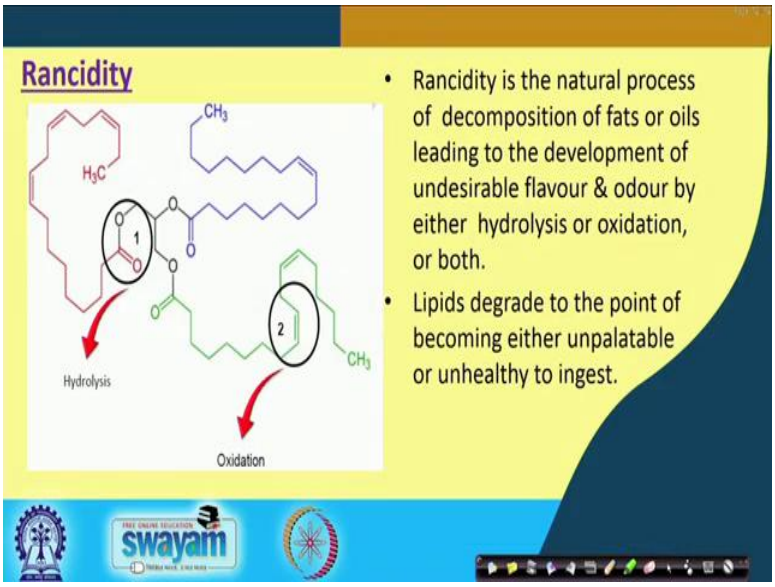
Novel Technologies for Food Processing and Shelf Life Extension

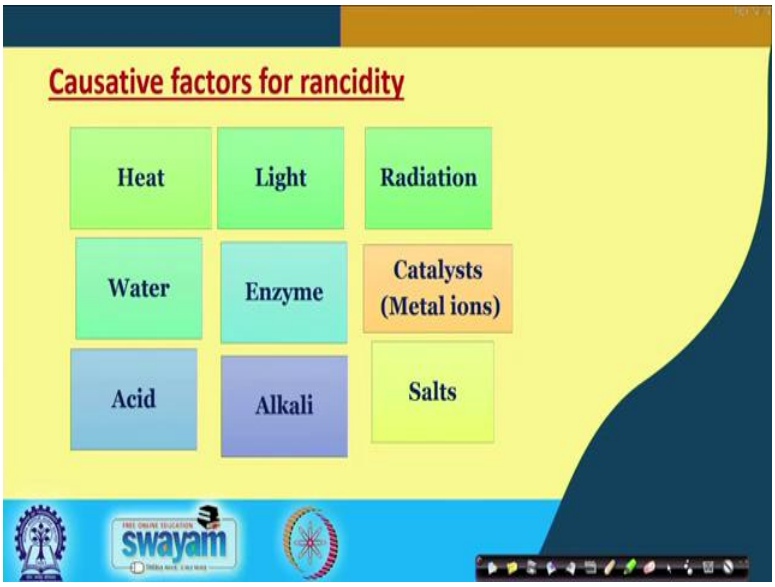
Prof. Hari Niwas Mishra
Department of Agricultural and Food Engineering
Indian Institute of Technology, Kharagpur

Lecture - 35
Rancidity

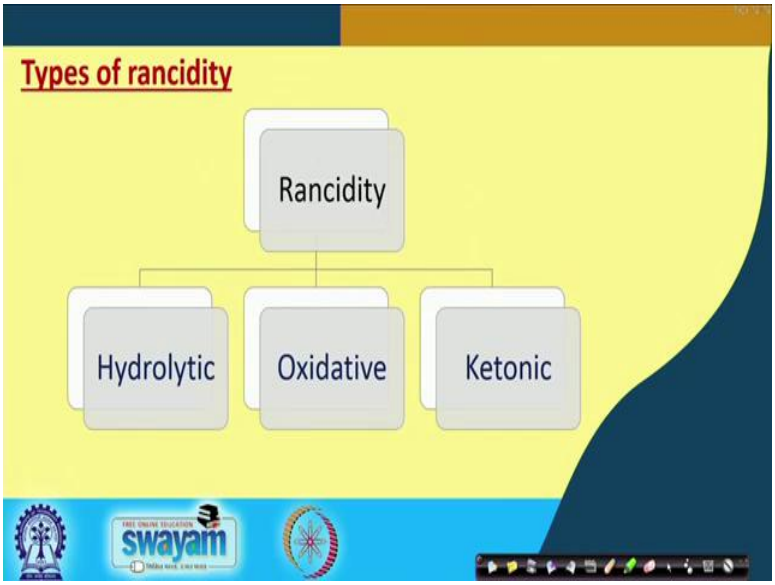
This lecture is on rancidity of oils and fats.



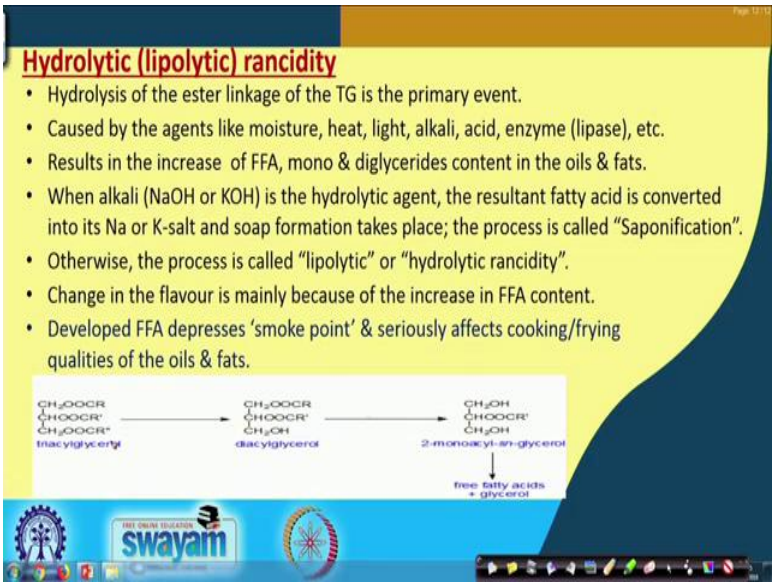
A very important process which takes place in fats and oils or the products containing fats and oil is known as rancidity. Rancidity is the natural process of decomposition of fats or oils leading to the development of undesirable flavor and odour which is either by hydrolysis or by oxidation. In rancidity by hydrolysis or oxidation, the lipids or fats and oils degrade to the point of becoming either unpalatable or unhealthy to ingest.



