Food Oils and Fats: Chemistry and Technology

Professor H N Mishra

Agricultural and Food Engineering Department

Indian Institute of Technology Kharagpur

Module 12: Packaging, Storage, & QA/QC

Lecture 59: Quality Analysis & Control

Hello everyone. Namaskar.

Concepts Covered

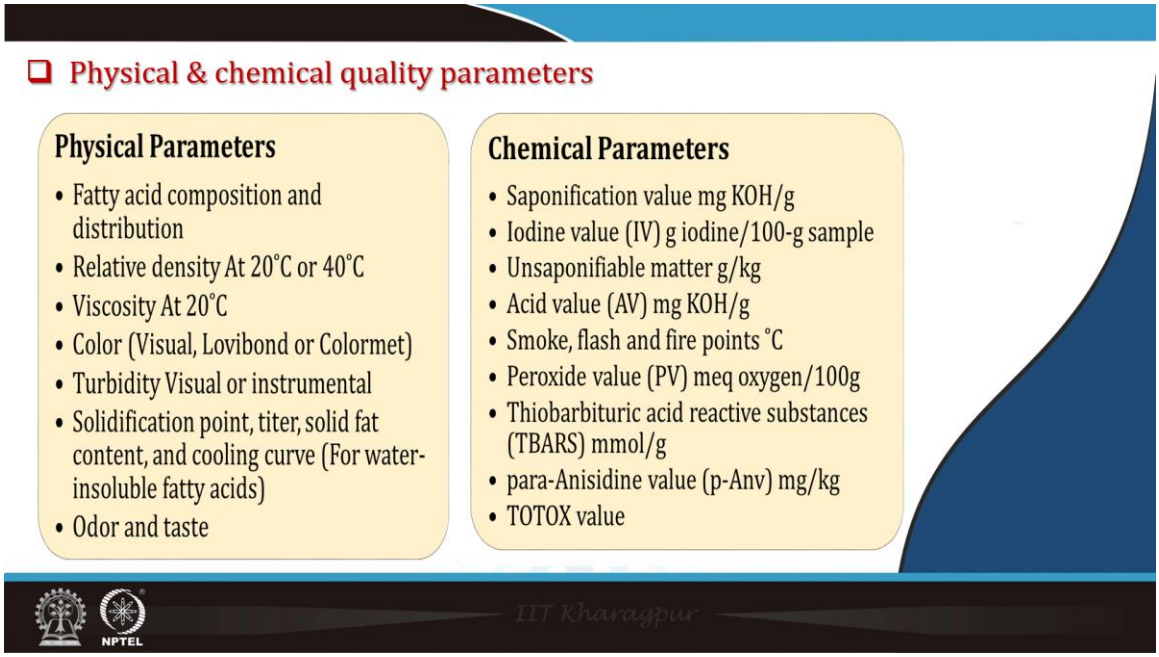
- Quality parameters for edible oils and fats
- Oxidative quality and stability tests
- Carbonyl compounds
- Chemical quick tests
- Adulteration

Today in lecture 59, we will discuss about Quality Analysis and Quality Control for Food Oil fats. We will discuss various quality parameters for edible oil fats, oxidative quality and stability tests, then various carbonyl compounds which are present in oil fats, then chemical quick test and also we will throw some light on adulteration in oil fats.

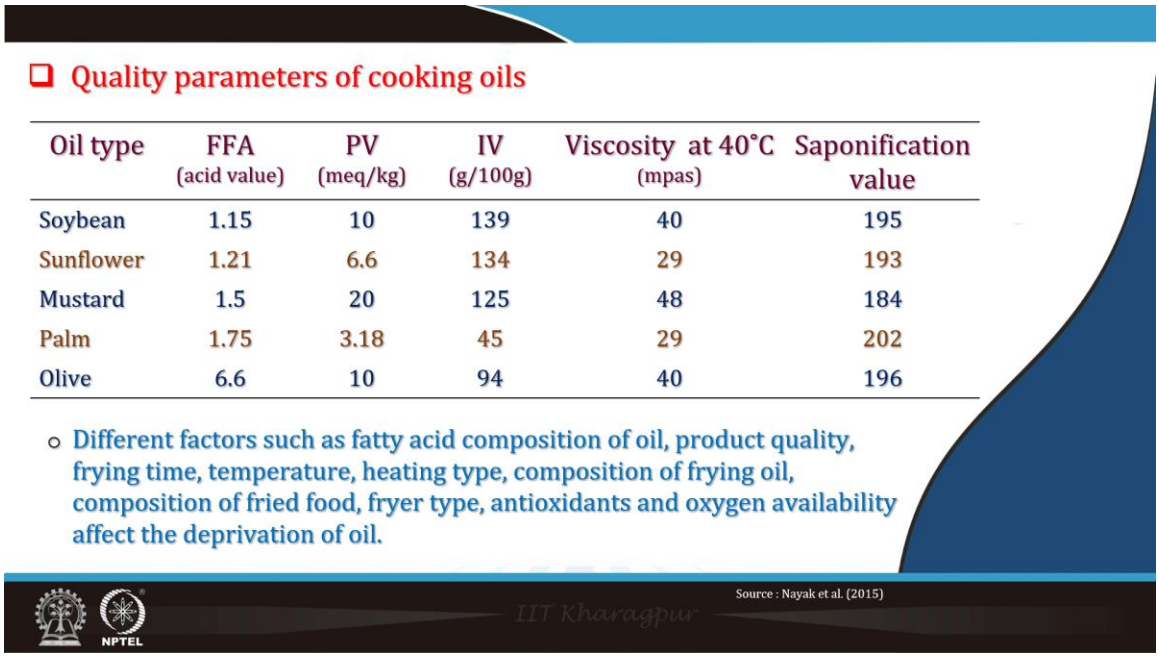
Quality parameters for fat and oils

- Edible oils are prone to quality deterioration through oxidation and microbial degradation resulting in nutritional loss and off-flavors.
- Quality deterioration may contribute in the formation of oxidation products that are reactive and toxic, which ultimately pose health risks including cancer and inflammation.
- Adulteration of fats and oils is increasing day by day throughout the world. Therefore, quality of oil is very important to regulate.
- Quality assurance criteria may depend partly on the type of oil under investigation as well as on other factors that may vary depending on the intended use and regulations that vary from country to country.

You know the various edible oils are prone to quality deterioration through oxidation and microbial degradation resulting in nutritional losses and off-flavor development. And some major aspects of this we already discussed in the various classes wherever it was necessary. Quality deterioration may contribute in the formation of oxidation products that are reactive and toxic which ultimately pose health risks including cancer and inflammation. Adulteration of fats and oils is increasing day by day throughout the world. Therefore, quality of oil is very important to regulate. Quality assurance criteria may depend partly on the type of oil under investigation as well as on other factors that may vary depending on the intended use and regulations that vary from country to country.



So, the various physical and chemical quality parameters include that is the physical parameters fatty acid composition and distribution, relative density at 20 °C and 40 °C, viscosity at 20-40°C, color may be both visual or colorimetry test, then turbidity visual or instrumental, solidification point, tighter or solid-fat content and cooling curve that is for water insoluble fatty acids and then odor and taste. So, these are the physical parameters which indicate the quality of fats and oils. Chemical parameters include saponification value, iodine value, un saponifiable matter, acid value, a smoke point, flash point, fire points, peroxide value, thiobarbituric acid value and para-Anisidine value and finally, the TOTOX value. So, these are the chemical parameters which indicate the quality of fats and oils.



