Food Oils and Fats: Chemistry & Technology
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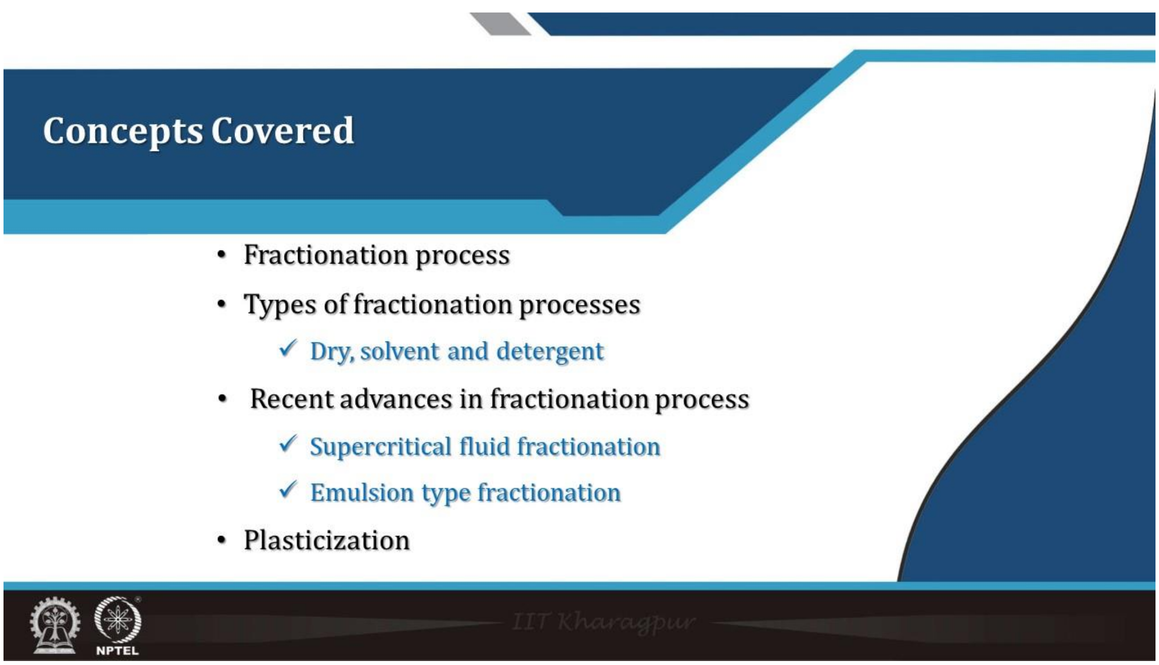
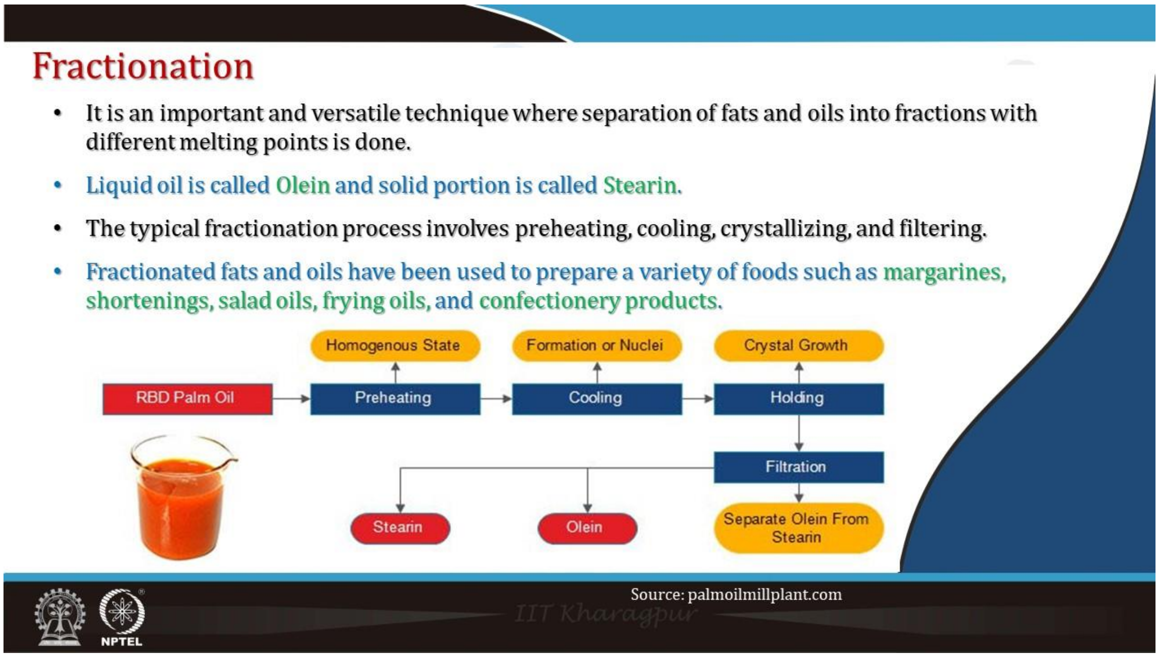
Module 7 : Modifications of Oils and Fats
Lecture 33 : Fractionation & Plasticization

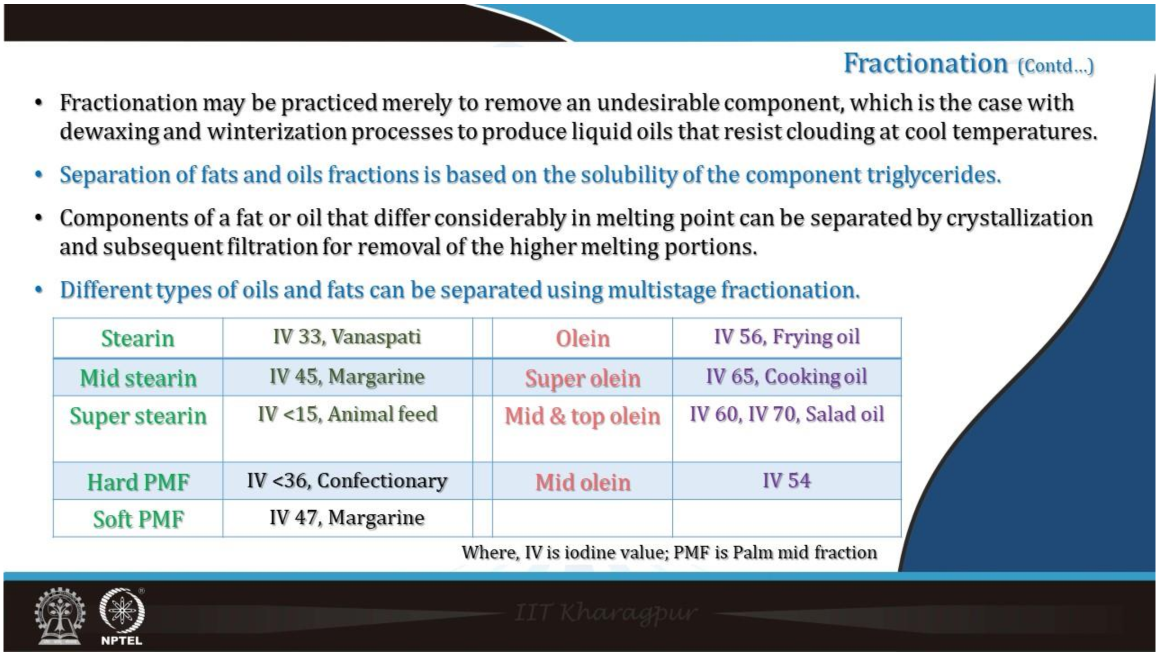
Hello, everybody. Namaste. Now, in this 33rd lecture today, we will discuss about Fractionation and Plasticization.



