Food Oils and Fats: Chemistry and Technology
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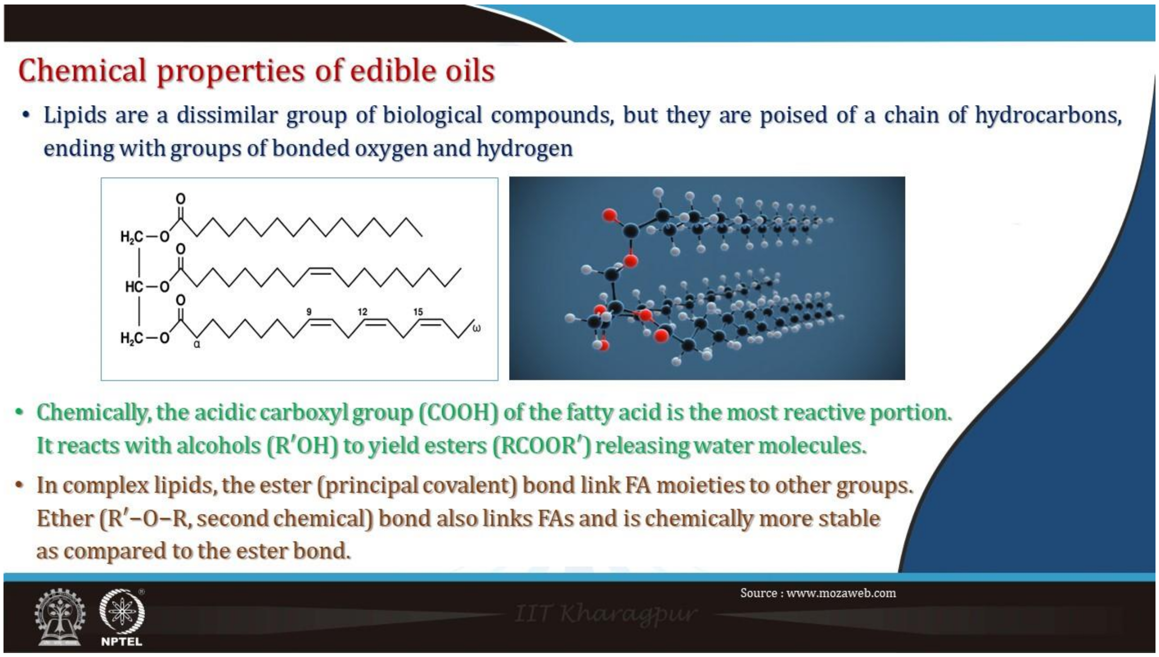
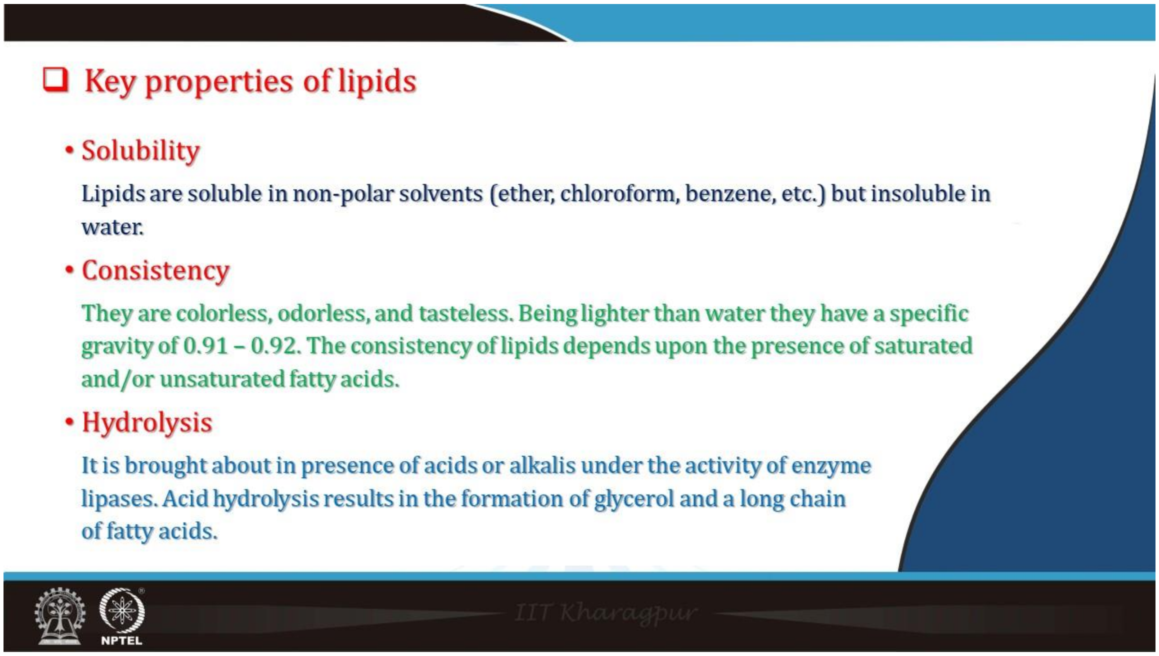
Week 03: Edible Oils - Chemistry & Properties
Lecture 12: Chemical Properties of Edible Oils

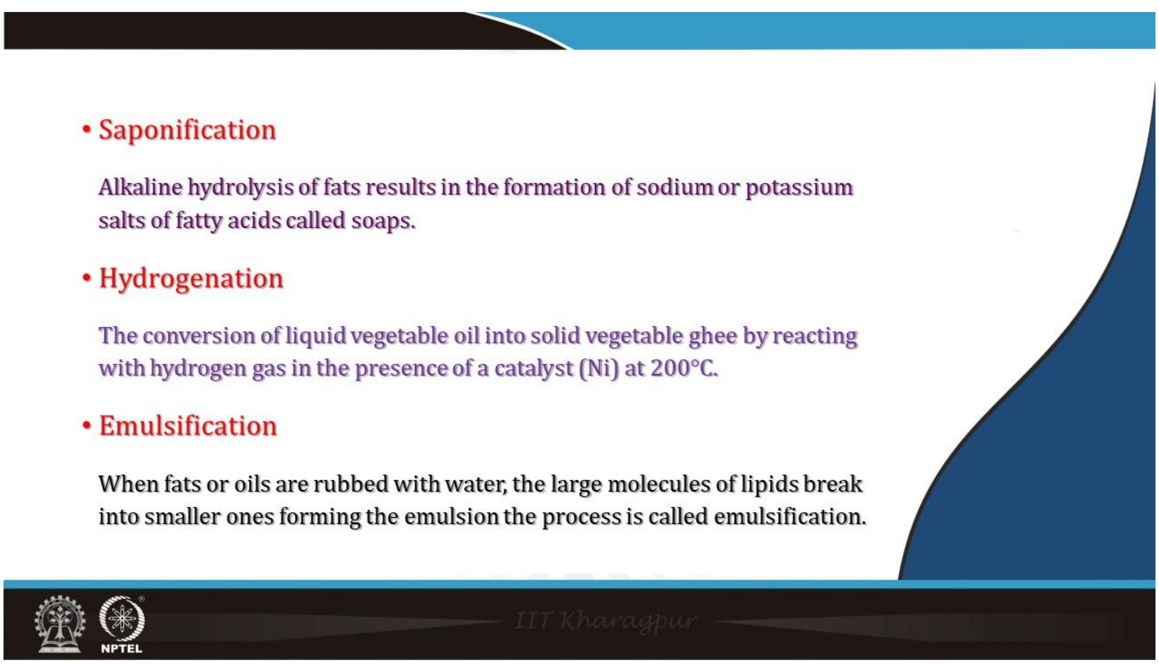
Hello everybody, Namaskar. Now, we are in lecture 12. In lecture 11, we discussed mainly the physical properties or engineering properties of oils, edible oils. Now, in this next half an hour in lecture 12, let us study the chemical properties of edible oils. Here, we will discuss key chemical properties and reactions, methylation of carboxyl groups, reactions of unsaturated fatty acids, halogen addition reaction, and then chemical quality parameters that is what are the various parameters which are evaluated and tested in the laboratory to assess the chemical characteristic, the chemical quality of the oils.