So, here in this table I just tried to give you some of the important quality parameters of major cooking oil. For example, soybean oil it should contain acid value not more than 1.15 percent, peroxide value maximum permitted is 10 milli equivalent per kg of the oil, iodine value it contains around 139 g per 100 g and viscosity at 40 °C is 40mpas and its saponification value is 195. Similarly this similar data for sunflower oil include 1.21 %FFA, 6.6 Meq/kg per oxide value, iodine value 134, viscosity 29MPas at 40°C and saponification value 193. For mustard oil again the FFA should be maximum 1.5 percent, maximum peroxide value should be 20 Meq/kg, then its iodine value is 125, viscosity at 40°C is 48 and saponification value is 184. And palm oil it has a that is free fatty acid 1.75, peroxide value 3.18, iodine value 45 because it contains more saturated fats. So, its iodine value is less, viscosity at 40°C of palm oil is 29 and saponification value is 202. Olive oil it contains more free fatty acids permitted maybe that is 6.6 percent up to acid value and then peroxide value again maximum is 10, iodine value 94, viscosity at 40°C is 40MPas and saponification value is 196. So, you can see that earlier also we discussed that different factors such as fatty acid composition of the oil, product quality, frying time, temperature, heating type, composition of the frying oil, composition of the fried food, fryer type, antioxidant and oxygen availability affect the deprivation of the oil.

Oil composition

- Fats and oils contain various classes of compounds. These compounds are primarily neutral lipids that include triacylglycerols (triglycerides) with lower amounts of diacylglycerols (diglycerides), monoacylglycerols (monoglycerides), and free fatty acids.
- Partial acylglycerols are produced by hydrolysis of triacylglycerols.
- The amount of free fatty acids should be less than 0.1%, preferably less than 0.05% in freshly refined oils.
- In addition, polar lipids, mainly phospholipids, and to a lesser extent, glycolipids are present.

Now, as regard to the oil composition earlier also in the beginning of this course we discussed that fats and oil contain various classes of compounds. These compounds are primarily neutral lipids that include triglycerides and diglycerides or some amount of monoglycerides and also there are some free fatty acids. So, partial acylglycerols are produced by the hydrolysis of triacylglycerols. So, the amount of free fatty acids should be less than 0.1 percent preferably less than 0.05 percent in freshly refined oils. In addition, polar lipids mainly phospholipids and to a lesser extent glycolipids are present in the oils.

Minor components

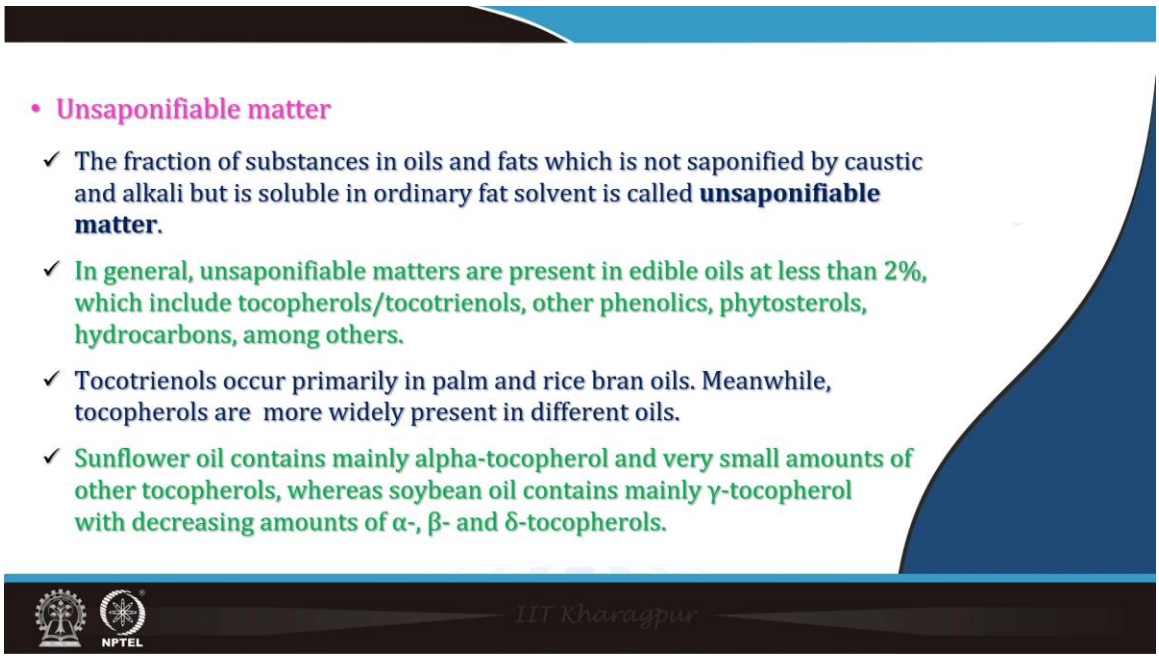
- Polar lipids

  These are mainly phospholipids, are present in fats and oils, and these originate primary as components of cell membranes and serve biological functions in the cells.

  Among phospholipids present are
  - ✓ Phosphatidylcholine (PC)
  - ✓ Phosphatidylethanolamine (PE)
  - ✓ Phosphatidylinositol (PI)

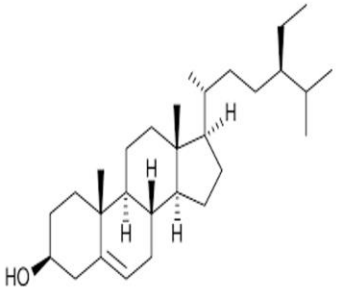
- Sphingolipids
  - ✓ These are also important bioactive components of all membranes.
  - ✓ The content of polar lipids is reduced during oil refining.
  - ✓ Degumming removes most polar lipids.
  - ✓ However, refining, bleaching, and deodorization would also bring about a reduction in the content of polar lipids.

The compound that is minor compounds which are present in the fats and oil that is the polar lipids as well as the sphingolipids. The polar lipids are the mainly phospholipids and these originate primarily as components of cell membrane and serve biological functions in the oil. Among phospholipids that present are phosphatidylcholine, phosphatidyl ethanolamine and phosphatidyl inositol. Sphingolipids are also important bioactive components of all membranes. The content of polar lipid is reduced during oil refining. Degumming removes most polar lipids. However, refining, bleaching and deodorization would also bring about a reduction in the content of polar lipids.



Regarding un-saponifiable manner, the fraction of substances in oils and fats which is not saponified by caustic and alkali, but is soluble in ordinary fat solvent is called un-saponifiable matter. In general, un-saponifiable matter are present in edible oils at less than 2 percent which includes tocopherols, tocotrienols, other phenolics, phytosterols, hydrocarbons among others. The tocotrienols are primarily in palm and rice bran oils. Meanwhile, tocopherols are more widely present in different oil. Sunflower oil contains mainly alpha tocopherols and very small amounts of other tocopherols. Whereas, soybean oil contains mainly gamma tocopherols with decreasing amounts of alpha, beta and delta tocopherols.

- Another group of unsaponifiable matter is phytosterols, fatty acid esters of phytosterols, and sterol glycosides.
- The hydrocarbons present in oils are composed mainly of squalene and carotenoids such as β-carotene, among other carotenes.
- In addition, oxygenated derivatives of carotenoids may be present.