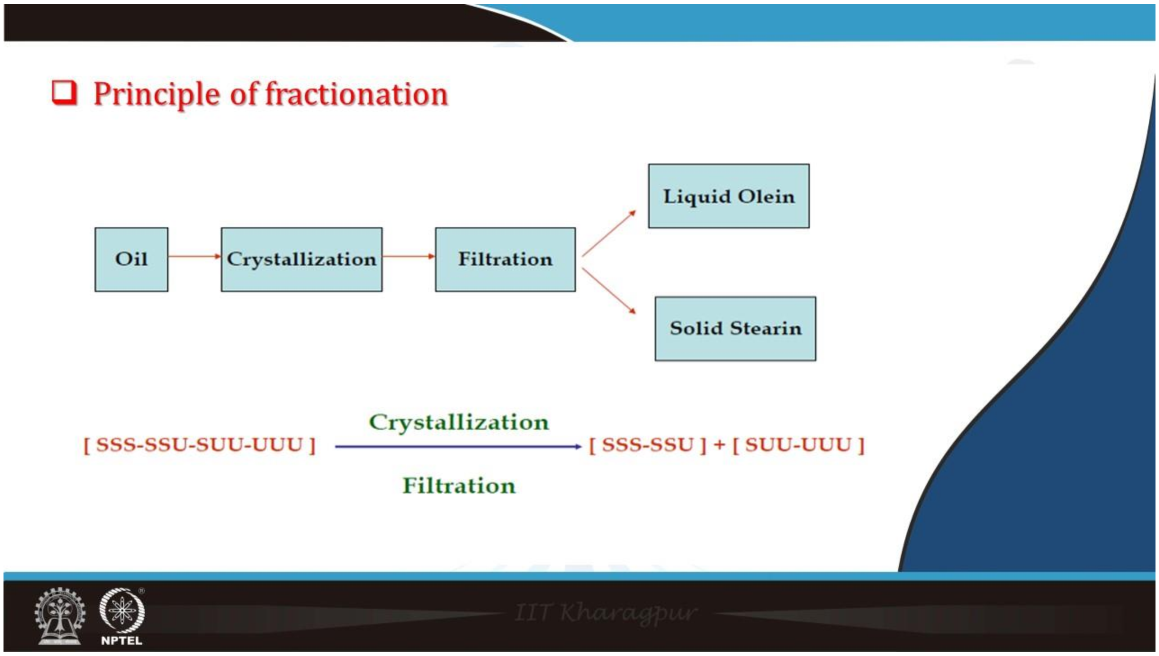
The concept which we will cover in today's lecture includes the fractionation process, and types of fractionation processes like dry fractionation, solvent fractionation, and detergent fractionation. Then we will also discuss some recent advances in the fractionation process like supercritical fluid fractionation, and emulsion type fractionation, and finally, we will conclude the lecture by discussing plasticization.



Let us see what fractionation means. It is an important and versatile technique where the separation of fats and oils into fractions with different melting points is done. Liquid oil is called Olein and solid portion is called Stearin. The typical fractionation process involves preheating, cooling, crystallizing, and filtering. Fractionated fats and oils have been used to prepare a variety of foods such as margarines, shortenings, salad oils, frying oils, and confectionery products. Oil is preheated and brought to a homogeneous state, then cooled where the formation of nuclei takes place and then it is held at specified conditions where crystal growth takes place. After that, it is exposed to a certain condition, and as the proper crystal growth conditions are different olein from stearin is separated and filtered. Fractionated fats and oils have been used to prepare a variety of foods such as margarine, chardonnay, salad oils, and frying oil and they have wide-ranging applications in confectionery products.



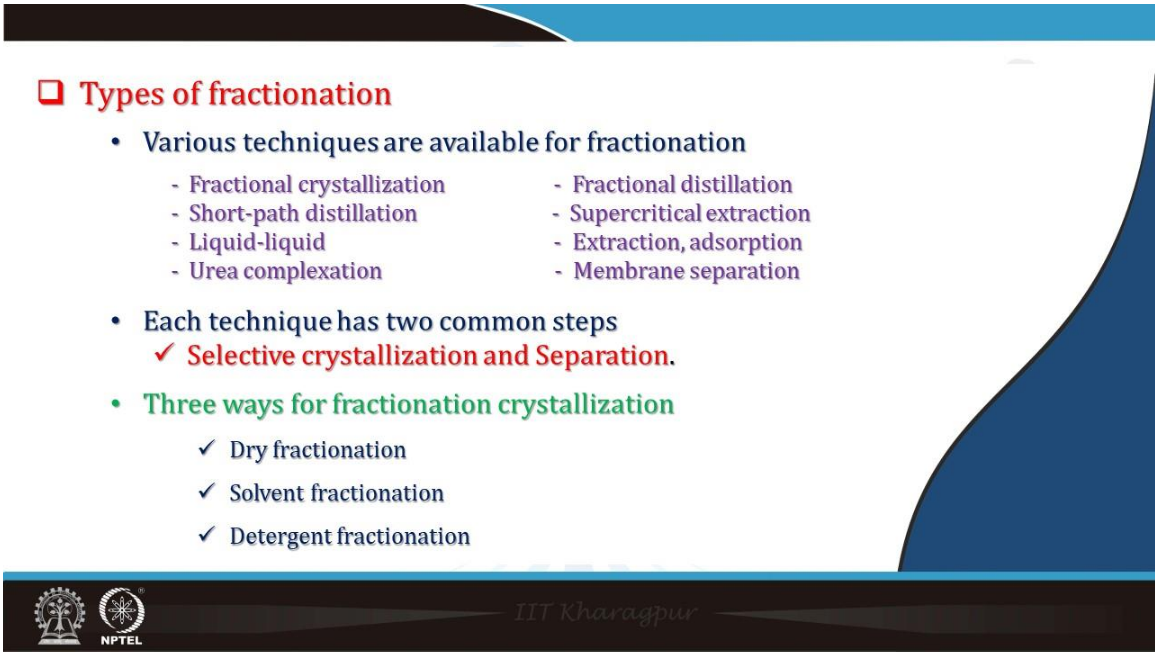
Fractionation may be practiced merely to remove an undesirable component, which is the case with dewaxing and winterization processes to produce liquid oils that resist clouding at cool temperatures. Separation of fats and oils fractions is based on the solubility of the component triglycerides. Components of a fat or oil that differ considerably in melting point can be separated by crystallization and subsequent filtration for removal of the higher melting portions. Different types of oils and fats can be separated using multistage fractionation may include stearin which is generally the vanaspati you know. It has an iodine value of around 33, then mid-stearin with an iodine value of about 45, it can be a margarine. Then super stearin with an iodine value of less than 15 which can sometimes be used as animal feed. The hard PMF like palm mid-fraction has an iodine value is less than 36. It is used in confectionery and soft PMF with an iodine value around 47 is used as margarine. Similarly, the oleine that is it is the liquid portion used in the frying oil has an iodine value of around 56. The super olein iodine value is 65 and it is cooking oil. The mid and top olein iodine values are 60 and 70. Top olein is used in salad oil and the mid oleine and another fraction which has an iodine value of 54.



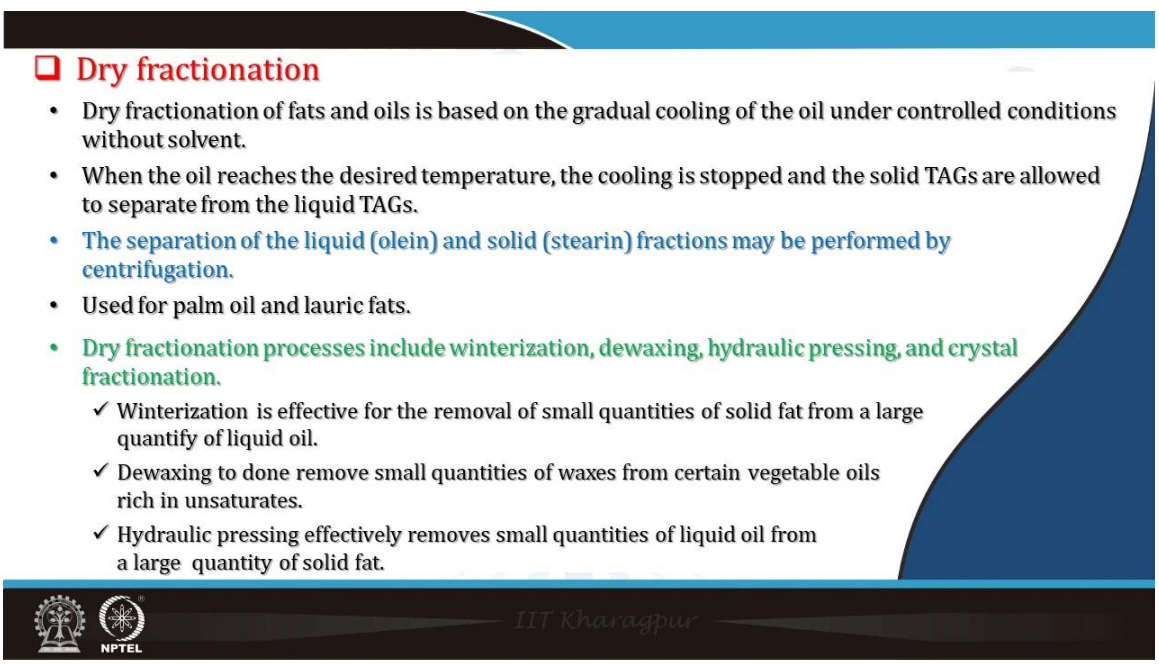
The principle of fractionation is the oil is crystallized first and then filtered, which means here in the crystallization and filtration the conditions are properly maintained in such a way that you can see in the figure

$$[\text{SSS-SSU-SUU-UUU}] \xrightarrow[\text{Filtration}]{\text{Crystallization}} [\text{SSS-SSU}] + [\text{SUU-UUU}]$$

