Food Oils and Fats: Chemistry & Technology
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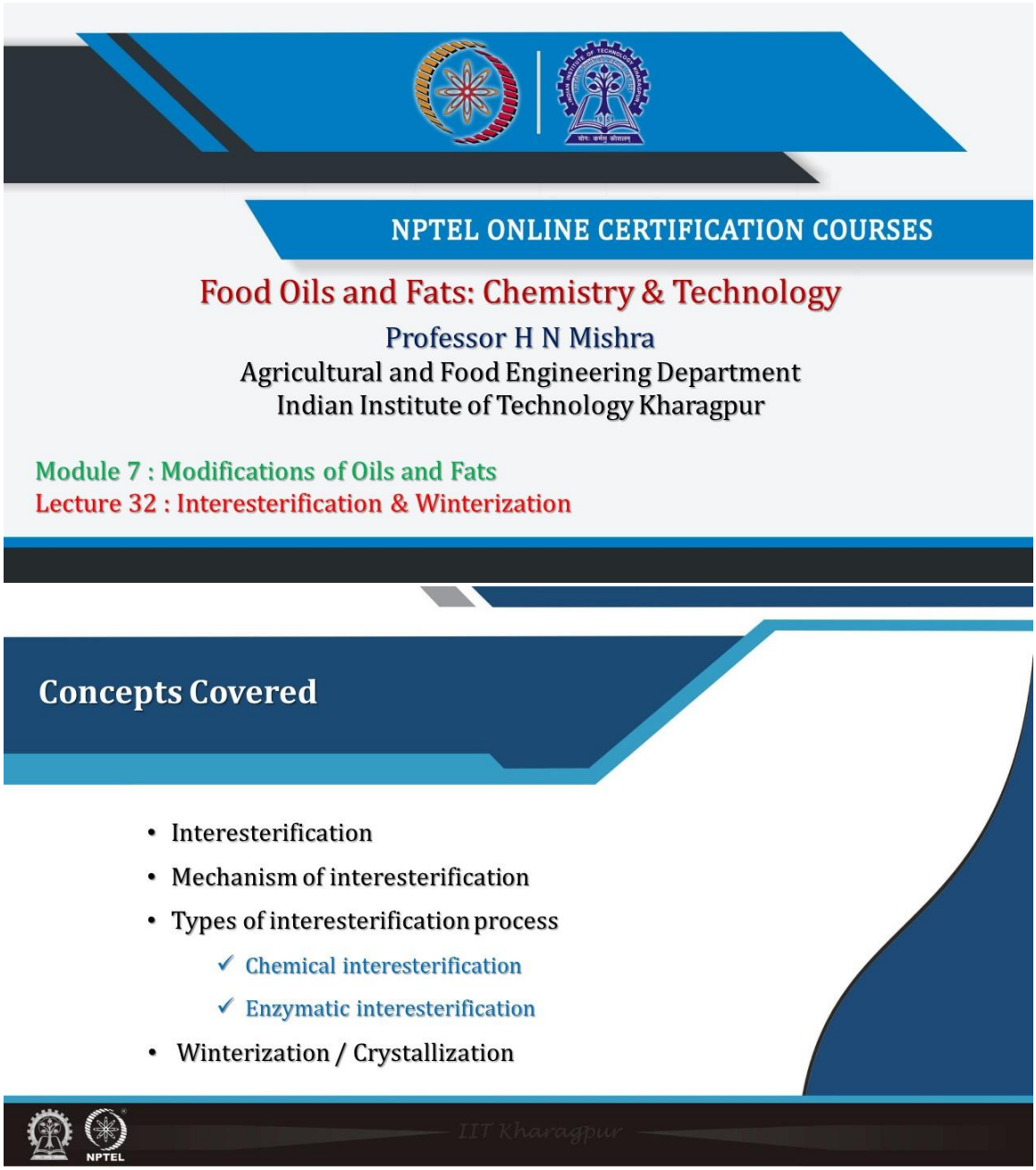
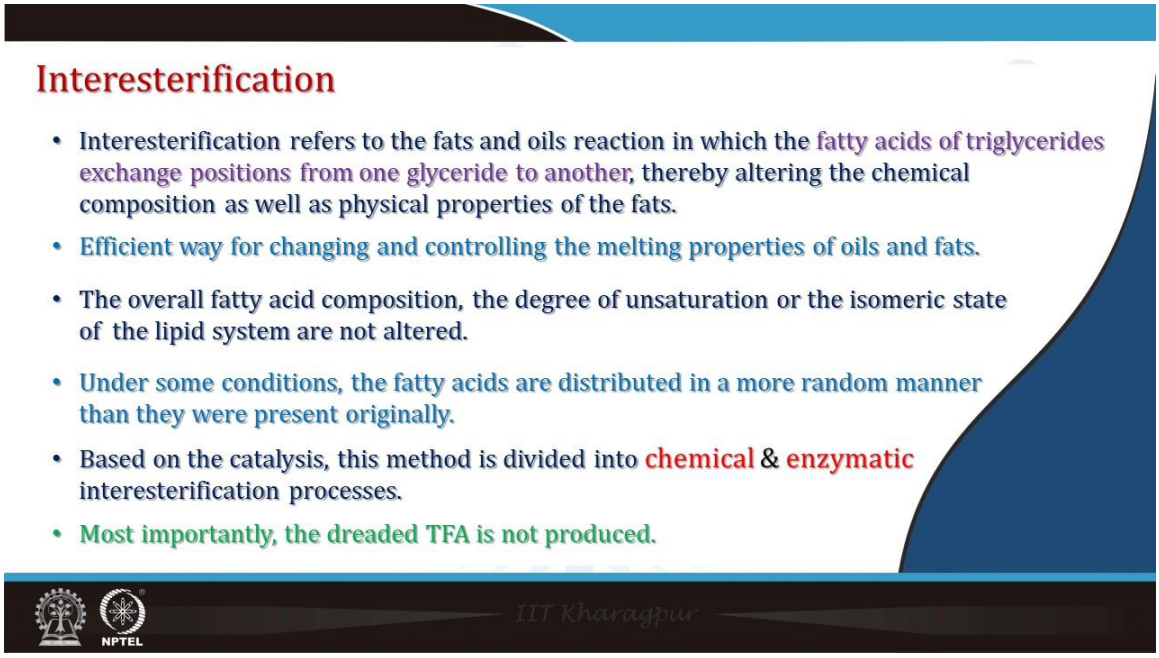
Module 7 : Modifications of Oils and Fats
Lecture 32 : Interesterification & Winterization

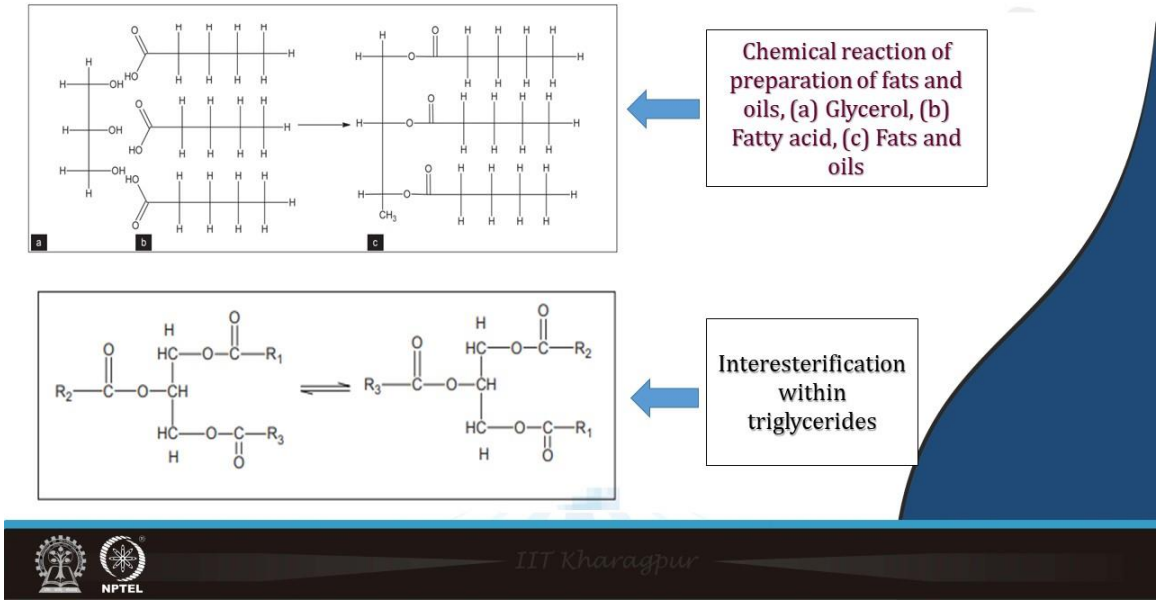


Hello, everybody. Namaskar. Now, in this lecture 32, we will discuss about Intersterification and Winterization Processes. We will talk about what is intersterification, what is the mechanism of intersterification and its type, which may be