Phytosterols

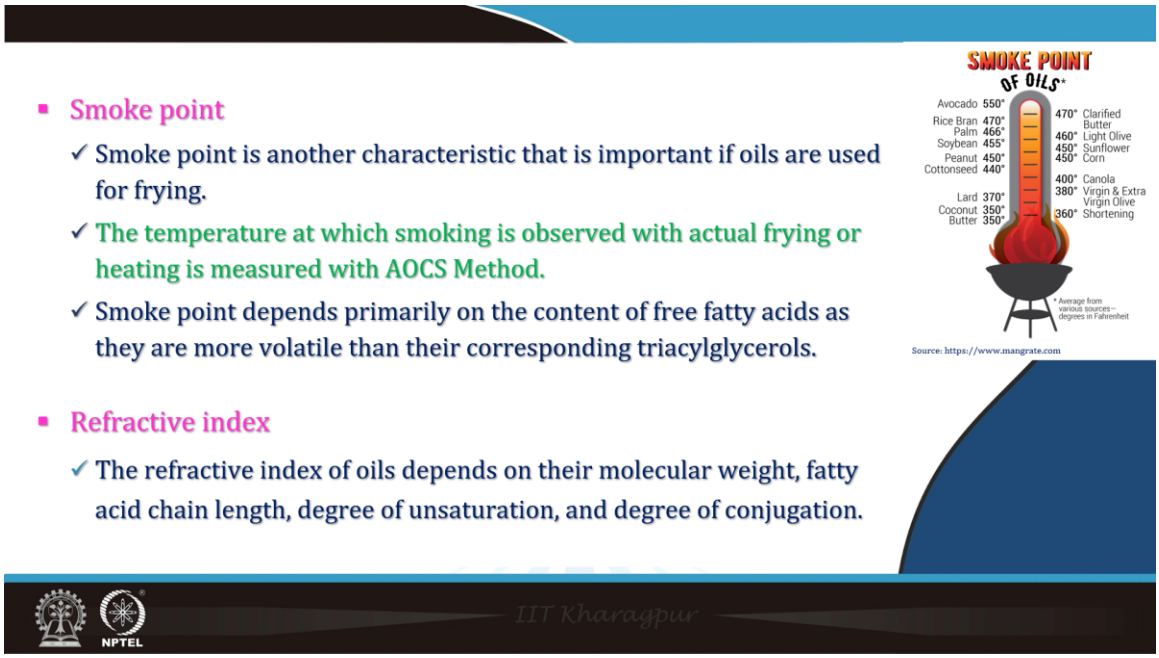
Another group of un-saponifiable matter is phytosterols that is fatty acid esters of phytosterols and sterol glycosides. The hydrocarbons present in oils are composed mainly of squalene and carotenoids such as beta carotene among others. In addition, oxygenated derivatives of carotenoids may also be present.

Characteristics of fats and oils

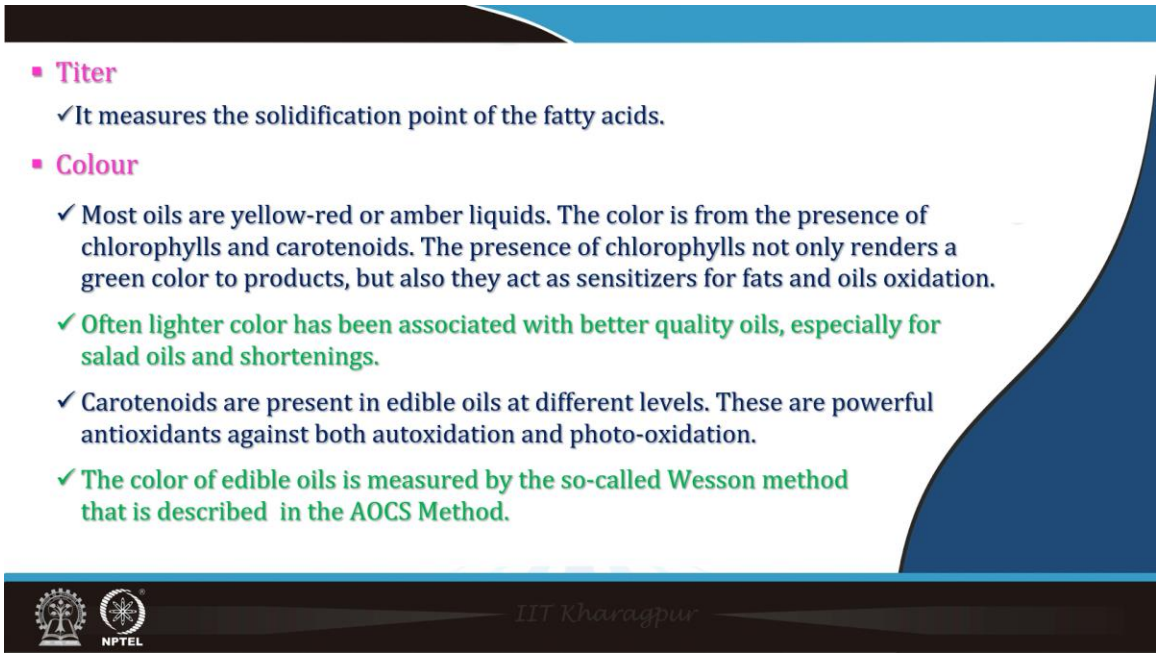
- Melting point
  - ✓ The melting points of fats and oils provides an estimate of their degree of saturation / unsaturation that parallels the saturation/unsaturation pattern dictated by their fatty acid constituents.
  - ✓ Trans-fats, when present, have a higher melting point than do their cis-counterparts because of better packing of trans-fatty acids when compared with their cis counterparts.
- Density
  - ✓ The density of liquid oils is dependent on their fatty acid composition, minor components, and temperature.

Now let us talk about characteristics of fats and oils. The important characteristics include melting point that is the melting point of fats and oils provides an estimate of the degree of saturation or unsaturation that parallels the saturation or unsaturation pattern dictated by their fatty acid constituents. Trans fats when

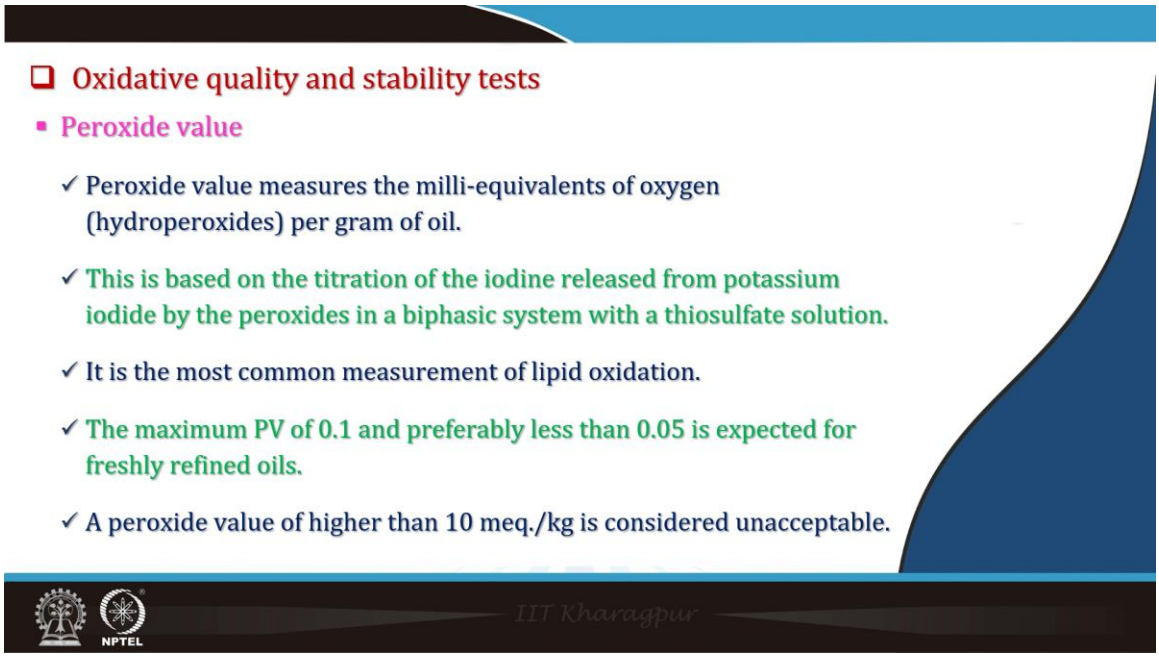
present have a higher melting point than do their *cis* counterparts because of better packing of trans fatty acids when compared with their *cis* counterparts. Density of liquid oil is dependent on their fatty acid composition, minor components present and the temperature of the oil.