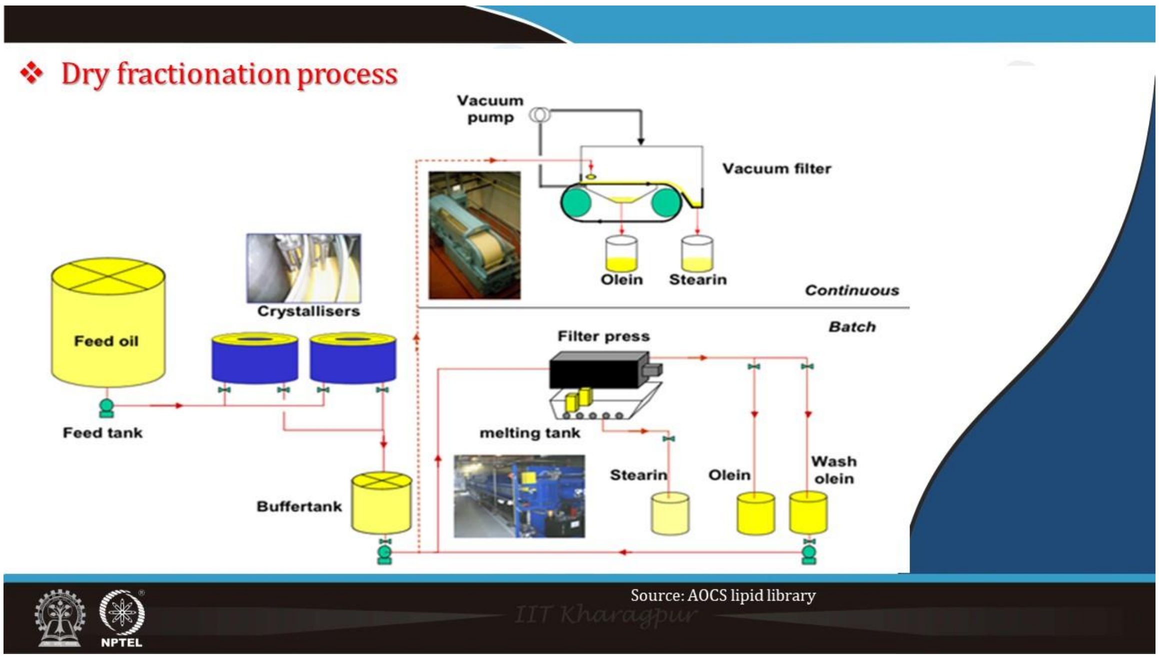
Where S is the solid fatty acid or saturated fatty acid and U is the unsaturated fatty acid. So, here you can see different two sets are thereafter crystallization and filtration that is one set which has more solid fatty acids and the other set which has more liquid fatty acids, and then different combinations and permutations can be done by properly selecting the crystallization and filtration conditions.



Various techniques are available for fractionation, which include fractional crystallization, short path distillation, liquid-liquid crystallization, urea complexation, fractional distillation, supercritical extraction, extraction, adsorption, and membrane separation. So, these are all various techniques that are available for the fractionation of oil and each technique you see has two common steps: selective crystallization and then separation. There are three ways of fractionation crystallization that are dry fractionation, solvent fractionation, and detergent fractionation.



So, let us discuss briefly the dry fractionation. Dry fractionation of fats and oils is based on the gradual cooling of the oil under controlled conditions without solvent. When the oil reaches the desired temperature, the cooling is stopped and the solid TAGs are allowed to separate from the liquid TAGs. The separation of the liquid (olein) and solid (stearin) fractions may be performed by centrifugation. Used for palm oil and lauric fats. Dry fractionation processes include winterization, dewaxing, hydraulic pressing, and crystal fractionation. Winterization is effective for the removal of small quantities of solid fat from a large quantity of liquid oil. Dewaxing removes small quantities of waxes from certain vegetable oils rich in unsaturated. Hydraulic pressing effectively removes small quantities of liquid oil from a large quantity of solid fat.



You can see here a schematic diagram of the dry fractionation process. It can be continuous or batch operations. This is a feed tank where the feed oil is there and then there are different crystallizers which are passed through these crystallizers and then there is a buffer tank. So, from this buffer tank, it may be sent to the vacuum filter if there is a continuous process or to the filter press in the batch process. In the buffer tank, it also crystallizes and then new crystal growth takes place, and then olein and stearin either in a continuous manner or in the batch process are removed.

❖ Advantages of dry fractionation

There are various advantages of dry fractionation

- ✓ Simple operating procedures
- ✓ Environmentally friendly (no need for chemicals as processing aids)
- ✓ Lower operational cost
- ✓ No effluent output

Disadvantage

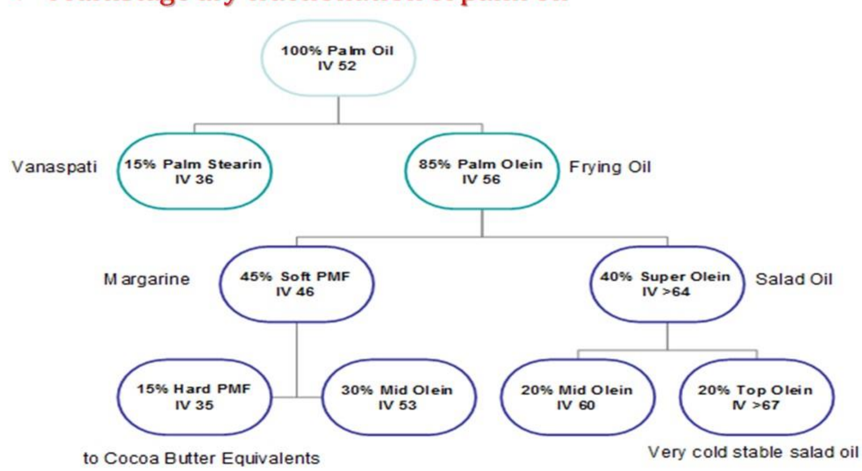
Dry fractionation has lower separation efficiency than the other two.

❖ Factors affecting dry fractionation

- ✓ Initial oil temperature
- ✓ Pre-crystallization
- ✓ Cooling rate
- ✓ Crystallization time
- ✓ Agitation
- ✓ Final crystallization
- ✓ Temperature
- ✓ Separation/filtration

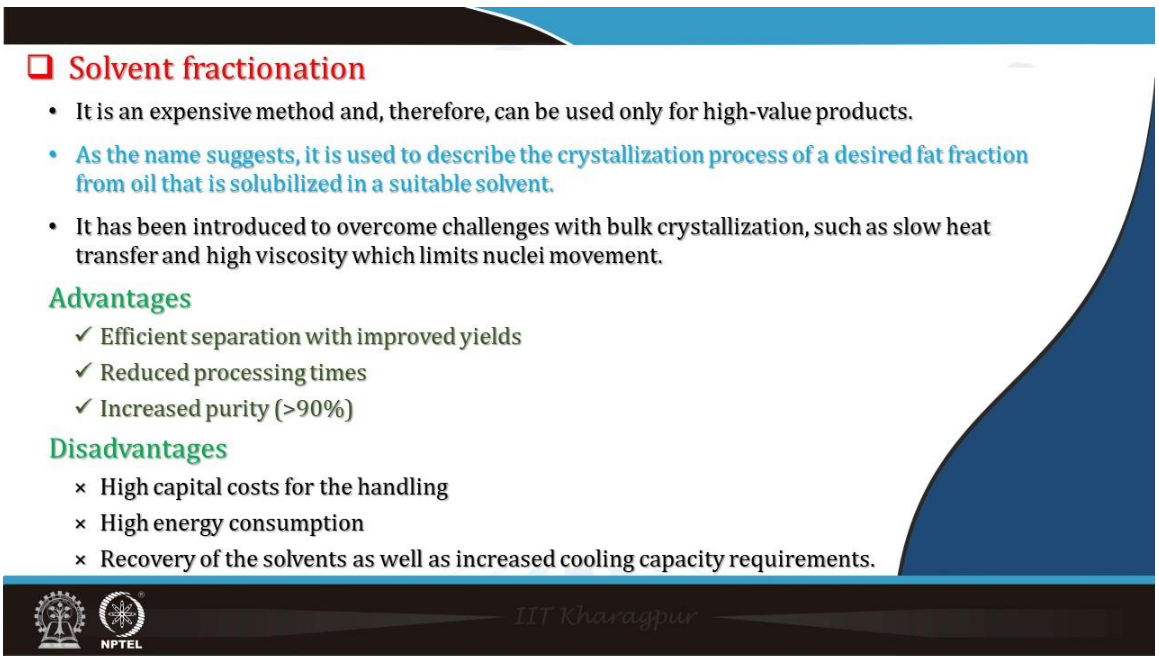
The advantages of dry fractionation include that it is the simple operating procedures involved. These are environmentally friendly processes there is no need for chemicals as processing aids, it has a lower operational cost and no effluent output problems. However, there are certain disadvantages is it has lower separation efficiency than the other two methods. The factors affecting the dry fractionation process include initial oil temperature, pre-crystallization process, rate of cooling, crystallization time, agitation of the oil, final crystallization, temperature, and separation or filtration process parameters. So, these are the various factors that should be properly controlled in order to get the desired result.

