**Food Oils and Fats: Chemistry & Technology**
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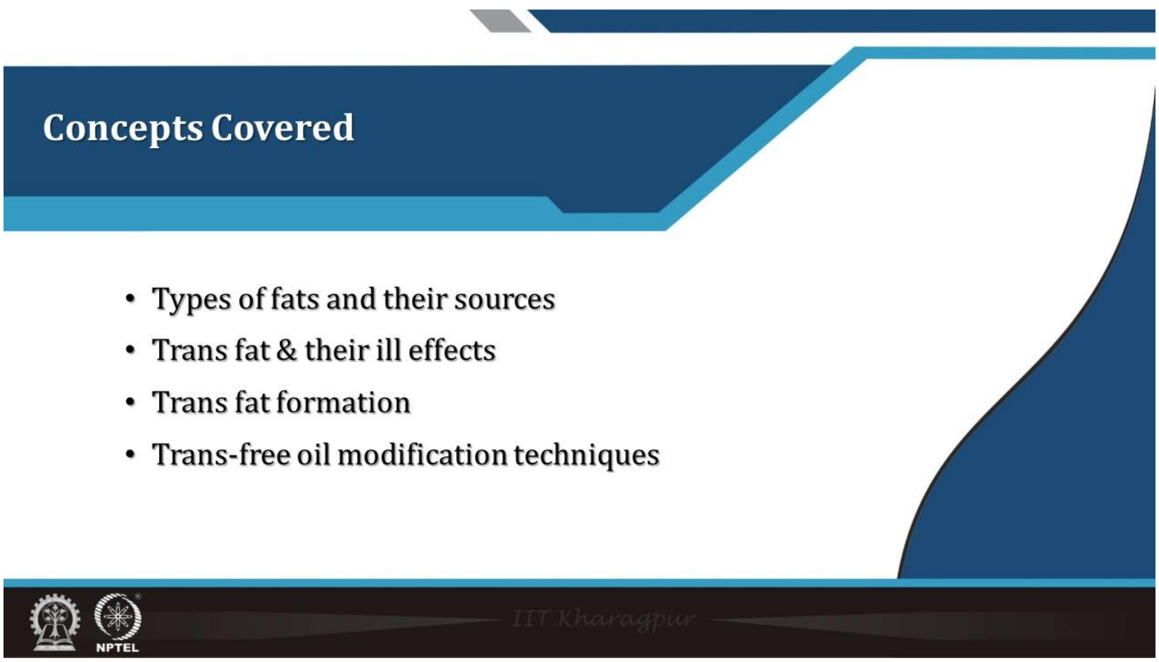
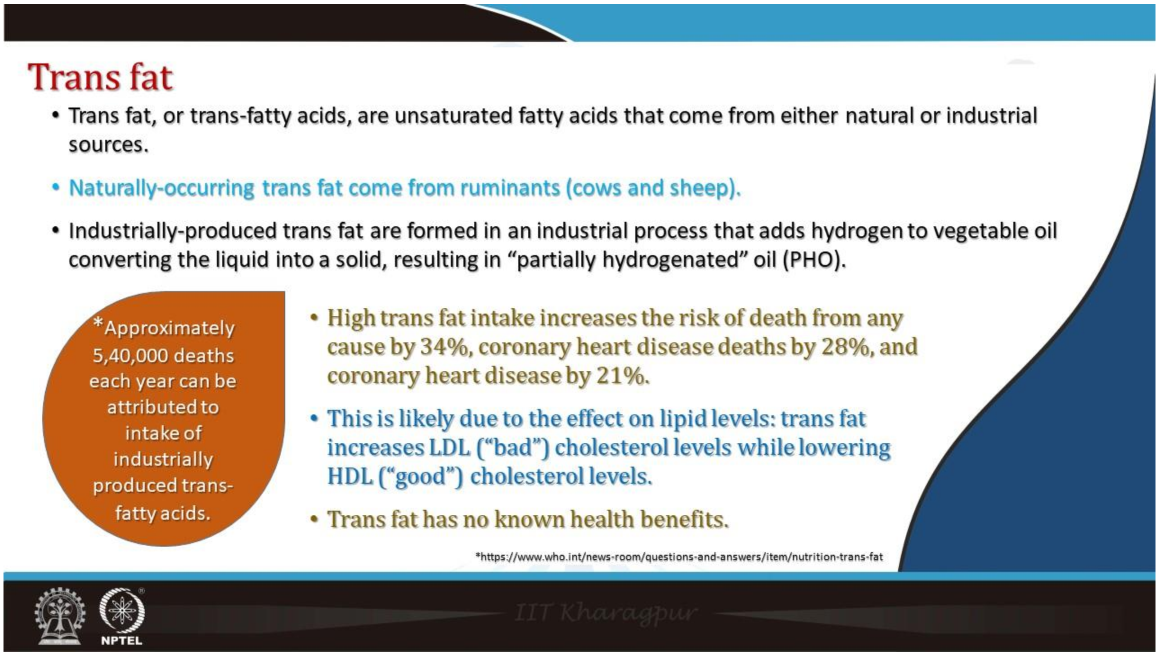
**Module 7 : Modifications of Oils and Fats**
**Lecture 35 : Trans-Free Modifications**


Hello everybody. Namaskar. Now, we are in the last lecture of the seventh module. In this lecture 35 for the next half an hour or so, we will discuss about Transfree Modifications. We will talk what are the types of fats and their sources, trans fat and their ill effects. Then what are trans fats, how the trans fats are formed during various modification techniques etc., and their mechanism of formation? Then we will see how this trans-free oil can be made, and how the formation of the trans fats can be minimized or can be reduced that is trans free modification techniques.

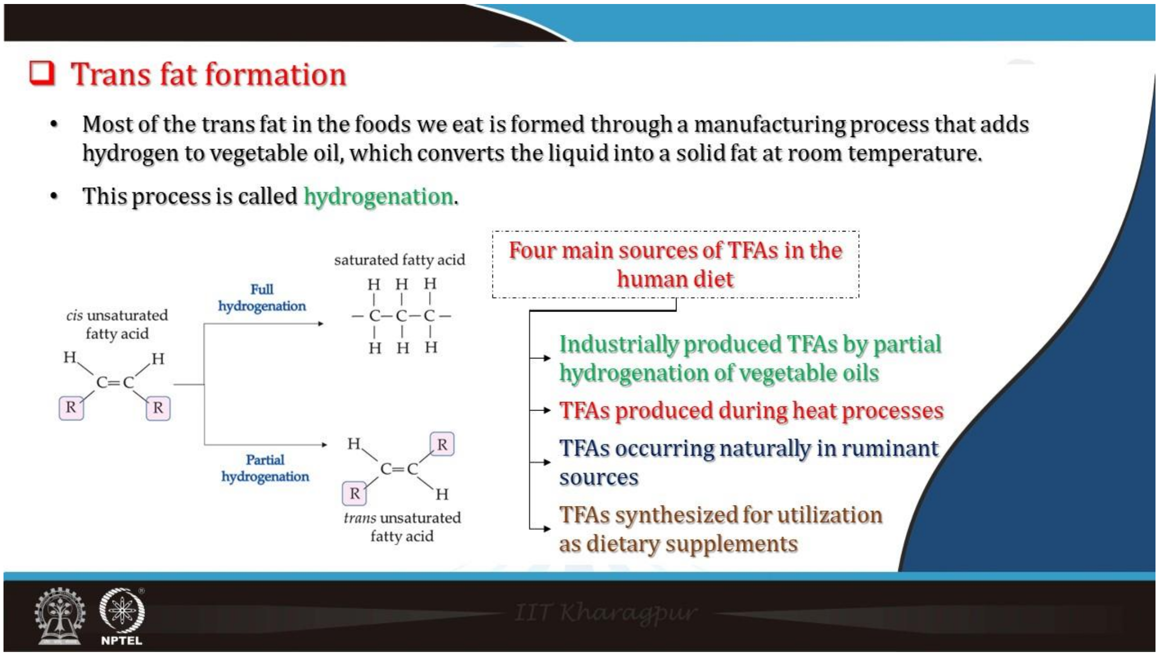

Fats are important for our body and it must be present in our diets to remain healthy. Not all fats are equal in terms of their effects on our health. Some are more beneficial and others may be unhealthy if one eats too much of them. Some fats correlate with the risk for heart disease while others have a protective effect. More important than the quantity of fat is the type (or mix) of fat. Frequently, the ratio of good fat to bad fat is very low.


Mainly if you see there are four types of fat that are mostly consumed through foods like polyunsaturated fats, monounsaturated fats, saturated fats, and trans fats. Polyunsaturated and monounsaturated are the preferred fats. Saturated fats and trans fats are those that we should consume the least. These fats are positively associated with the development of insulin resistance and heart disease. Trans fats have received much interest in recent years because of several bad health effects as trans fats raise LDL (bad) cholesterol, they lower HDL (good) cholesterol. High LDL along with low HDL levels can cause cholesterol to build up in arteries (blood vessels). This increases risk for heart disease and stroke.