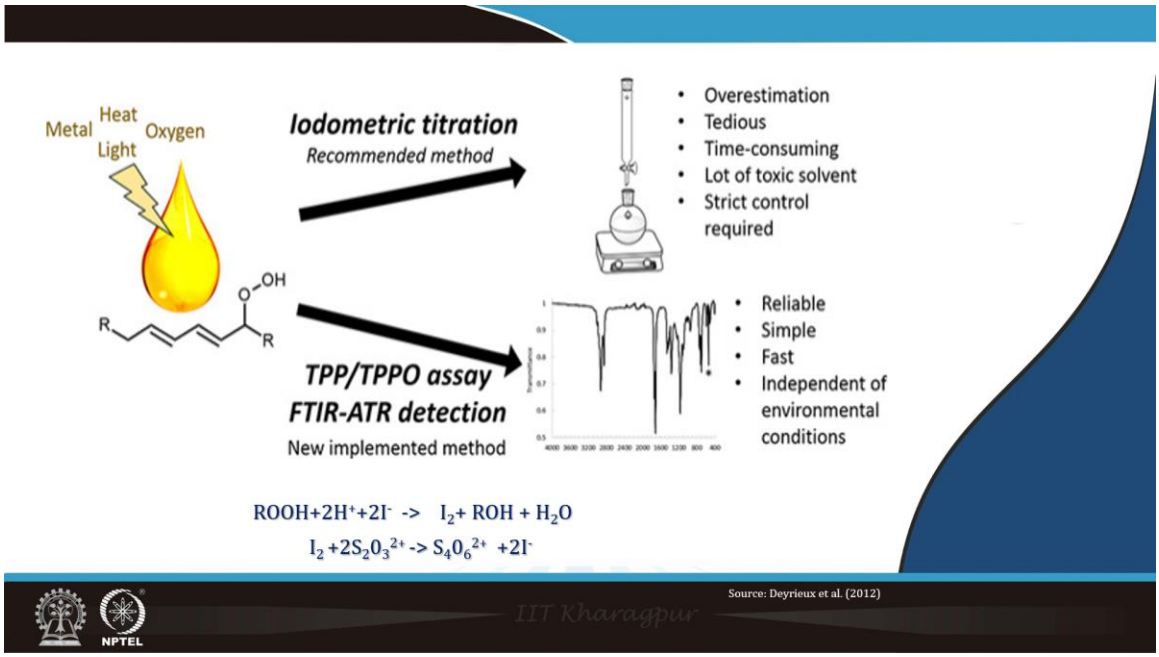
A smoke point is another characteristic that is important if oils are used for frying. The temperature at which smoking is observed with actual frying or heating is measured with AOCS methods. Smoke point depends primarily on the content of free fatty acids as they are more volatile than their corresponding triacylglycerol. The refractive index of the oil depends upon the molecular weight, fatty acid chain length, degree of unsaturation and degree of conjugation.



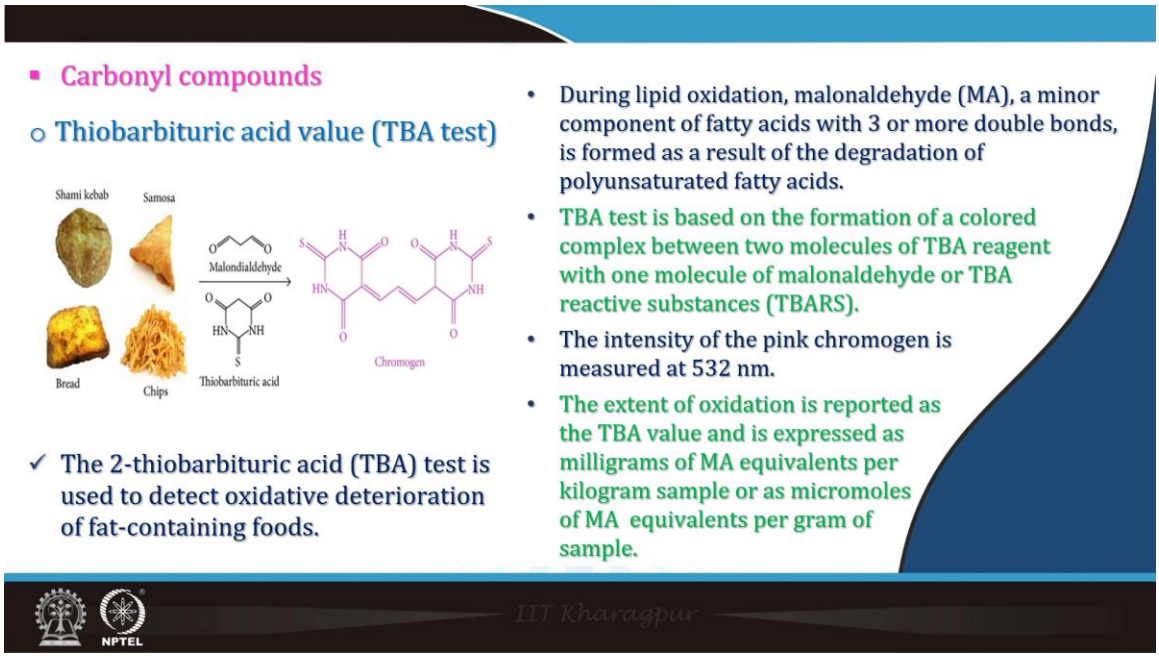
Titer is the measure of solidification point of the fatty acids. As regard to the color, most oils are yellow red or amber liquids. The color is from the presence of chlorophylls and carotenoids. The presence of chlorophylls not only render a green color to the product, but also they act as sensitizers for fats and oil oxidation. Often lighter color has been associated with better quality of oils, essentially for solid oils as well as for shortening. Carotenoids are present in edible oils at different levels. These are powerful antioxidants against both autooxidation and photooxidation. The color of edible oil is measured by the so-called Vason method that is described in the AOCS methods.



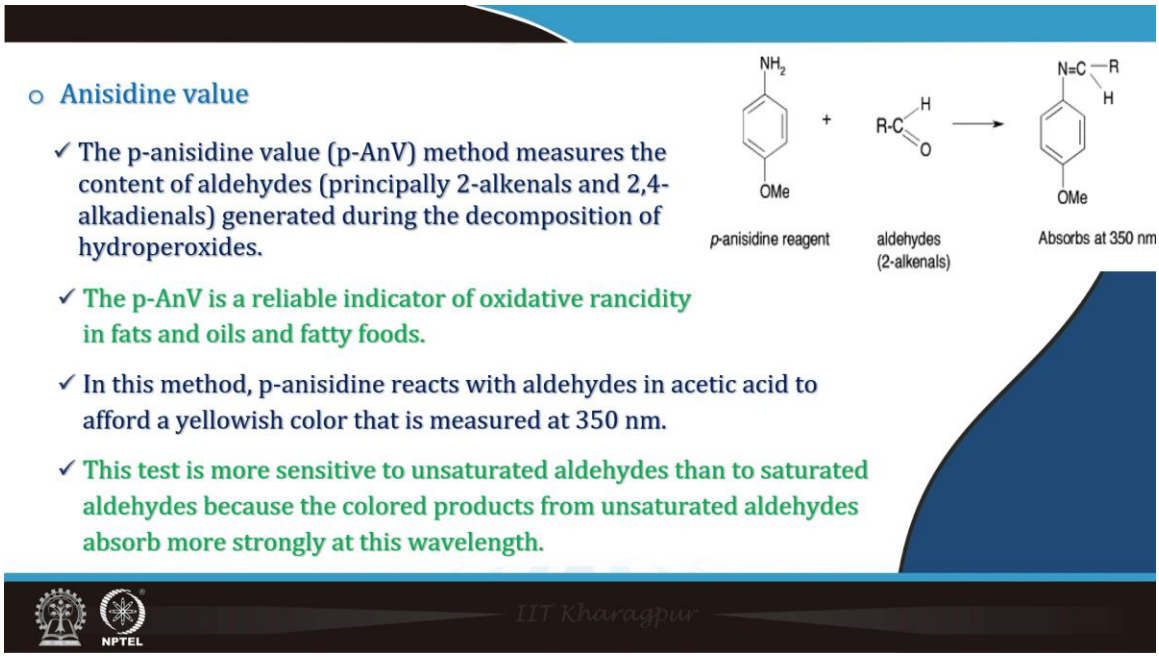
Then oxidative quality and stability tests are available. To determine the oxidative quality of the oils or its stability of the oil, various tests are available. These tests are detailed in AOCS methods. Standard Laboratory Manuals and Protocols are there. So, once you refer to that. Here I will briefly tell you that what are these tests and how they are mainly measured. Like peroxide value, it measures the mainly equivalent of oxygen that is hydroperoxide per gram of oil. This is based on the titration of the iodine released from potassium iodide by the peroxides in a biphasic system with a thiosulfate solution. It is the most common measurement of lipid oxidation. The maximum peroxide value of 0.1 and preferably less than 0.05 is expected for freshly refined oil. The peroxide value of higher than 10 meq/kgper kg is considered unacceptable.