Different causative factors for the rancidity include heat, light, radiation, water, enzymes, even catalysts like metal ions, acids, alkali, salt, etc. These are the conditions or agents to which the foods containing fats and oils or even the individual fats and oils come in direct contact during various operations like heating, frying, etc. During storage, they may come in contact with the light.



All these factors bring about certain changes in the odour, flavor, nature and characteristics of the material. The rancidity may be broadly categorized into three groups: hydrolytic rancidity, oxidative rancidity and ketonic rancidity.



Hydrolytic (lipolytic) rancidity

- Hydrolysis of the ester linkage of the triglyceride is the primary event.
- Caused by the agents like moisture, heat, light, alkali, acid, enzyme (lipase), etc.
- Results in the increase of FFA, mono & diglycerides content in the oils & fats.

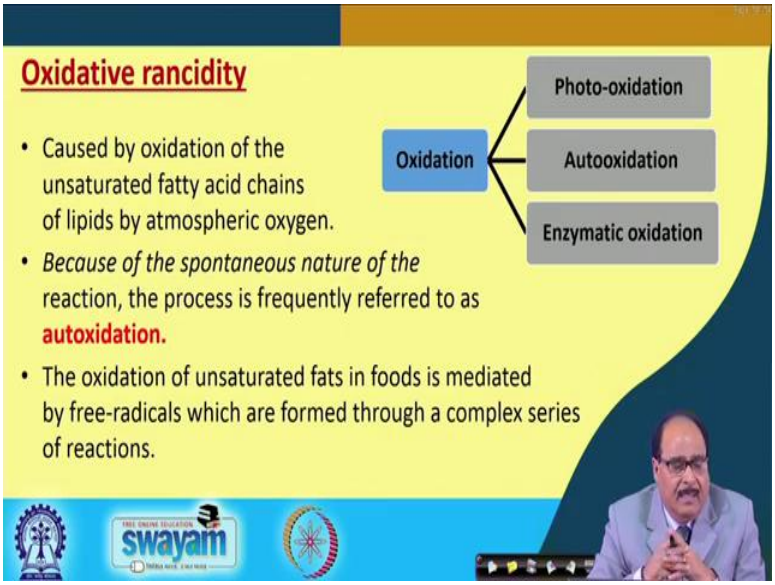
A triglyceride (see Fig.) contains 3 fatty acids attached with a glycerol molecule. When the ester linkage is hydrolyzed depending upon the extent of hydrolysis, the system will get more free fatty acids plus there may be some monoglyceride, diglyceride and triglyceride. In fact, generally oil or fat which was earlier a triglyceride because of this hydrolysis, it becomes a mixture of triglyceride, diglyceride, monoglyceride and free fatty acids. This hydrolysis may be caused by the different agents like moisture, heat, light, alkali, acid, enzymes like lipase etc.

- When alkali (NaOH or KOH) is the hydrolytic agent, the resultant fatty acid is converted into its Na or K-salt and soap formation takes place; the process is called "Saponification". So, this alkali reacts with the released free fatty acids and sodium or potassium salt of the respective fatty acids are formed and the resultant product is called soap and actually that is the principal of the soap formation in the industrial sector.
- Otherwise, when other causative agents bring about hydrolysis, the process is called "lipolytic" or "hydrolytic rancidity".
- Change in the flavour is mainly because of the increase in FFA content.

- Developed FFA depresses 'smoke point' & seriously affects cooking/frying qualities of the oils & fats.

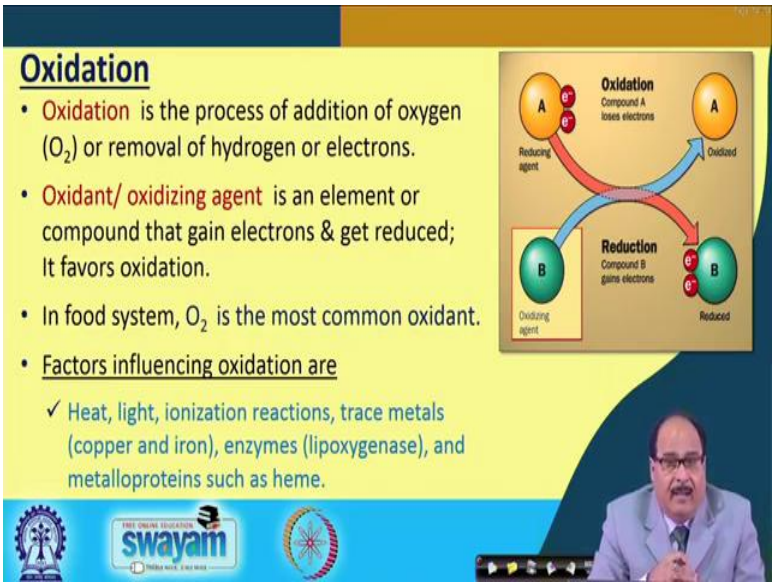
For example, cotton seed oil which has a smoke point of about 232 ℃; even 1 % development of FFA in the cotton seed oil reduces its smoke point to 160 ℃ means that the cotton seed oil which was earlier able to be heated up to 232 ℃; with 1 % developed free fatty acids, it cannot be heated more than 160 ℃.