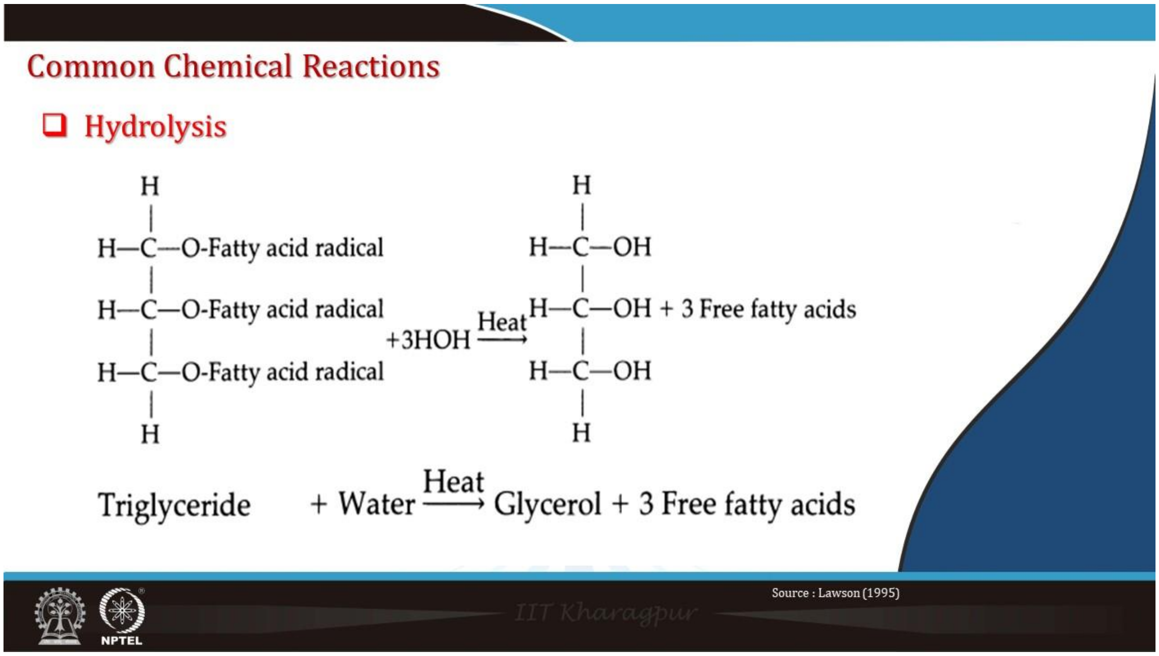
Lipids are a dissimilar group of biological compounds, but they are poised of a chain of hydrocarbons ending with the groups of bonded oxygen and hydrogen. Chemically the acidic carboxyl group of the fatty acid is the most reactive portion. It reacts with the alcohol to yield esters releasing water molecules and that is how triglyceride, monoglyceride, diglycerides are formed. In the earlier classes we have had a glimpse of this. In complex lipids, the esters, which is principal covalent bond link the fatty acid moieties to other groups like ROR that is the second chemical. Ether bonds also links fatty acids and is chemically more stable as compared to the ester bond.



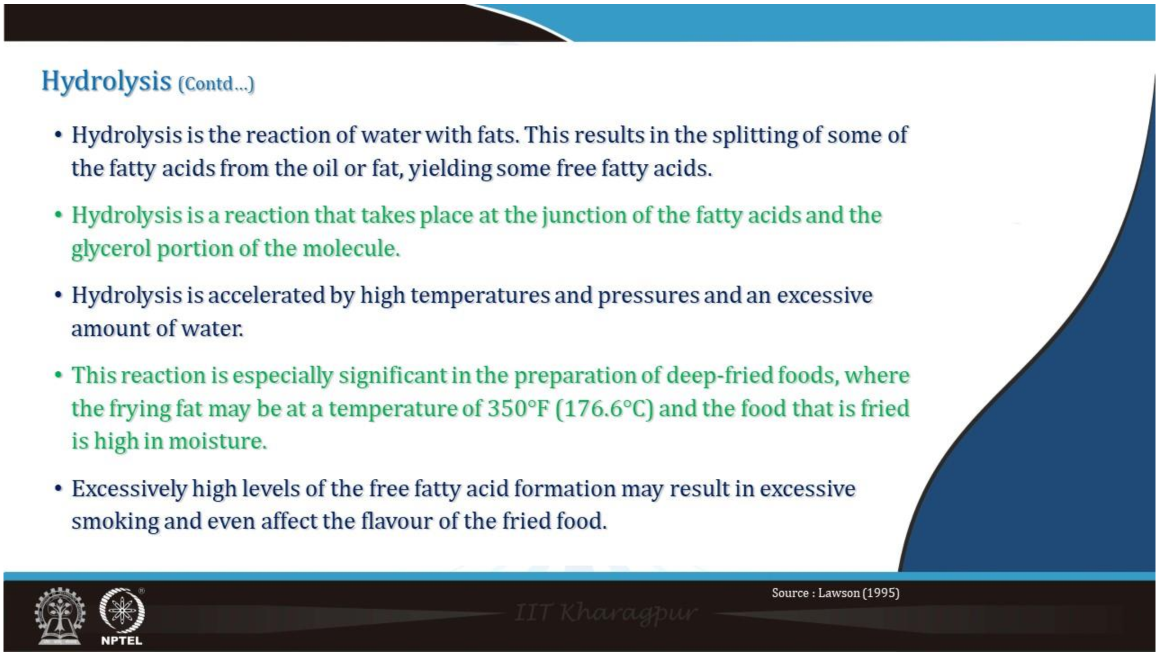
Key properties of the oil lipids, that is the chemical properties etcetera may be solubility that is the lipids are soluble in nonpolar solvents like ether, chloroform, and benzene, but they are insoluble in water. Consistency is another important property. Most of the lipids are colorless, odorless, and tasteless. Being lighter than water, they have a specific gravity in the range of 0.91 to 0.92. The consistency of lipids depends upon the presence of saturated and/or unsaturated fatty acids. Hydrolysis is brought about in the presence of acids or alkalis under the activity of enzyme lipases. Acid hydrolysis results in the formation of glycerol and a long chain of fatty acids.



Saponification value or saponification reaction is another important property that is alkaline hydrolysis of fat results in the formation of sodium or potassium salts of the fatty acid called soaps, that is if the hydrolytic agent is an alkali. So, the free fatty acids that are released react with the alkali and they form sodium salt of fatty acid or potassium salt of fatty acid and that is the soap formation. The hydrogenation reaction is the conversion of liquid vegetable oil into solid vegetable ghee by reacting with hydrogen gas in the presence of a catalyst. The reaction catalyst is nickel and the reaction takes place at around 200 degree Celsius. Another important chemical property is the emulsification. When the fats and oils are rubbed with water, the large molecules of lipids break into smaller ones forming the emulsion, and the process is called emulsification.

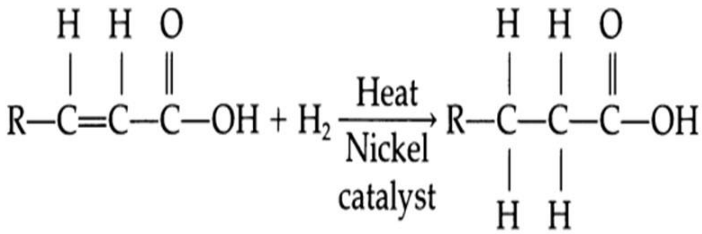


So, let us see the chemistry of all these reactions, which we have discussed. Hydrolysis is the reaction of the three fatty acids of the triglycerides with three molecules of water. On heating three free fatty acids are released and water molecules replace the fatty acids in the triglycerides thus forming glycerol. So, the triglycerides and water on heating release glycerol plus three fatty acids which is the hydrolysis reaction.



Hydrolysis is the reaction of water with fats. This results in the splitting of some of the fatty acids from the oil or fat, yielding some free fatty acids. This hydrolysis reaction takes place at the junction of the fatty acid and the glycerol portion of the molecule. Hydrolysis is accelerated by high temperatures and the presence of an excessive amount of water. This reaction is especially significant in the preparation of deep-fried foods where the frying fat may be at a temperature of 170 to 180 degrees Celsius and the food that is fried is high in moisture. In that case, the moisture content present in the food also causes the lipids to hydrolyze and therefore, more amount of free fatty acids is formed. Excessive free fatty acids influence the frying properties, heat transfer capacities, and other engineering properties of the fats and oils. Excessively high levels of free fatty acids may result in excessive smoking and even affect the flavor of the fried food. If the oil has more amount of free fatty acids, then the food fried will have more absorption of oil into it, it will have cracked surfaces, it will develop a darker brown color.

Hydrogenation



Fatty acid radical + Hydrogen   Hydrogenated fatty acid

Hydrogenation Reaction

Source : Lawson (1995)

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Then the other reaction is hydrogenation as I told you that is where you see fatty acid which has unsaturated linkage. So, hydrogenation is basically the addition of hydrogen under controlled conditions into the unsaturation bond, and then unsaturated fatty acids become saturated fatty acids where nickel is a catalyst. The unsaturated fatty acid triglyceride is liquid at room temperature and then when it becomes saturated it becomes solid at room temperature.