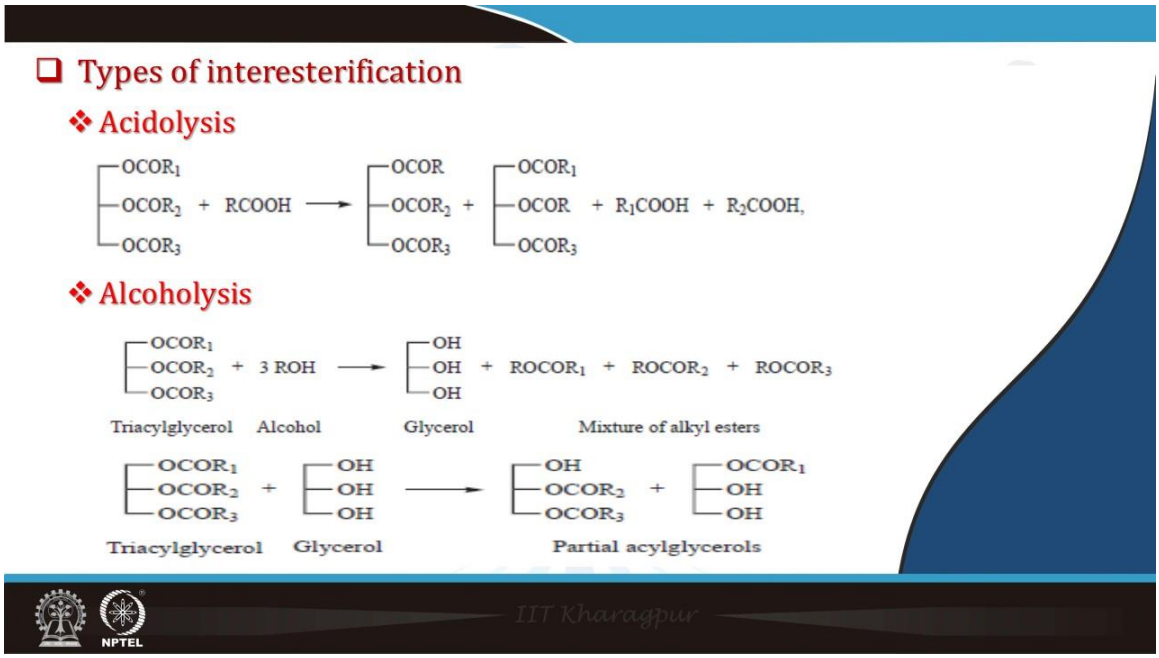
chemical intersterification or enzymatic intersterification and finally, we will also discuss winterization or crystallization processes.



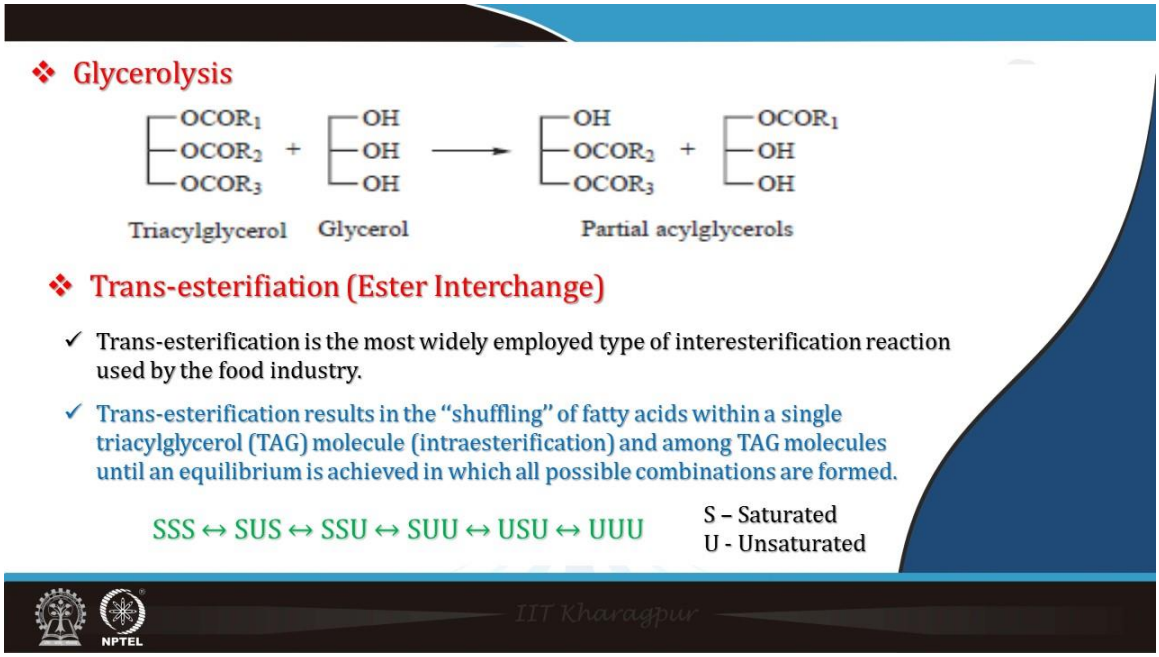
So, let us see what intersterification is. Interesterification refers to the fats and oils reaction in which the fatty acids of triglycerides exchange positions from one glyceride to another, thereby altering the chemical composition as well as physical properties of the fats. Efficient way to change and control the melting properties of oils and fats. The overall fatty acid composition, the degree of unsaturation, or the isomeric state of the lipid system are not altered. Under some conditions, the fatty acids are distributed in a more random manner than they were present originally. Based on the catalysis, this method is divided into chemical & enzymatic interesterification processes. Most importantly, the dreaded trans fatty acids are not produced unlike those in the hydrogenation and other heat process.



You can see here in the picture the chemical reaction of the preparation of fats and oils. 'A' is glycerol, 'b' is three molecules of fatty acids and combine to form triglyceride 'c'. So, R 1, R 2 and R 3 this is a triglyceride. So, in the intersterification process, the position of R 1, R 2, or R 3 is interchanged. It is there is intersterification that ester linkages are formed that R 1 comes to the position of R3, R 2 goes to the R1 position, R 3 goes to the R2 or vice versa. Random distribution change is what is done in the intersterification.



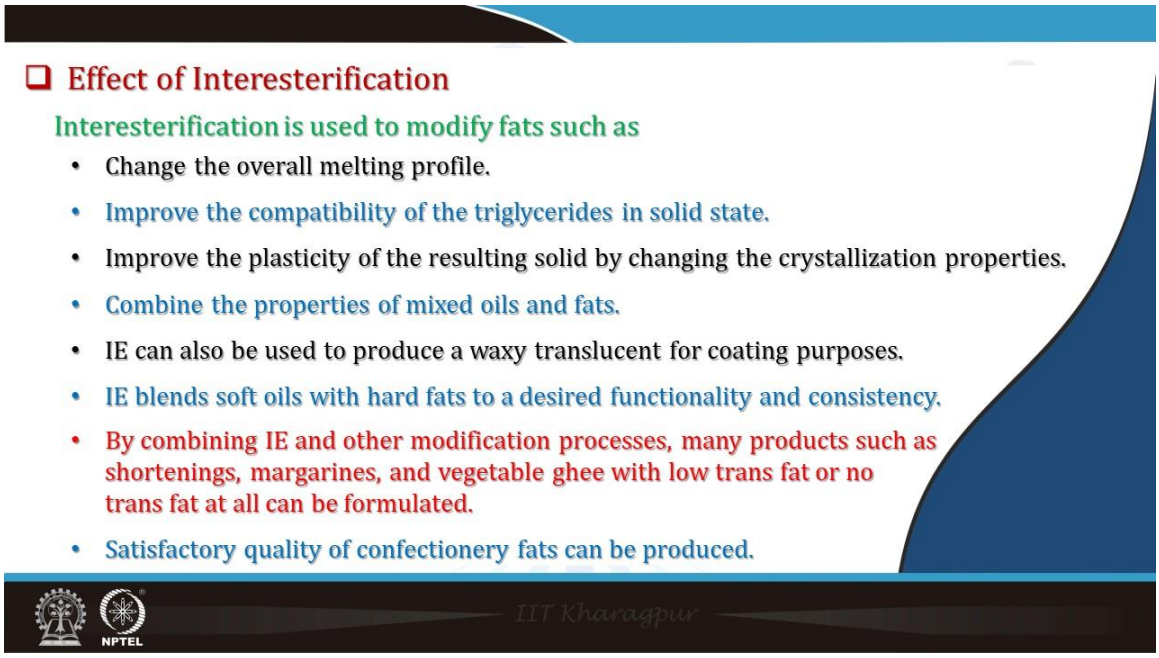
The intersterification types may be different ways it can be done like acidolysis and alcoholysis. In acidolysis you see there is an organic acid, carbolic acid is used to change the position. In alcoholysis that is it is basically alcohol is used. So, R 1, R 2, and R 3 is a triglyceride, that reacts with alcohol it gives glycerol plus a mixture of alkyl esters different ROCOR1, RCORO2, and ROCOR3.