Earlier classes also we discussed that the heat, metal, light, oxygen etc. These cause the oxidation of the fats and oils and it result into the formation of various peroxides and other component by the reactions which we have already discussed. So, these are determined that is the peroxide or other compound they are determined either by hydrometric titration or by TPP/TPPO or FTIR-ATR detection. Hydrometric titration method is the most commonly followed it is the recommended method whereas, the TPP/TPPO or FTIR-ATR detection are new methods and they are of course, they are also used, but they are novel methods are later recent. So, these hydrometric methods are that is here sometime there are problem that overestimation ok, it is tedious method time consuming, there are lot of solvents are required and strict control required in these method and these problems has been to great extent overcome by the new method that TPP/TPPO that is these methods are new methods are reliable, simple, they are fast and they are independent of environmental conditions. So, this would be now used.

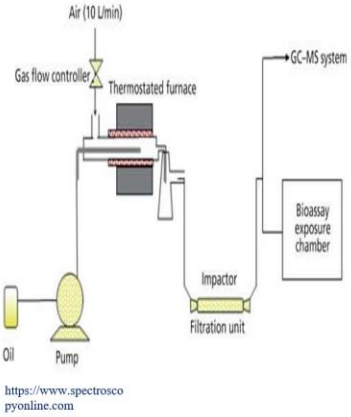


Then carbonyl compounds that is the peroxide that are oxidation test also if there is a thiobarbituric acid or other compounds are present in it indicates that oxidation of the iron. Normally, the two thiobarbituric acid test is used to detect oxidative deterioration of fat containing foods. So, in earlier class we discussed during lipid oxidation, malonaldehyde a minor component of fatty acids with three or more double bonds is formed as a result of degradation of polyunsaturated fatty acid. So, TBA test is based on the formation of a colored complex between two molecules of TBA reagent and one molecule of malonaldehyde or TBA reactive substance. The intensity of the pink chromosome is measured at 532 nm and the extent of oxidation is reported as the TBA value and is expressed as milligrams of malonaldehyde equivalents per kilogram sample or as micromoles of malonaldehyde equivalent per gram of sample.



Then p-anisidine value is another indicator of oxidation. The para anisidine value method measures the content of aldehydes, principally two alkenes and two four alkadienals. These are which are generated during the decomposition of hydroperoxide. The para anisidine value is a reliable indicator of oxidative rancidity in fats and oils and fatty foods. In this method, para anisidine reacts with aldehydes in acetic acid to afford an alloys color that is measured at 350 nm. This test is more sensitive to unsaturated aldehydes than to saturated aldehydes because of the colored products from unsaturated aldehydes as they are more strongly at this wavelength.

Gas chromatographic methods



https://www.spectroscopyonline.com

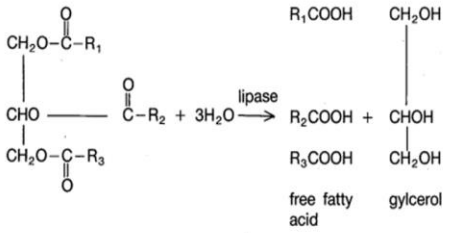
- Gas chromatographic methods may be used for measuring volatile oxidation products.
- Static headspace, dynamic headspace, or direct injection methods may be employed.
- Specific aldehydes may be measured as indicators for oxidative stability of oils and fats.
- Thus, propanal is an indicator for stability of ω-3 fatty acids, whereas hexanal is best for following the oxidative stability of ω-6 fatty acids.

GC-MS system

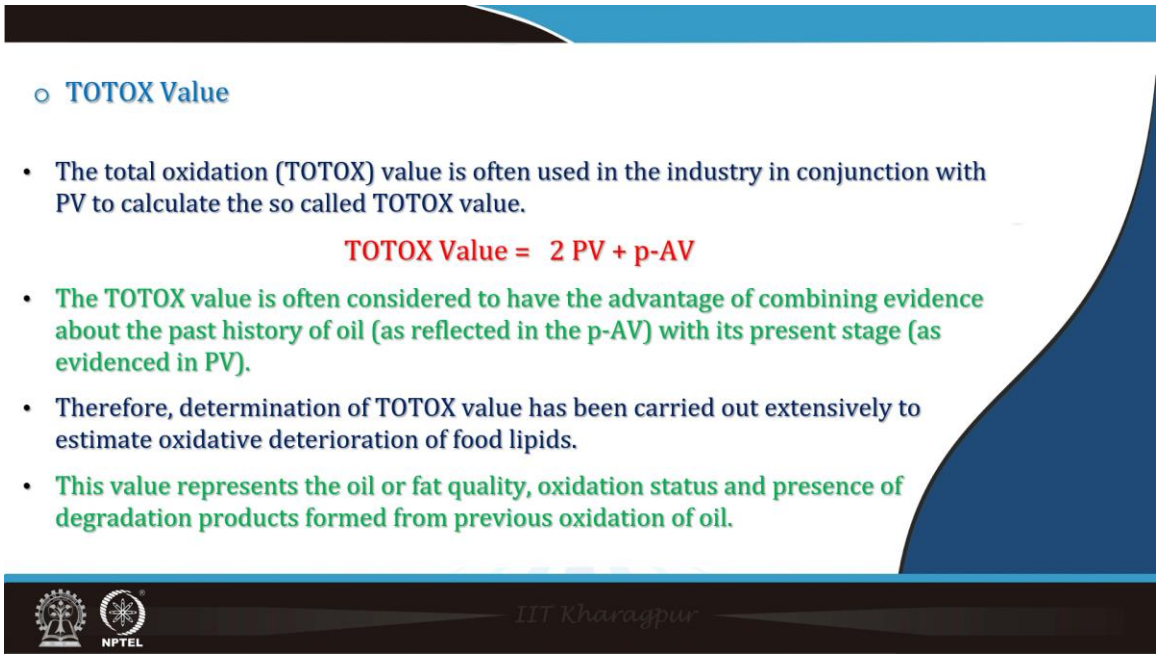
Then gas chromatographic methods are also used. Gas chromatographic method that is it is generally used it may be used for measuring volatile oxidation product. A static headspace, dynamic headspace or direct injection method may be employed. A specific aldehyde may be measured as indicators of oxidative stability of oils and fats. Thus propanol is an indicator for stability of omega 3 fatty acid whereas, hexanol is the best for following the oxidative stability of omega 6 fatty acids. So, there are standard GCMA protocols which can be used for detecting the oxidative stability.

Free fatty acid/Acid value

- ✓ Free fatty acids are normally calculated as free oleic acids on a percentage basis.
- ✓ The free fatty acids in an oil is estimated by titrating it against KOH in the presence of phenolphthalein indicator.
- ✓ The acid value is defined as mg of KOH required to neutralize the free fatty acids present in 1 g of sample.
- ✓ They are also found during frying of fats and oils. The amount of moisture from foods fried and the frying temperature are important.



