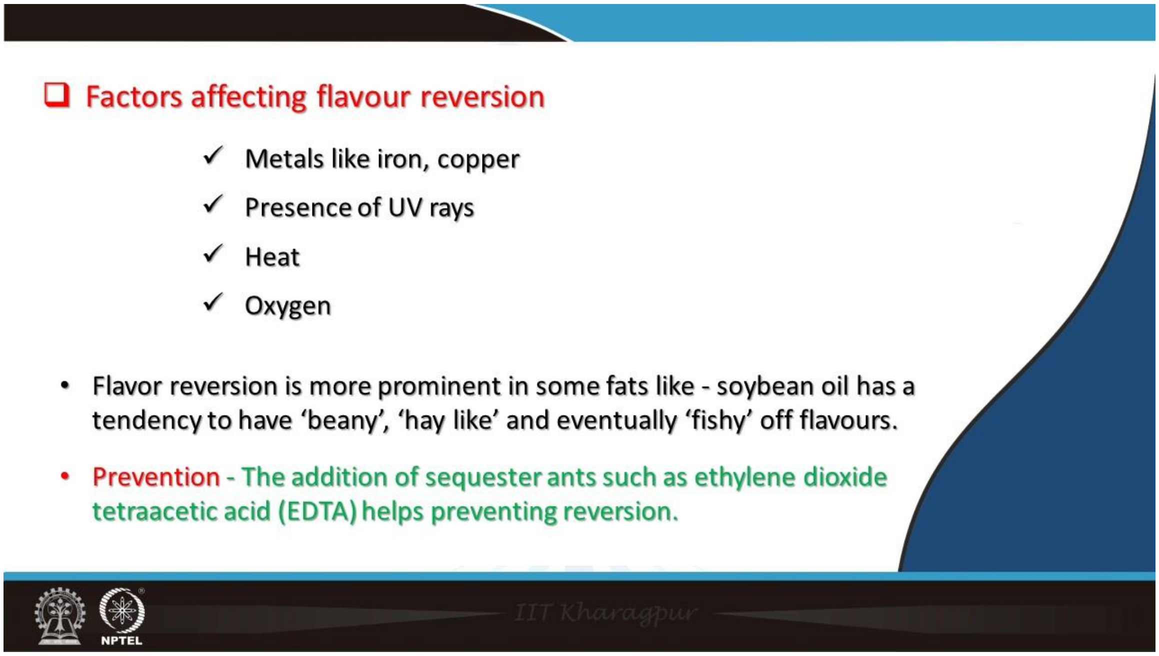
Let us take a case study particularly the ketonic rancidity in coconut oil. Coconut oil has a higher concentration of medium-chain fatty acids (C6:0 - C12:0). The triacylglycerols of coconut oil has a high concentration of lauric acid (C12:0) and myristic acid (C14:0). Ketonic rancidity involves the fungal conversion of medium chain fatty acids (C6- C~2) to the methyl ketone one carbon atom less. The conversion of triacylglycerols to methyl ketones involves two reactions. The first reaction involves lipolysis of triacylglycerols containing medium chain length fatty acids to release free fatty acids. The second reaction involves the conversion of free medium chain fatty acids to the methyl ketone one carbon atom less. Thus, lauric acid (C12:0) is converted to 2-undecanone (C11:0), capric acid (C10:0) is converted to 2-nonanone (C,~) and caprylic acid (C8:0) is converted to 2-heptanone (Cv). So, this is these are with particular relation to the ketonic rancidity of coconut oil.