Then triacylglycerol plus glycerol it gives partial acylglycerol. So, different types of products depending upon the conditions can be made. Then it may be glycerolysis, glycerolysis means triacylglycerol is reacted with glycerol which gives partial acylglycerols. Then transesterification means ester interchange. Trans-esterification is the most widely employed type of interesterification reaction used by the food industry. Trans-esterification results in the ‘‘shuffling’’ of fatty acids within a single triacylglycerol (TAG) molecule (intraesterification) and among TAG molecules until an equilibrium is achieved in which all possible combinations are formed. You can see that if you say that saturated S and unsaturated U may be

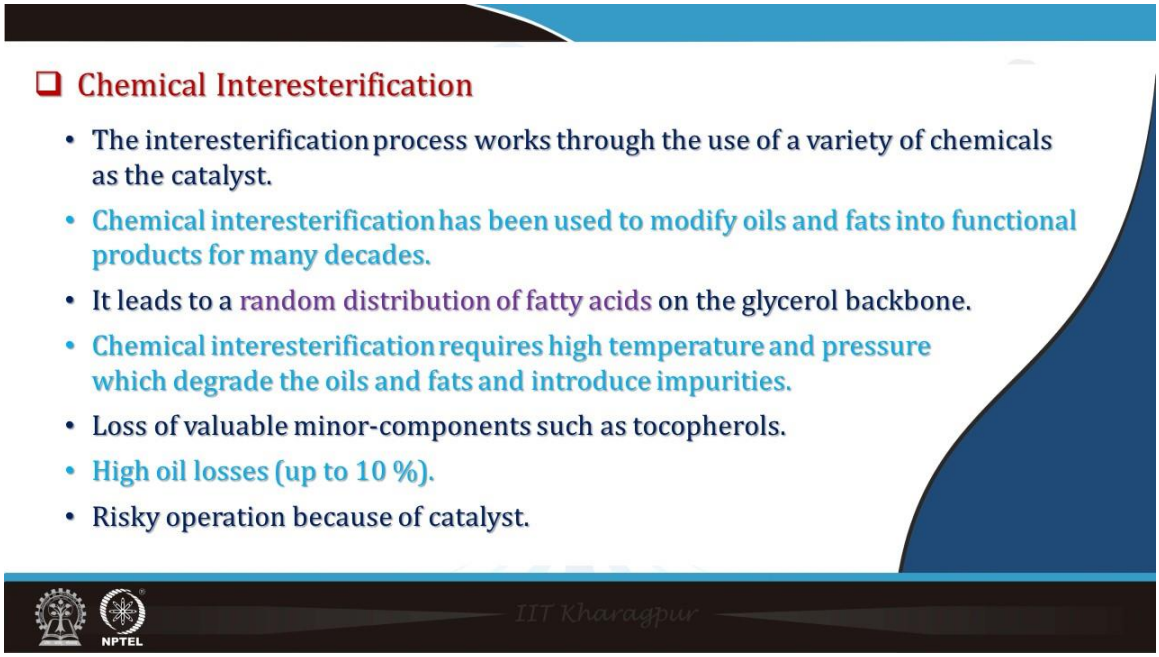
$$SSS \leftrightarrow SUS \leftrightarrow SSU \leftrightarrow SUU \leftrightarrow USU \leftrightarrow UUU$$

where that is all saturated here all unsaturated and then a combination of saturated unsaturated. So, all these combinations and permutations are done and these are all achieved by controlling the proper conditions during the process.

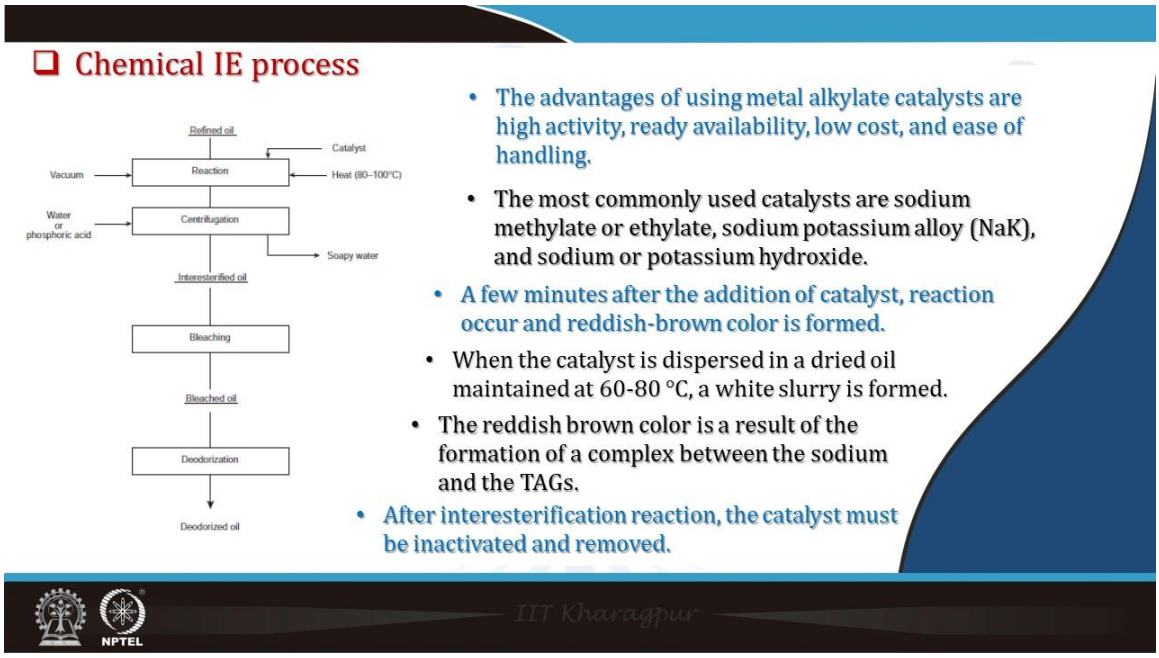


The effect of inter-esterification is a process used to modify fats such as to change the overall melting profile, improve the compatibility of the triglycerides in the solid state, improve the plasticity of the resulting solid by changing the crystallization properties, combine the properties of mixed oils and fat. IE can also be used to produce a waxy translucent for coating purposes and blend soft oils with hard fats to a desired functionality and consistency. By combining IE and other modification processes, many products such as shortenings, margarine, and vegetable ghee with low trans-fat or no trans-fat at all can be formulated satisfactory quality of confectionery fats can be produced. So, this is used to get again that various fats and oils of required consistency

for required functional usage.