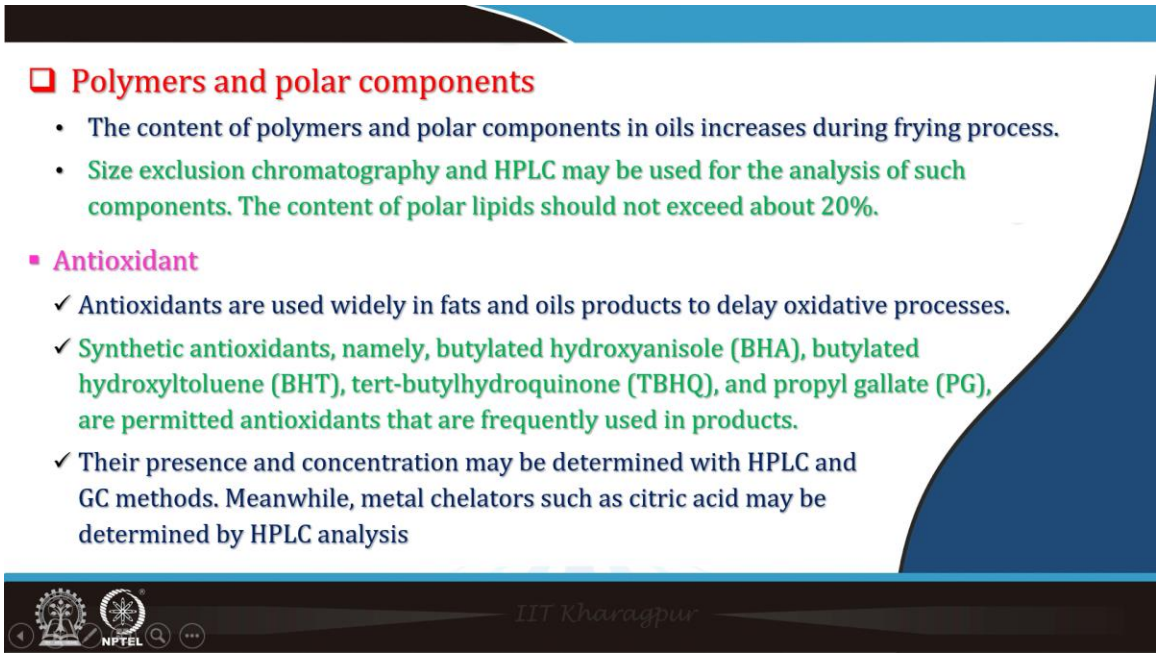
Then free fatty acids are acid value. The free fatty acids are normally calculated as a free oleic acid on a percentage basis. The free fatty acids in an oil is estimated by titrating it against potassium hydroxide in the presence of phenolphthalein indicator. The acid value is defined as milligrams of potassium hydroxide required to neutralize the free fatty acid present in 1 gram of sample. They are also found during frying of fats and oils. The amount of moisture from foods fried and the frying temperature are very important.



Then TOTOX value. The TOTOX value means total oxidation value that is it is often used in the industry in conjunction with the PV value to calculate the so-called TOTOX value that is the total what is the total amount of oxidation.

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

The TOTOX value is often considered to have the advantage of combining evidence about the past history of oil as reflected by the PV value. Then it is present stage as evidenced by peroxide value. So, both peroxide value and para-acidin value these both are taken into account while considering or calculating TOTOX value. Therefore, the determination of TOTOX value has been carried out extensively to estimate oxidative deterioration of food lipids. This value represents the oil or fat quality, oxidation status and presence of degradation products formed from previous oxidation of oil.



Then the polymers and polar compounds which are present which might be present in the oil these contain the content of the polymers and polar component in oil increases during frying process . Particularly if the oil is cooked it is heated the polymerization takes place in the earlier classes we discussed in detail about all these things. So, size exclusion chromatography and HPLC may be used for the analysis of such component like polymers or polar components. The content of polar lipids should not exceed about 20 percent in the oil in any case . Antioxidants are used widely in fired cyanide products to delay the oxidation process. Synthetic antioxidants such as hydroxyl butylated hydroxy anisole commonly known as BHA butylated hydroxyl toluene BHT or tertiary butyl hydroquinone TBHQ and propyl gallate PG. These are permitted antioxidant that are frequently used in the products their presence and concentration may be determined with HPLC and GC methods. Meanwhile metal chelators such as citric acid may also be determined by the HPLC analysis.

Chemical quick tests

There are several test kits available for detection of various chemical parameters like FFA or oxidation products using color reactions, pH indicators, or redox indicators.

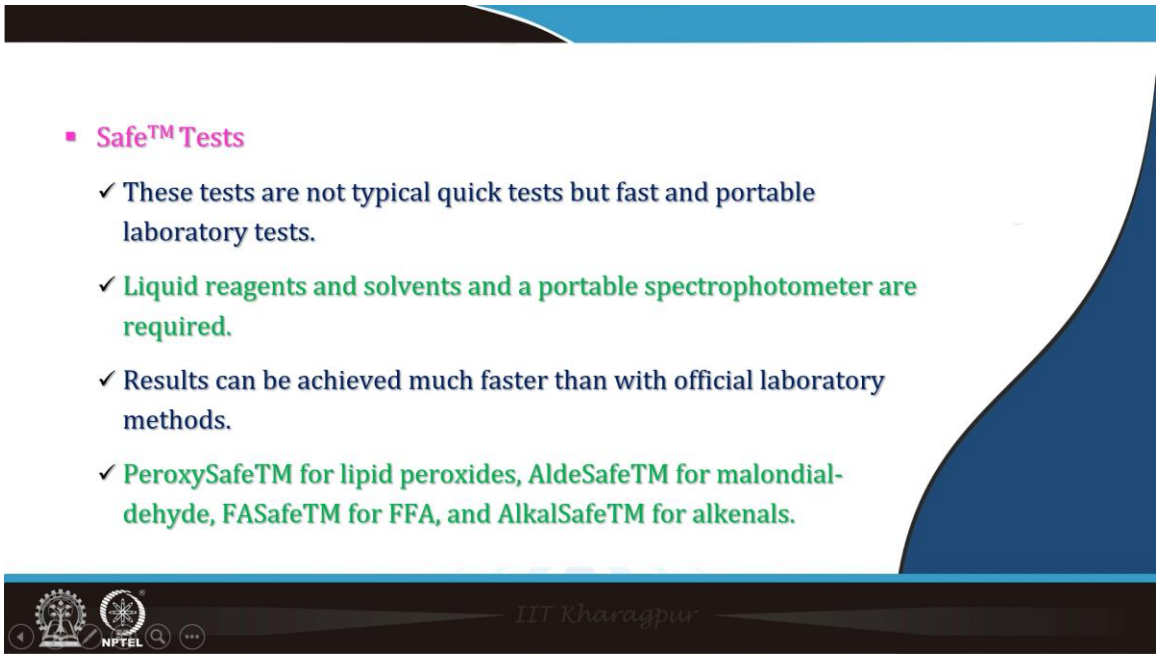
- 3M™ Shortening monitor
  - ✓ With these test strips FFA in the range of 0–2.5% (lower range)and 0–7% (higher range) can be detected.
  - ✓ As mentioned above, there is only very poor correlation between free fatty-acid level and frying fat quality measured by polymer triglycerides and total polar material.

Then quick chemical test quick tests there are several test kits available for detection of various chemical parameters like free fatty acids or oxidation products using color reactions pH indicators redox indicators and so on. And one among them is the 3 M™ shortening monitor. With these test strips FFA in the range of 0 to 2.5 percent that is the lower range and 0 to 7 percent higher range can be detected. As mentioned above there is only very poor correlation between free fatty acid level and frying fat quality measured by the polymer triacylglycerols and total polar materials.