Its frying qualities and moreover the production are hampered when they are fried in an oil which has more free fatty acids, there is more absorption of oil or fat by the products. Also the products tend to develop more browning and they give the cracked surfaces i.e. smoothness on the surface may not be there. So, these are some of the problems for which the rancidity should be avoided.



Oxidative rancidity

Oxidation is a process where addition of oxygen takes place on the molecule; it may be a photo oxidation, it may be auto-oxidation or enzymatic oxidation. The oxidative rancidity basically is caused by oxidation of the unsaturated fatty acid in the chain and because of the spontaneous nature of the reaction, the process is frequently referred to as auto-oxidation and oxidation of unsaturated fat in food is generally mediated by free radical which are formed through a complex series of reactions.

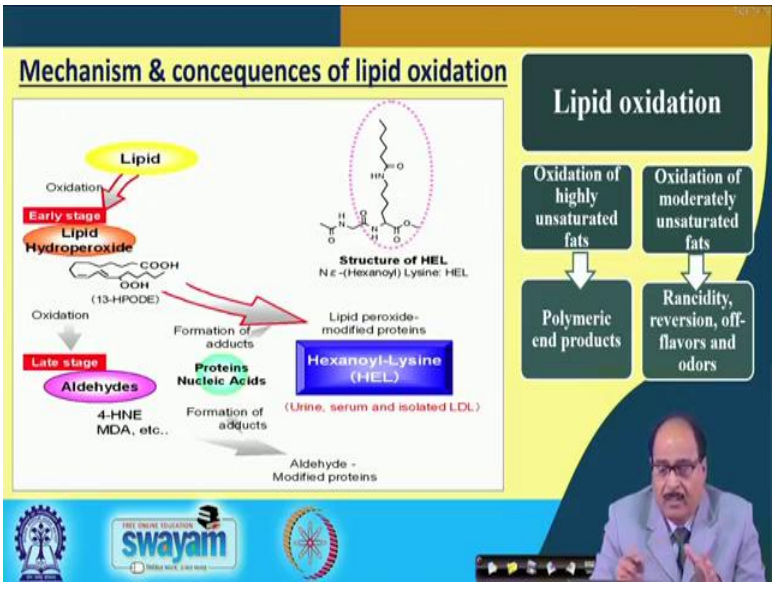


Oxidation

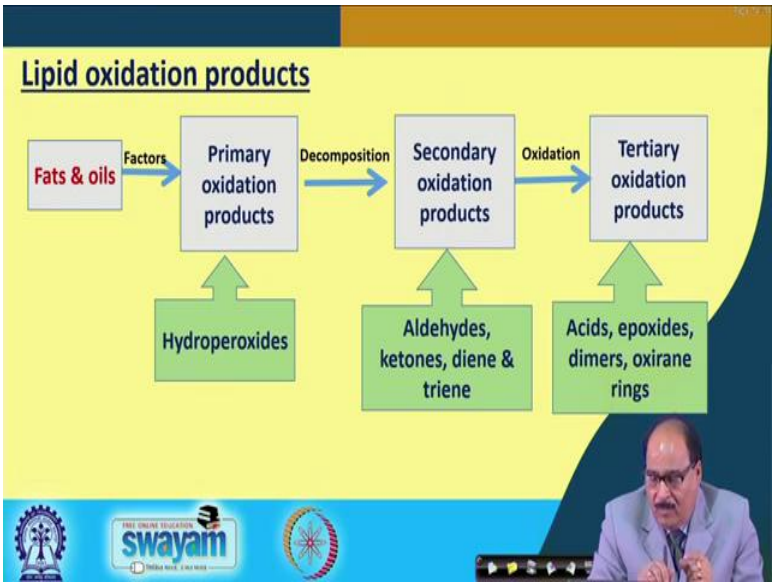
- Oxidation is the process of addition of oxygen (O_2) or removal of hydrogen or electrons.
- Oxidant/ oxidizing agent is an element or compound that gain electrons & get reduced; it favors oxidation.
- In food system, O_2 is the most common oxidant.

Factors influencing oxidation are

✓ Heat, light, ionization reactions, trace metals (copper and iron), enzymes (lipoxygenase), and metalloproteins such as heme.

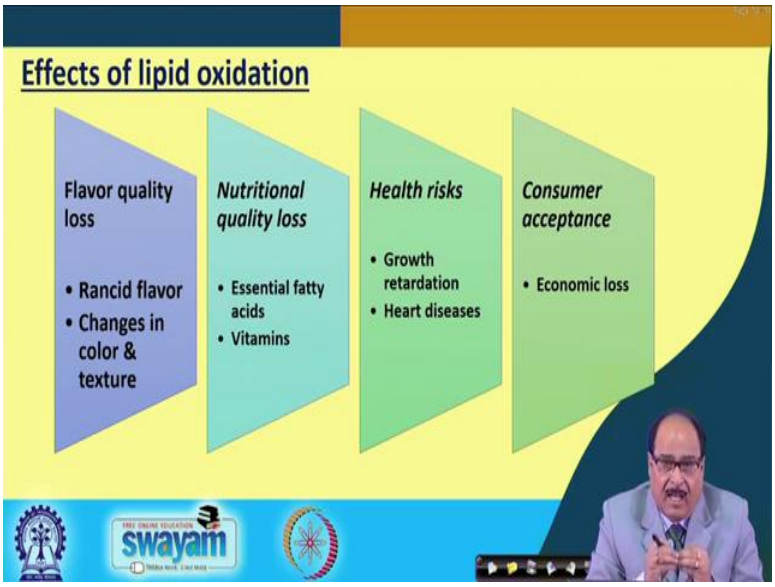


The lipid oxidation may be of two types. Actually higher the degree of unsaturation, higher is the instability or more prone the oil will be to the oxidative processes. So, oxidation of highly unsaturated fats may result in the polymeric end product formation whereas, oxidation of moderately unsaturated fats results in the development of rancidity reversion, off flavor, odours, etc.