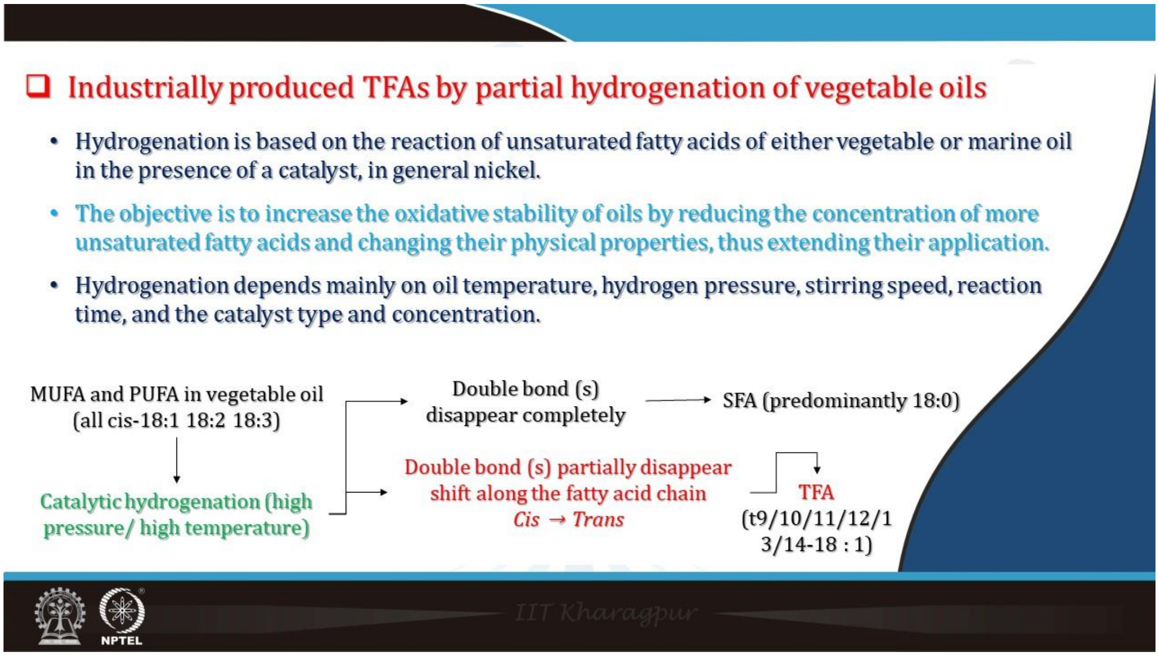



So, let us see what is the trans fat, how it is formed. Trans fat, or trans-fatty acids, are unsaturated fatty acids that come from either natural or industrial sources. Naturally-occurring trans fat come from ruminants (cows and sheep). Industrially-produced trans fat are formed in an industrial process that adds hydrogen to vegetable oil converting the liquid into a solid, resulting in "partially hydrogenated" oil (PHO). High trans fat intake increases the risk of death from any cause by 34%, coronary heart disease deaths by 28%, and coronary heart disease by 21%. This is likely due to the effect on lipid levels: trans fat increases LDL ("bad") cholesterol levels while lowering HDL ("good") cholesterol levels. Trans fat has no known health benefits. Approximately 5,40,000 deaths each year can be attributed to intake of industrially produced trans-fatty acids.

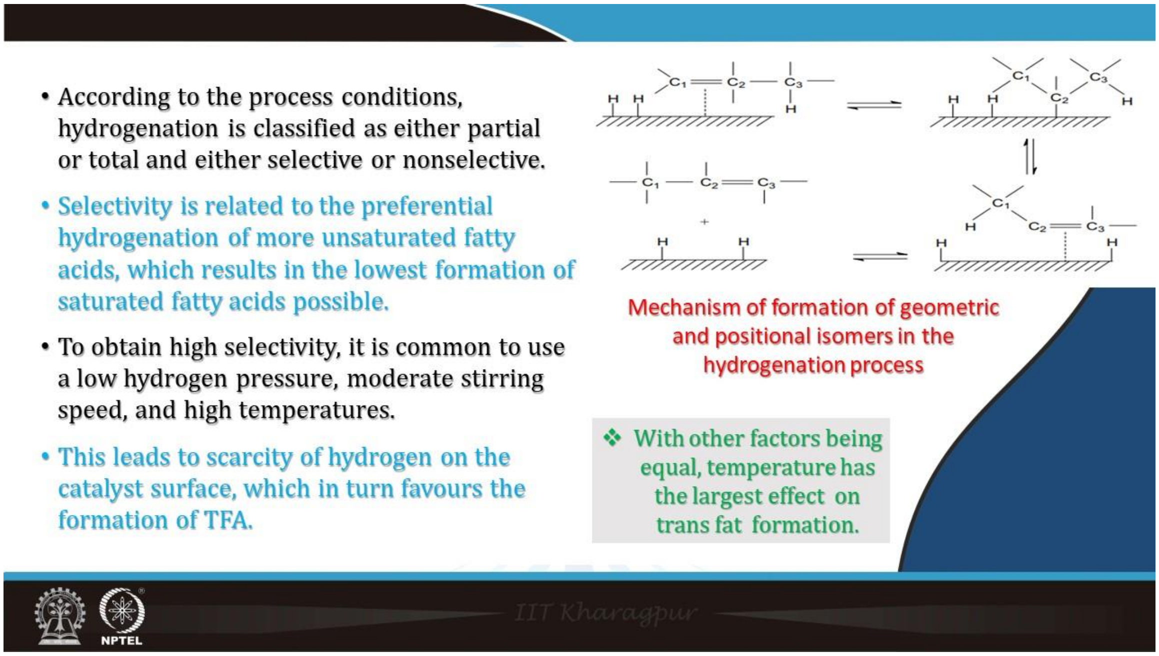

The effects on blood lipids from naturally occurring trans fat & industrially-produced trans fat are the same. So, whether you are consuming trans fat in the form of junk food like fried food etcetera fried oil, or hydrogenated oil or you are taking the trans fat from ruminant animal sources etcetera, it is its effect on the health of the body will be almost same International expert groups and public health authorities recommend limiting consumption of trans fat (industrially-produced and ruminant) to less than 1% of total energy intake, which translates to less than 2.2 g/day for a 2,000-calorie diet. Margarine, vegetable shortening, vanaspati ghee, fried foods, baked goods, doughnuts, etc. are some foods containing trans fat in significant amounts. So, any heated oil if you are taking it will contain trans fat.



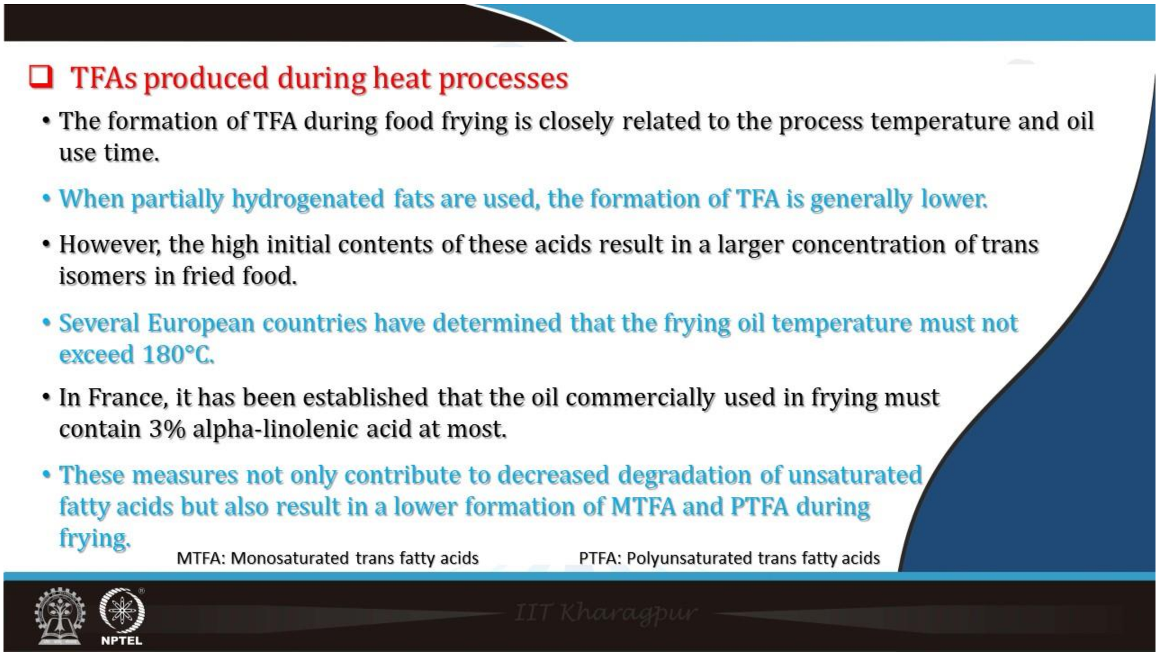

Let us see how trans fat is formed. Most of the trans fat in the foods we eat is formed through a manufacturing process that adds hydrogen to vegetable oil, which converts the liquid into solid fat at room temperature. This process is called hydrogenation. You can see here the process of hydrogenation, in the earlier class also we discussed the details of the hydrogenation process in this module itself. Naturally unsaturated oils position are generally present in the cis form. So, when it is fully hydrogenated fully saturated fatty acids are formed, there is no problem and this is H-H only, but when it is partial hydrogenation it gives H and H comes in the transposition and the opposite side of the bond. So, partially hydrogenated fats contain more amount of trans fatty acids. Four main sources of trans fatty acids in the human diet include Industrially produced TFAs by partial hydrogenation of vegetable oils, TFAs produced during heat processes, TFAs occurring naturally in ruminant sources, and TFAs synthesized for utilization as dietary supplements.