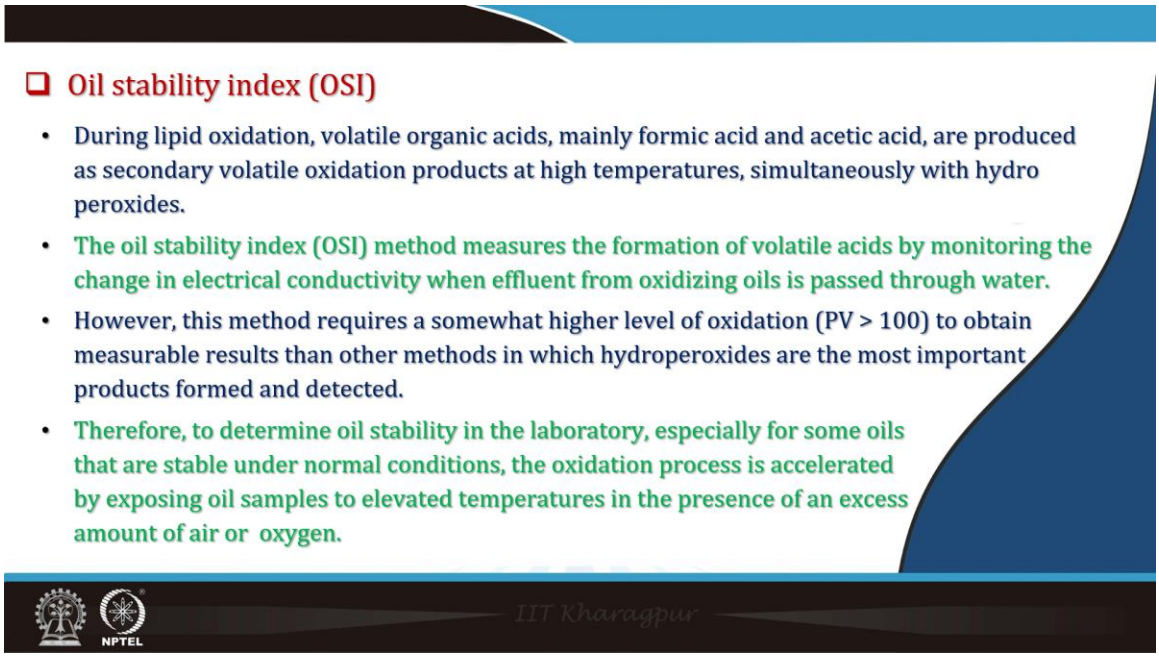
- Oxifrit-test and Fritest
  - ✓ Oxifrit-test can detect OXF using a redox indicator, Fritest can detect carbonyl compounds measuring alkaline color by comparing with a color scale.
  - ✓ With these tests frying oils can be classified in four categories from "good" to "bad.

Source: Weisshaar (2014)

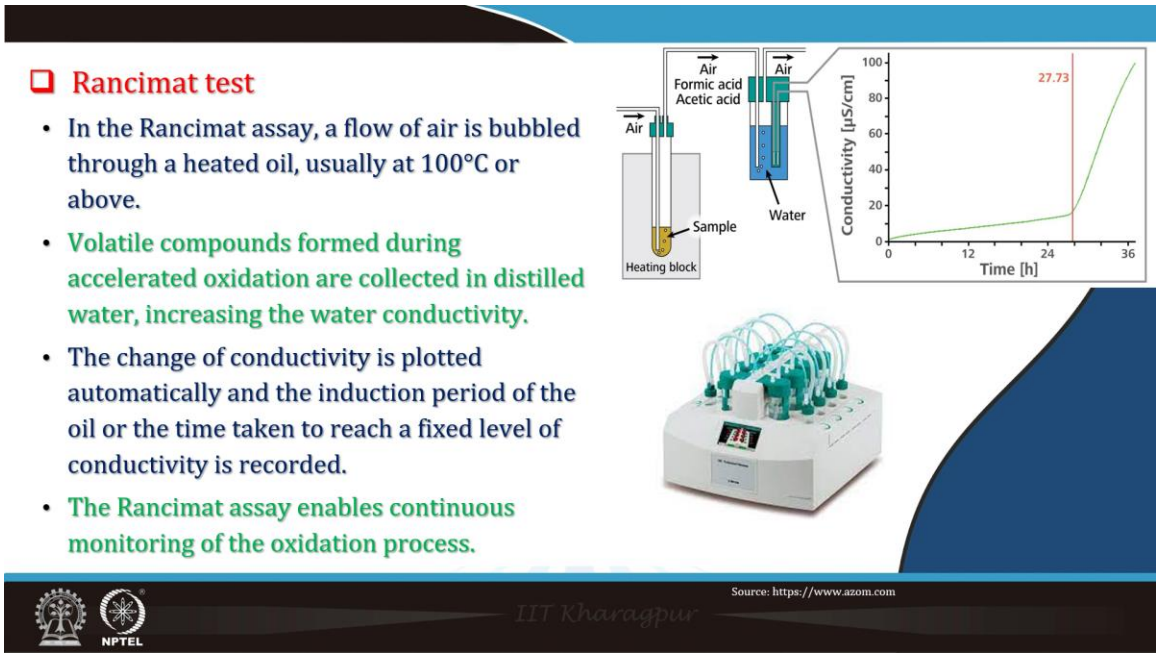
Then Oxyfrit-test and Fritest. Oxyfrit-test can detect OXF using a redox indicator, fry test can detect carbonyl compounds measuring alkaline color and by comparing with it a color scale. With these test frying oils can be classified into four general category from good to bad.



Then Safe™ test these tests are not typical quick test, but fast and portable laboratory test liquid reagents and solvents and a portable spectrophotometer are required for this test. Results can be achieved much faster than with the official laboratory methods. PeroxySafeTM for lipid peroxides, AldeSafeTM for malondial-dehyde, FASafeTM for FFA, and AlkalSafeTM for alkenals and so on that is it.



Then oxidation stability index or you can say oil stability index . During lipid oxidation volatile organic acids mainly formic acid and acetic acid are produced as secondary volatile oxidation product at higher temperature and simultaneously with hydroperoxide. So, the oil stability index method measures the formation of volatile acids by monitoring the changes in the electrical conductivity when effluent from oxidizing oil is passed through water. However, this method requires a somewhat higher level of oxidation that is peroxide value should be more than 100 to obtain measurable results that than the other method in which hydroperoxides are the most important products formed and detected. Therefore, to determine the stability or oil stability in the laboratory especially for some oils that are stable under normal conditions, the oxidation process is accelerated by exposing oil samples to elevated temperatures in the presence of an excess amount of air or oxygen.



The Rancimat test equipment in the Rancimat assay a flow of air is bubbled through a heated oil usually at 100°C temperature or even more than 100°C. The temperature oil is heated to accelerate the oxidation process that is bollock pile compounds formed during the accelerated oxidation are collected in distilled water which causes the increase in the conductivity of the water. And this change of conductivity in water is plotted automatically and the induction period of the oil or that is normally taken at the time taken to reach a fixed level of conductivity is recorded that is the induction period that is at that particular temperature what is the minimum time that is required to reach the fixed level. The after conductivity means that is the conductivity of the water beyond which you can see that is now the oil becomes rancidar it is oxidized. So, the Rancimat assay enables continuous monitoring of the oxidation process. So, this is you can see here in the figure it is shown that is the sample it is heated here then air is continuously and this is the Rancimat apparatus. And then this formic acid is it comes in the air water it is dissolved and then finally, it is in the it is in will provided in the equipment it is measured and this found you see the maximum conductivity here it is obtained beyond the result. So, that is taken as a induction period it is induction period is indication of oil stability index.