Hydrogenation (Contd...)

- This is one of the more important chemical reactions of food oils and fats, especially oils.
- It is a typical example of a reaction that occurs at points of unsaturation or double bonds.
- Hydrogen is added directly to points of unsaturation in the fatty acids.
- Gaseous hydrogen is used at elevated oil temperatures under increased pressure and in the presence of a suitable catalyst such as a nickel compound.
- This reaction is used to make fat products with greater flavour stability.
- Hydrogenation also permits the conversion of liquid vegetable oils into fluid shortenings and semisolid plastic shortenings that are better adapted for use in deep-frying, baking, and so on.

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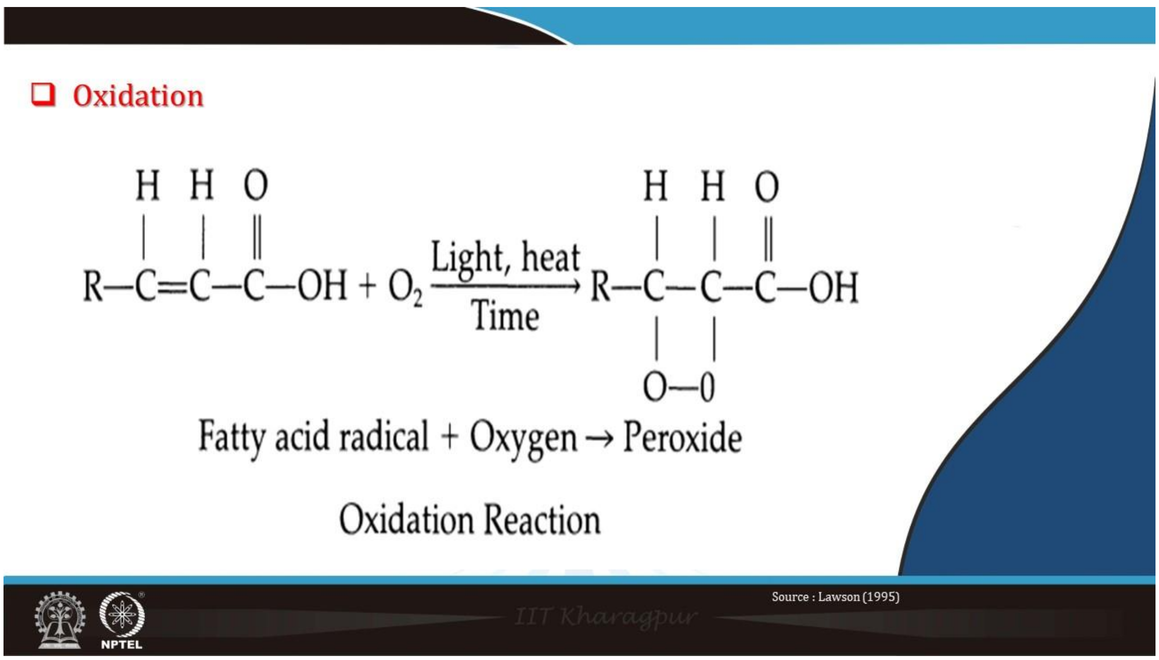
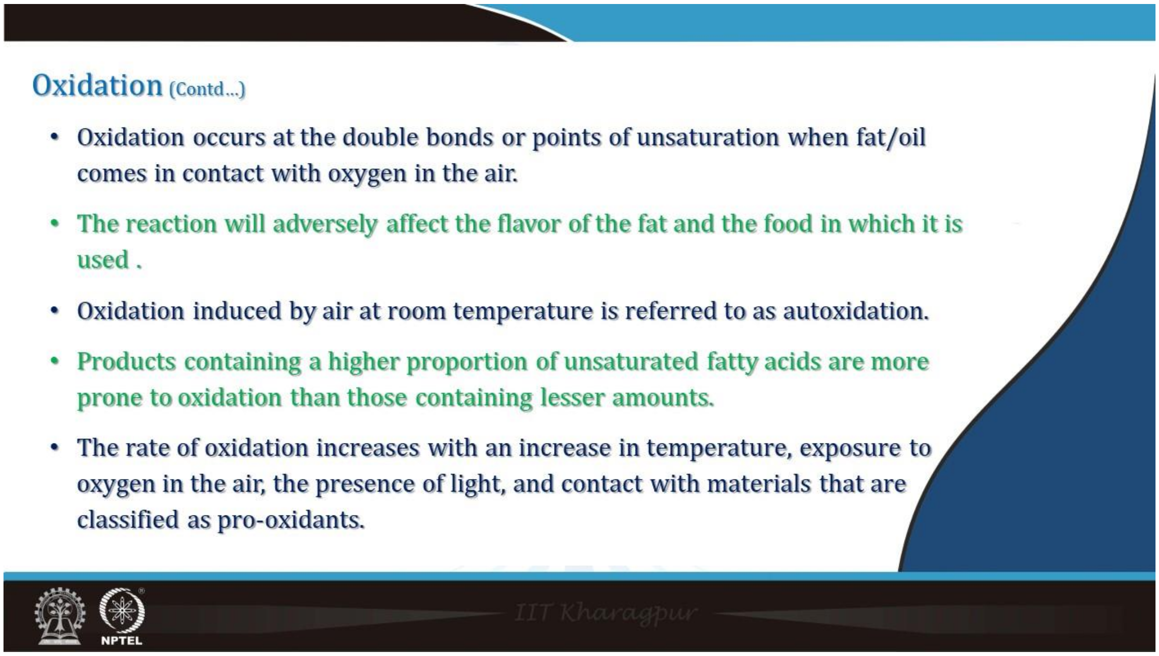
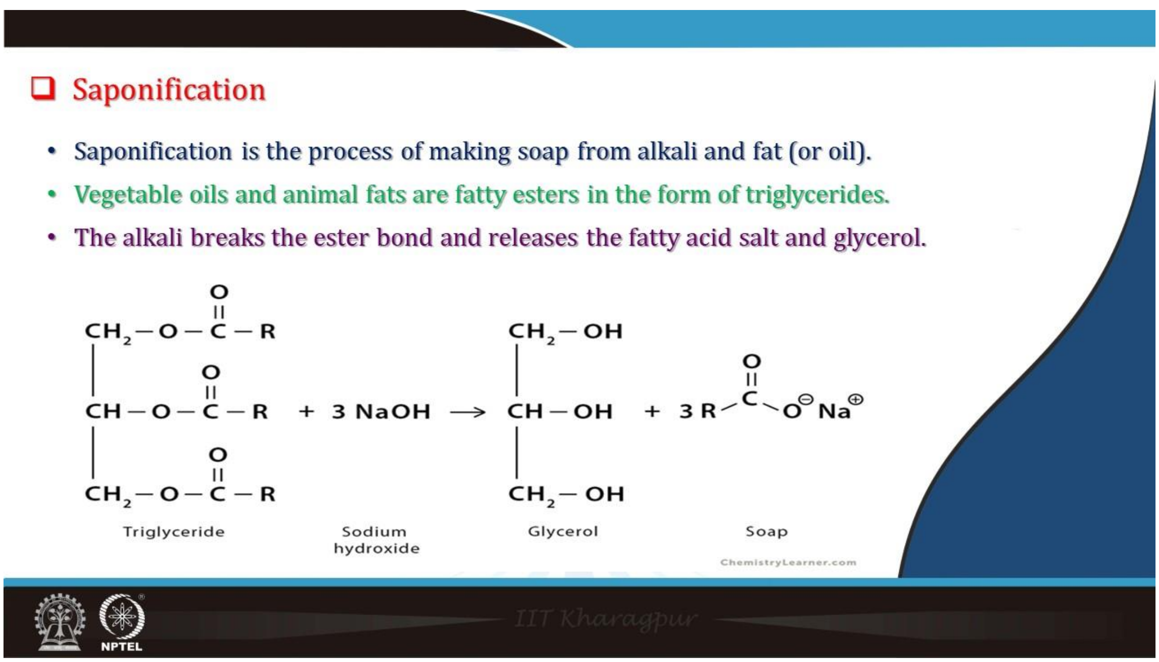
This is one of the more important chemical reactions of food oils and fats, especially the oils. It is one of the important modification reaction details of its chemistry and technology that we will discuss separately when we discuss the modification processes of fats and oils. It is a typical example of the reaction that occurs at the point of unsaturation or double bond. Hydrogen is added directly to the point of unsaturation in the fatty acids. Gaseous hydrogen is used at elevated oil temperatures under increased pressure and in the presence of a suitable catalyst such as nickel compound. This reaction is used to make fat products with greater flavor stability. Hydrogenation also permits the conversion of liquid vegetable oil into solid shortening and semi-solid plastic shortening that are better adapted for use in deep frying, baking, and so on. So, by controlling the hydrogenation, one can go even with the selective hydrogenation to produce the solid fat having proper characteristics, proper melting characteristics, proper molecular packing etcetera.