❖ Multistage dry fractionation of palm oil

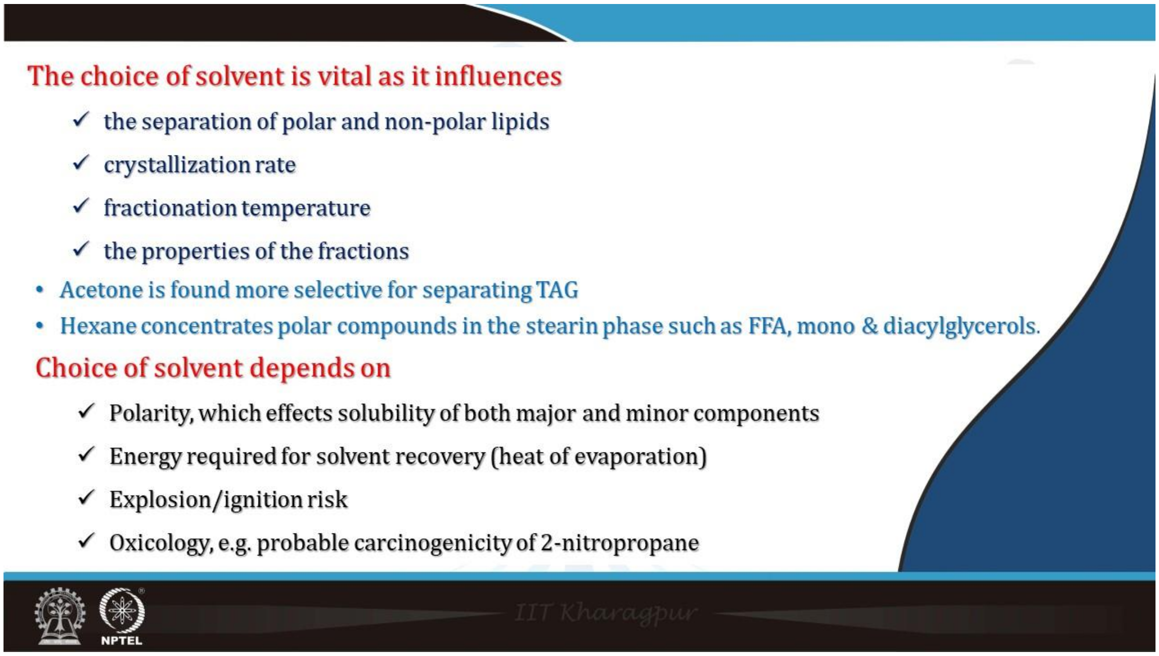


Source: AOCS lipid library

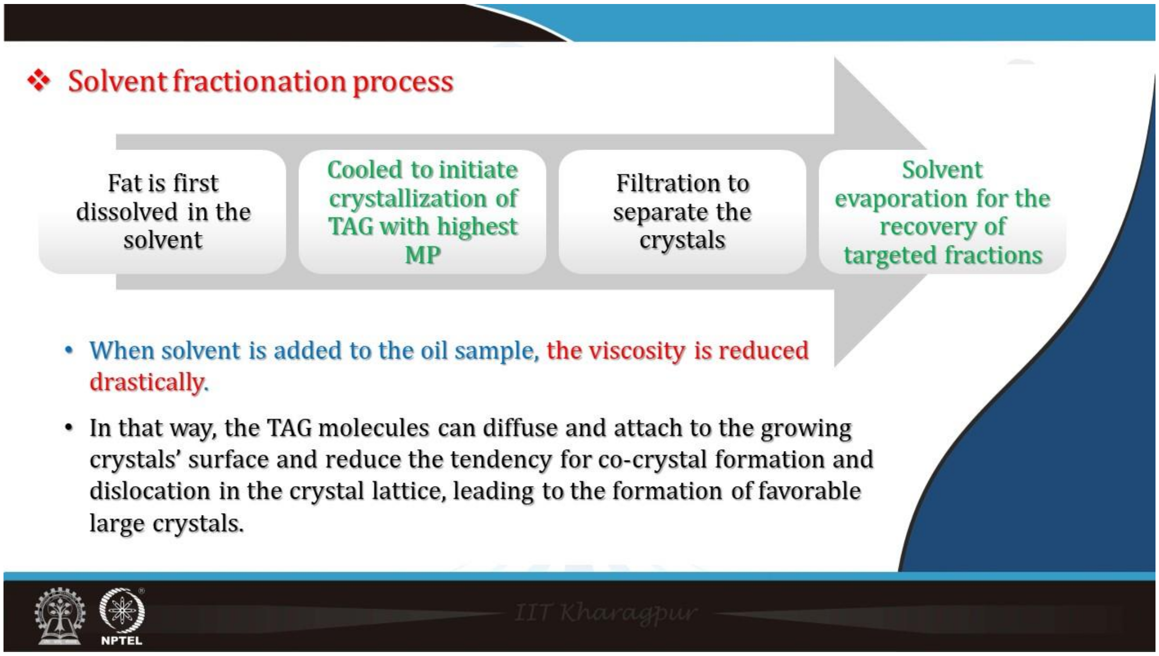
This slide shows the multi-stage dry fractionation of palm oil. So, you see there is a 100 percent palm oil with an iodine value of around 52 and then here it is palm stearin with an iodine value of 36. So, it has about 15 percent palm stearin in this as this is vanaspati and the remaining 85 percent is palm olein with an iodine value of around 56. It is used as a frying oil. So, this again is prime palm olein again has a 45 percent soft palm mid fraction iodine value of 46, it is margarine. About 40 percent of it is the salad oil that is it has a iodine value of more than 64. This is a soft PMF, it has a 15 percent hard PMF with an iodine value of 35, 30 percent mid olein with an iodine value of 53 whereas, the salad oil has about 20 percent mid oleine with an iodine value of 60 and 20 percent top oleine iodine value more than 67. So, these salad oils these are they can be considered very cold stable oils and these margarine or soft can be considered cocoa butter equivalents because of their property and their melting characteristics.



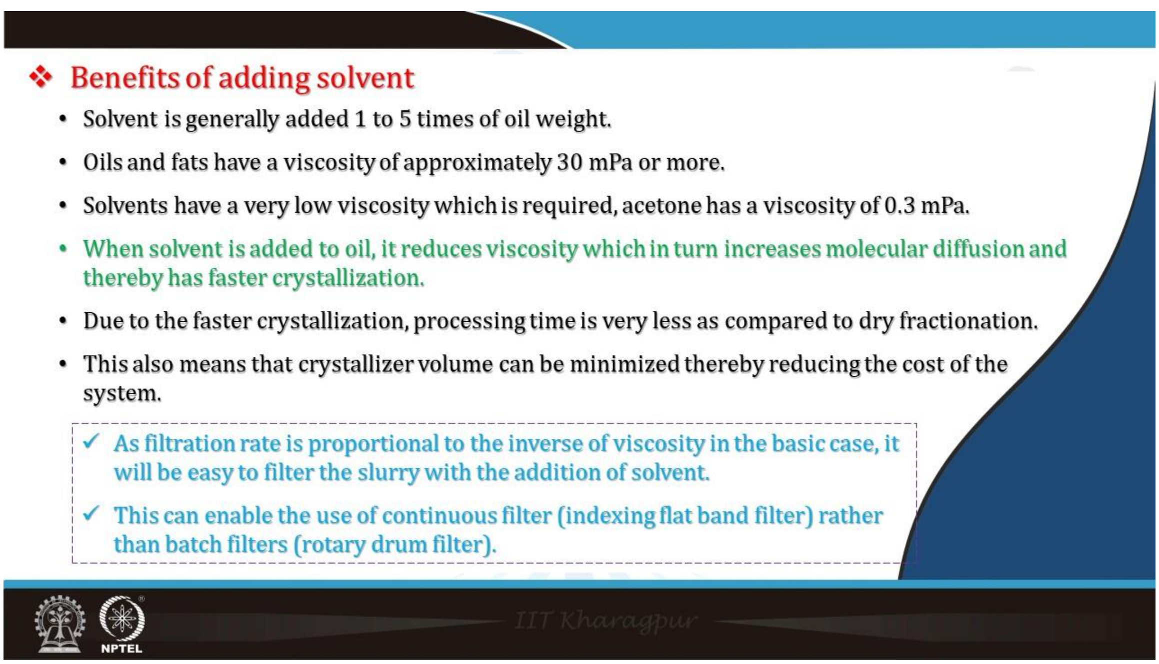
Now let us discuss the second topic which is solvent fractionation. It is an expensive method and, therefore, can be used only for high-value products. As the name suggests, it is used to describe the crystallization process of a desired fat fraction from oil that is solubilized in a suitable solvent. It has been introduced to overcome challenges with bulk crystallization, such as slow heat transfer and high viscosity which limits nuclei movement. So, the advantages of solvent fractionation include efficient separation with improved yields, reduced processing times, and increased purity which is more than 90 percent purity. However, the disadvantages of the process are high capital cost for the handling, high energy consumption and recovery of the solvent as well as increased cooling capacity requirements.