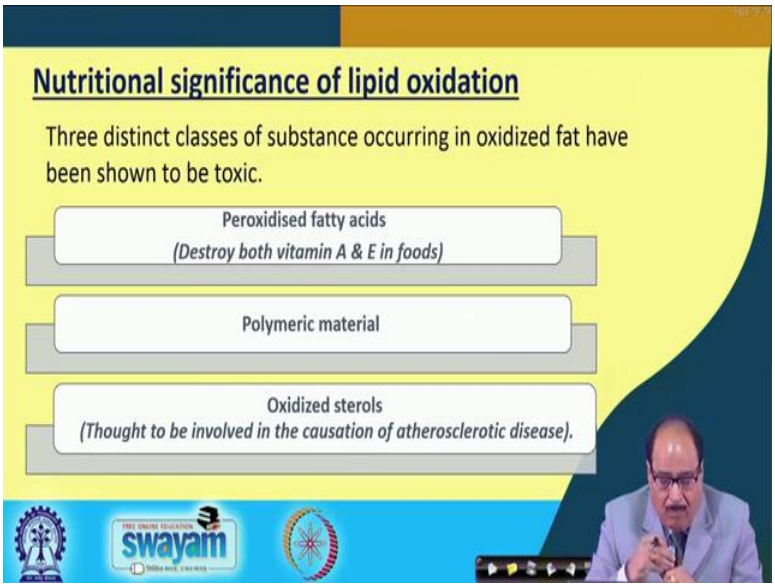
Lipid oxidation products

Depending upon the stages and extent of oxidation, different products are formed. Accordingly, primary oxidation products are decomposed into secondary oxidation products and which may further be oxidized into tertiary oxidation product. The primary oxidation products in the fats and oil include hydroperoxides; secondary oxidation products may be aldehydes, ketones, dienes, trienes, etc. and the tertiary oxidation products are acids, epoxide, dimers and oxirane rings and so on.



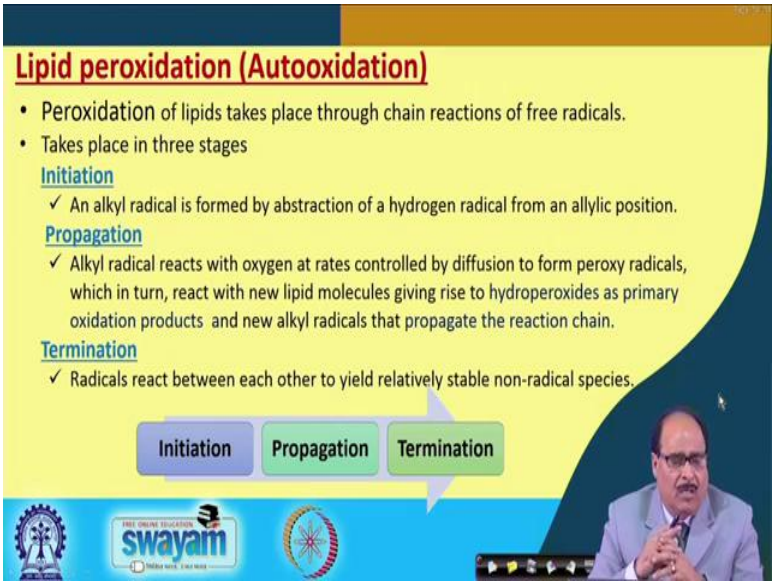
Effects of lipid oxidation

The lipid oxidation has several influences on the quality of the products of lipid, fats and oils. There may be flavor loss like rancid flavor, change in the color and texture of the food, nutritional quality loss particularly the essential fatty acids if involved or vitamins etc. Even this lipid oxidation end products may be sometime health risk also, there will be growth retardation, heart diseases etc. sometime reported due to the oxidation products and ultimately the consumer acceptance of the product is adversely affected. So, there is economic loss.



As far as the nutritional significance of the lipid oxidation is concerned, there are certain products which might be formed as a result of oxidation of lipids or fats which have

important influence on the health like for example, peroxidised fatty acids. They destroy both vitamin A and vitamin E in foods. Similarly polymeric materials may have different effects. Oxidized sterols are thought to be involved in the causation of atherosclerotic disease and so on.



Lipid peroxidation (Autooxidation)

- Peroxidation of lipids takes place through chain reactions of free radicals.
- Takes place in three stages

Initiation

✓ An alkyl radical is formed by abstraction of a hydrogen radical from an allylic position.

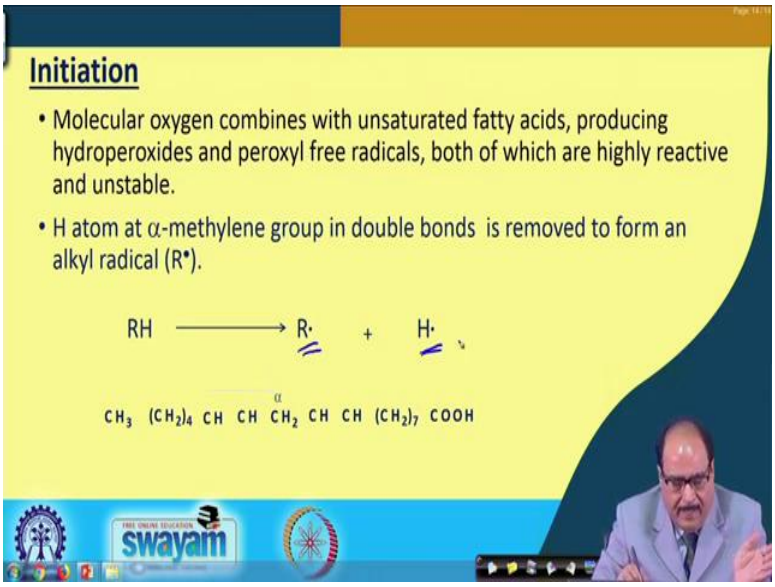
Propagation

✓ Alkyl radical reacts with oxygen at rates controlled by diffusion to form peroxy radicals, which in turn, react with new lipid molecules giving rise to hydroperoxides as primary oxidation products and new alkyl radicals that propagate the reaction chain.