Let us discuss the different types, chemical interesterification or enzymatic interesterification. In the chemical inter-esterification process, works through the use of a variety of chemicals as the catalyst. Chemical interesterification has been used to modify oils and fats into functional products for many decades. It leads to a random distribution of fatty acids on the glycerol backbone. Chemical interesterification requires high temperature and pressure which degrade the oils and fats and introduce impurities. Loss of valuable minor components such as tocopherols. There may be high oil losses that is up to 10 percent or it is a risky operation because of the use of the chemical catalyst

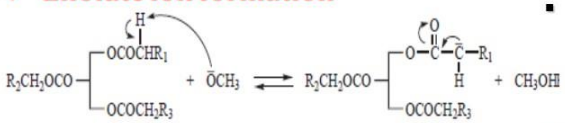


In the chemical catalyst process, you can see here it is that inter-esterification results when the oil is heated relatively to a high temperature of about 200 degree Celsius for a considerably long period of time. Chemical Interesterification can be performed at lower temperatures (as low as 50 °C) than when it is carried out without catalyst. Wwhen it is carried out without catalyst and approximately 0.1 percent weight percent of the catalyst on the basis of the weight of the oil is used. So, the advantage of using metal alkylates catalysts are high activity, ready availability, low cost and ease of handling. The most commonly used catalyst are sodium methylates or ethylate, sodium potassium alloy and sodium or potassium hydroxide. A few minutes after the addition of the catalyst reaction occur and reddish brown color is formed. When the catalyst is dispersed in a dried oil maintained at 60 to 80 degree Celsius a white slurry is formed. So, the reddish brown color is a result of the formation of the complex between the sodium and the TAGs. After the interesterification reaction the catalyst must be inactivated and removed by a suitable process.

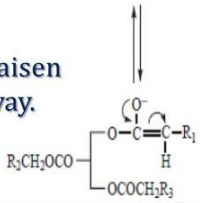
Mechanism for chemical IE

- Two mechanisms have been proposed for alkaline-catalyzed chemical interesterification, viz. (i) enolate anion formation & (ii) carbonyl addition.

Enolate ion formation



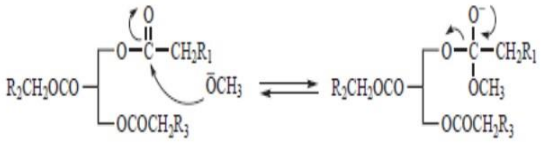
Carbanion



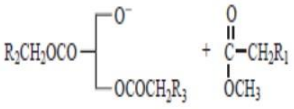
- The reaction begins when the sodium methoxide (catalyst) attacks the acidic hydrogen from the carbon α to the carbonyl carbon to produce an enolate structure.
- This reaction produces a carbanion, which is a strong nucleophile.
- This enolate anion reacts continuously with other ester groups till all ester groups in TAG may react and move around from their initial position.
- This mechanism is referred to as the Claisen condensation pathway.

Two mechanism for chemical IE has been put forward that is enolate anion formation and carbonyl addition. In the enolate anion formation as you see here the reaction begins when the sodium methoxide catalyst attacks the acid hydrogen from the carbon alpha carbon to the carbonyl carbon to produce an enolate structure. This reaction produces a carbonation which is a strong nucleophile. This enolate anion reacts continuously with other ester to groups till all the ester group in the TAG may interact and move around from their initial position. So, this reaction continues. This mechanism is referred to as a Claisen condensation pathway.

Carbonyl addition



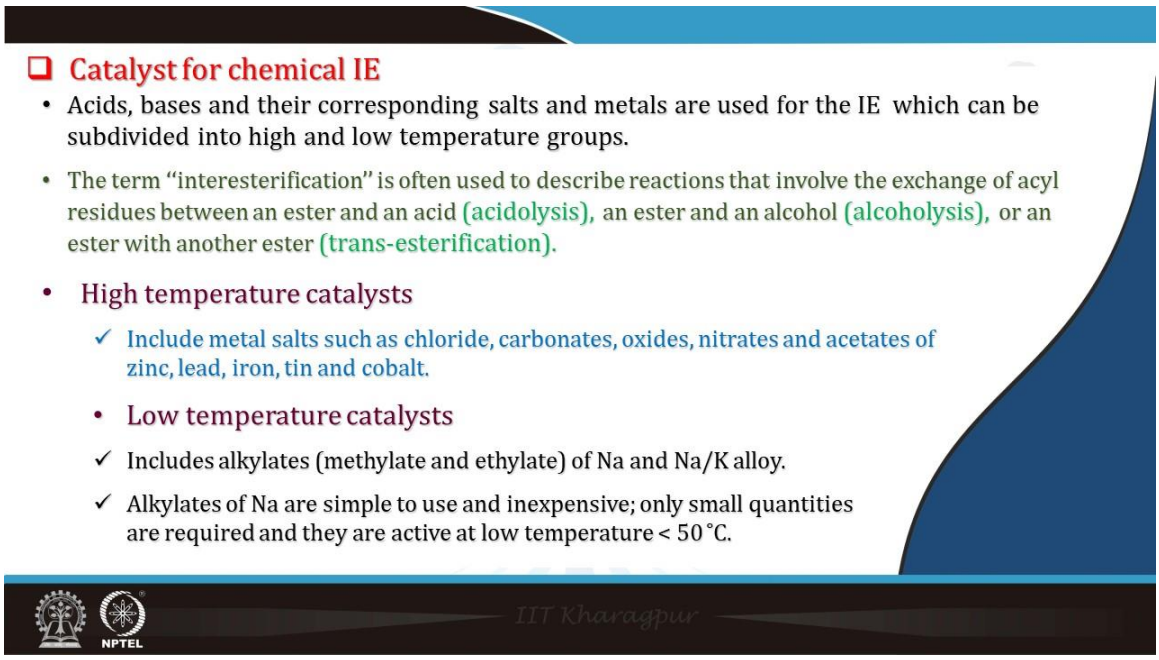
Teterahedral intermadiate



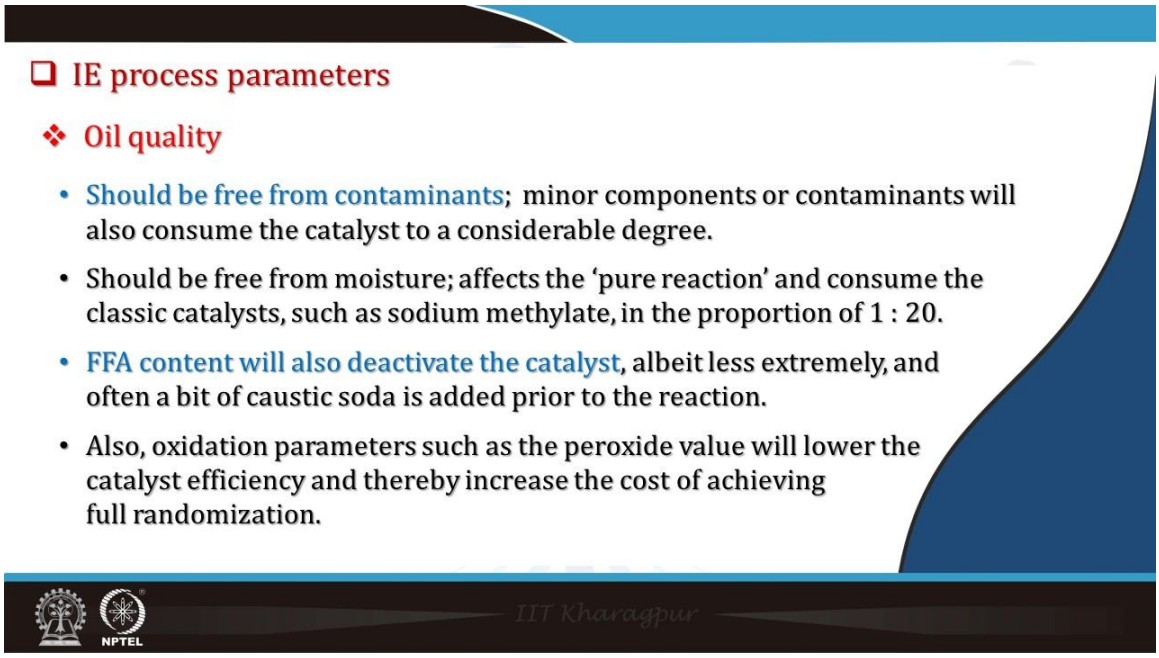
Glycerylate anion

- In this reaction, the alkylate ion (nucleophile) adds on to the slightly positively-charged carbonyl carbon at one of the three fatty acylglycerol ester bonds and forms a tetrahedral intermediate.
- The fatty acid methyl ester is then released, regenerating a glycerylate anion for further reaction.
- The glycerylate anion acts as a catalyst and transfer acyl group around the glycerol.
- It should be noted that with the carbonyl addition mechanism, both intra- and interesterification reactions are possible.