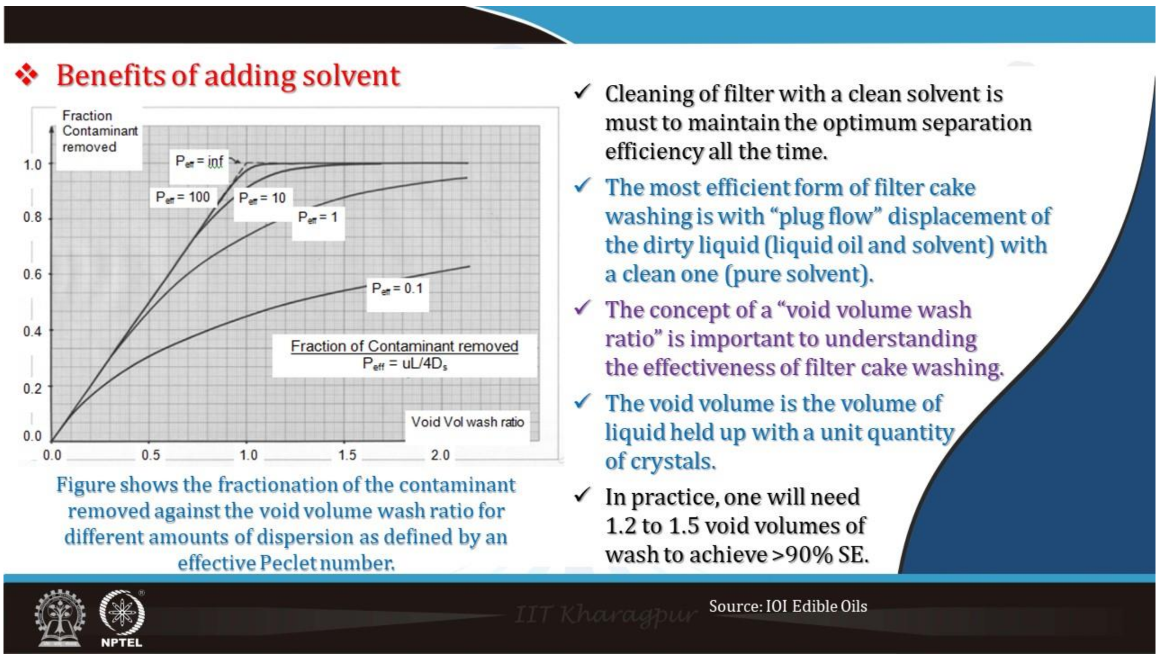
The choice of the solvent is vital as it influences the separation of polar and nonpolar lipids, it influences the crystallization rate, it influences the fractionation temperature and also the solvent influences the properties of the fractions. Acetone is found more selective in separating TAG. Hexane concentrates polar compounds in the stearin phase such as FFA, mono, and diacylglycerols. The choice of the solvent depends on polarity which affects solubility of both major and minor components. The energy required for solvent recovery is particularly the heat required for the evaporation, explosion, or ignition risk and oxicology, which is probable carcinogenicity of the 2-nitropropane. So, these are the factors on which this choice of the solvent is considered.



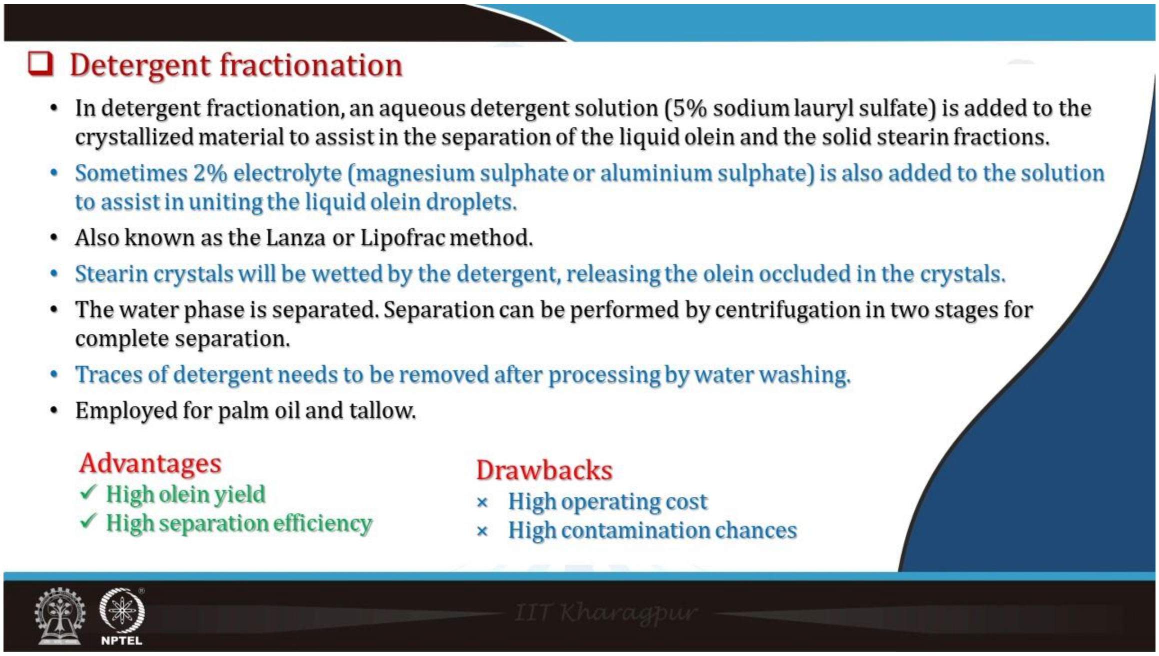
If you look at the technology of the solvent fractionation process fat is first dissolved in the solvent and then it is cooled to initiate crystallization of the triglyceride with the highest melting point. Then filtration is done to separate the crystals and finally, solvent evaporation for the recovery of the targeted fractions. When solvent is added to the oil sample, the viscosity is reduced drastically. In this way, the TAG molecule can diffuse and attach to the growing crystals on the surface and reduce the tendency of co-crystal formation and dissolution in the crystal lattice leading to the formation of favorable large crystals.



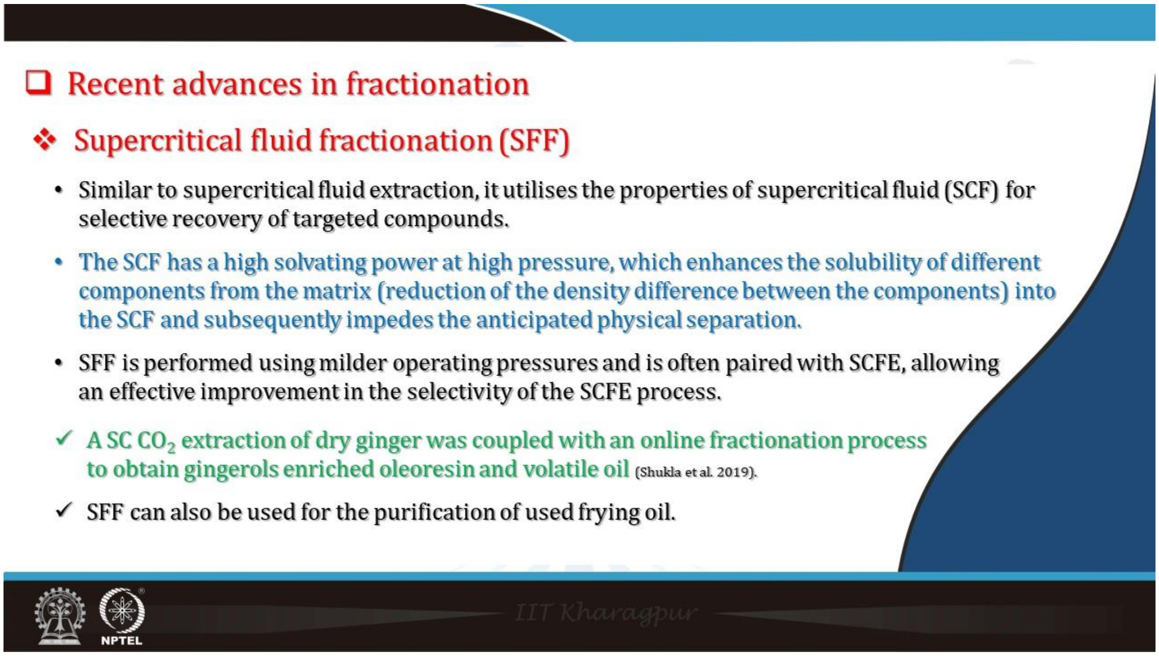
Benefits of adding solvent include Solvent is generally added 1 to 5 times of oil weight. Oils and fats have a viscosity of approximately 30 mPa or more. Solvents have a very low viscosity which is required, acetone has a viscosity of 0.3 mPa. When solvent is added to oil, it reduces viscosity which in turn increases molecular diffusion and thereby has faster crystallization. Due to the faster crystallization, processing time is much less as compared to dry fractionation. This also means that crystallizer volume can be minimized thereby reducing the cost of the system. As the filtration rate is proportional to the inverse of viscosity in the basic case, it will be easy to filter the slurry with the addition of solvent. This can enable the use of continuous filters (indexing flat band filter) rather than batch filters (rotary drum filter).