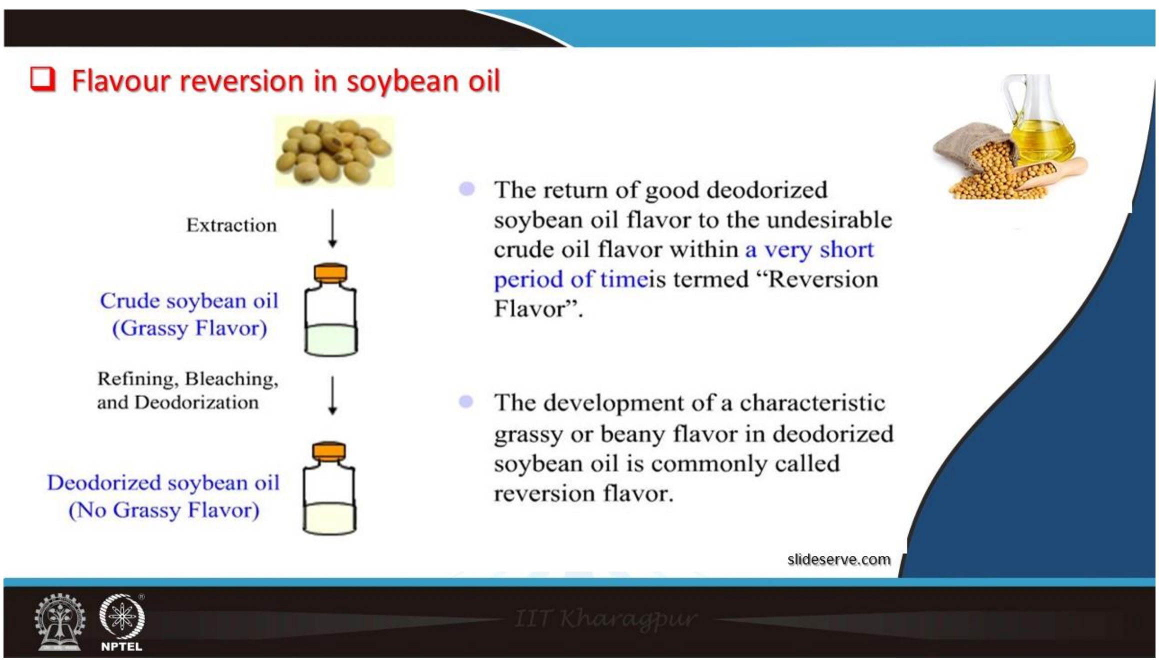
Then how can we control the ketonic rancidity? Most preservation factors operate through the inhibition of or slowing of microbial growth. Both extrinsic factors related to the environment and intrinsic factors related to the food products that can control the growth of mold are used here. Ketonic rancidity can be controlled by controlling the temperature because the temperature is an important requirement for every microorganism, even in the case of mold. They require optimum temperature for their growth. They require oxygen for their growth therefore, ketone production was not observed in the absence of oxygen. So, if there is an environment that is oxygen-free then ketonic rancidity can be controlled. The preservatives like sorbic acid at the rate of 1000 milligrams per kg of oil inhibited ketone production because this preservative is effective against molds. The fatty acid composition of the oil is an important factor that contributes to the formation of ketones that is more the short-chain fatty acids more the concentration of ketones formed. In the oils which have more polyunsaturated fatty acid this is generally not a problem.



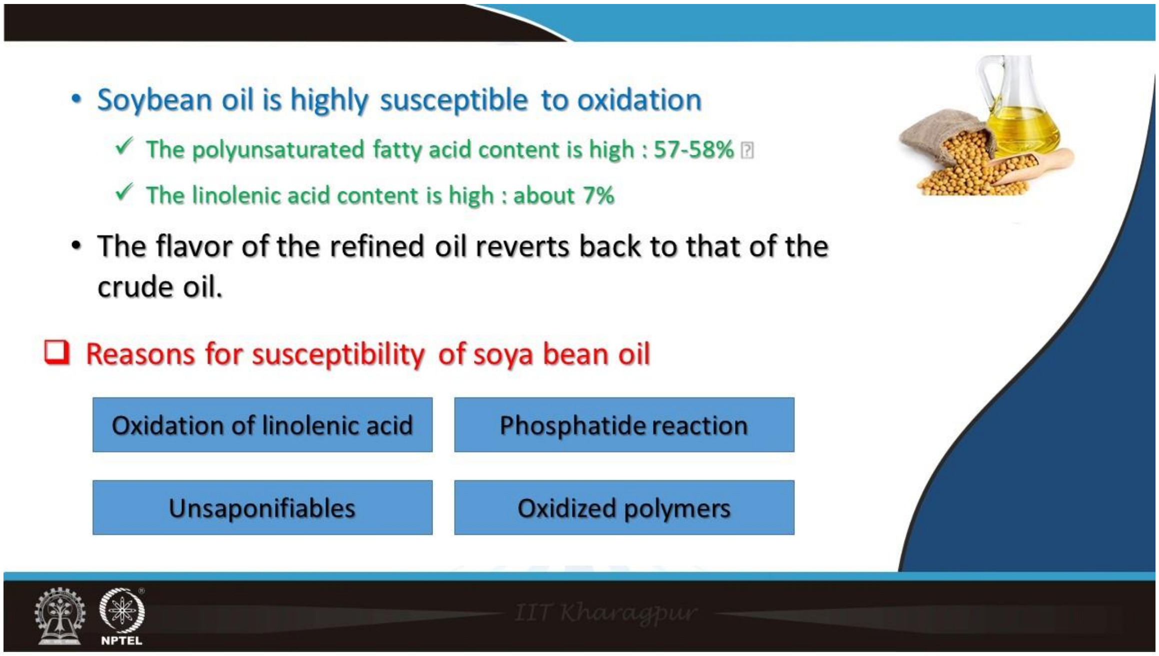
Then let us see flavor reversion. Many oils and fats undergo a change in the flavor before becoming rancid. This change in the flavor of the oil because of some other action that is may not be actually the rancidity that is hydrolytic ketonic or oxidative rancidity, but the other flavor change. This change in flavor which is different than the rancid flavor is known as reversion and this is more of a problem in the oil which has higher amount of polyunsaturated fatty acids. Flavor reversion is defined as a change in edible fats that is characterized by the development in the refined material of an objectionable flavor prior to the onset of the true rancidity. It may develop during the exposure of the fat to ultraviolet or visual light or by heating because they all catalyze these conditions then more unsaturated fatty acids change even without going to the oxidate process. A small amount of oxygen seems to be necessary for the reaction that is catalyzed by the presence of small amounts of metals such as iron and copper. Selective hydrogenation decreases the amount of linolenic acid and aids in preventing flavor reversal. Soybean oil is the most susceptible oil to flavor reversion because it has more amount of polyunsaturated fatty acids.