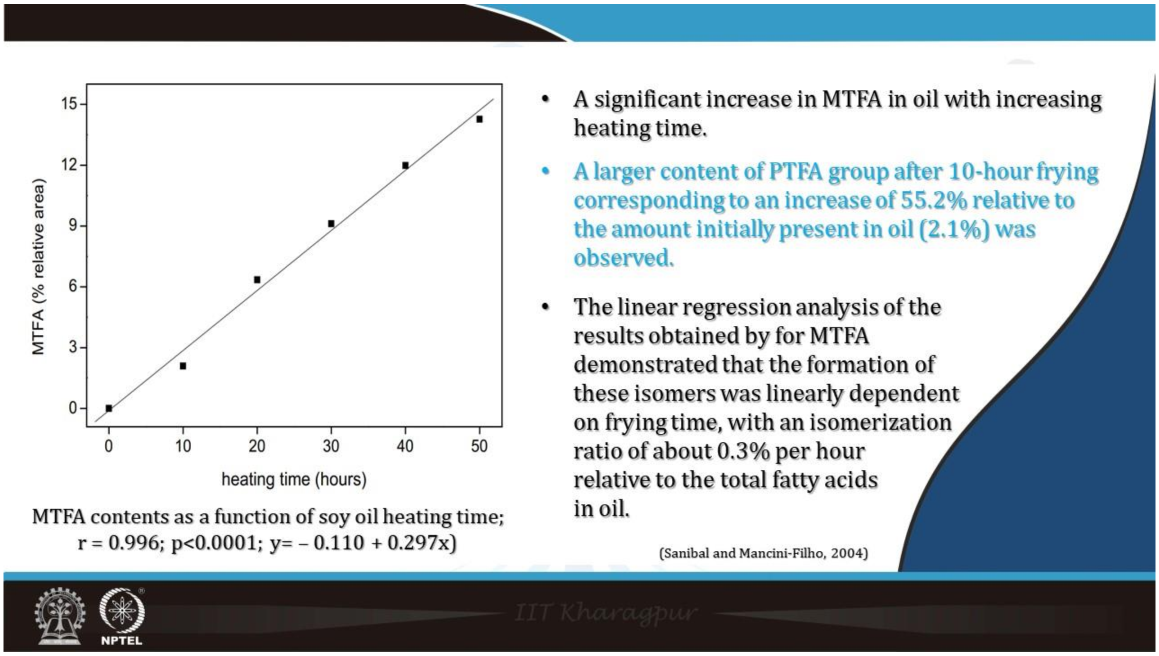

Industrially produced trans fatty acids that by the partial hydrogenation of vegetable oils and in the again we discussed earlier that is in the hydrogenation process reaction hydrogen is added to convert vegetable unsaturated fat into saturated fat. Hydrogenation is based on the reaction of unsaturated fatty acids of either vegetable or marine oil in the presence of a catalyst, in general nickel. The objective is to increase the oxidative stability of oils by reducing the concentration of more unsaturated fatty acids and changing their physical properties, thus extending their application. Hydrogenation depends mainly on oil temperature, hydrogen pressure, stirring speed, reaction time, and the catalyst type and concentration. Hydrogen as you can see here MUFA and PUFA in the vegetable oils, are all cis as I told you 18:1, 18:2, and 18:3. So, in the natural they are all cis position. Catalytic hydrogenation at high pressure and high temperature particularly the double bond will disappear completely you will get saturated fatty acids, predominantly 18:0 which is stearic acid. When double bonds partially disappear, that is they shift along the fatty acids chain, and in this process, trans fatty acids are formed. The cis form is converted into transform, it may be T 9/10/11/12/13/14-18: 1, and different forms of the trans fatty acid depending upon the hydrogenation conditions are produced.



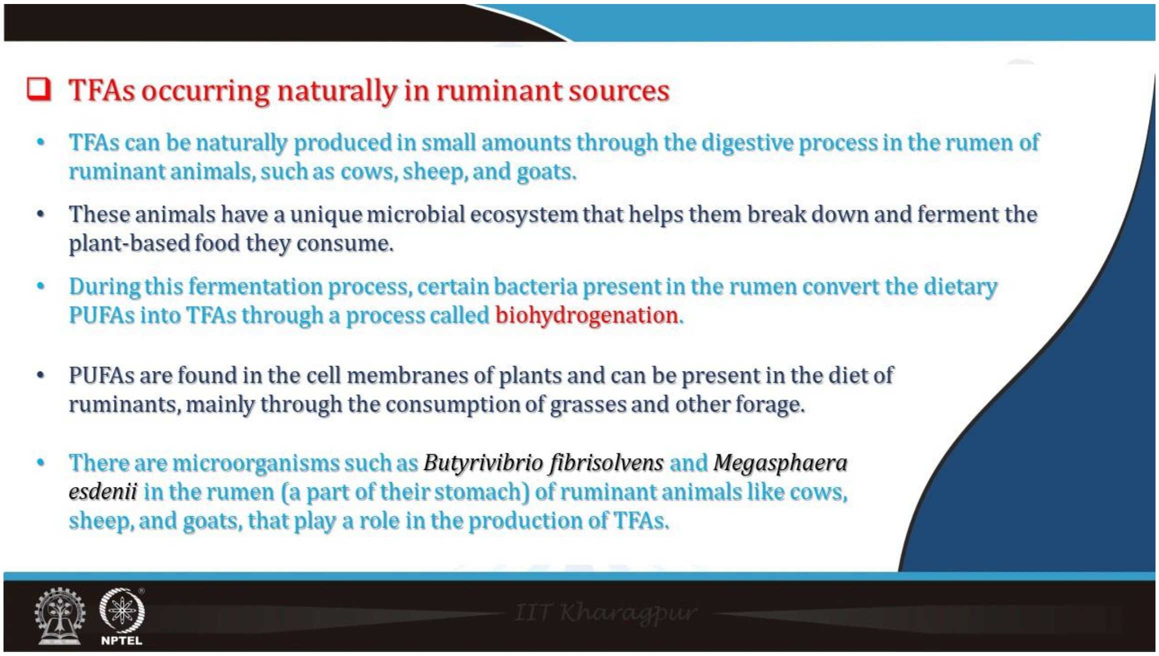

According to the process conditions, hydrogenation is classified as either partial or total and either selective or nonselective. So, this is the mechanism of the formation of the geometric and positional isomers in the hydrogenation process you can see here it is shown in these figures. Selectivity is related to the preferential hydrogenation of more unsaturated fatty acids, which results in the lowest formation of saturated fatty acids possible. To obtain high selectivity, it is common to use a low hydrogen pressure, moderate stirring speed, and high temperatures. This leads to scarcity of hydrogen on the catalyst surface, which in turn favors the formation of TFA. With other factors being equal temperature has the larger effect on the trans fat formation during the hydrogenation process.



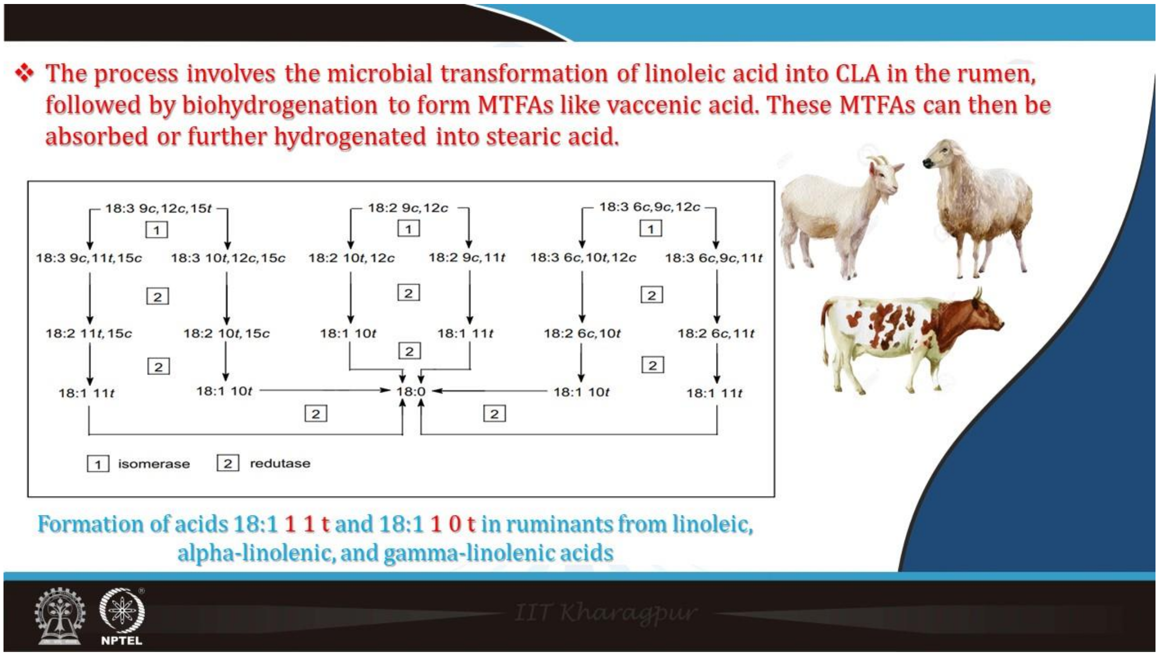

The formation of TFA during food frying is closely related to the process temperature and oil use time. When partially hydrogenated fats are used, the formation of TFA is generally lower. However, the high initial contents of these acids result in a larger concentration of trans isomers in fried food. Several European countries have determined that the frying oil temperature must not exceed 180°C. In France, it has been established that the oil commercially used in frying must contain 3% alpha-linolenic acid at most. These measures not only contribute to decreased degradation of unsaturated fatty acids but also result in a lower formation of MTFA and PTFA during frying.  So, in that sense, the conditions of the heating oil type of oil which is being used, the degree of unsaturation present in the 3-alpha-linolenic acids, etc. should be properly controlled during frying to minimize the formation of monosaturated trans fatty acids or polyunsaturated trans fatty acids.