The other is the carbonyl addition as you can see here In this reaction, the alkylate ion (nucleophile) adds on to the slightly positively-charged carbonyl carbon at one of the three fatty acylglycerol ester bonds and forms a tetrahedral intermediate. The fatty acid methyl ester is then released, regenerating a glycerylate anion for further reaction. The glycerylate anion acts as a catalyst and transfer acyl group around the glycerol. So, it should be noted that with the carbonyl addition mechanism both intra and inter esterification reactions are possible that is within the same triglyceride or in various triglyceride molecules also.



Acids, bases and their corresponding salts and metals are used for the IE which can be subdivided into high and low temperature groups. The term ‘‘interesterification’’ is often used to describe reactions that involve the exchange of acyl residues between an ester and an acid (acidolysis), an ester and an alcohol (alcoholysis), or an ester with another ester (trans-esterification). High temperature catalysts include metal salts such as chloride, carbonates, oxides, nitrates and acetates of zinc, lead, iron, tin and cobalt. Low temperature catalysts includes alkylates (methylate and ethylate) of Na and Na/K alloy. Alkylates of Na are simple to use and inexpensive; only small quantities are required and they are active at low temperature less than 50 degree Celsius.



In inter esterification process, one important parameter is the oil quality. Oil should be free from contaminants; minor components or contaminants will also consume the catalyst to a considerable degree. Should be free from moisture; affects the 'pure reaction' and consume the classic catalysts, such as sodium methylate, in the proportion of 1: 20. FFA content will also deactivate the catalyst, albeit less extremely, and often a bit of caustic soda is added prior to the reaction. Also, oxidation parameters such as the peroxide value will lower the catalyst efficiency and thereby increase the cost of achieving full randomization. So, the free fatty acid peroxide value etcetera should be as low as possible with the oil before the inter esterification.

Catalyst

- In the light of the interesterification reaction, the active catalyst species needs to be an electron donor.
- Pure alkali metals such as Na or K were ideal for such reactions, and in small scale operations these proved successful.
- However, for larger operations alkoxides (sodium methoxide or sodium methylate) are the principal catalyst, because of their high reaction rate at rather low temperatures.
- This catalyst allows for a relatively clean separation after the reaction.
- The applied concentrations of catalysts generally range between 0.05 and 1.5%.
- The relatively broad range of catalyst dosage is due to the large influence of the feed oil purity on the catalyst activity.

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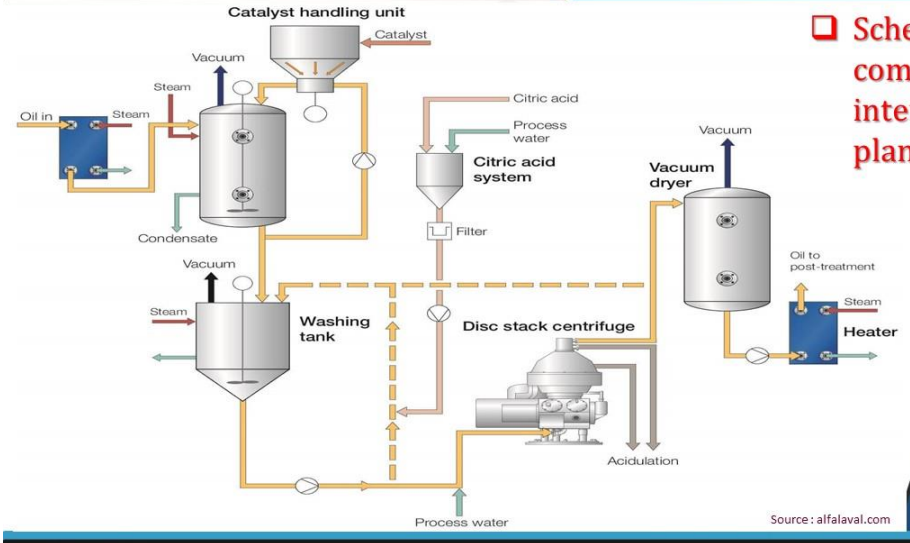
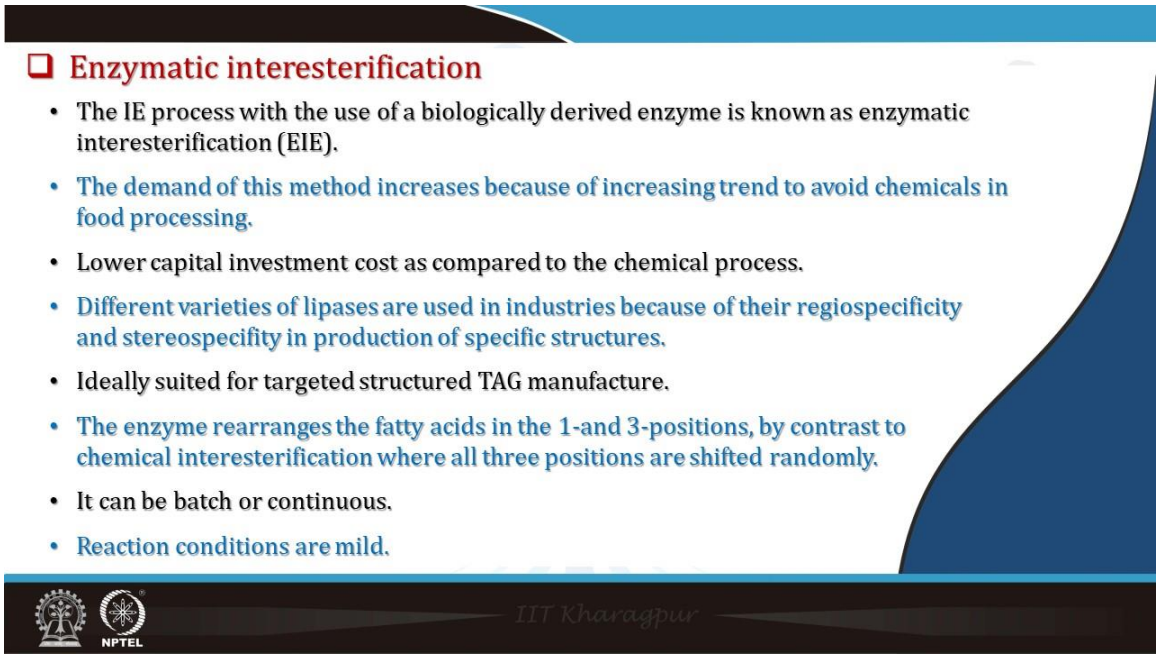
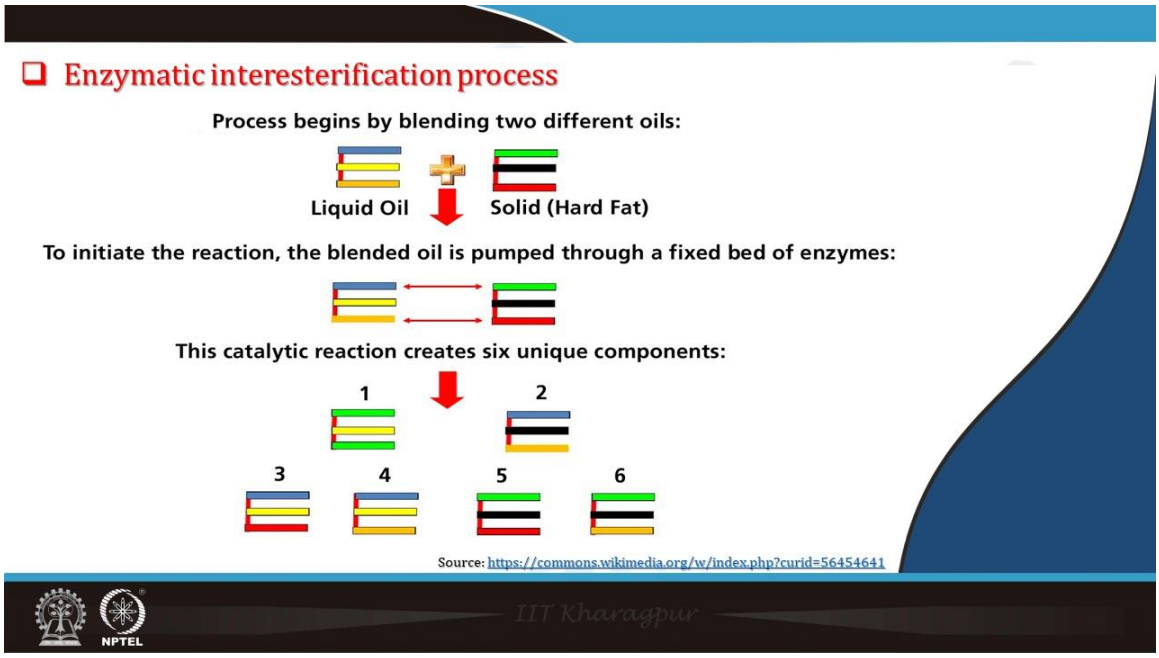
Schematic of a commercial oil interesterification plant