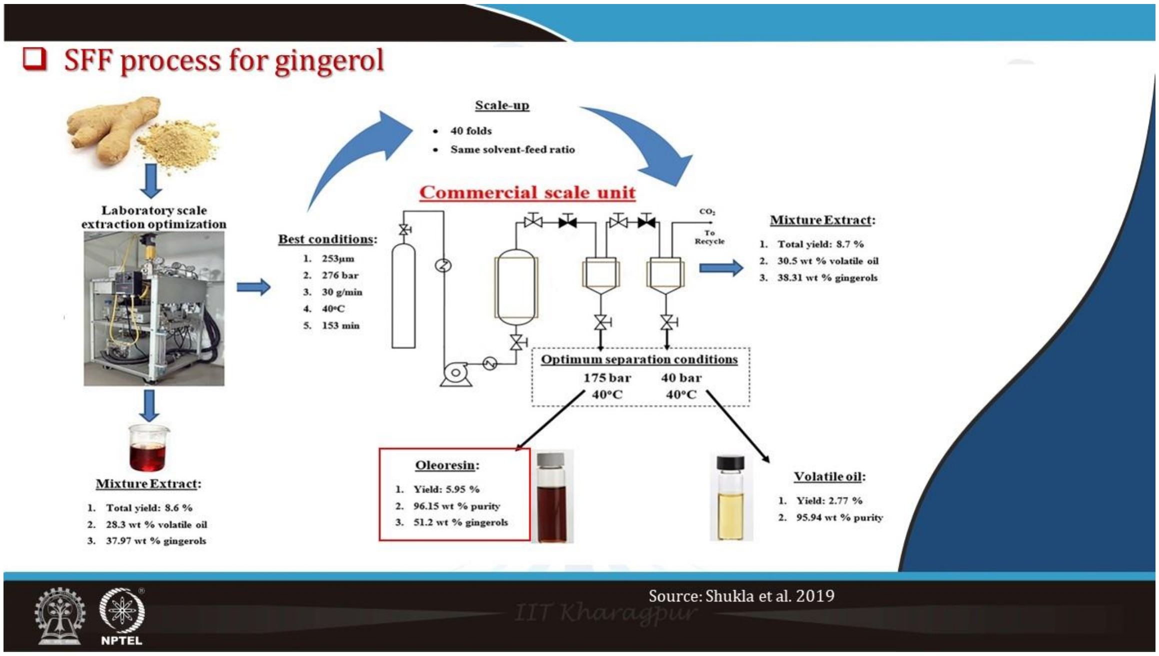
Here you can see that in this figure, the fractionation of the contaminant removed from the void volume wash ratio of different amounts of the dispersion as defined by the effective peclet number. You can see on the x-axis the void volume wash ratio and the axis contains the fractionation contaminant removed and the effective peclet number is here. When the effective peclet number is more than contamination more amount of contamination or rate of contamination removed is increased. It is increasing with both the void volume ratio and the contamination removed. Cleaning of filter with a clean solvent is a must to maintain the optimum separation efficiency all the time. The most efficient form of filter cake washing is with "plug flow" displacement of the dirty liquid (liquid oil and solvent) with a clean one (pure solvent). The concept of a "void volume wash ratio" is important to understanding the effectiveness of filter cake washing. The void volume is the volume of liquid held up with a unit quantity of crystals. In practice, one will need 1.2 to 1.5 void volumes of wash to achieve more than 90% SE.



In detergent fractionation, an aqueous detergent solution (5% sodium lauryl sulfate) is added to the crystallized material to assist in the separation of the liquid olein and the solid stearin fractions. Sometimes 2% electrolyte (magnesium sulfate or aluminum sulfate) is also added to the solution to assist in uniting the liquid olein droplets. Also known as the Lanza or Lipofrac method. Stearin crystals will be wetted by the detergent, releasing the olein occluded in the crystals. The water phase is separated. Separation can be performed by centrifugation in two stages for complete separation. Traces of detergent need to be removed after processing by water washing. Employed for palm oil and tallow. The advantages of detergent fractionation include high olein yield and it has high separation efficiency, the drawbacks are high operating cost and high contamination chances.



The recent advance in the fractionation process is supercritical fluid fractionation. Similar to supercritical fluid extraction, it utilizes the properties of supercritical fluid (SCF) for selective recovery of targeted compounds. The SCF has a high solvating power at high pressure, which enhances the solubility of different components from the matrix (reduction of the density difference between the components) into the SCF and subsequently impedes the anticipated physical separation. SFF is performed using milder operating pressures and is often paired with SCFE, allowing an effective improvement in the selectivity of the SCFE process. A supercritical carbon dioxide extraction of dry ginger was coupled with an online fractionation process to obtain gingerols-enriched oleoresin and volatile oil and this was reported by Shukla et al in 2019. The SFF can also be used for the purification of used frying oils.



Shown here is the process reported by Shukla et al., 2019. You can see that laboratory-scale extraction equipment is used to extract ginger and the total yield is around 8.6 percent, it has around 28.3 percent volatile oil and 37.97 percent gingerols. Then the best conditions were reported as 253-micron meter particle size, 276 bar pressure, 130 gram per minute feed rate, 40 degree Celsius temperature, and 153 minutes and then this process was scaled up to 40 folds, and the same solvent to feed ratio was used and you can see that as a mixture extract here total yield almost remain the similar to that of the the laboratory scale process. But when the conditions were optimized like 175 bar 40 degrees Celsius, the weight of the gingerol as you can see increased to about 37 percent or approximately 51 percent, and its purity was around 96 percent. This volatile oil yield was 2.77 percent and purity was 95.9 weight percent. The pressure was 40 bar and the temperature was 40 degrees Celsius. This shows how the solvent and operating conditions influence the initial conditions.

Advantages

- ✓ Mild fractionation temperature making it Ideal for thermolabile components.
- ✓ The solvent can be easily separated from the end product.
- ✓ The SC CO_2 is non-toxic and traces of residual CO_2 do not pose health hazards.

Disadvantages

- × Low polar affinity
- × High molecular weight components

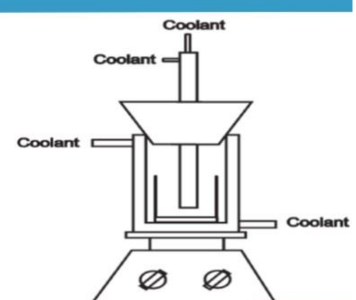
- Use of co-solvent can address this issue. A small volume of co-solvent (0-20 mol%) can be added to increase the polarity of SC CO_2, increase the solvating power and enhances the quantitative extraction.

➢ Organic solvents (e.g., Methanol, ethanol, hexane) are commonly used as co-solvents.

The advantages are mild fractionation temperature making it Ideal for thermolabile components. The solvent can be easily separated from the end product. The SC CO2 is non-toxic and traces of residual CO2 do not pose health hazards. The disadvantages are low polar affinity and high molecular weight components. The use of co-solvent can address this issue. A small volume of co-solvent (0-20 mol%) can be added to increase the polarity of SC CO2, increase the solvating power, and enhance the quantitative extraction. Organic solvents like methanol, ethanol, and hexane are commonly used as co-solvents.

Emulsion fractionation

- It is a very novel technique where emulsion was developed followed by dry fractionation.
- This fractionation method is carried out based on the crystallization of low-viscous emulsion in which water and emulsifier are employed to reduce the viscosity of the oil system.
- The prepared emulsion was fractionated according to the layer-melt crystallization method using a cold finger apparatus under optimized conditions.