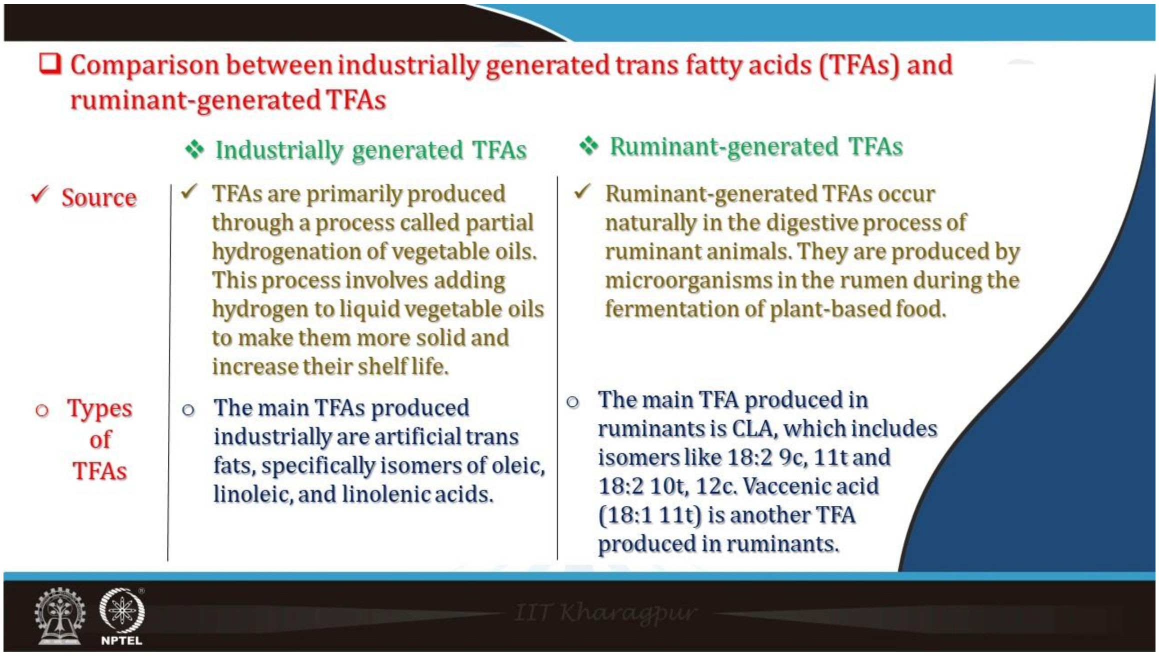

Here you can see the effect of heating time in hours on the formation of MTFA monosaturated trans fatty acids and obviously, the effect of heating time increases the percent relative area of the MTFA, that is the formation of MTFA increases. A significant increase in MTFA in oil with increasing heating time. A larger content of the PTFA group after 10 hours of frying corresponding to an increase of 55.2% relative to the amount initially present in oil (2.1%) was observed. The linear regression analysis of the results obtained by MTFA demonstrated that the formation of these isomers was linearly dependent on frying time, with an isomerization ratio of about 0.3% per hour relative to the total fatty acids in the oil.



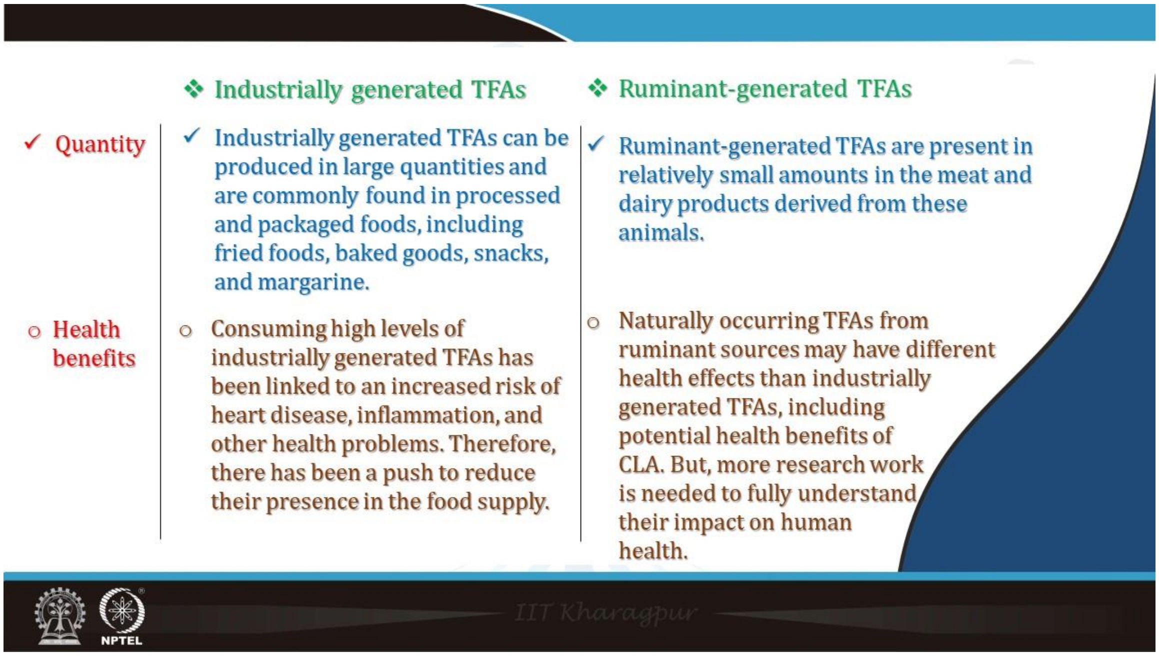

Trans fatty acid occurs naturally in ruminant sources, let us talk about it. TFAs can be naturally produced in small amounts through the digestive process in the rumen of ruminant animals, such as cows, sheep, and goats. These animals have a unique microbial ecosystem that helps them break down and ferment the plant-based food they consume. During this fermentation process, certain bacteria present in the rumen convert the dietary PUFAs into TFAs through a process called biohydrogenation. PUFAs are found in the cell membranes of plants and can be present in the diet of ruminants, mainly through the consumption of grasses and other forage. There are microorganisms such as *Butyrivibrio fibrisolvens* and *Megasphaera esdenii* in the rumen (a part of their stomach) of ruminant animals like cows, sheep, and goats, that play a role in the production of TFAs. These microorganisms can transform polyunsaturated fatty acids (PUFAs), specifically linoleic acid, into different forms through a process called isomerization. As a result, two types of fatty acids called conjugated linoleic acid (CLA) are formed: 18:2 9c, 11t and 18:2 10t, 12c. These CLAs can be absorbed by the animal or further processed through biohydrogenation involving the conversion of these fatty acids into other forms viz. 18:1 11t, also known as vaccenic acid, and 18:1 10t. These two forms can also be derived from other types of fatty acids like alpha and gamma-linolenic acids. These modified trans fatty acids (MTFAs), including vaccenic acid, can either be absorbed by the animal's body or undergo further hydrogenation which can lead to the formation of stearic acid (18:0), which is a saturated fatty acid. When these fatty acids are absorbed, they are incorporated into the adipose (fat) and muscle tissues of the animal.



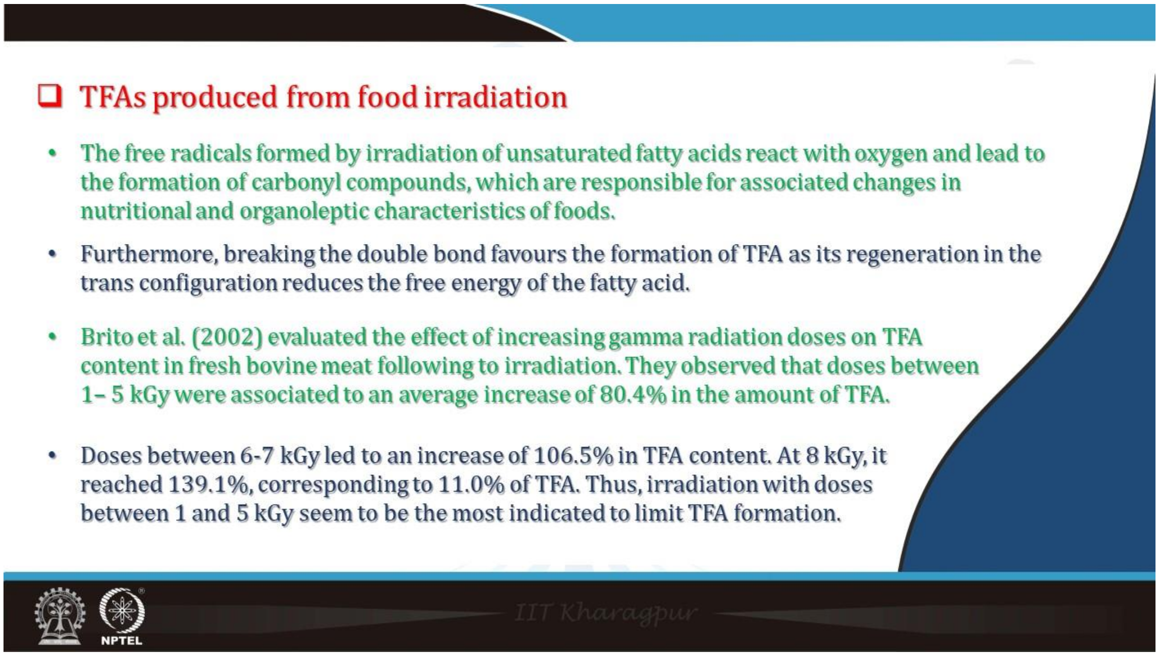

The process involves the microbial transformation of linoleic acid into CLA in the rumen, followed by biohydrogenation to form MTFAs like vaccenic acid. These MTFAs can then be absorbed or further hydrogenated into stearic acid. The schematic diagram shows the isomerases and reductases involved in the formation of acids 18:1 1 1 t and 18:1 1 0 t in ruminants from linoleic, alpha-linolenic, and gamma-linolenic acids. As you see, 18:3, 9 C, 12 C, 15 t are converted into either 18:3, 9 C, 11 t, 15 C or 18:3, 10 t, 12 C, 15 C by isomerase and reduced to 18:2, 11 t, 15 C by reductase. Thus, this whole series that is either 18:3, 18:2, or again 18:3 with 6 C, 9 C, 12 C gives by these processes, either a different type of MTF is produced or finally, they can come to the 18:0 that is steric acid which we discussed in the earlier.