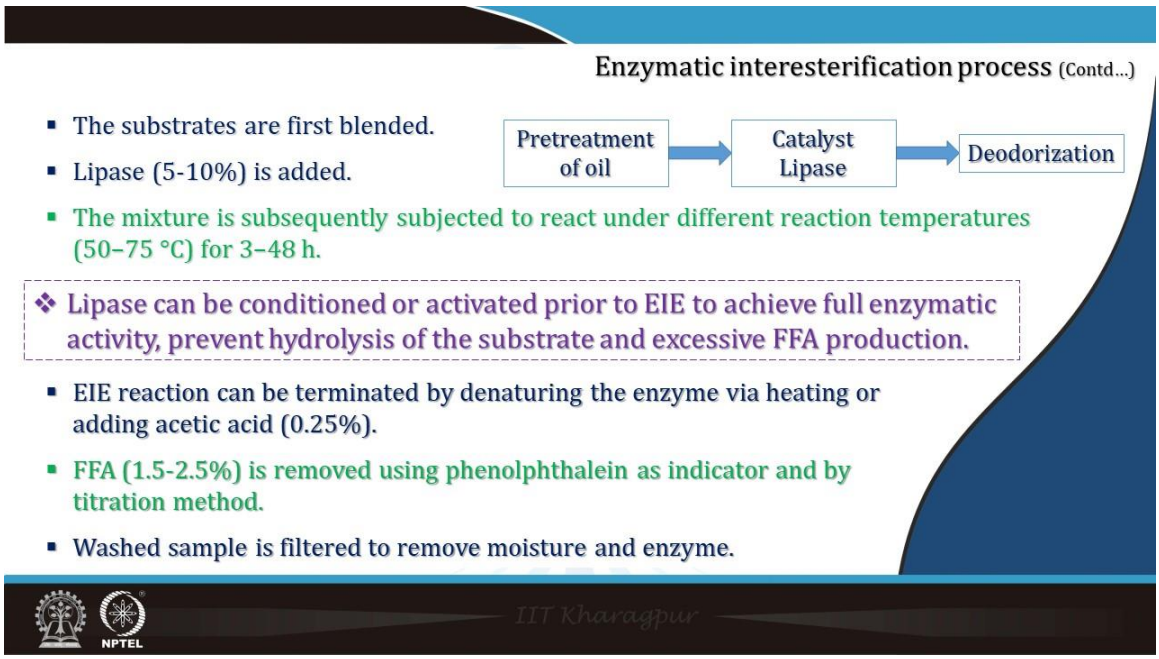
So, this is a schematic of the commercial oil inter esterification plant. The yellow line shows the oil movement. There is a catalyst handling unit, a reaction vessel, washing tank, vacuum dryer, then citric acid as a system, stack centrifuge and an oil treatment cooler. So, this is a alfalaval schematic setup they provide the inter esterification plant.



Then we come to the enzymatic inter esterification. The IE process with the use of a biologically derived enzyme is known as enzymatic interesterification (EIE). The demand of this method increases because of increasing trend to avoid chemicals in food processing. Lower capital investment cost as compared to the chemical process. Different varieties of lipases are used in industries because of their regiospecificity and stereospecifity in production of specific structures. Ideally suited for targeted structured TAG manufacture. The enzyme rearranges the fatty acids in the 1-and 3-positions, by contrast to chemical interesterification where all three positions are shifted randomly. It can be batch or continuous. Reaction conditions are mild.

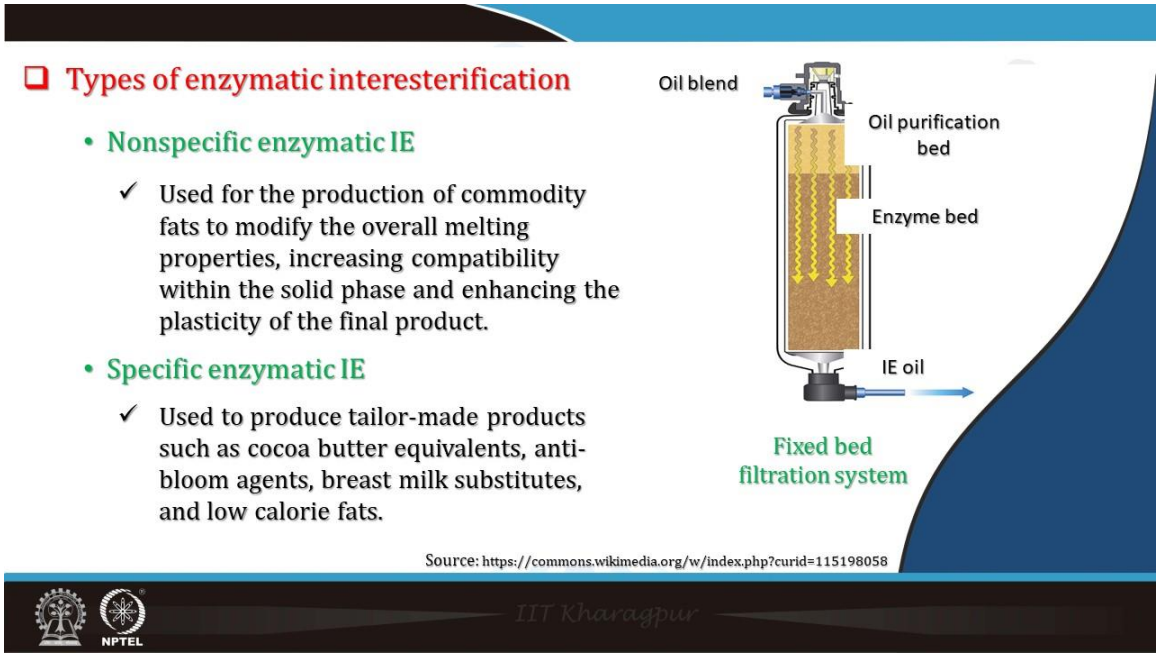


This is the enzymatic inter esterification as you can see the process begins by blending two different oils liquid oil and little solid oil of a particular consistency. These are blended and to initiate the reaction the blended oil is pumped through a fixed bed of enzymes and this catalytic reaction creates six unique components where this you see that different colors shows the different types of the fatty acids the interchange takes place.

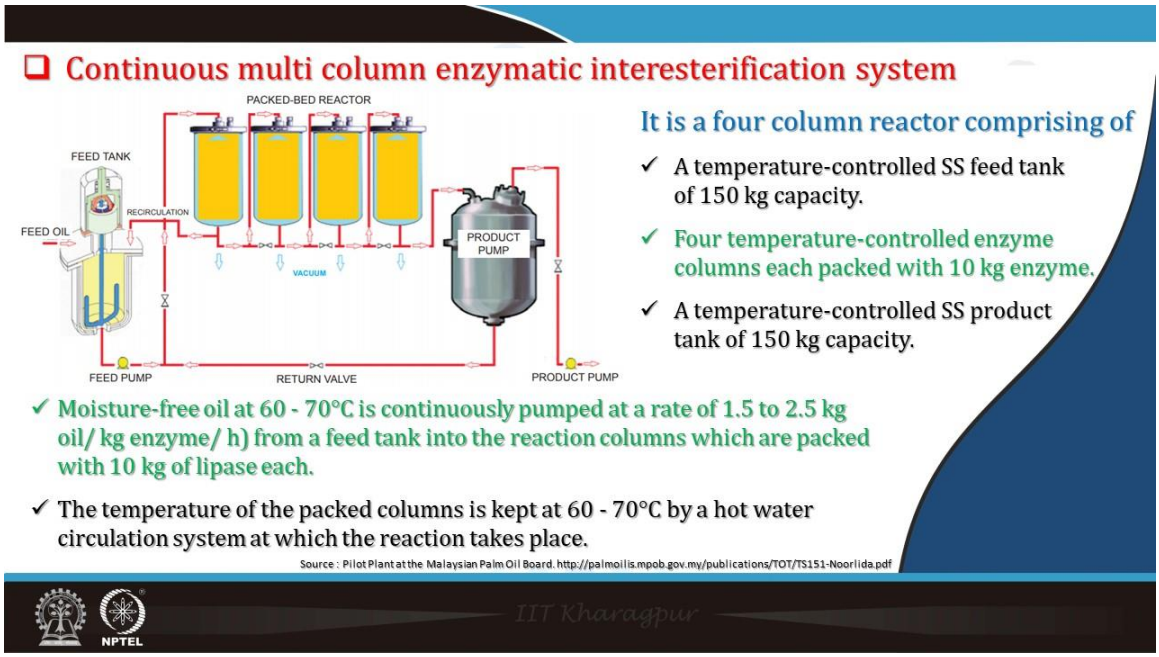


The substrate are first blended and then lipase 5 to 10 percent is added. There is pretreatment process of oil and catalyst lipase addition, deodorization, and finally, the