Cold finger apparatus

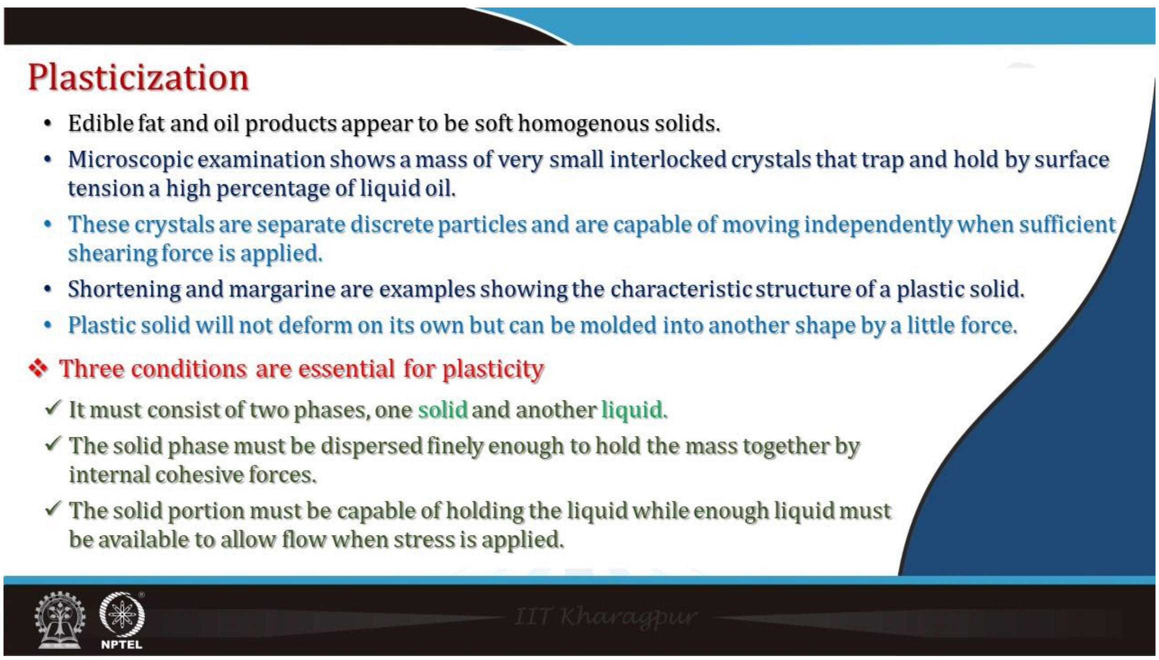
Factors affecting efficiency

- ✓ Cold finger temperature
- ✓ Temperature of melt
- ✓ Agitation speed
- ✓ Cooling rate

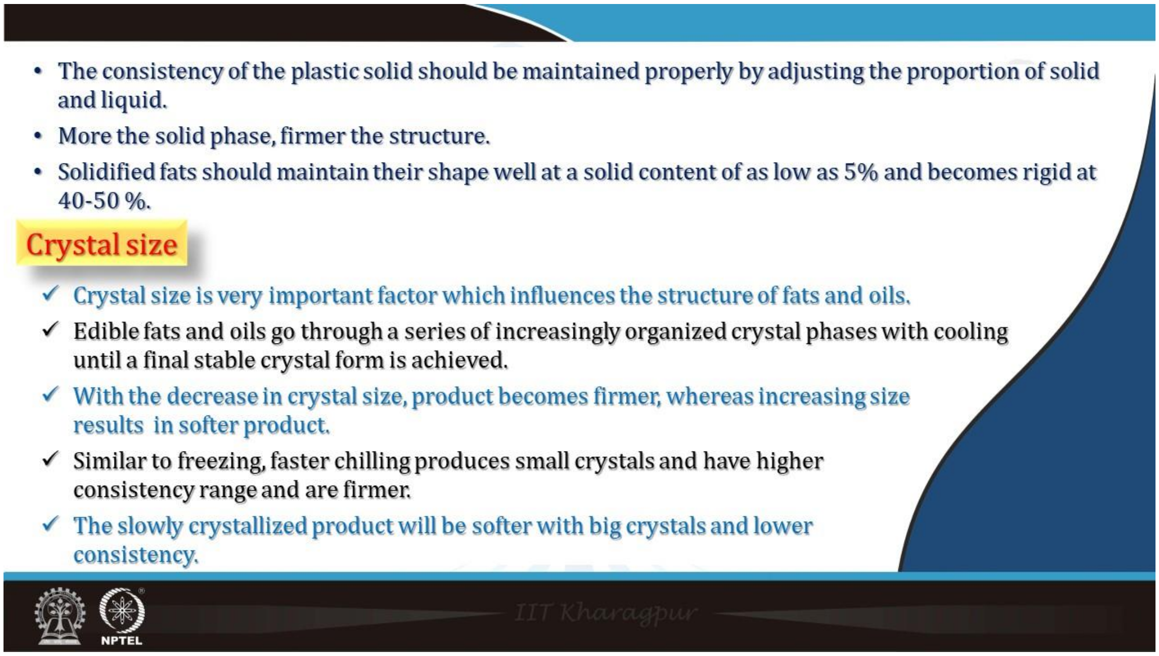
- Emulsion fractionation shows great potential as a green alternative lipid fractionation technology because the process requires only water and a food emulsifier, as well as the capacity to address the oil entrainment issue from the dry fractionation.

Source: Chaleepa & Ulrich (2011)

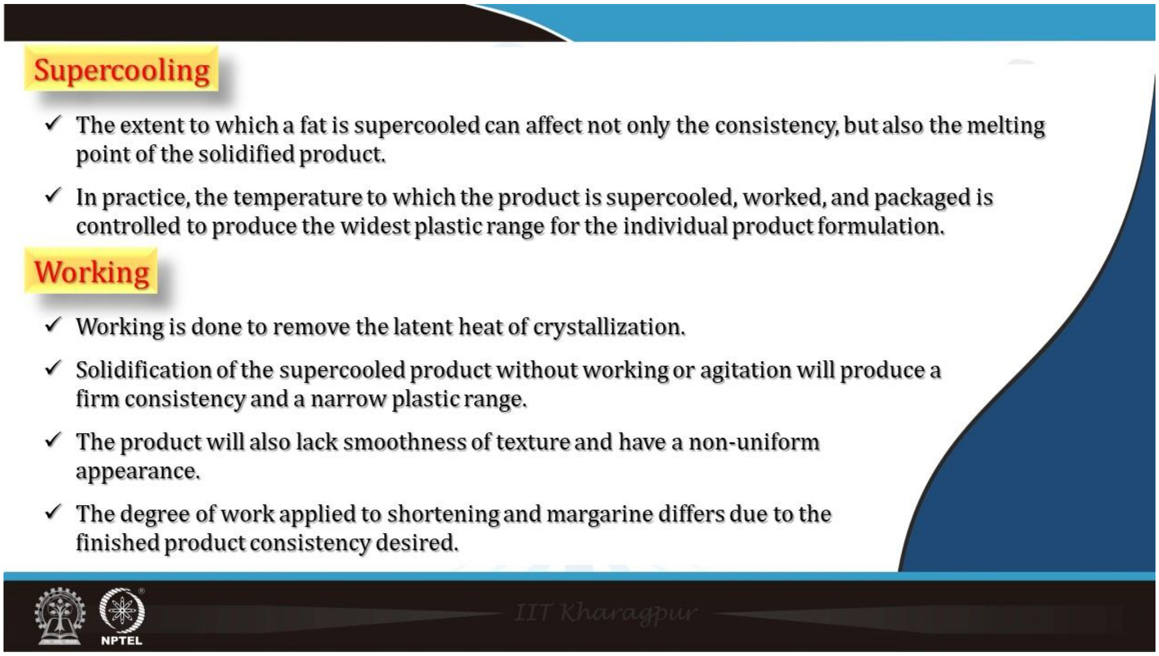
Then emulsion fractionation is another novel technique where emulsion was developed followed by dry fractionation. This fractionation method is carried out based on the crystallization of low-viscous emulsion in which water and emulsifier are employed to reduce the viscosity of the oil system. The prepared emulsion was fractionated according to the layer-melt crystallization method using a cold finger apparatus under optimized conditions, which is shown here in this schematic diagram. Factors affecting efficiency are cold finger temperature, temperature of melt, agitation speed, and cooling rate. Emulsion fractionation shows great potential as a green alternative lipid fractionation technology because the process requires only water and a food emulsifier, as well as the capacity to address the oil entrainment issue from the dry fractionation. So, this is a very good potential technology for fractionation.