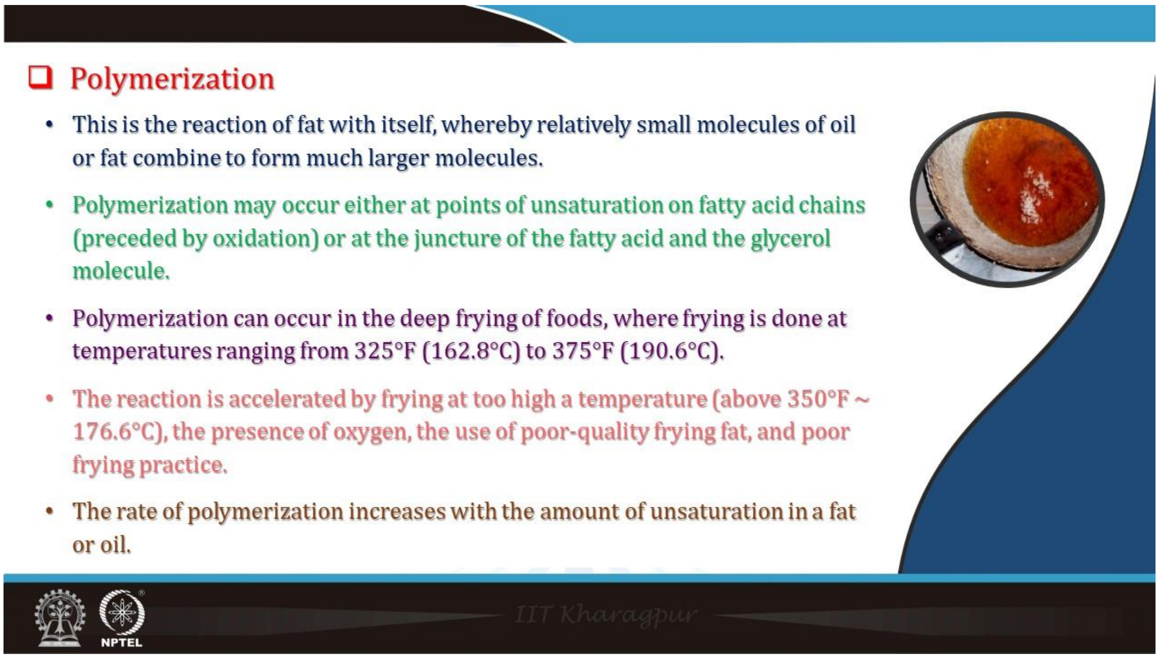
Another important reaction that oils undergo is oxidation. The oil fatty acids and unsaturated fatty acids, etcetera, when they come in contact with air and heat, light, time, etc. act as catalysts. Then peroxide is formed, that is free fatty acid plus oxygen which gives peroxide free radicals. And this is basically peroxide formation is the basic oxidation reaction and this again has a very important role to play in the development of rancidity, that is auto-oxidation process by which the oil becomes rancid. The oxidation reaction will adversely affect both the flavor of the fat and the food in which it is used.



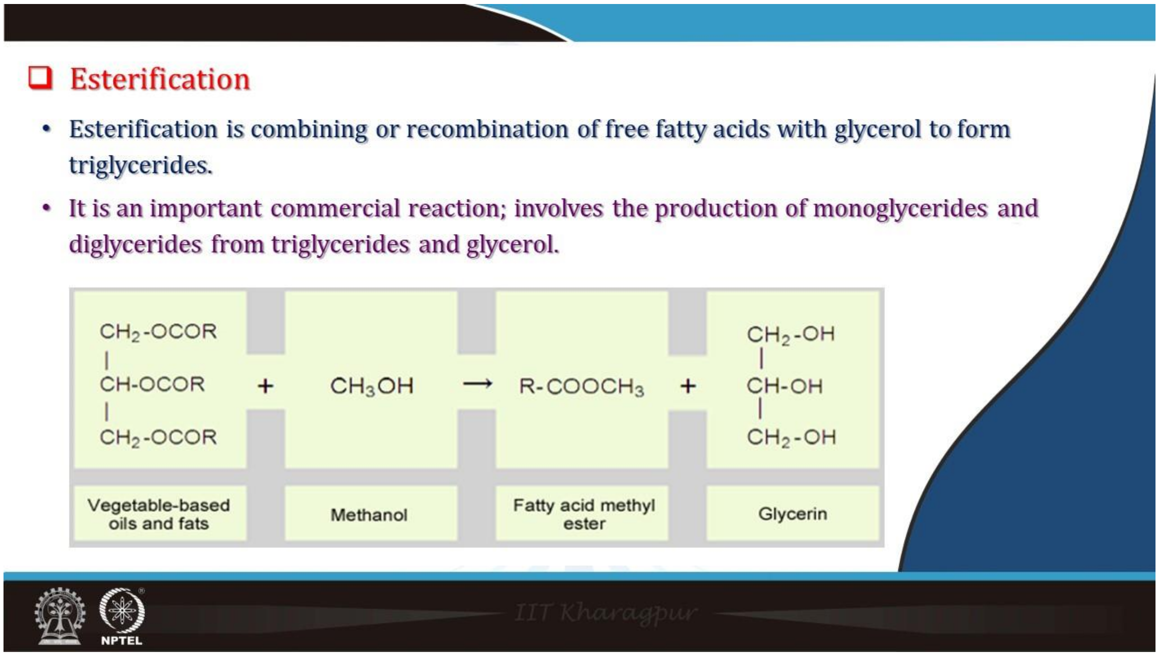
Oxidation induced by air at room temperature is referred to as auto-oxidation. As I told you products containing a higher proportion of unsaturated fatty acids are more prone to oxidation than those containing lesser amounts. The rate of oxidation increases with an increase in temperature, exposure to oxygen in the air, the presence of light, and contact with the materials that are classified as pro-oxidants because these increase the rate of oxidation.



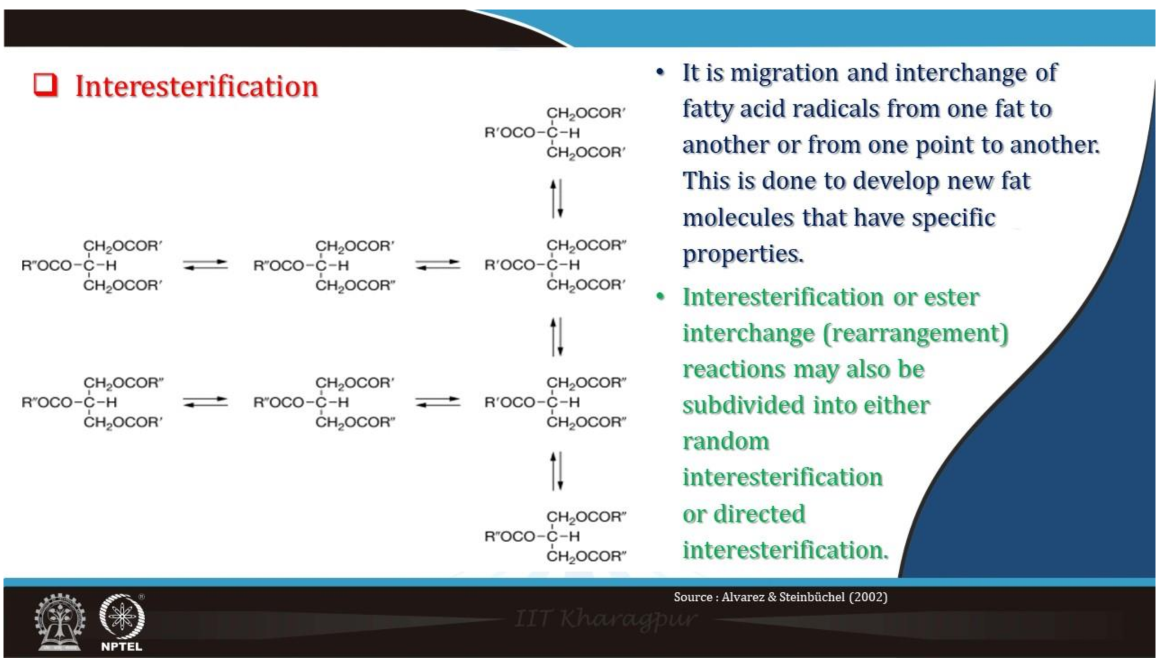
Now next important reaction is the saponification reaction which in the introductory slide I gave you that is what is saponification. It is basically the process of making soap from alkali and fat or oil, vegetable oil, and animal fats or fatty acid esters in the form of triglyceride you know it. So, the alkali when it is used breaks the ester bond as you can see in these reactions that is the RRR shown are the ester linkages. So, when it comes in contact with an alkali, strong alkali like sodium hydroxide solution, it will break this ester linkage, but these 3 fatty acids react with sodium and this OH goes here. So, it becomes CH2OH, CHOH, and CH2OH, and the 3 fatty acids form sodium salt of these fatty acids, and this sodium salt of fatty acids is basically called soap. So, this is the saponification reaction.