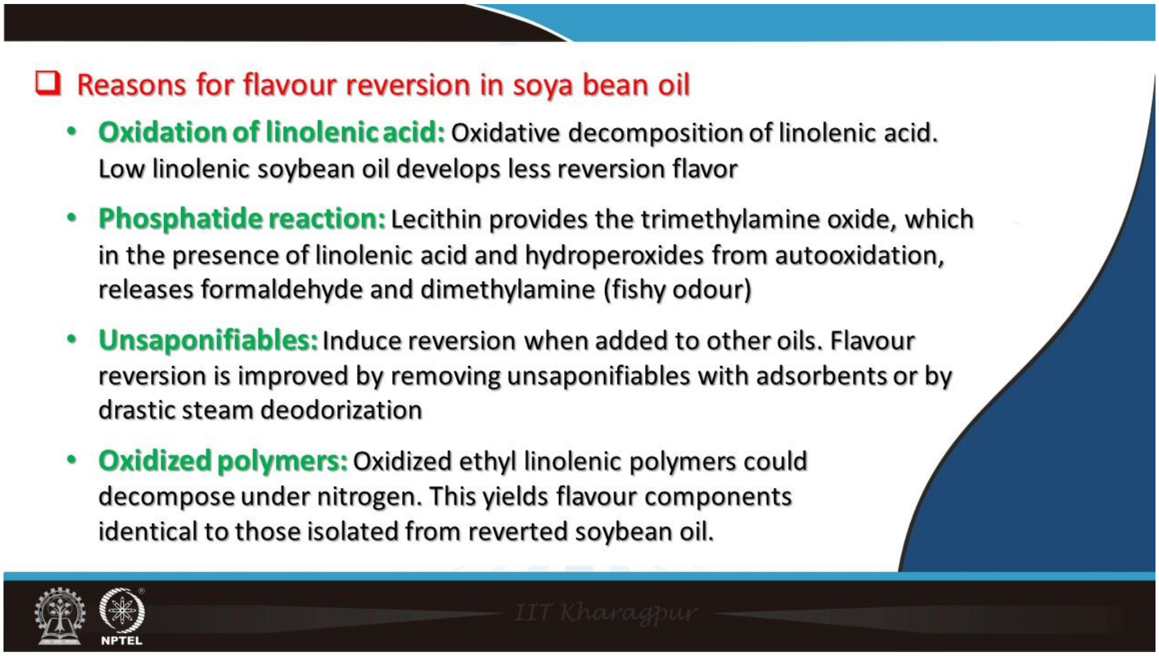
The factors that affect the flavor reversion include metals like iron and copper, presence of ultraviolet rays, heat, light and oxygen. Flavor reversion is more prominent in some fats like soybean oil. It has a tendency to have beanie, hay like or eventually the fishy off flavor. The addition of sequester such as ethylene dioxide tetra acetic acid that is the EDTA helps preventing reversion.