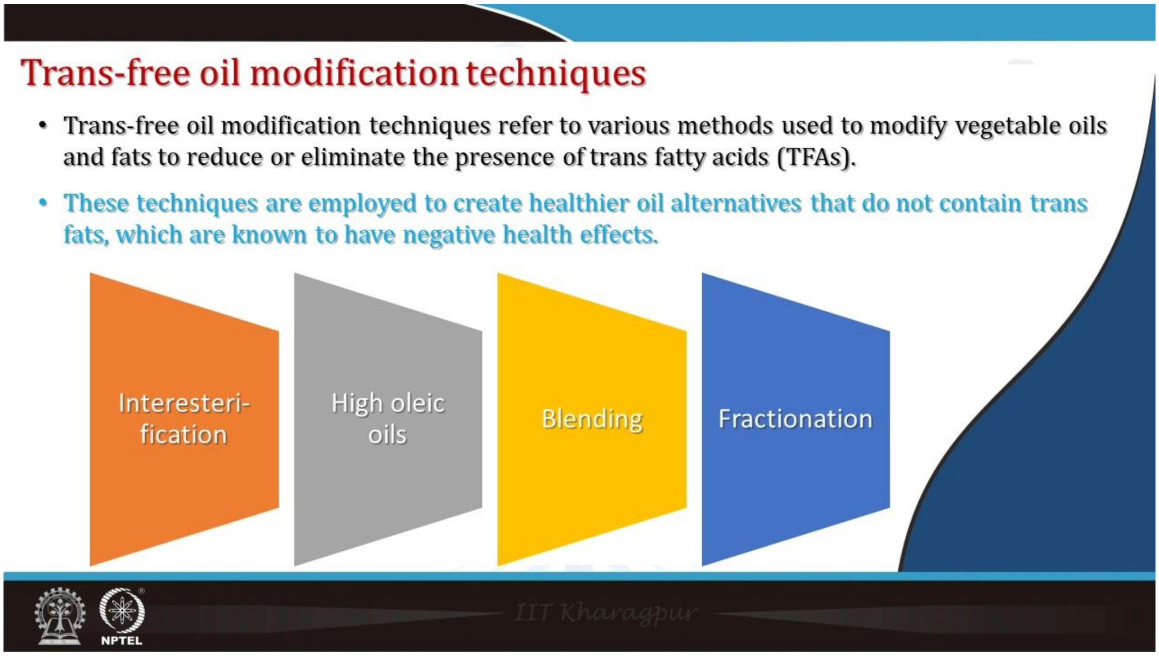

If we compare the industrially generated trans fatty acids and ruminant-generated trans fatty acids we see that is particularly the sources that is TFAs are primarily produced through a process called partial hydrogenation of vegetable oils. This process involves adding hydrogen to liquid vegetable oils to make them more solid and increase their shelf life in the case of industrially generated and Ruminant-generated TFAs that occur naturally in the digestive process of ruminant animals. They are produced by microorganisms in the rumen during the fermentation of plant-based food. The main TFAs produced industrially are artificial trans fats, specifically isomers of oleic, linoleic, and linolenic acids. The main TFA produced in ruminants is CLA, which includes isomers like 18:2 9c, 11t and 18:2 10t, 12c. Vaccenic acid (18:1 11t) is another TFA produced in ruminants.



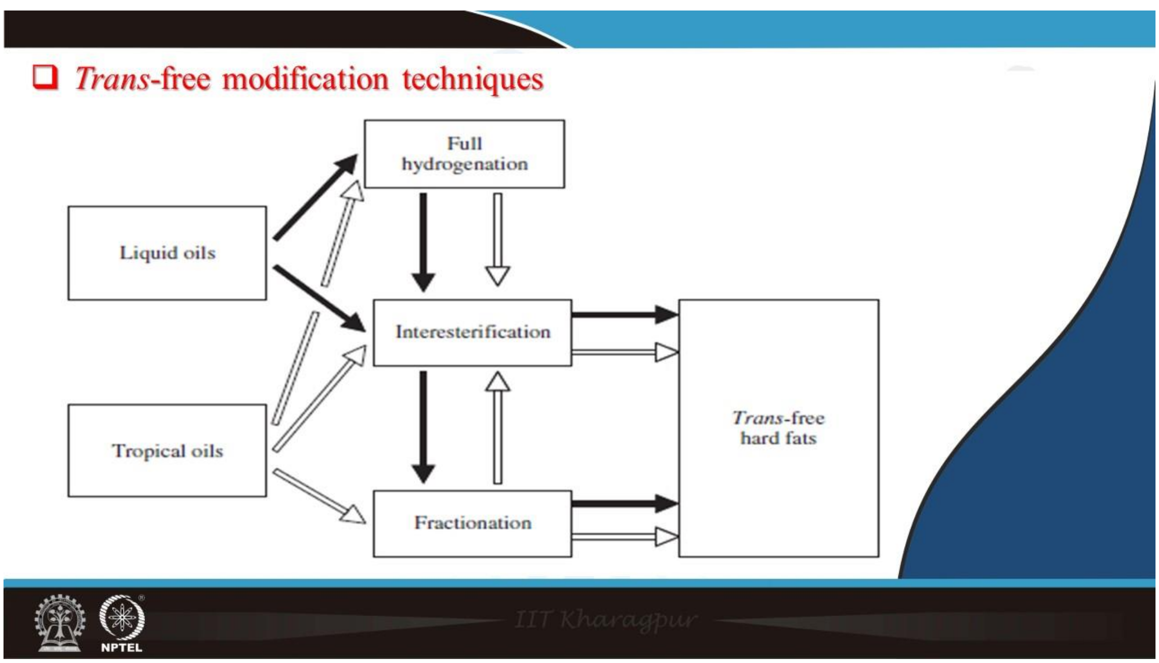

Industrially generated TFAs can be produced in large quantities and are commonly found in processed and packaged foods, including fried foods, baked goods, snacks, and margarine. Ruminant-generated TFAs are present in relatively small amounts in the meat and dairy products derived from these animals. Consuming high levels of industrially generated TFAs has been linked to an increased risk of heart disease, inflammation, and other health problems. Therefore, there has been a push to reduce their presence in the food supply. Naturally occurring TFAs from ruminant sources may have different health effects than industrially generated TFAs, including potential health benefits of CLA. However, more research work is needed to fully understand their impact on human health.



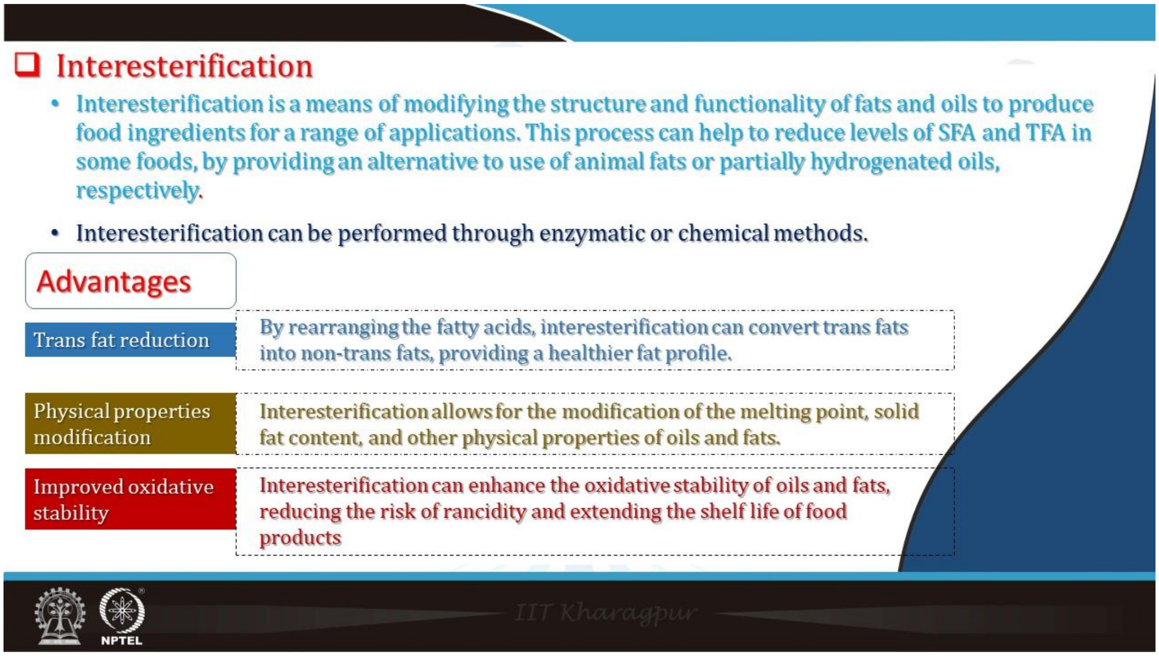

Literature reports show that trans fatty acids are also produced during food irradiation. The free radicals formed by irradiation of unsaturated fatty acids react with oxygen and lead to the formation of carbonyl compounds, which are responsible for associated changes in the nutritional and organoleptic characteristics of foods. Furthermore, breaking the double bond favors the formation of TFA as its regeneration in the trans configuration reduces the free energy of the fatty acid. Brito et al. (2002) evaluated the effect of increasing gamma radiation doses on TFA content in fresh bovine meat following to irradiation. They observed that doses between 1– 5 kGy were associated to an average increase of 80.4% in the amount of TFA. Doses between 6-7 kGy led to an increase of 106.5% in TFA content. At 8 kGy, it reached 139.1%, corresponding to 11.0% of TFA. Thus, irradiation with doses between 1 and 5 kGy seem to be the most indicated to limit TFA formation.