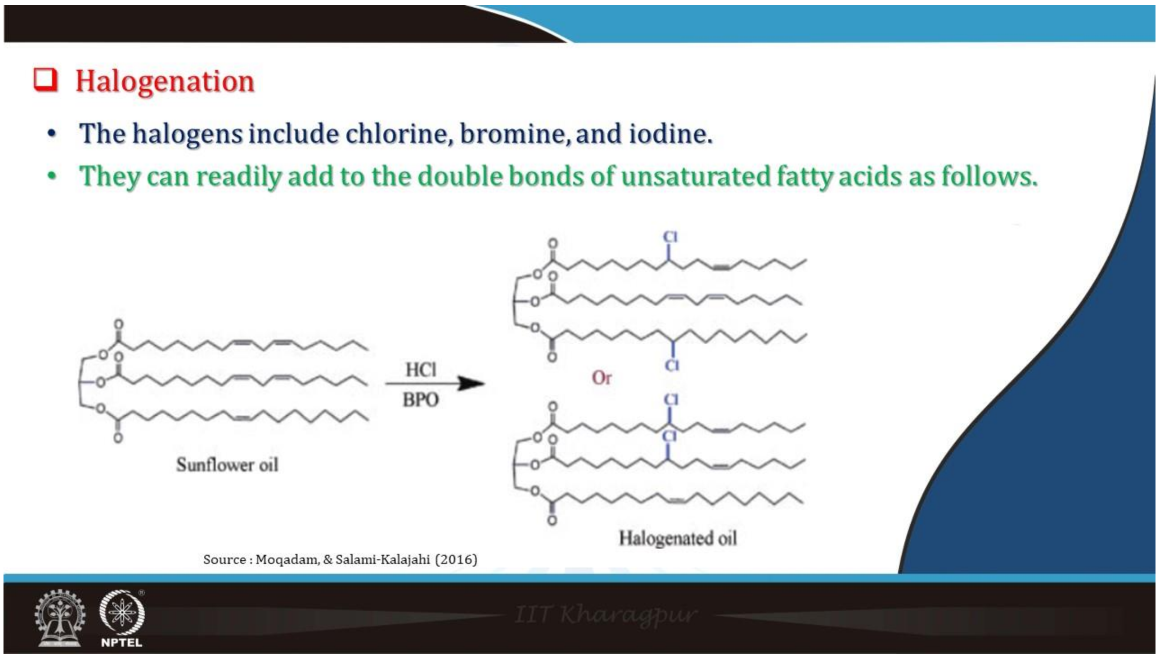
Then next is the polymerization. Polymerization is the reaction of fat with itself whereby relatively small molecules of oils or fat combine to form much larger molecules. Polymerization may occur either at the point of unsaturation on fatty acid chains or at the juncture of the fatty acids and the glycerol molecule. Polymerization can occur in the deep frying of foods where frying is done at temperatures ranging from around 163 to 190 degrees Celsius. The reaction is accelerated by frying at too high a temperature, above 180 degrees Celsius, the presence of oxygen, the use of poor quality frying fat, and poor frying practice. The rate of polymerization increases with the amount of unsaturation in the fat or oil.



Another important reaction is esterification you know which is the combining or recombination of the free fatty acids with the glycerol molecule. It is an important commercial reaction. It involves the production of monosylglyceerides, diaglycerides from triglycerides and glycerols etcetera. The vegetable-based oils and fats are reacted with methyl alcohol methanol, and then fatty acid methyl ester and glycerin are formed.

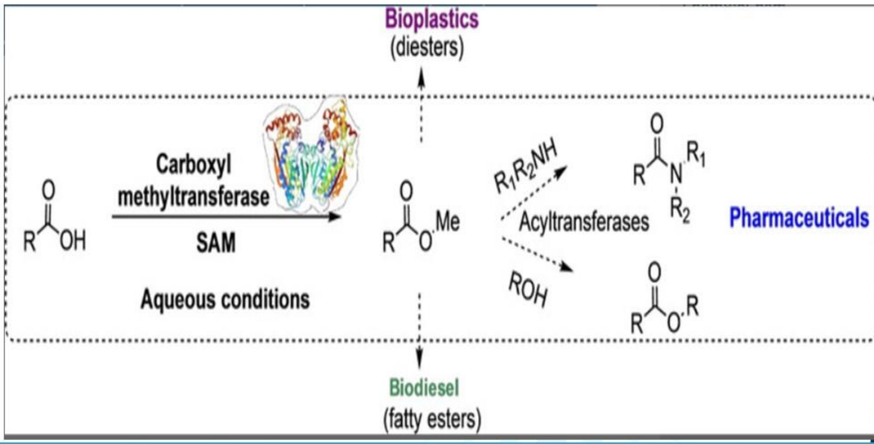


Then inter esterification reaction is another very important process reactions as these allows to have the oils and fats of specific properties. Inter esterification, the name itself indicate it is the migration and interchange of fatty acid radicals from one fat to another or from one point to another. This is done to develop new fat molecules that have specific properties. Inter esterification or ester interchange rearrangement reactions may also be subdivided into either random inter esterification or directed inter esterification and you can see here, that in the triglyceride there is R 1, R1, and R 2 that is R 1 is 2, R 2 is the 2nd position. Then it can interchange the R2 position, here in R 1, R 2, and R 2, which is R double prime. So, this can be in various positions that are there is and in within the same molecule the positioning of fatty acids is interchanged. This interchange, it changes the characteristic, particular properties, etcetera of the fatty acids.



Halogenation includes chlorine, bromine, and iodine and they can readily add to the double bond of the unsaturated fatty acids. As you can see here in this sunflower oil, for example, this is unsaturated linkages. In this R 1 and R 2 position, there are 2 unsaturated bonds and in R 3 there is one. So, in these 2 positions, this can be either in the first or in the second unsaturated position becomes halogenated. So, this halogenated oil like even brominated vegetable oil you must have heard that sometimes this addition of halogens etcetera in oil may adversely affect the properties and characteristics of the oils.

Methylation of carboxyl groups



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Source : Ward et al. (2021)

Then methylation of the carboxyl group like carboxyl methyl transferase there is there have course conditions and they can transfer like fatty acid esters or di esters or bioplastic or fatty acid esters are used in biodiesel production acyl transferases may help in re-methylation of carboxyl group which can be used in the for specific suitable for the pharmaceutical and other applications ok.

Methylation of carboxyl groups (contd…)

- Methylation is a common modification in biological systems which involves the transfer of a methyl group (CH_3) from a donor molecule to a substrate.
- Carboxyl group methylation of fatty acids using MT enzymes is a route currently being explored for production of biodiesel.
- Biodiesel is composed of fatty acid methyl esters (FAMEs) and is a sustainable alternative to petroleum fuels.
- The standard approach to produce FAMEs is through transesterification of triglycerides (from vegetable oil) with methanol, using an alkaline catalyst.