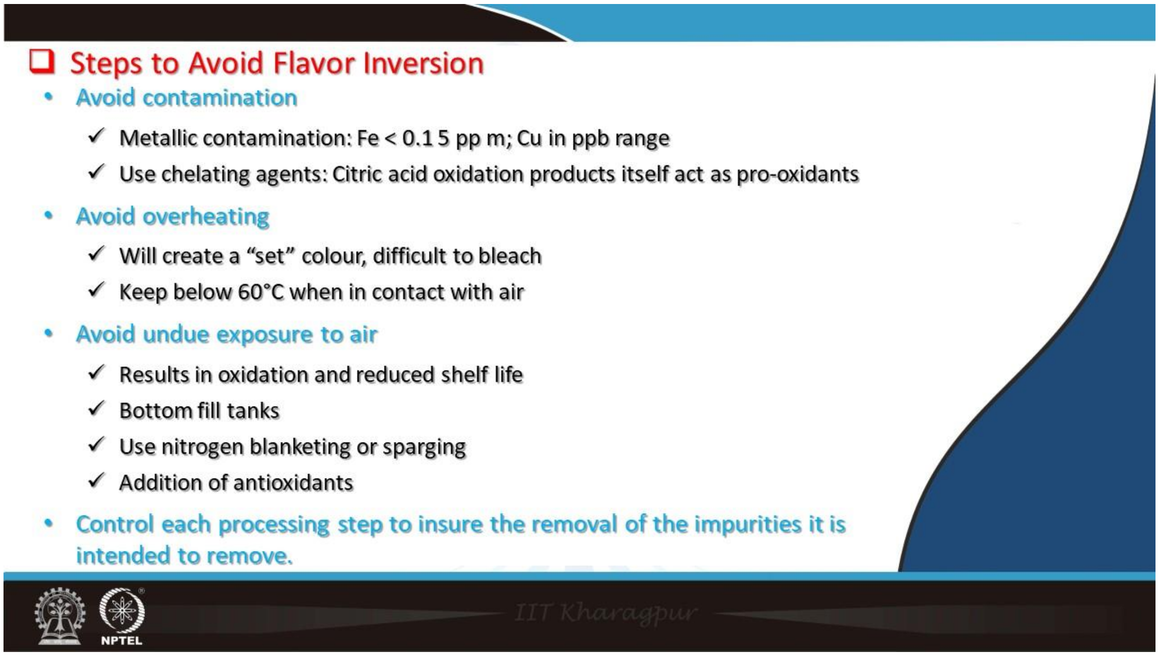
Let us see a case study of flavor reversion in soybean oil. The soybean oils that are extracted, that is the crude soybean oil have a grassy flavor. Then at refining, bleaching, and deodorization, this grassy flavor is removed. The return of good deodorized soybean oil flavor to the undesirable crude oil flavor within a very short period of time takes place and that is termed as flavor reversion. This development of a characteristic grassy or beanie flavor in deodorized soybean oil is commonly called flavor reversion. So, both there is in these flavors develop after the refining of oil is very probably because of the presence of the more polyunsaturated fatty acids.