Termination

✓ Radicals react between each other to yield relatively stable non-radical species.

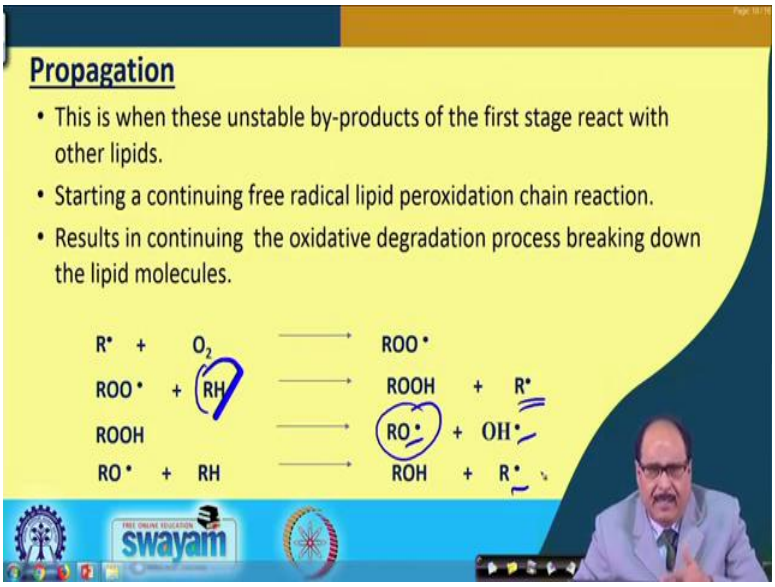
This is generally the end of the process, but this is a continuous process. Once that free radical chain has started, the mechanism if not taken care of may take place simultaneously.



Initiation

- Molecular oxygen combines with unsaturated fatty acids, producing hydroperoxides and peroxyl free radicals, both of which are highly reactive and unstable.
- H atom at α-methylene group in double bonds is removed to form an alkyl radical ($R^{\bullet}$).

$$RH \text{ -----> } R^{\bullet} + H^{\bullet}$$

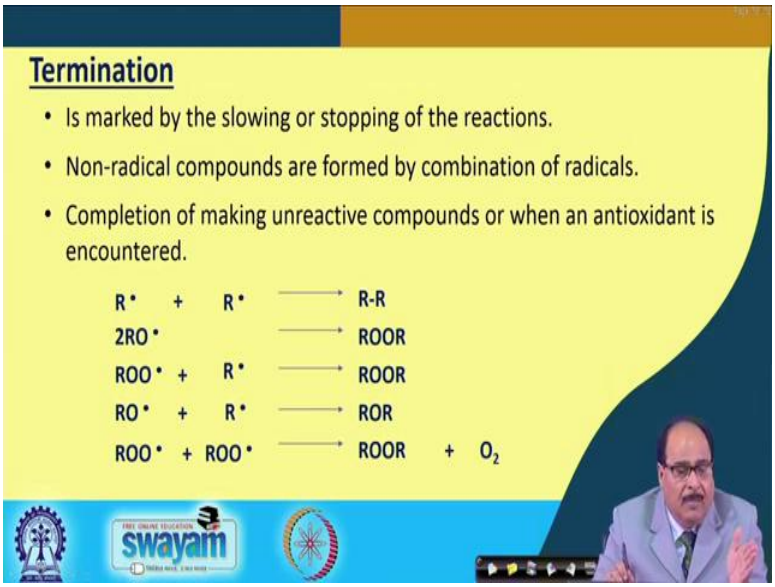


Propagation

- This is when these unstable by-products of the first stage interact with themselves or react with other fatty molecules (lipids).
- Starting a continuing free radical lipid peroxidation chain reaction.
- Results in continuing the oxidative degradation process breaking down the lipid molecules.

The equations are written in slide that can be referred and understood.

So, in this manner the reaction proceeds with time and even the reaction rate etc. increases with the progress of time if not checked or controlled.

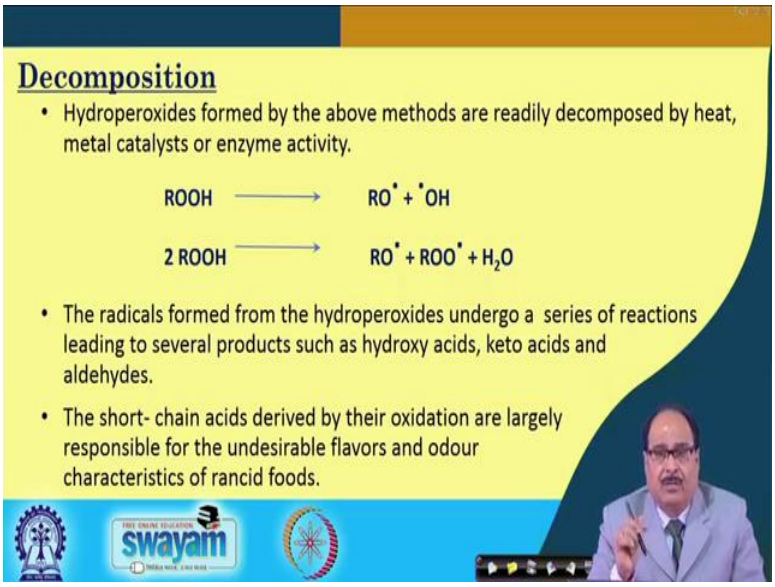


Termination

- Is marked by the slowing or stopping of the reactions.
- Non-radical compounds are formed by combination of radicals.
- Completion of making unreactive compounds or when an antioxidant is encountered.

The equations are written in slide which can be referred and understood.