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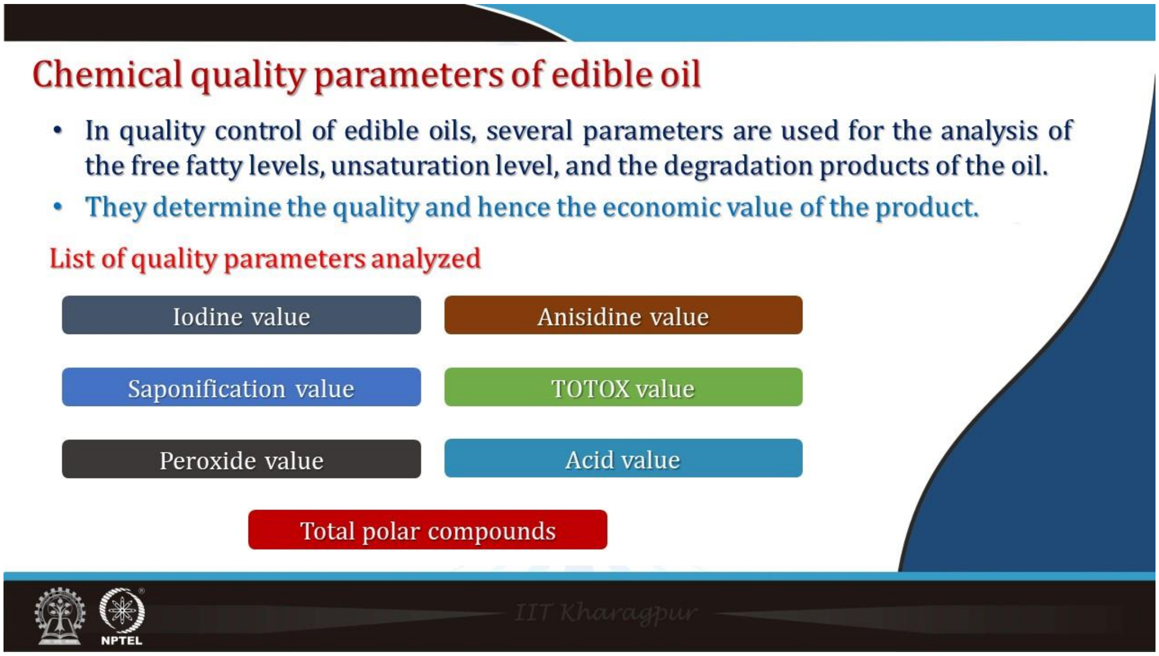
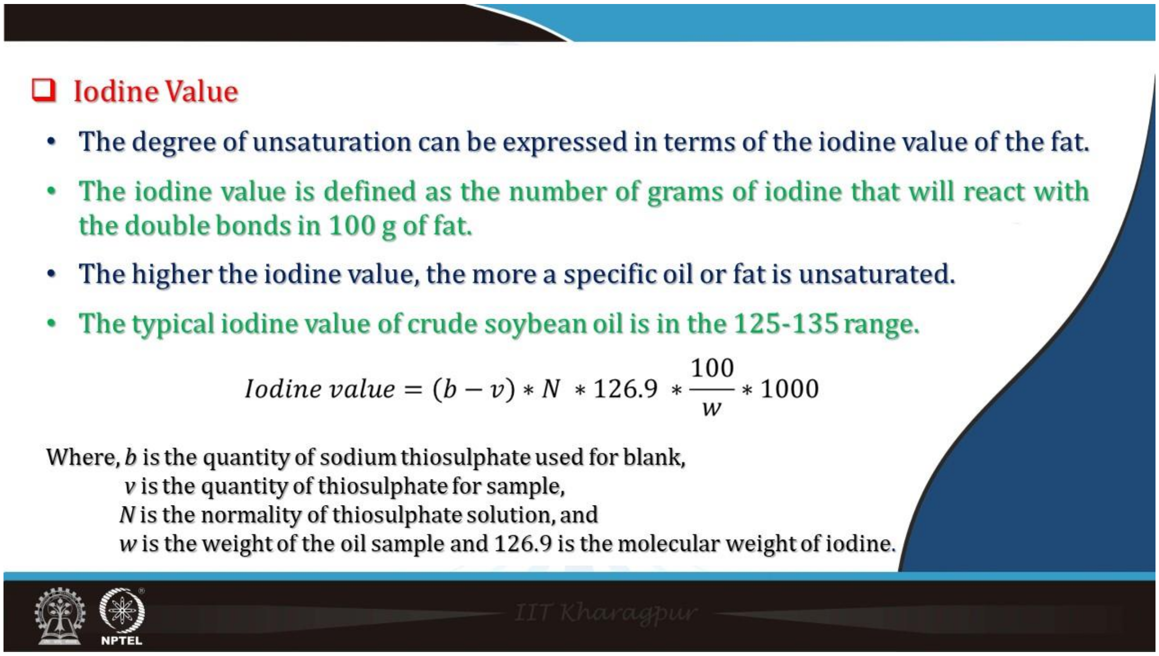


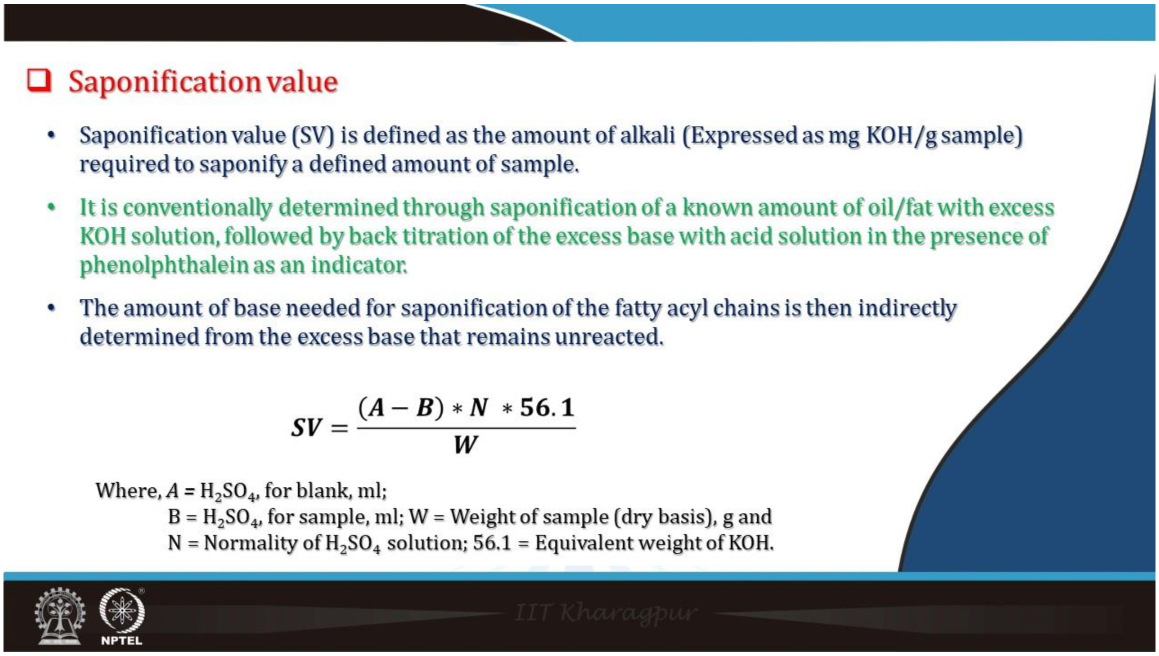
Then let me discuss some of the chemical quality parameters of edible oil. In quality control of edible oils, several parameters are used for the analysis of these values like free fatty acid level, unsaturation level, and degradation of products which are analyzed in the laboratory and these values can be used to indicate to assess the quality of the oil. Also, they determine the quality and hence the economic value of the product. So, the quality parameters which are generally analyzed include iodine value, saponification value, peroxide value, anisidine value, totox value, acid value as well as the total polar compounds.



The iodine value is the degree of unsaturation that can be expressed in terms of the iodine value of the fat. The iodine value is defined as the number of grams of iodine that will react with the double bond in 100 grams of fat. The higher the iodine value the more a specific oil or fat is unsaturated. So, the typical iodine value of crude soybean oil is in the range of 125 to 135. So, there is a specific protocol that is used in the laboratory for the determination which is the titration method.

$$Iodine\ value = (b - v) * N * 126.9 * \frac{100}{w} * 1000$$

That is B is the quantity of sodium thiosulfate used for the blank titration, v is the quantity of thiosulphate for the sample, that is oil sample in which we are analyzing the iodine value and then N is the normality of sodium thiosulfate solution, W is the weight of oil sample and 126.9 is the molecular weight of iodine. So, using this process one can find out the iodine value.



The saponification value is defined as the amount of alkali expressed in milligrams of KOH per gram sample required to saponify a defined amount of sample. It is conveniently determined through saponification of a known amount of oil or fat with excess KOH solution followed by back titration of the excess base with the acid solution in the presence of phenolphthalein as an indicator. The amount of base needed for saponification of the fatty acid chains is then indirectly determined from the excess base that remains unreacted.