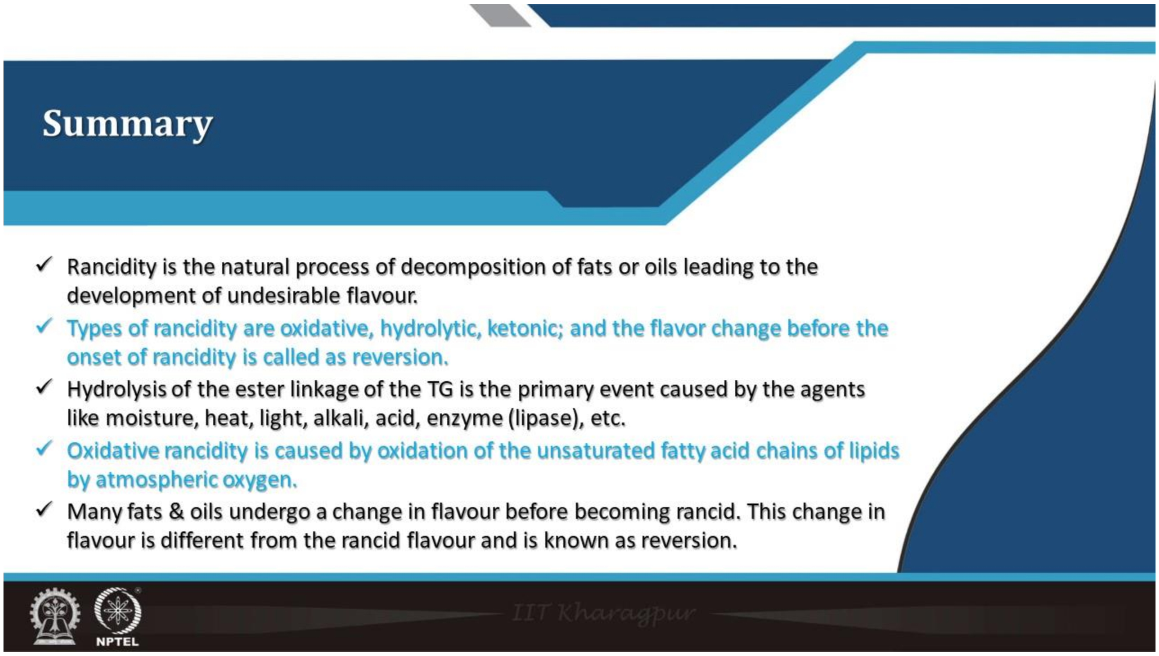
Soybean oil is highly susceptible to oxidation as the polyunsaturated fatty acid content is high like 57 to 58 percent. The linolenic acid content is high about 7 percent. So, the flavor of the refined oil reverse back to that of the crude oil, and the reason for the susceptibility of soybean oil include oxidation of linolenic acid, unsponifiable matters, phosphatide reactions, and oxidized polymers.



The reason for flavor reversion in soya bean oil is the oxidation of linolenic acid which is the oxidative decomposition of linolenic acid, and lower linolenic soybean oil develops less reversion in flavor. Then lecithin provides the trimethylamine oxide which in the presence of linolenic acid and the hydroperoxides from auto-oxidation releases formaldehyde and dimethylamine which gives a fishy odor. Then unsponifiable matters induce reversion when added to other oils. Flavor reversion is improved by removing the unsaponifiable with adsorbents or by drastic steam deodorization. So, deodorization, degumming, and removing the unsponifiable matters control the reversion problem. Then oxidized polymers like oxidized ethyl linolenic polymers could decompose under nitrogen and this yields flavor components identical to those isolated from the reverted soybean oil.



Then steps to avoid flavor reversion or flavor inversion include avoiding metallic contamination that is iron in the oil should be less than 0.15 ppm or so copper in the ppb range. Then chelating agents like citric acid oxidation products themselves act as a pro-oxidant. The chelating agents if they are used bind to the metal ions. Then avoid overheating, overheating will create a set color that is difficult to bleach and keep below 60 degree Celsius when in contact with the air. Then avoid exposure of the oil to air, as it results in oxidation and reduces the shelf life. Use bottom fill tanks and nitrogen blanketing or sparging. Bottom-filling tanks mean that the tank is filled from the bottom rather than from the top as in the top filling containers the oxygen can get easy entry. Then addition of antioxidants and controlled each processing step to ensure the removal of the impurities it is intended to remove.



Finally, I would like to summarize this lecture by saying that yes rancidity is a natural process of decomposition of fats or oil which lead to the development of undesirable flavour and may cause health problem, and the oil becomes unacceptable. Types of rigidity are oxidative, hydrolytic, and ketonic and the flavor change before the onset of rancidity is called reversal. Hydrolysis of the ester linkage of the triglyceride is a primary event that is caused by agents like moisture, heat, light, alkali, acid, enzyme etcetera. Then oxidative rancidity is caused by the oxidation of unsaturated fatty acid chains of the lipid by atmospheric oxygen and most fats and oils undergo change in the flavour before becoming rancid. And this stage is known as reversion which is the flavour change before the onset of the rancidity. So, one should take proper care to handle the oil during handling of the oil storage processing etcetera, one should take care that these causative agents are eliminated from the oil. This rancidity and reversion are the major problems that deteriorate the quality of oil during its handling.

These are the references that we used in this lecture. Finally, thank you very much for your patience hearing.