Adulteration

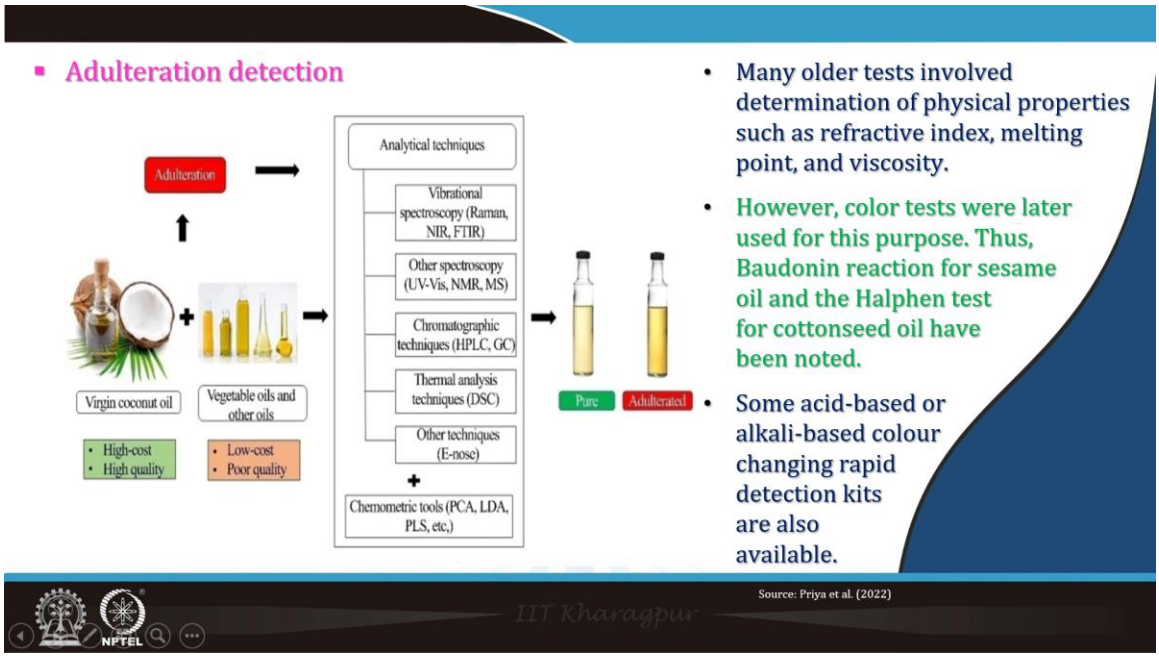
There are two major adulterations in edible oils and fats, namely

- Admixing cold press oil with refined one, and
- Replacement of more expensive oils and fats with cheaper ones.

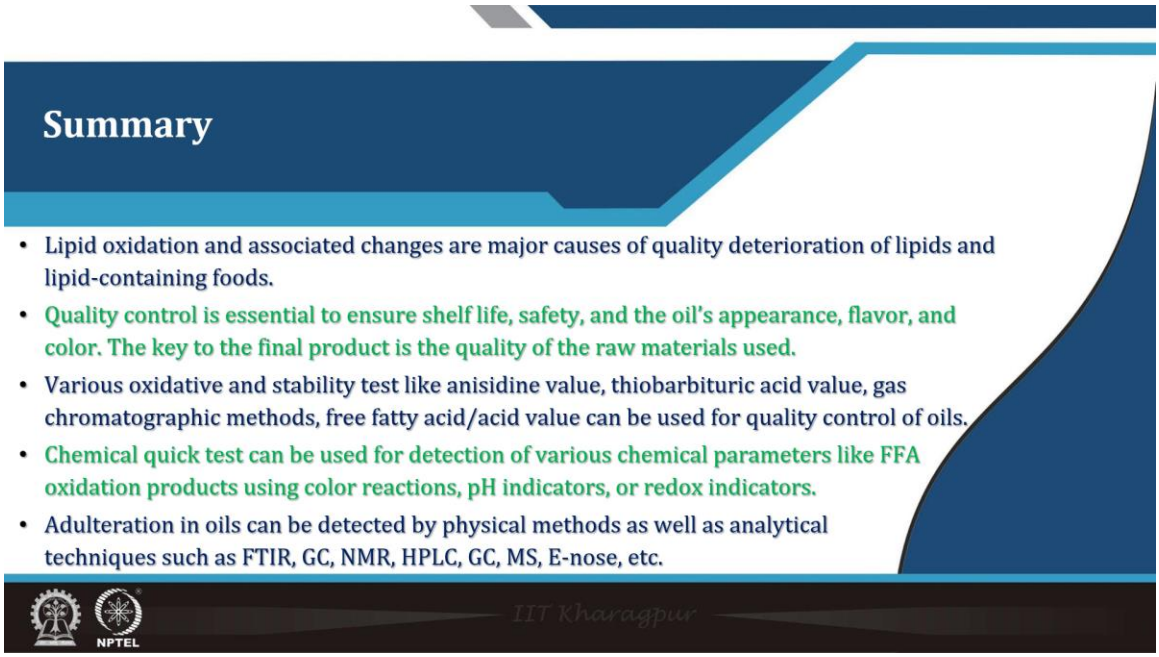
Examples

- ✓ Mustard oil adulterated with argemone oil.
- ✓ Animal fats and hydrogenated oils are often mixed with ghee to adulterate it.
- ✓ In several cases, it has been observed that castor oil, karanja oil, mineral oil, and artificial colors are profoundly used to adulterate edible oils.
- ✓ Soybean oil is adulterated with linseed oil.
- ✓ Virgin olive oil is adulterated with cottonseed oil and sunflower oils.

Then adulteration another very common meanings there are two major adulterations in edible oils and fats namely admixing cold press oil with the refined ones and another type is replacement of more expensive oils and fats with cheaper ones. For example, the common adulteration being done for that is various regions to have to get more margin of profit etc intentional addition of one thing into the other that is like mustard oil adulterated with argemone oil. Edible fats and hydrogenated oils are often mixed with the ghee to adulterate it. In several cases it has been observed that the castor oil, carangia oil, mineral oils and artificial colors are profoundly used to adulterate edible oils. Swabian oil is adulterated with linseed oil, virgin olive oil is adulterated with cotton seed oil and sunflower oil etc.



So, the purpose of this is here is that is to replace the good quality oil with the inferior quality oil and obviously, the purpose of adulteration is the to achieve that financial when the more economical profit, but this adulteration already also it creates health hazard. So, it must be prevented. For detection of adulteration there are various test available many older test involved it is determination of physical properties such as refractive index, melting point, viscosity etc or the color test we have later used for this purpose like boudomain reaction for sesame oil and health and test for the cotton seed oil have been noted. Some acid based or alkali based color charging rapid detection kits are also available. So, various methods like vibrational spectroscopy like Raman NIR, FTIR spectroscopy or UV-Vis, NMR or MS mass spectroscopy, chromatographic technique like HPLC, GC, thermal analysis technique, differential scanning chromatography (DSC) or other techniques like e-nose etc are now become popular which can be used to determine this test. Then chemometric tools like PCA, LDA, PLS etc are used to analyze these results and get the data. So, you can see that the various test. So, the purpose is that is this test should be conducted to control the adulteration.



So, finally, I will summarize this lecture by saying that lipid oxidation and associated changes are major causes of primary quality deterioration of lipids and lipid containing foods. Quality control is essential to ensure shelf life, safety and oil's appearance, flavor and color. The key to the final product is the quality of raw material used. Gas oxidative and stability test like an acid in value, thiobarbitalic acid value, gas chromatographic methods, free fatty acid, acid value can be used for quality control of oils. Chemical quick test can be used for detection of various chemical parameters like FFA, oxidation products using color reactions, pH indicators or redox indicators etc. Adulteration in oil can be detected by physical methods as well as analytical techniques such as FTIR, GC, NMR, HPLC, GC, MS, E-nose, etc. So, the whatever is required that is industry must follow the standard procedures and protocol to analyze the quality parameters of oil and this analysis helps in maintaining the quality of the oil and to maintain it to safe level quality and safety of oil which is very important. And this various adulteration detection tests are available now just to ensure that as there is this maintenance of adulteration is minimized or completely prevented. Even there are various regulation in force in the country and various agencies are there which can detect which can help the industry in getting these tests done and therefore, getting helping them to maintain the quality and safety of their products.

These were the references that is used in this lecture. This thank you very much for your patience here. Thank you.