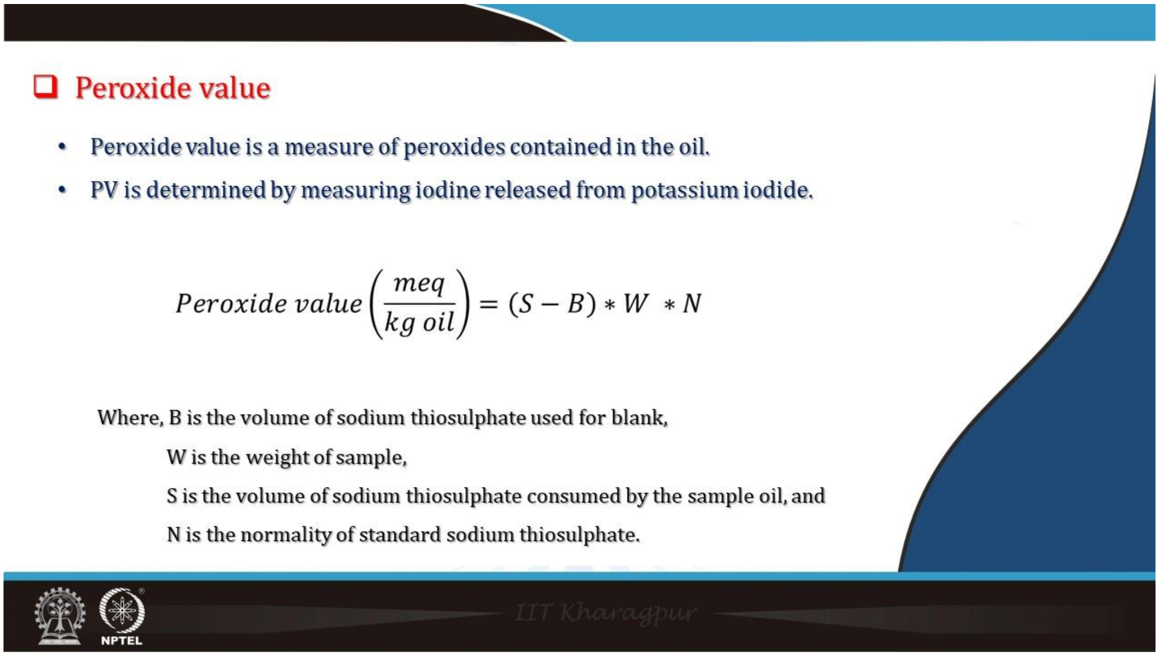
$$SV = \frac{(A - B) * N * 56.1}{W}$$

where A is the amount of sulfuric acid for the blank in ml,

B is the amount of sulfuric acid used for the sample in ml,

W is the weight of sample in dry basis g and

N is the normality of sulfuric acid solution and 56.1 is the equivalent weight of KOH.



Peroxide value is the measure of peroxide contained in the oil, peroxide value is determined by measuring iodine released from potassium iodide.

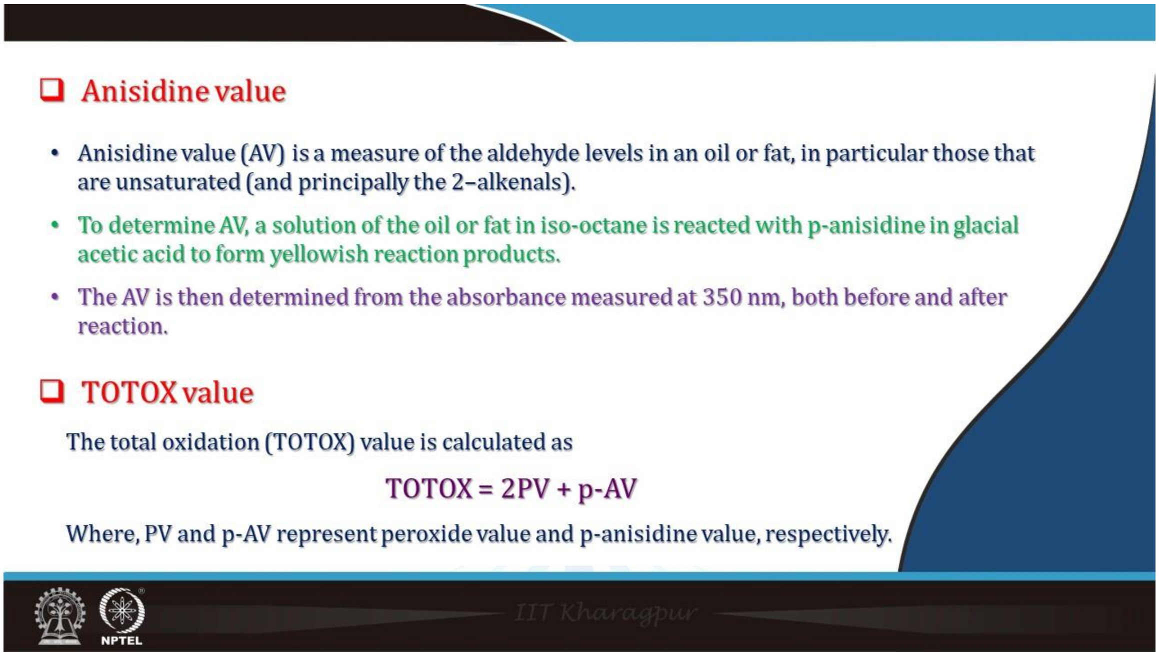
$$peroxide\ value\ \left(\frac{meq}{kg\ oil}\right) = (S - B) * W * N$$

where B is the volume of sodium thiosulfate used for blank,

W is the weight of the sample,

S is the volume of sodium thiosulfate consumed by the sample and

N is the normality of the standard sodium thiosulfate.



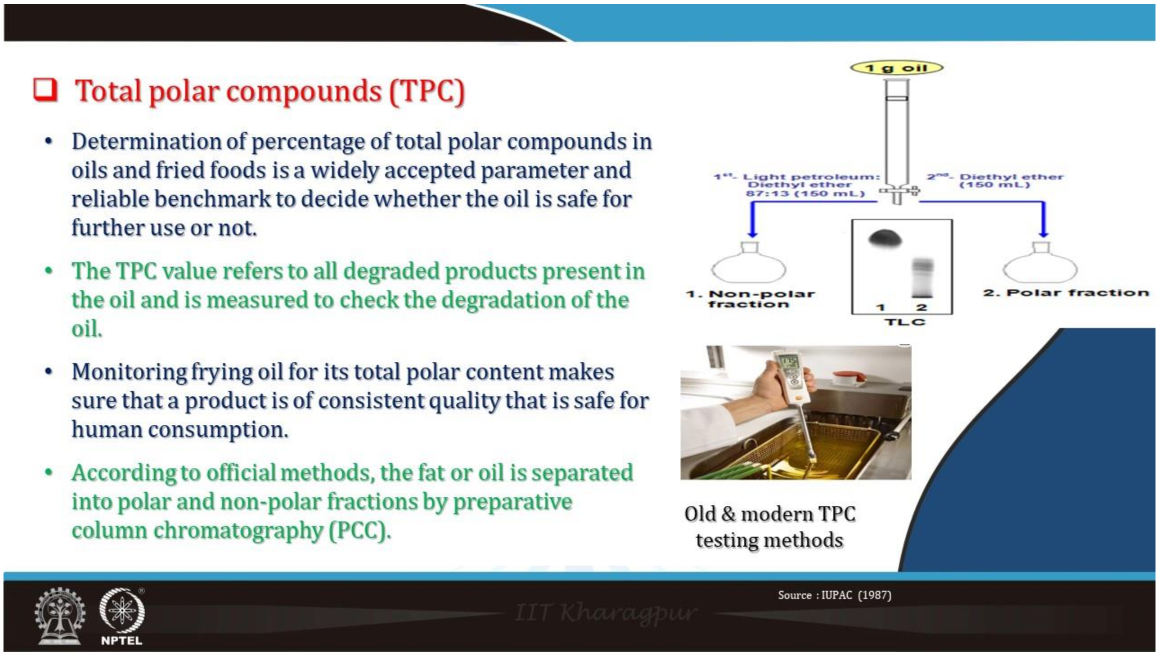
Anisidine value is measure of the aldehyde level of an oil or fat, in particular those that are unsaturated and principally the two alkenals. To determine the anisidine value a solution of oil or fat in iso-octane is reacted with p-anisidine in a glacial acetic acid to form yellowish reaction products. The anisidine value is then determined from the absorbance measured at 350 nanometers both before and after the reaction. TOTOX value indicates the oxidation level of the oil.

$$TOTOX = 2PV + p - AV$$

where PV is the peroxide value and

p-AV is the p-anisidine value, respectively.

So, 2 multiplied by PV plus the p-anisidine value gives total oxidation TOTOX value.



Determination of a percentage of total polar compounds in oils and fried foods is a widely accepted parameter and reliable benchmark to decide whether the oil is safe for further use or not. The TPC value refers to all degraded products present in the oil and is measured to check the degradation of the oil. Monitoring frying oil for the total polar content makes sure that a particular product is of consistent quality and is safe for human consumption. According to the official methods the fat or oil is separated into polar and nonpolar compound fractions by preparative column chromatography. Here you can see that,1 gram of oil is taken then 150 ml of light petroleum and diethyl ether in ratio 87: 13 and then diethyl ether 150 ml is added. These fractions are the nonpolar and polar compounds and these are generated by the TLC plate (thin liquid chromatography).