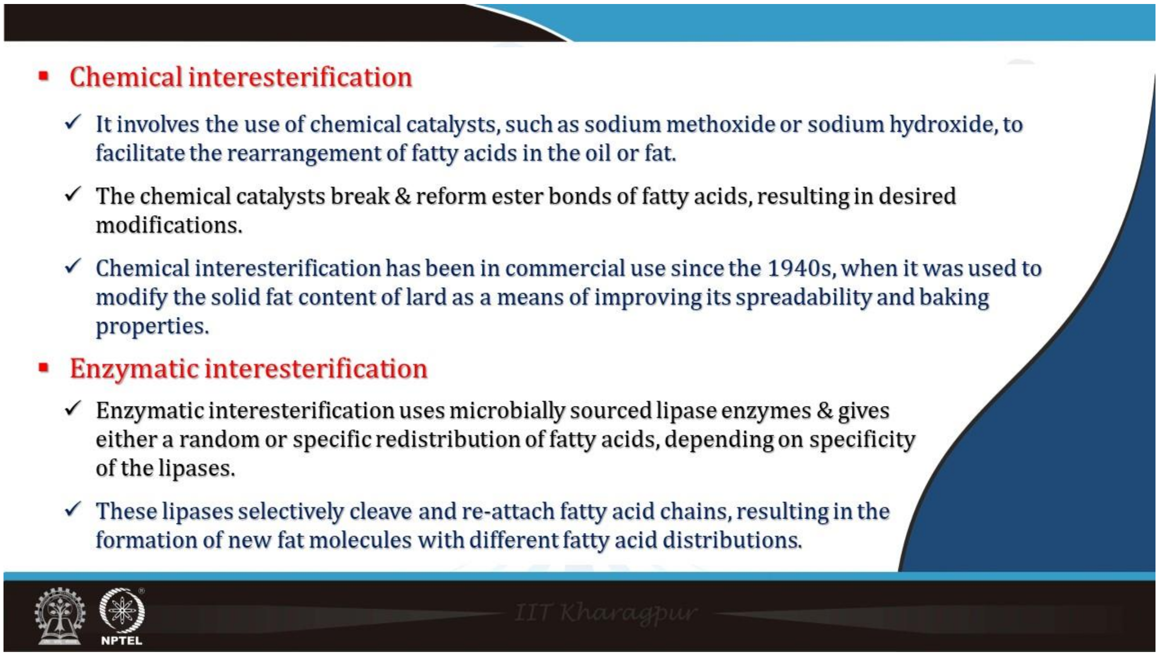

So, now that having known how these are the trans fatty acids and how they are formed, let us discuss about what are the different trans-free oil modification techniques. Trans-free oil modification techniques refer to various methods used to modify vegetable oils and fats to reduce or eliminate the presence of trans fatty acids (TFAs). These techniques are employed to create healthier oil alternatives that do not contain trans fats, which are known to have negative health effects. The techniques used are inter-esterification, high oleic oils, blending of oil, and fractionation.



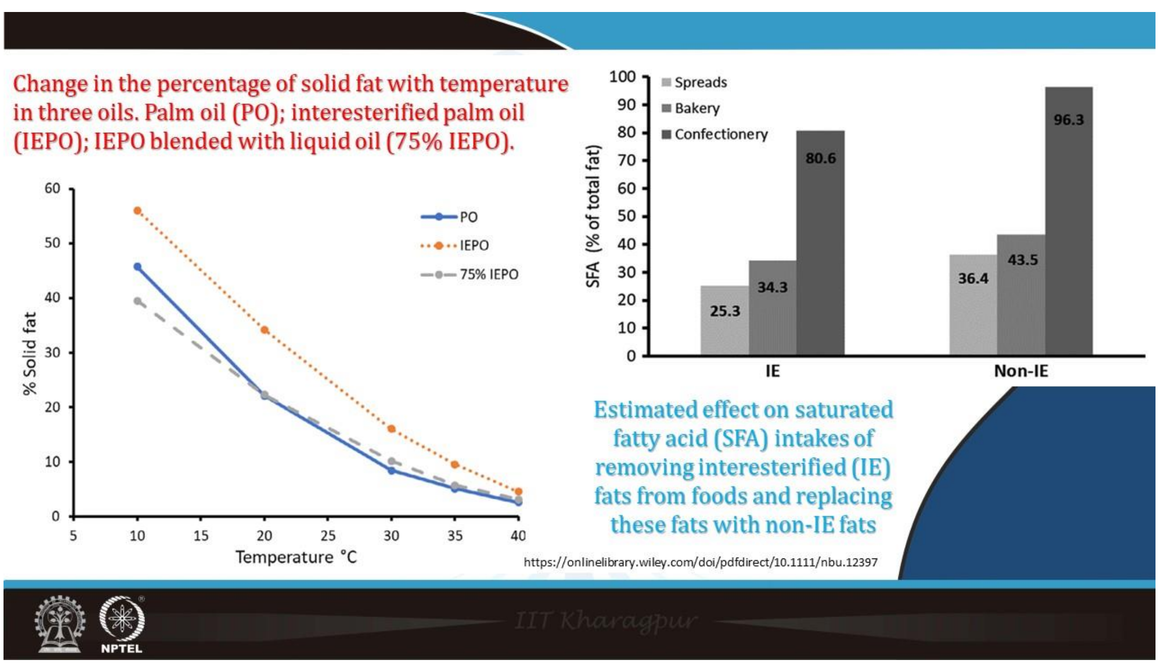
The liquid oils and tropical oils can be subjected to full hydrogenation, interesterification, and fractionation, and obviously, the conditions of the process should be properly maintained in such a way that it will lower the trans-fat generation.



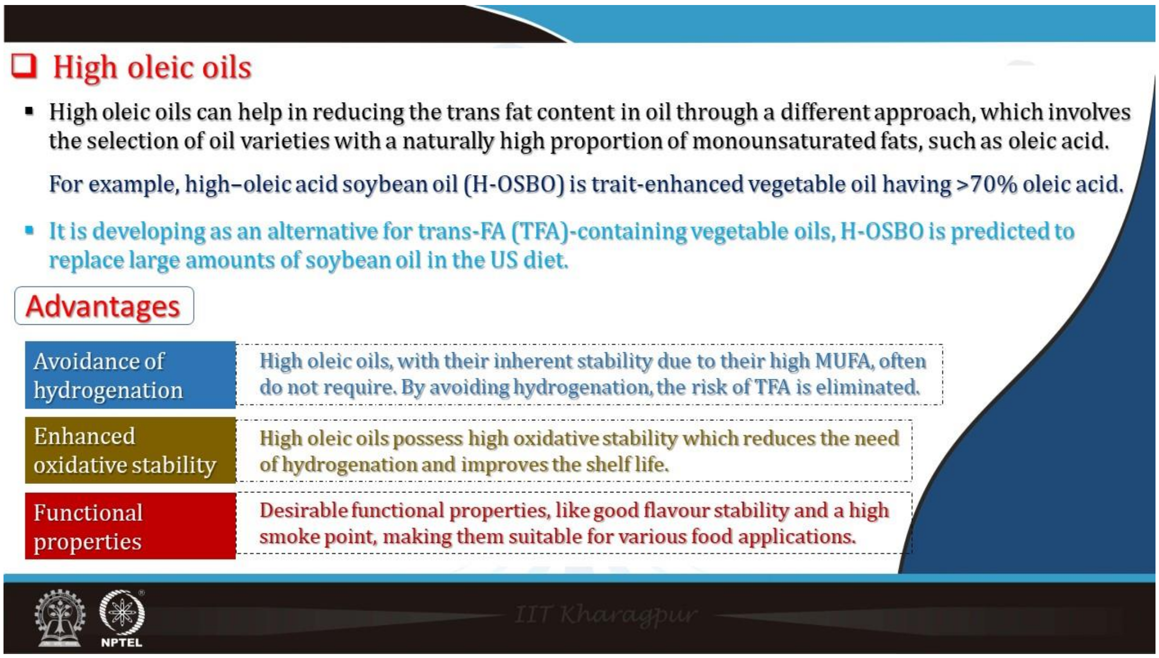

Inter esterification we have discussed earlier, is a means of modifying the structure and functionality of fats and oils to produce food ingredients for a range of applications. This process can help to reduce levels of SFA and TFA in some foods, by providing an alternative to the use of animal fats or partially hydrogenated oils, respectively. Interesterification can be performed through enzymatic or chemical methods. By rearranging the fatty acids, interesterification can convert trans fats into non-trans fats, providing a healthier fat profile. It allows for the modification of the melting point, solid fat content, and other physical properties of oils and fats and can enhance the oxidative stability of oils and fats, reducing the risk of rancidity and extending the shelf life of food products.