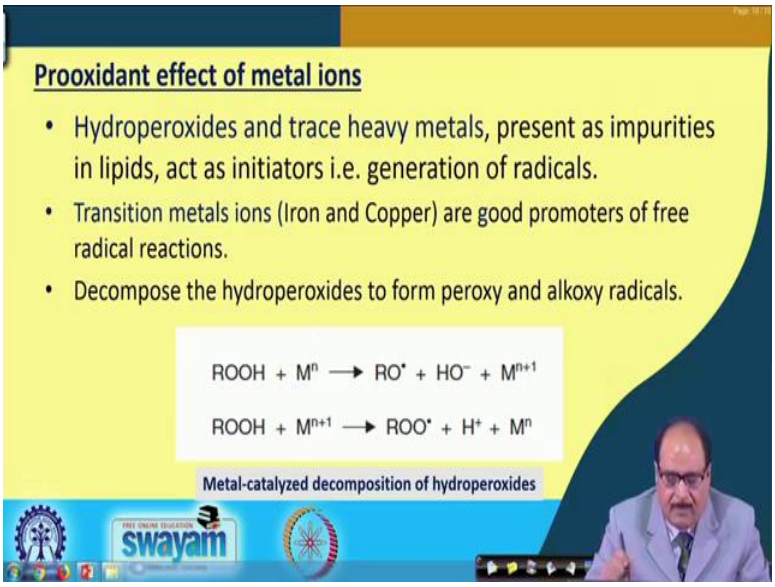
Different non-radical compounds hydroperoxides and others are formed here in the termination process.



Decomposition

- Hydroperoxides formed by the above methods are readily decomposed by heat, metal catalysts or enzyme activity.
- The radicals formed from the hydroperoxides undergo a series of reactions leading to several products such as hydroxy acids, keto acids and aldehydes.
- The short- chain acids derived by their oxidation are largely responsible for the undesirable flavors and odour characteristics of rancid foods.

In case of hydrolytic rancidity, the changed flavor is mainly because of the development of free fatty acid. But in oxidative rancidity, many new compounds like hydroxy acid, keto acid, aldehydes, etc. are formed and the flavor is because of these new compounds and at times these new compounds which are formed may be even carcinogenic or toxic.

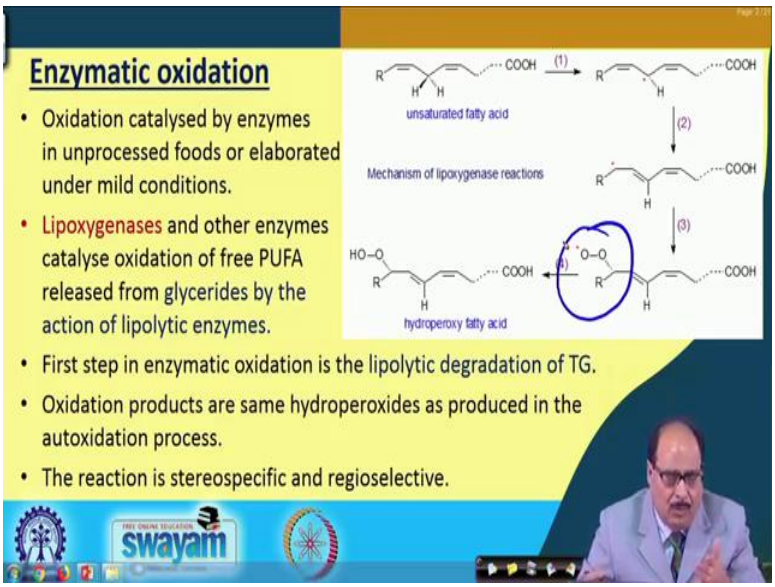


Prooxidant effect of metal ions

There are certain agents which are prooxidant which accelerate the rate of oxidation reactions.

- Hydroperoxides and trace heavy metals, present as impurities in lipids, act as initiators i.e. they initiate generation of radicals.
- Transition metals ions (Iron and Copper) are good promoters of free radical reactions.
- Decompose the hydroperoxides to form peroxy and alkoxy radicals.

Equations can be referred from the slide.



Enzymatic oxidation

- Oxidation catalyzed by enzymes in unprocessed foods or elaborated under mild conditions.
- Lipoxygenase and other enzymes catalyse oxidation of free PUFA released from glycerides by the action of lipolytic enzymes. Lipase enzyme is the one which brush the ester linkage but lipoxygenase it adds oxygen at the point of unsaturation.
- First step in enzymatic oxidation is the lipolytic degradation of TG. Unsaturated fats are more prone to oxidation.
- Oxidation products are same hydroperoxides as produced in the autoxidation process.
- The reaction is stereospecific and regioselective.

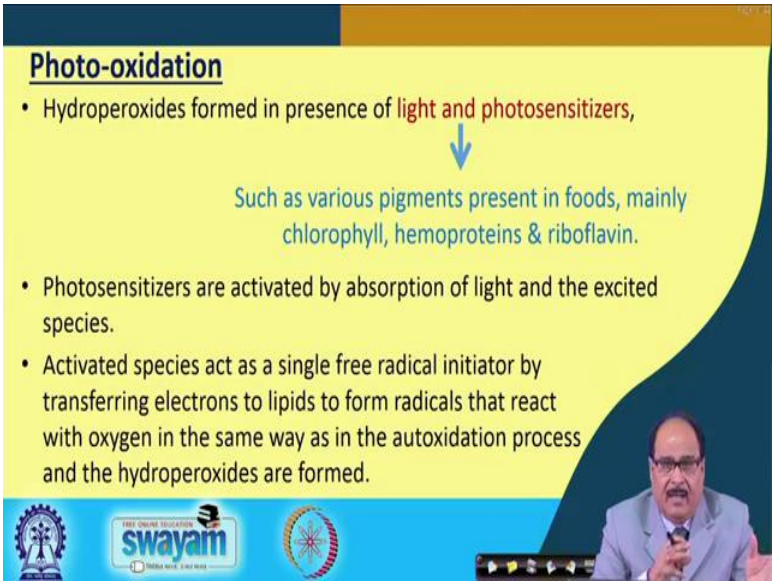


Photo-oxidation

- Hydroperoxides formed in presence of light and photosensitizers such as various pigments in foods, mainly chlorophyll, hemoproteins and riboflavin.
- Photosensitizers are activated by absorption of light and the excited species.
- The activated species act as a single free radical initiator by transferring electrons to lipid to form radicals that react with oxygen in the same way as we have discussed in the earlier auto oxidation process.