❑ Acid value

- Free fatty acids (FFA) are hydrolysis products of triglycerides (TG) in vegetable oils.
- In edible oils, their formation occurs primarily during the production and the storage procedures of the oil and, in general, during handling of the raw material.
- An established method to measure the content of FFA is the so-called "acid value" (AV), referred to as the amount of potassium hydroxide (mg of KOH) required to neutralize the acidic fraction in one gram of sample (mg KOH/g oil).
- The AV is a volumetric method for the determination of FFA in lipids (fatty oils and waxes), that consists in the titration of the sample with a standardized ethanolic solution of KOH using phenolphthalein as an endpoint indicator.

Free fatty acids are hydrolysis products of triglycerides in vegetable oil. In edible oils their formation occurs primarily during the production and the storage procedures of the oil and in general during the handling of the raw materials. An established method to measure the content of free fatty acids is the so-called acid value, referred to as the amount of potassium hydroxide per milligram of KOH required to neutralize the acidic fraction in 1 gram of the sample that is milligram KOH per gram of oil. The acid value is a volumetric method for the determination of free fatty acids in lipids that consists of the titration of the sample with a standardized ethanolic solution of KOH using phenolphthalein as an end-point indicator.

Comparison of chemical properties of commercial edible oils

Oil type	Free fatty acid (as % oleic)	Acid value (mg OH per gm)	Saponification value (mg KOH/g oil)	Peroxide value (Meq/Kg)	Ash content %	Smoke point, ^{0}c
Soybean oil	-	0.6	189-195	10	1.5-2.5	232
Sunflower oil	-	0.6	188-194	10	1.5-2.5	232
Sunlit oil	-	0.6	188-194	10	1.5-2.5	232
Hayat oil	0.15%	0.6	190-209	10	1.5-2.5	230
Avena oil	0.15%	0.6	190-209	10	1.5-2.5	230
USA oil	-	0.6	-	10	1.5-2.5	high
Niger oil	-	0.6	189-193	10	1.5-2.5	-

Chemical parameters set by FOA/WHO as standards for seven edible oils

(Asean Manual of Food Analysis, 2011; Codex Alimentarius Commission, 1995).

In this table there is chemical properties of some of the commercial edible oils are given and these parameters are set by FOA/WHO as standard for these seven edible oils. The free fatty acid content in the soybean oil should be nil, an acid value maximum of 0.6, a saponification value that is milligram KOH per gram of oil maybe 189 to 195, a peroxide value maximum of 10, an ash content percent should be 5 to 2.5 percent and a smoke point is 232 degree Celsius. Sunflower oil its acid value is 0.6 milligram OH per gram, its saponification value is 188 to 194, peroxide value in milli equivalent per kg is 10, in fact same for all these oils, and most of these oils their ash contents ranges from 1.5 to 1.25 and for soybean oil, sunflower oil, sunlit oil, hayat oil, Avena oil, their smoke point is from 230 to 232 degree Celsius, their acid value is 0.6 and free fatty acid may be for hayap oil 0.15 percent, Avena oil 0.15 percentage of oleic acid.

Chemical properties of common edible oils

Chemical Parameters	Smoke point (°C)	Free fatty acid (as % oleic acid)	Acid value, %	Saponification value (mg KOH/g oil)	Peroxide value (Meq/Kg)	Ash content %
Soybean oil	224.33±0 .58	0.75±0.16	1.49±0.32	195.56±1.35	9.26±0.11	0.015±0.00
Sunflower oil	221.66± 1.52	1.21±0.16	2.43±0.32	197.14±0.56	8.80±0.20	0.925±0.00
Sunlit oil	219.00±1.00	1.31±0.16	0.61±0.32	194.75±1.39	8.52±0.15	0.020±0.00
Hayat oil (palm oil)	215.00±5.00	2.07±0.58	3.17±0.32	213.18±1.40	4.33±0.11	0.053±0.00
Avena oil (palm oil)	209.00± 1.00	2.05±0.25	4.48±0.57	210.84± 0.80	4.93±0.11	0.012±0.00
USA oil	239.00±1.00	1.40±0.28	2.80±0.56	199.48±0.58	6.73±0.11	0.016±0.00
Niger oil	161.66±1.53	7.98±0.81	5.89±1.62	197.00±1.93	8.00±0.20	0.022±0.00

(Mengistie et al., 2018)

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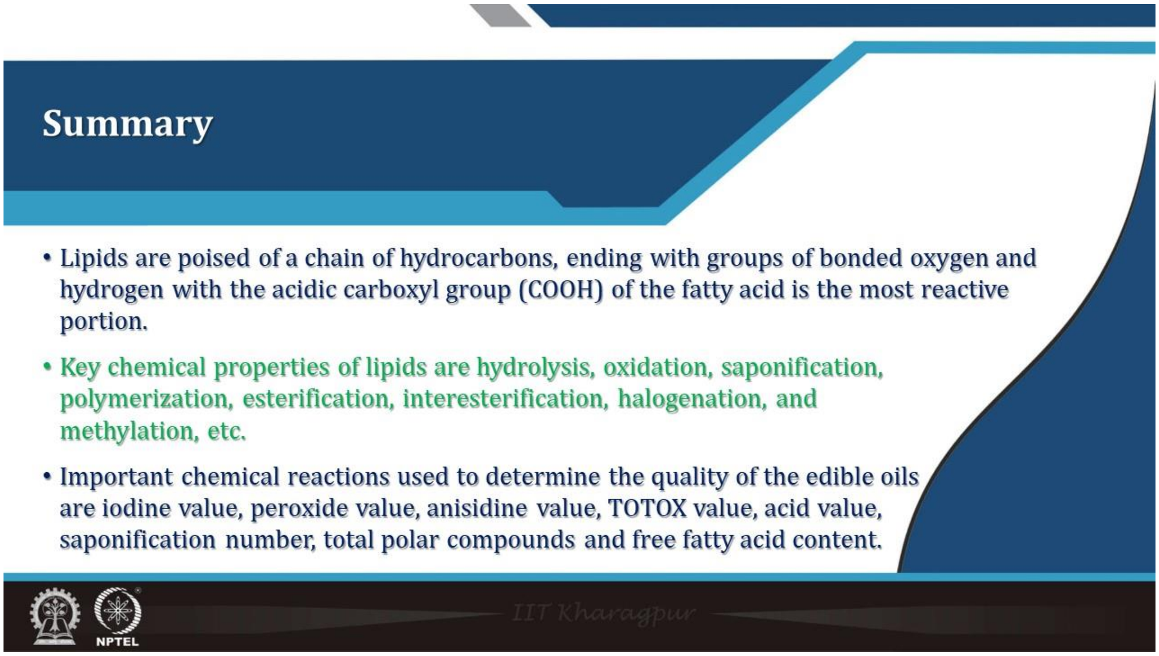
The smoke point-free fatty acid, acid value, saponification value, peroxide value, and ash content of oils like soybean oil, sunflower oil, sunlit oil, etc. are given. All these parameters of the chemical properties of common edible oils are given in this, this has been taken from the Mengistie et al. 2018, reference. And you can see here there is most of these oils have a smoke point above 200 except that niger oil which has around 161 degrees Celsius. Free fatty acid in most of the cases is less than 1 to 2 percent, but in the niger oil, it is around 8 percent. Similarly, the acid value of niger oil has more than USA oil, for which it is 2.8, Avena (palm oil) has 4.48, hyat (palm oil) is 3.17, and others are very less. Similarly, the saponification value peroxide value of niger oil and USA oil are more, sunlit and sunflower oil also has 8.52 and 8.80. In most cases, these oils have 8, but the lowest peroxide value is observed for hyath palm and Avena palm oil.



Finally, I summarize this lecture, lipids are poised of a chain of hydrocarbon ending with groups of bonded oxygen and hydrogen with the acidic carboxyl group of the fatty acid and this carboxyl group is the most reactive. It is the most reactive, that is one is the carboxyl group and the other is the unsaturation point in the chain fatty acid chain. The key chemical properties of the lipids are hydrolysis, oxidation, saponification, polymerization, esterification, interesterification, halogenation, and methylation, etc. Important chemical reactions that are used to determine the quality of edible oils are iodine value, peroxide value, anisidine value, TOTOX value, acid value, saponification number, total polar compound, and free fatty acid content. So, by determining these parameters in the laboratory there are standard protocols one can use and one can get for example, if you get a higher TOTOX value, or higher peroxide value, it indicates that the oil is oxidized or auto-oxidized. If you get more amount of free fatty acids in the oil it means that there is a significant substantial hydrolysis of the fat has taken place. If you get more iodine value means the oil has more amount of unsaturated fatty acids. So, these values give an indication of the fatty acids or triglycerides.

These are the references that are used in this lecture. Thank you very much for your patience here. Thank you.

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