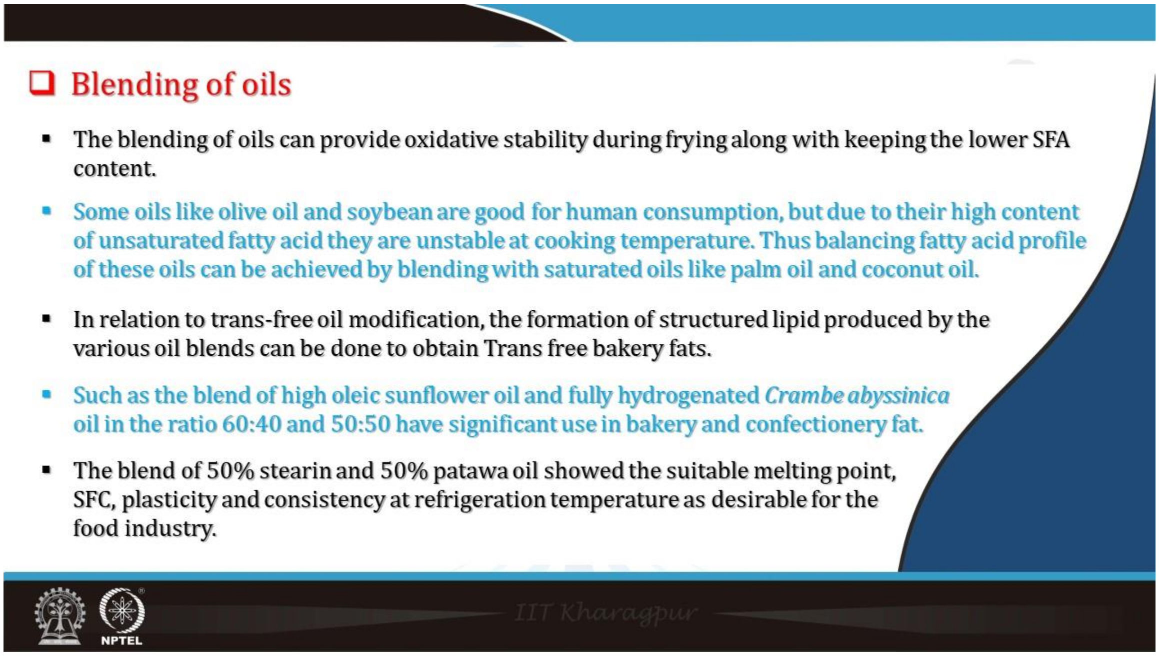

There are two methods of interesterification chemical interesterification and enzymatic interesterification. Just for reference, I have included this slide, but details of the interesterification process we had already discussed in the earlier class. Enzymatic interesterification uses microbial-sourced enzymes and gives either a random or specific distribution of fatty acid, depending on the specificity of the lipases, and by this one can lower the formation of trans fatty acids.




Here it shows the change in the percentage of solid fat with the temperature in 3 oils, which are palm oil, inter-esterified palm oil, and inter-esterified palm oil that is blended with the liquid oil and you can see PO, IEPO, and 75 percent IEPO. For both the temperature and solid fat content the effect is shown in the figure. Also, the here the saturated fatty acids percentage in IE and non-IE oils used in the application of spreads bakery and confectionery is shown. So, this bar diagram and the line show the estimated effect of saturated fatty acids intake and removing the inter-esterified fats from foods by replacing those with non-inter-esterified fats.




High oleic oils can help in reducing the trans fat content in oil through a different approach, which involves the selection of oil varieties with a naturally high proportion of monounsaturated fats, such as oleic acid. For example, high–oleic acid soybean oil (H-OSBO) is a trait-enhanced vegetable oil having >70% oleic acid. It is developing as an alternative for trans-FA (TFA)-containing vegetable oils, H-OSBO is predicted to replace large amounts of soybean oil in the US diet. The advantage of the high oleic oils is the avoidance of hydrogenation as high oleic oils with their inherent stability due to their high MUFA, often do not require it. By avoiding hydrogenation, the risk of TFA is eliminated. High oleic oils possess high oxidative stability which reduces the need of hydrogenation and improves the shelf life. Desirable functional properties, like good flavour stability and a high smoke point, making them suitable for various food applications.



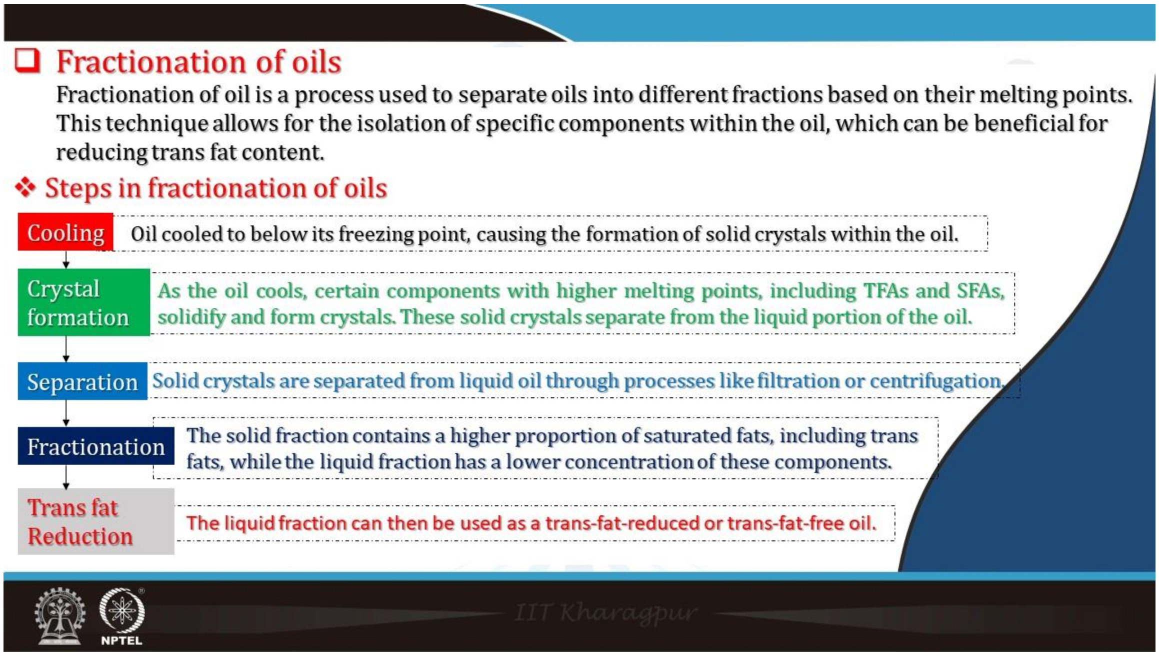

The blending of oils can provide oxidative stability during frying along with keeping the lower SFA content. Some oils like olive oil and soybean are good for human consumption, but due to their high content of unsaturated fatty acid they are unstable at cooking temperature. Thus balancing fatty acid profile of these oils can be achieved by blending with saturated oils like palm oil and coconut oil. In relation to trans-free oil modification, the formation of structured lipid produced by the Such as the blend of high oleic sunflower oil and fully hydrogenated Crambe abyssinica oil in the ratio 60:40 and 50:50 have significant use in bakery and confectionery fat. various oil blends can be done to obtain Trans free bakery fats. The blend of 50% stearin and 50% patawa oil showed the suitable melting point, SFC, plasticity and consistency at refrigeration temperature as desirable for the food industry.

| Blends | Application |
|---|---|
| Rapeseed oil: fish oil : lard (70:20:10) | Fat base for cookies |
| Cotton seed : palm oil (75:25) | Trans free Cookies production |
| Palm stearin: Acer truncatum oil : palm kernel oil (50:40:10, 60:30:10, 60:20:20) | Trans free Margarine fats |
| Palm mid-fraction: palm stearin: olive oil (16.7:66.7:16.7) | Trans free shortening |
| Palm olein : Moringa oleifera oil (50:50) | Vanaspati substitute |
| palm stearin: mango or sal fats (70:30, 80:20) | Trans free plastic fats |
| Palm stearin fractionate: fish oil (2:1) | Human milk fat substitute |
| High oleic sunflower oil: mixture of ethyl palmitate and ethyl stearate | Cocoa butter equivalent |
| Ethyl behenate: sunflower or soya bean oil | Low calorie fat |
| High oleic sunflower oil: fully hydrogenated Crambe abyssinica oil (60:40, 50:50) | Low calorie fat |