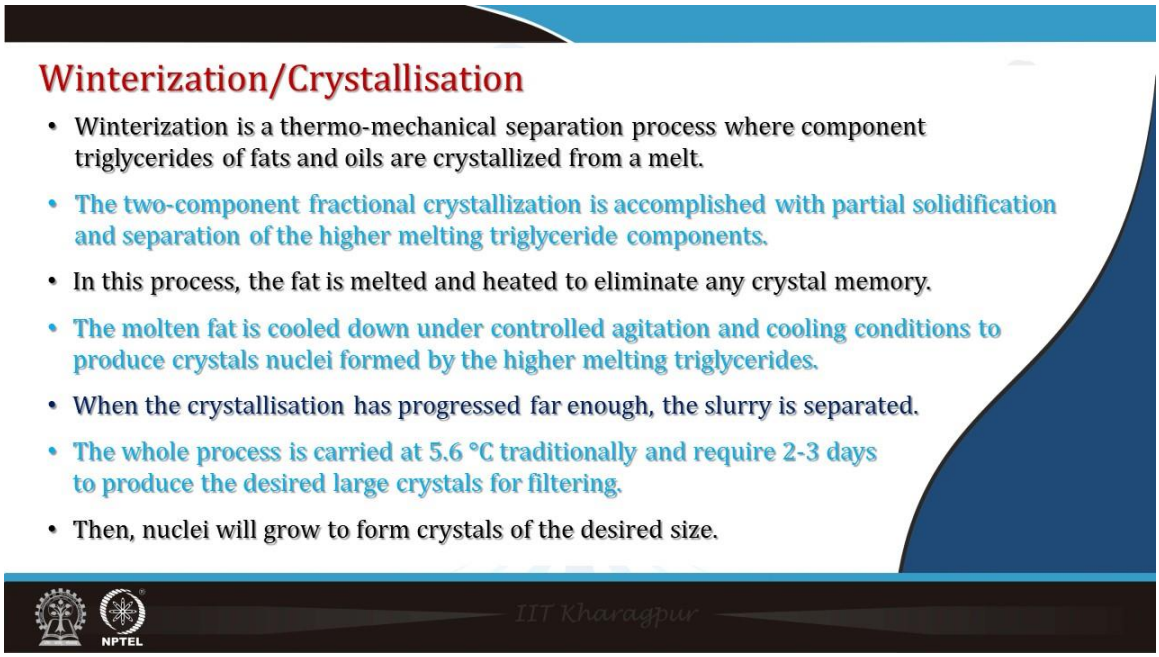
inter esterification. The mixture is subsequently subject to react under different reaction temperatures 50 to 75 degree Celsius for 3 to 48 hours. Lipase can be conditioned or activated prior to EIE to achieve full enzymatic activity, prevent hydrolysis of the substrate and excessive FFA production. Accordingly the enzyme can be properly conditioned or it can be properly activated. Enzymatic inter esterification reaction can be terminated by denaturing the enzyme via heating or adding acetic acid (0.25%). FFA (1.5-2.5%) is removed using phenolphthalein as indicator and by titration method. Washed sample is filtered to remove moisture and enzyme.



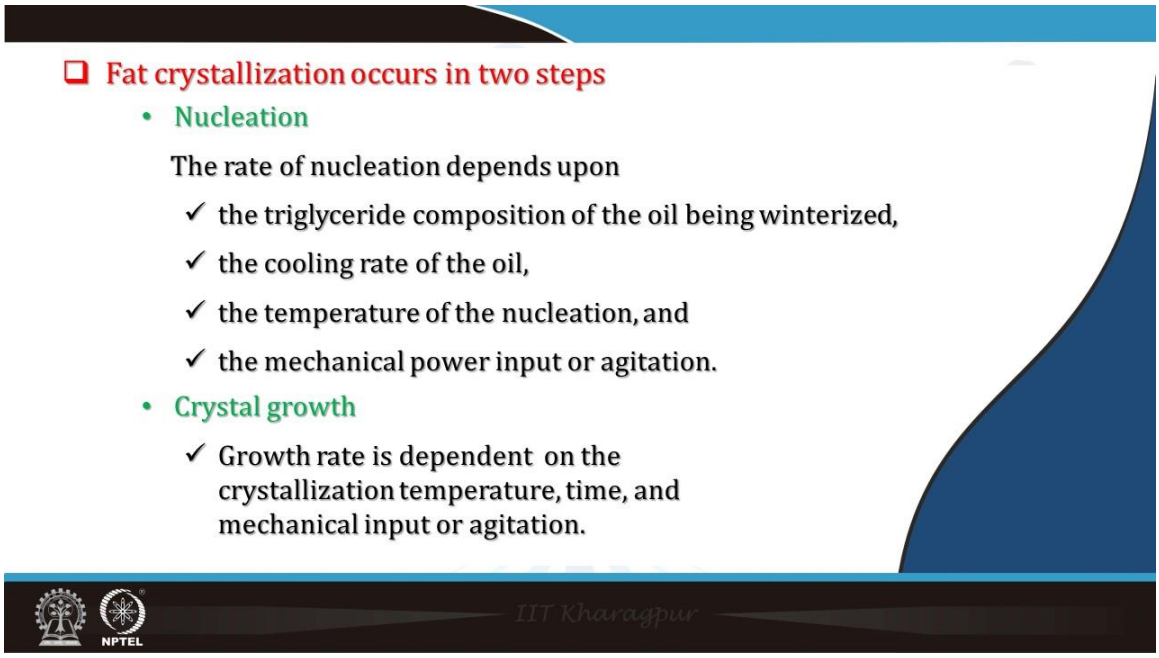
Types of enzymatic inter esterification are non specific enzymes inter esterification these are used for the production of commodity fats to modify the overall melting properties, increasing compatibility within the solid phase and enhancing the plasticity of the final product. The other type is specific enzymatic inter esterification, which to produce tailor-made products such as cocoa butter equivalents, anti-bloom agents, breast milk substitutes, and low calorie fats. Shown here is a fixed bed filtration system that is oil blend filtration with enzyme bed added and inter esterification oil is obtained.