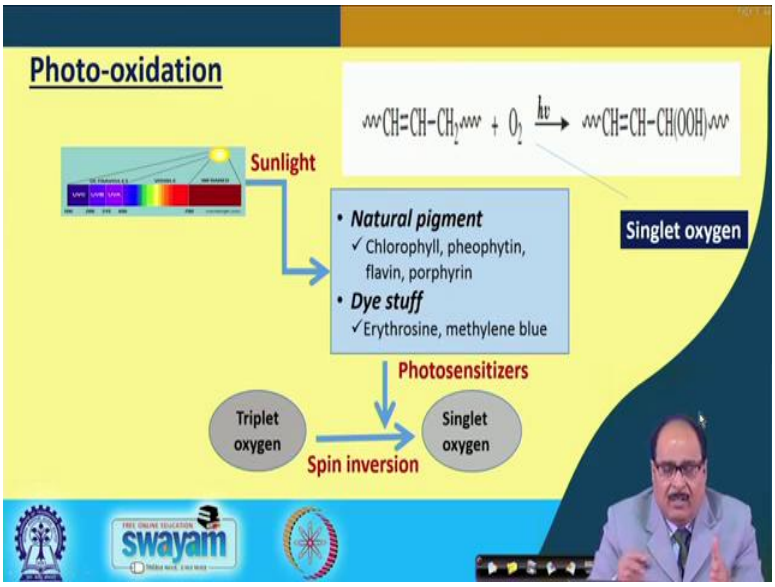
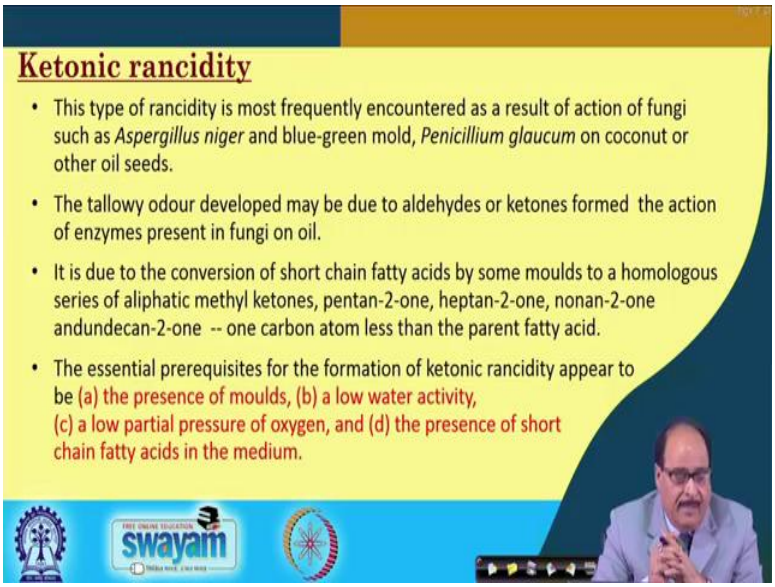


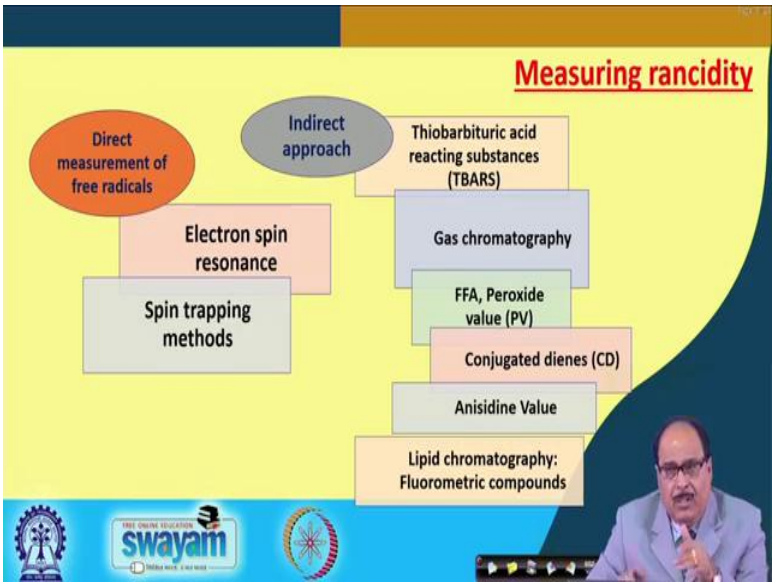
Photo-oxidation

The sunlight passes through the food containing natural pigments like chlorophyll, pheophytin etc. and dye stuff like erythrosine, methylene blue etc. These are considered to be photo-synthesizer. Triplet oxygen is converted into singlet oxygen by spin inversion and this singlet oxygen provides oxygen that causes the oxidation of the unsaturated fatty acids. So, that is why the ions particularly poly unsaturated ions etc. should be stored in a dark place. Their exposure to direct sunlight etc. should be avoided otherwise it will catalyze their oxidation and oil will become rancid.