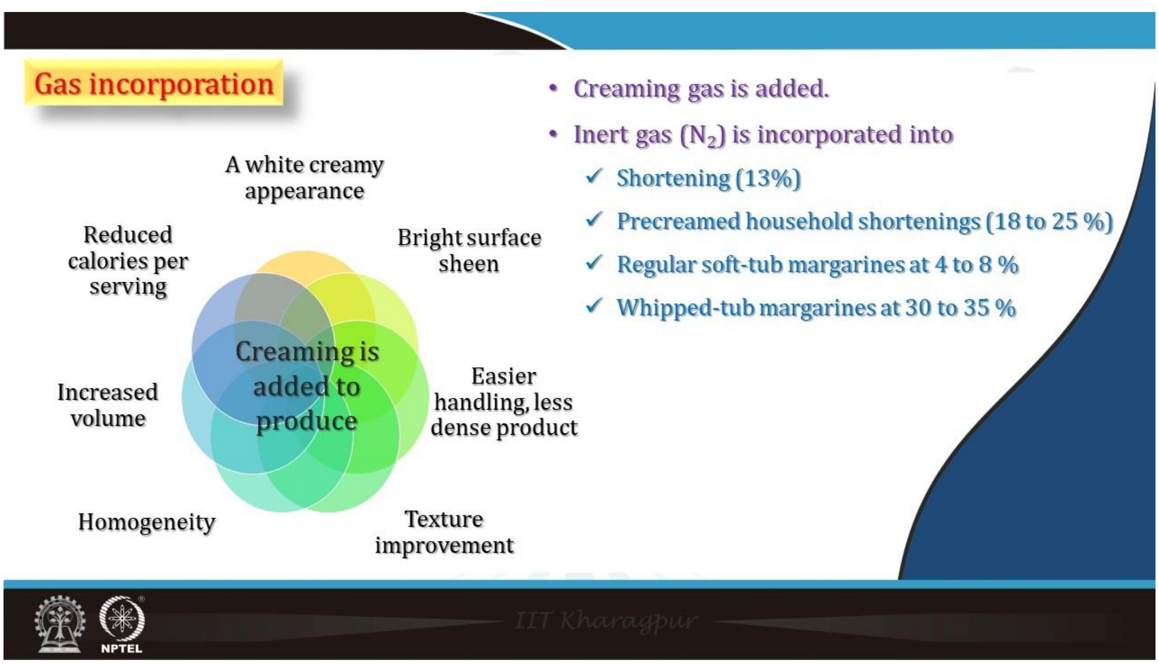
Now, let us talk about plasticization. Edible fat and oil products appear to be soft homogenous solids. Microscopic examination shows a mass of very small interlocked crystals that trap and hold by surface tension a high percentage of liquid oil. These crystals are separate discrete particles and are capable of moving independently when sufficient shearing force is applied. Shortening and margarine are examples showing the characteristic structure of a plastic solid. Plastic solid will not deform on its own but can be molded into another shape by a little force. Three conditions are essential for plasticity, which are, it must consist of two phases, one solid and another liquid, the solid phase must be dispersed finely enough to hold the mass together by internal cohesive forces, the solid portion must be capable of holding the liquid while enough liquid must be available to allow flow when stress is applied.



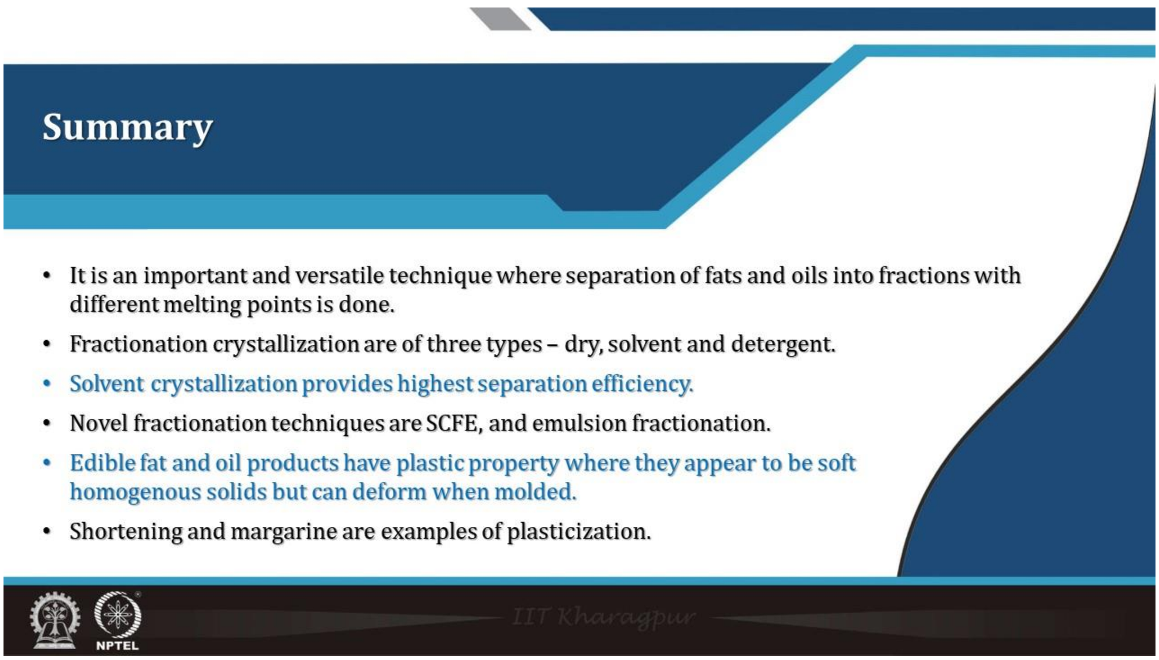
The consistency of the plastic solid should be maintained properly by adjusting the proportion of solid and liquid. The more the solid phase, the firmer the structure. Solidified fats should maintain their shape well at a solid content of as low as 5% and become rigid at 40-50 %. Crystal size is a very important factor that influences the structure of fats and oils. Edible fats and oils undergo a series of increasingly organized crystal phases with cooling until a final stable crystal form is achieved. With the decrease in crystal size, the product becomes firmer, whereas increasing size results in a softer product. Similar to freezing, faster chilling produces small crystals have higher consistency range and are firmer. The slowly crystallized product will be softer with big crystals and lower consistency.



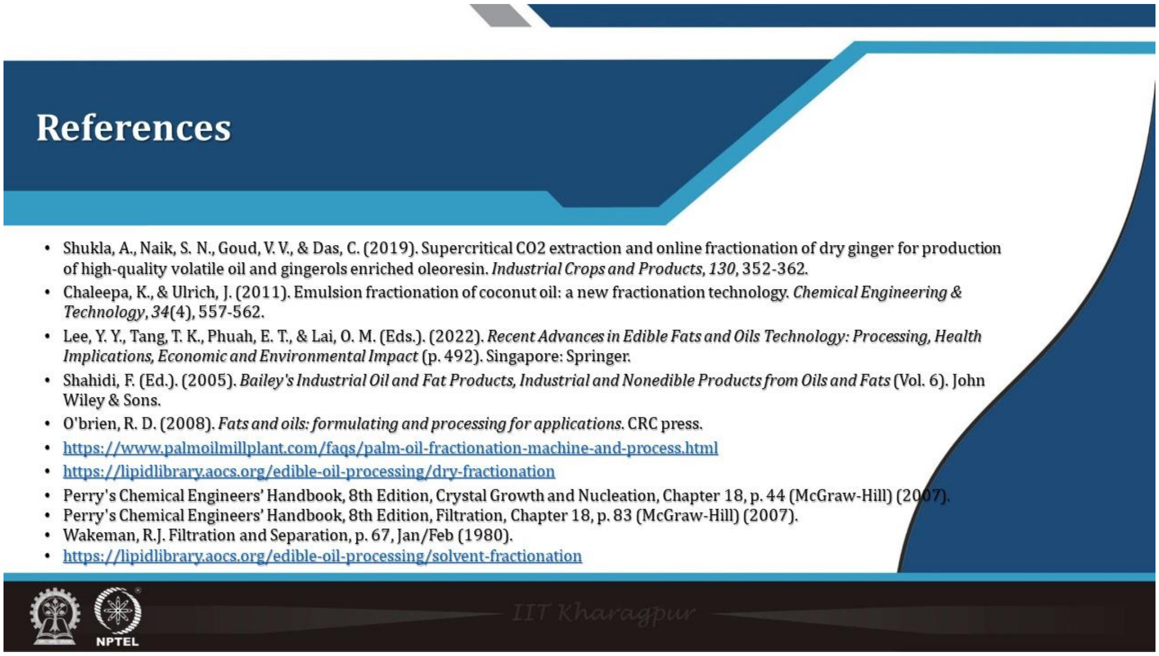
The extent to which a fat is supercooled can affect not only the consistency but also the melting point of the solidified product. In practice, the temperature to which the product is supercooled, worked, and packaged is controlled to produce the widest plastic range for the individual product formulation. Working is done to remove the latent heat of crystallization. Solidification of the supercooled product without working or agitation will produce a firm consistency and a narrow plastic range. The product will also lack smoothness of texture and have a non-uniform appearance. The degree of work applied to shortening and margarine differs due to the finished product consistency desired.



Another parameter is gas incorporation. Normally the creaming gas is added to these fats to incorporate plasticity. The creaming gas in a normally inert gas such as nitrogen is incorporated up to 13 percent into the shortening. Pre-creamed household shortening has around 18 to 25 percent air, regular soft tub margarine has 4 to 8 percent, and whipped tub margarine has as high as 30 to 35 percent. So, the incorporation of gas into the product is done to give a white creamy appearance. Also, the incorporation of gas gives a bright surface sheen, the product becomes easier to handle, and it becomes a less dense product. There is texture improvement, its homogeneity improves, and it has an increased volume because of the incorporation of gas and also reduced calories per serving. So, these are the advantages of the gas incorporation.



Now, I would like to summarize this lecture by saying that it is an important and versatile technique where the separation of fats and oils into fractions with different melting points is done. Fractionation crystallization is of three types – dry, solvent, and detergent. Solvent crystallization provides the highest separation efficiency. Novel fractionation techniques are SCFE and emulsion fractionation. Edible fat and oil products have plastic properties that appear to be soft homogenous solids but can deform when molded. Shortening and margarine are examples of plasticization.



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