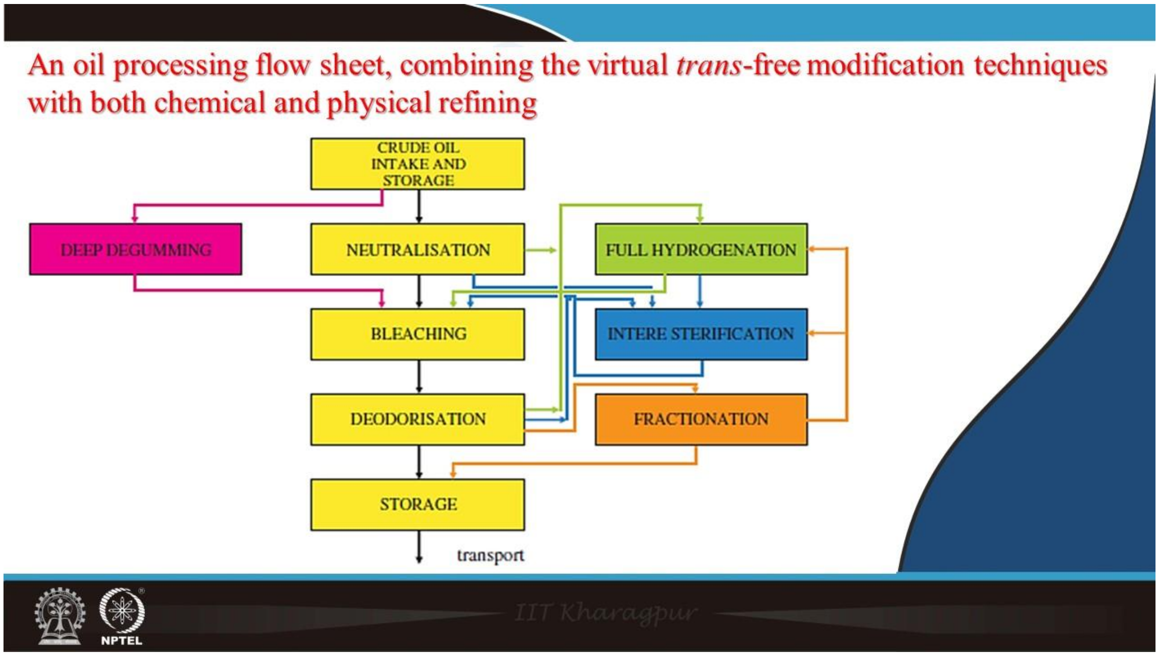
- Cocoa butter is a major ingredient for confectionery fat. Cocoa butter equivalent, an alternative to cocoa butter, can be prepared by using a blend of 1,3- dipalmitoyl- 2-oleoyl-glycerol (POP) rich fats with fats rich in 1,3-distearoyl-2-oleoyl-glycerol (SOS).
- Blend of palm mid-fraction (PMF), palm stearin (POs) and olive oil (OO) could be used as manufacturing shortening and cocoa butter substitutes with improved features than individual oil.
- Interesterified blends of lard and soybean oil can be used as a substitute for human milk fat.



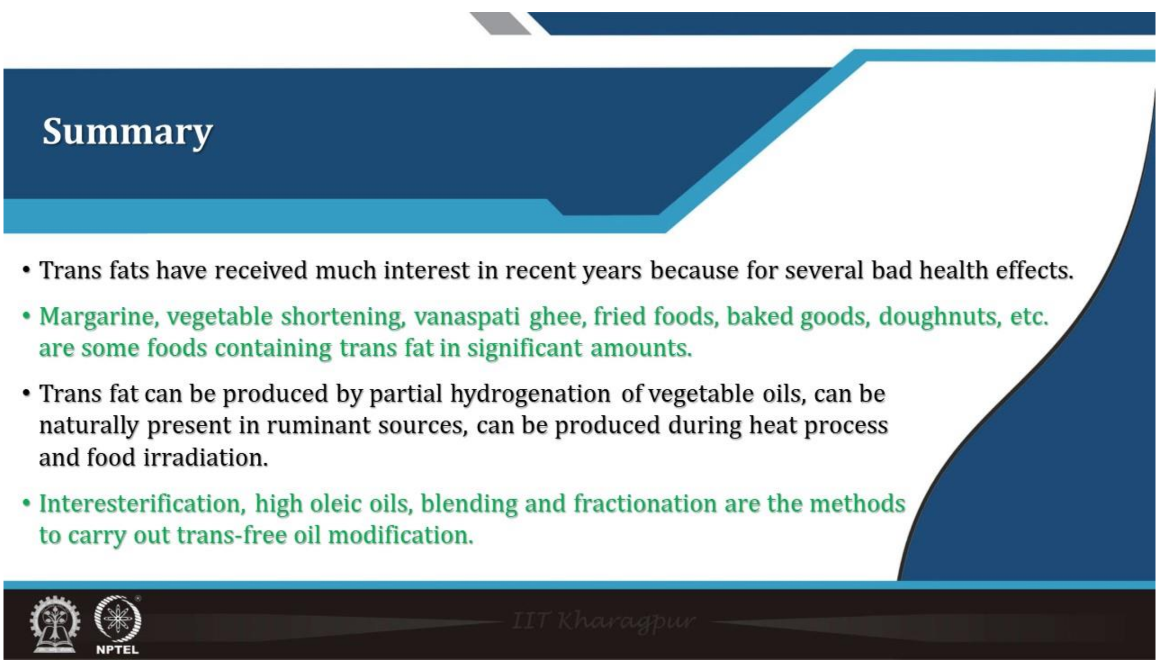
So, here in this table, we have given some of the common blends of the different types of oil and their possible application. But of course, for the blending of the oil every country has specific regulations, in India also in the FSSAI there are specific regulations that industries should follow for blending protocol as per the recommended guidelines. Cocoa butter is a major ingredient for confectionery fat. Cocoa butter equivalent, an alternative to cocoa butter, can be prepared by using a blend of 1,3- dipalmitoyl- 2-oleoyl-glycerol (POP) rich fats with fats rich in 1,3-distearoyl-2-oleoyl-glycerol (SOS). A blend of palm mid-fraction (PMF), palm stearin (POs), and olive oil (OO) could be used as manufacturing shortening and cocoa butter substitutes with improved features than an individual oil. Interesterified blends of lard and soybean oil can be used as a substitute for human milk fat.



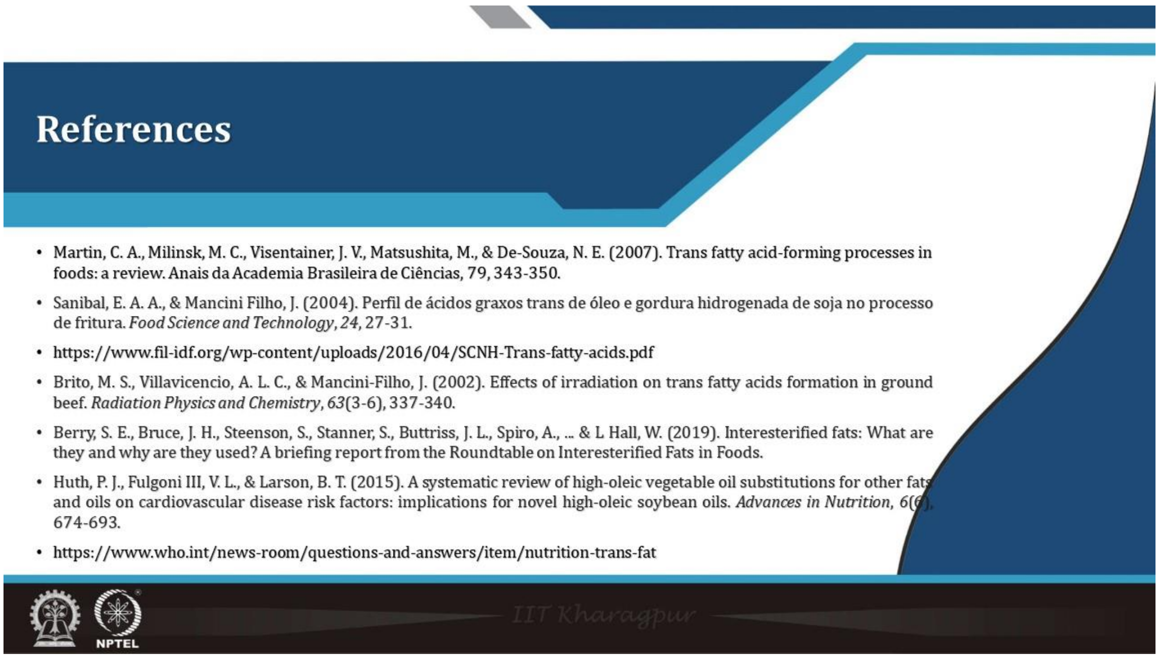

Then fractionation of oil we discussed the fractionation technology in the earlier class. Fractionation of oil is a process used to separate oils into different fractions based on their melting points. This technique allows for the isolation of specific components within the oil, which can be beneficial for reducing trans fat content. The steps in fractionation of oils are, oil cooled to below its freezing point, causing the formation of solid crystals within the oil, as the oil cools, certain components with higher melting points, including TFAs and SFAs, solidify and form crystals. These solid crystals separate from the liquid portion of the oil. The solid fraction contains a higher proportion of saturated fats, including trans fats, while the liquid fraction has a lower concentration of these components. The liquid fraction can then be used as a trans-fat-reduced or trans-fat-free oil. The involvement of the temperature is much more here. Theprocess parameters in this process can be adjusted in such a way properly optimized to reduce the TFA formation.




So, here an oil processing flow sheet combining virtual trans-free modification techniques with both chemical and physical refining is shown. See all the processes involved are neutralization, bleaching, deodorization, and storage. It has deep degumming, full hydrogenation, interesterification, and fractionation as an additional process. These are the conditions where there is a greater possibility of trans fat formation, in all that process the parameters would be properly optimized, and as we discussed in the earlier classes sometimes controlling the pressure, the temperature, and other factors in a proper level so as to have minimum or no trans fat formation.



To summarize the lecture, trans fats have received much interest in recent years because for several bad health effects. Margarine, vegetable shortening, vanaspati ghee, fried foods, baked goods, doughnuts, etc. are some foods containing trans fat in significant amounts. Trans fat can be produced by partial hydrogenation of vegetable oils, can be naturally present in ruminant sources, and can be produced during heat process and food irradiation. Interesterification, high oleic oils, blending, and fractionation are the methods to carry out trans-free oil modification.




So, these are the references that are used in this lecture. Thank you very much for your patience hearing. Thank you.