Ketonic rancidity

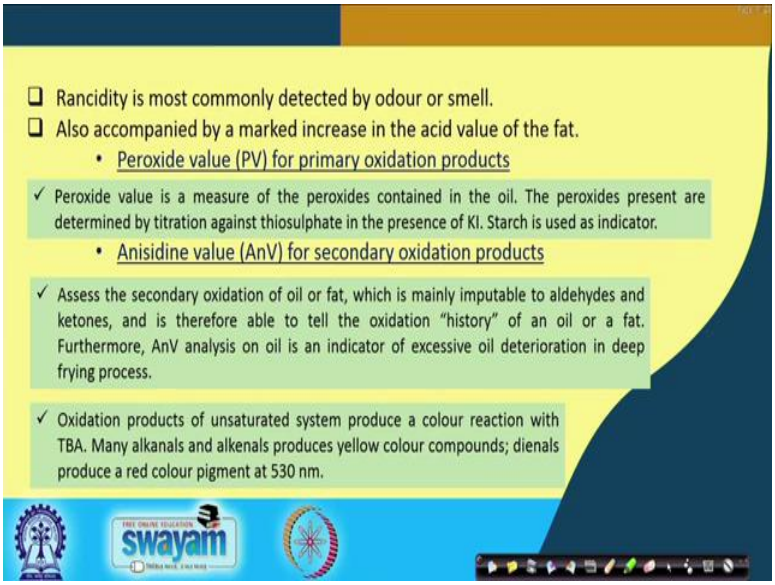
- This type of rancidity is most frequently encountered as a result of action of fungi such as *Aspergillus niger* and blue-green mold, *Penicillium glaucum* on coconut or other oil seeds.
- The tallowy odour developed may be due to aldehydes or ketones formed the action of enzymes present in fungi on oil. The fungal enzymes turn the oil or fats into short chain fatty acids which are more prone to ketonic rancidity.
- It is due to the conversion of short chain fatty acids by some moulds to a homologous series of aliphatic methyl ketones, pentan-2-one, heptan-2-one, nonan-2-one and undecan-2-one -- one carbon atom less than the parent fatty acid.
- The essential prerequisites for the formation of ketonic rancidity appear to be (a) the presence of moulds, (b) a low water activity, (c) a low partial pressure of oxygen, and (d) the presence of short chain fatty acids in the medium.



Measuring rancidity

One important method is just by visual observation or just by sensory (smell) whether the oil is rancid or not. Direct measurement of the free radicals are electron spin resonance method or spin trapping methods. Indirect approaches can be used like thiobarbituric acid reacting substances or gas chromatography can be used because

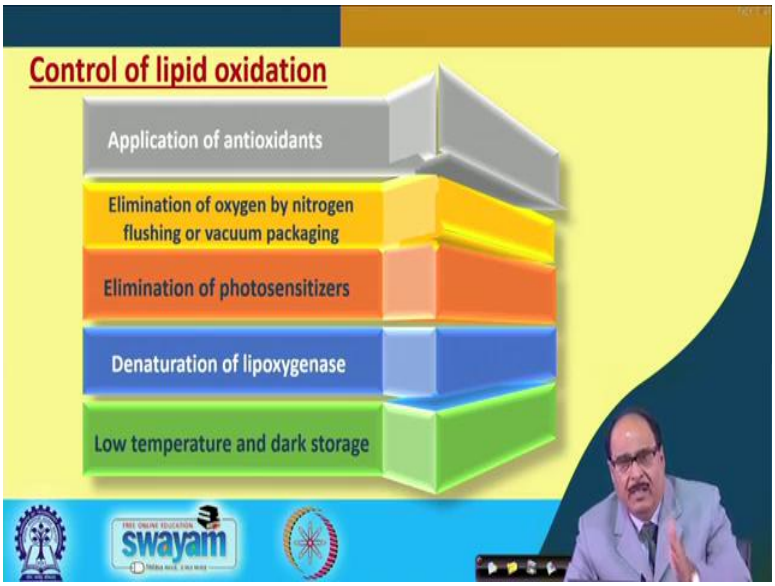
during this rancidity either in the oxidative or hydrolytic, different aldehydes and other compounds are formed. These fatty acids and carbonyl compounds can be measured spectrophotometrically or the peroxides can be measured using peroxide value etc. The conjugated diene, anisidine value, lipid chromatography, fluorometric compound etc. are also used. So, there are different methods both indirect method as well as direct approach for measuring free radicals which can be used to measure the rancidity oxidative, hydrolytic or ketonic.



Rancidity is most commonly detected by odour or smell and regarding the peroxide value or the measurement of the primary oxidation product, the peroxide value is generally measure of the peroxides contained in the oil; the peroxides present are determined by titration against thiosulfate in the presence of potassium iodide; starch is used as an indicator.

Anisidine value is measured for the determination of secondary oxidation products. It assess the secondary oxidation product of oil or fat which is mainly imputable to aldehydes and ketones and is therefore, able to tell the oxidation history of an oil or a fat. Furthermore anisidine value of an oil is an indicator of excessive oil deterioration in deep fried oil. So, anisidine value, peroxide value, thiobarbituric acid test, etc. are such other measurements. Oxidation products of unstaturated system produce color reaction with thiobarbituric acid. So, many alkanals and alkenals produce yellow colour compound, dienals produce red colour pigment at 530 nm.

These various approaches apart from the rancimat system where oxidation stability, induction period of oil or fat can be measured give the suitable idea of oxidation and stability of the oil. Depending upon its induction etc., it can be calculated.



Control of lipid oxidation

In the lipid and oil or the food containing oil, lipid peroxidation or oxidation or hydrolysis become major problem which result to the change in their flavor, odour etc. The appropriate methods that are followed to prevent lipid oxidation are derived from those factors which accelerate them like oxidation prevention of pro-oxidants.

Using appropriate antioxidants, the oxidation can be avoided. Similarly elimination of oxygen can be done by keeping the oil or fats away from oxygen either by nitrogen flushing or by vacuum packaging etc. or even avoiding their contact with photosensitizers, direct exposure to light etc., or even by using appropriate means to denature the causative enzymes like lipase, lipoxygenase etc. or even low temperature and dark room storage of oil.

So, these are some of the ways by which one can minimize the rancidity of oils and fat. In fact, the refined oil and such other oil which are available in the market for cooking and frying operations, are extensively used to improve their stability. The industry uses antioxidants both synthetic and natural antioxidants which become very valuable component in the oils and fats.