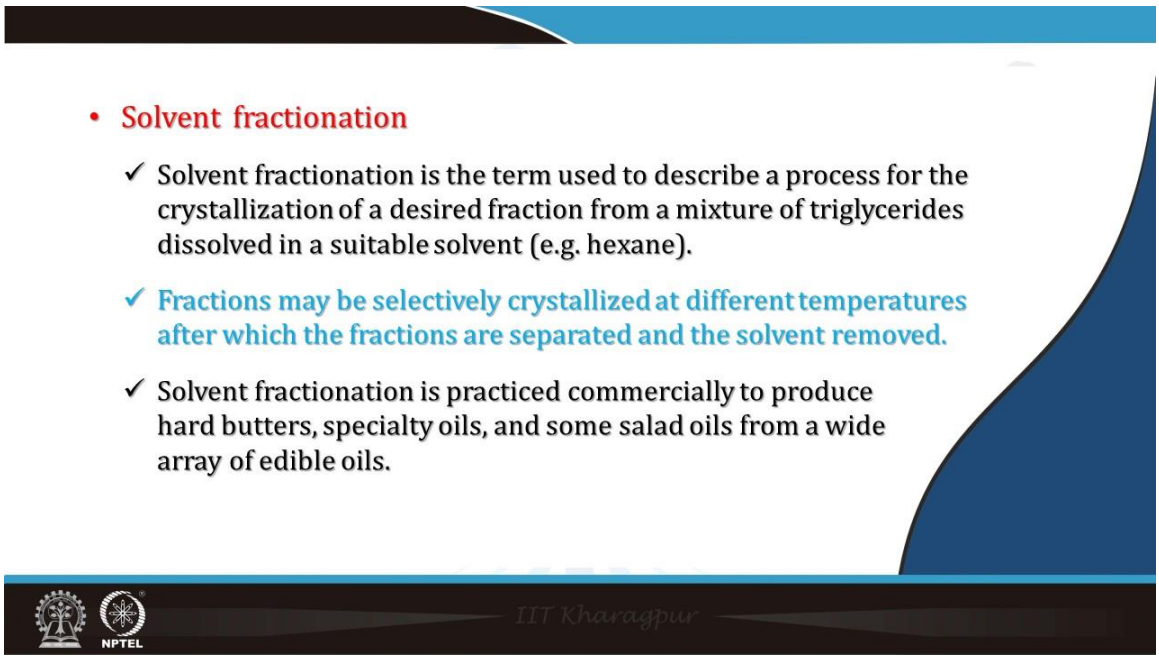
Then continuous multi column enzymatic inter esterification system. As you see it is a 4 column reactor comprising of a temperature controlled SS feed tank of 150 kg capacity. The 4 temperature controlled enzyme columns each packed with 10 kg enzyme and a temperature controlled SS product tank of around 150 kg capacity as you could see here is the figure. Moisture free oil enters in the tank at 60 to 70 degree Celsius and it is continuously pumped at a rate of 1.5 to 2.5 kg oil per kg enzyme per hour from the feed tank into the reaction columns which are packed with the 10 kg of lipase in each. The temperature of the packed column is kept at 60 to 70 degree Celsius by a hot water circulation system at which the reaction takes place and finally, inter esterified product is taken into the product container tank. So, this is a continuous operation.



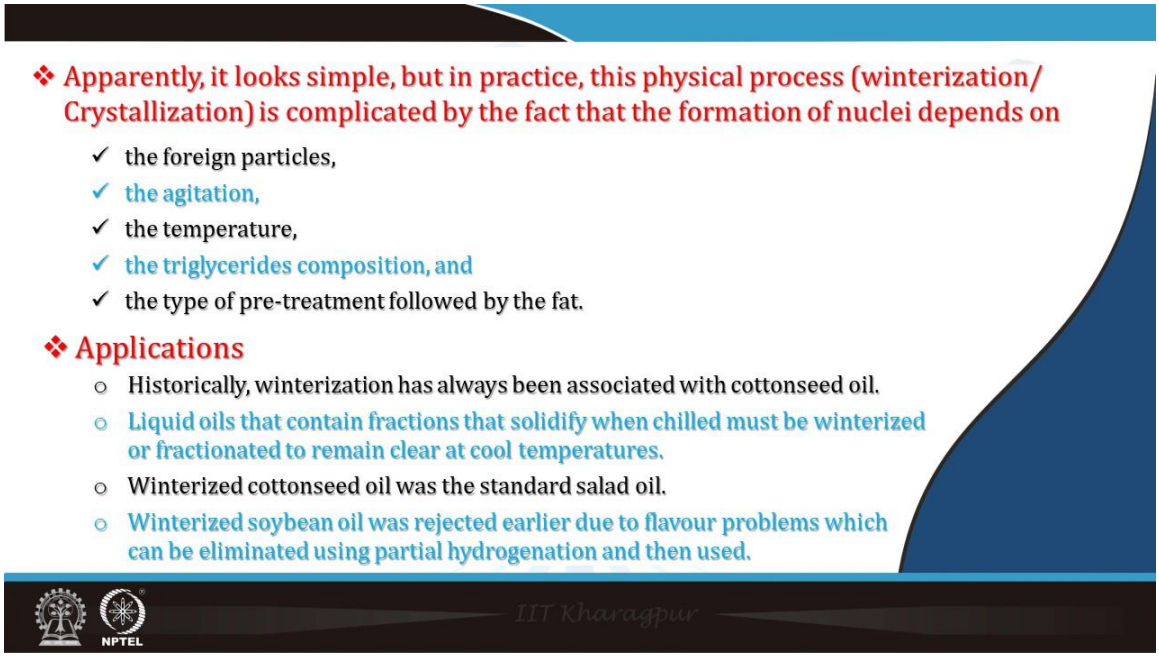
Now, we will see the crystallization or winterization process. Winterization is a thermo-mechanical separation process where component triglycerides of fats and oils are crystallized from a melt. The two-component fractional crystallization is accomplished with partial solidification and separation of the higher melting triglyceride components. In this process, the fat is melted and heated to eliminate any crystal memory. The molten fat is cooled down under controlled agitation and cooling conditions to produce crystals nuclei formed by the higher melting triglycerides. When the crystallisation has progressed far enough, the slurry is separated. The whole process is carried at 5.6 °C traditionally and require 2-3 days to produce the desired large crystals for filtering. Then, nuclei will grow to form crystals of the desired size. So, basically the here the oil is cooled down and that is the cool down which is kept. So, this oils that is crystals are formed they are converted into form crystals that is the crystallization process.



Fat crystallization occurs in two steps. One is the nucleation and then the growth of the crystal. In the nucleus the rate of nucleation depends upon the triglyceride composition of the oil being winterized, the cooling rate of the oil, the temperature of the nucleation and the mechanical power input or agitation. Then once the nucleus is formed then crystal enlarges. The growth rate is dependent on the crystallization temperature time and mechanical input or agitation. So, on this the growth of the crystal will take place it will vary.

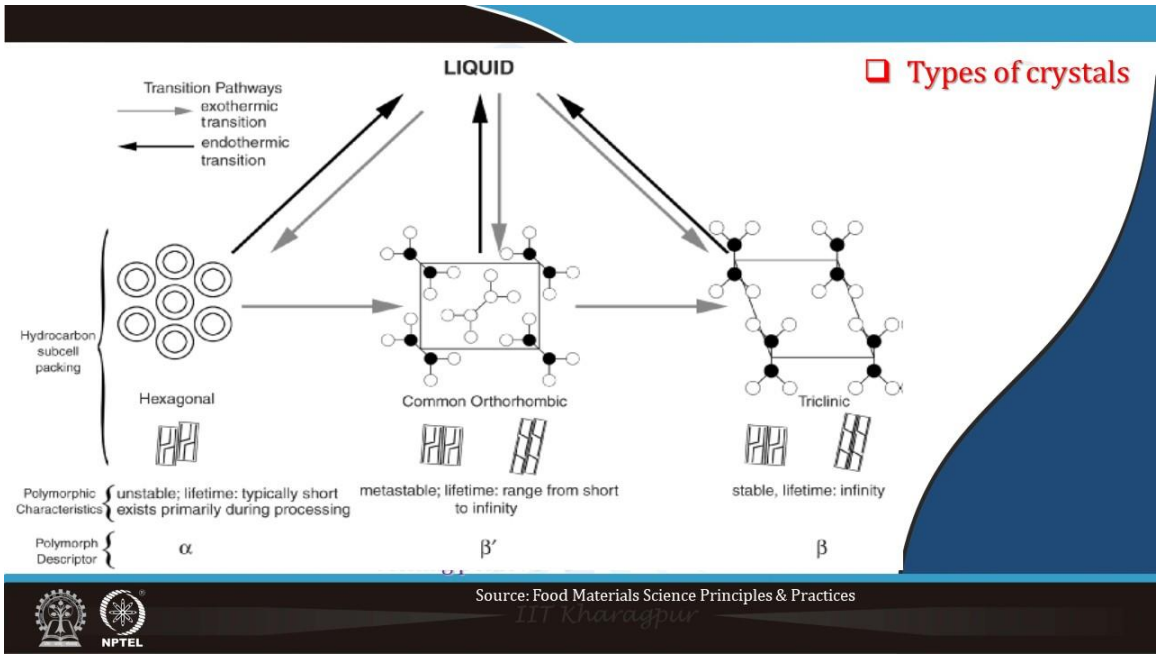


Then there is also a solvent fractionation. Solvent fractionation is the term used to describe a process for the crystallization of a desired fraction from a mixture of triglycerides dissolved in a suitable solvent (e.g. hexane). Fractions may be selectively crystallized at different temperatures after which the fractions are separated and the solvent removed. Solvent fractionation is practiced commercially to produce hard butters, specialty oils, and some salad oils from a wide array of edible oils.



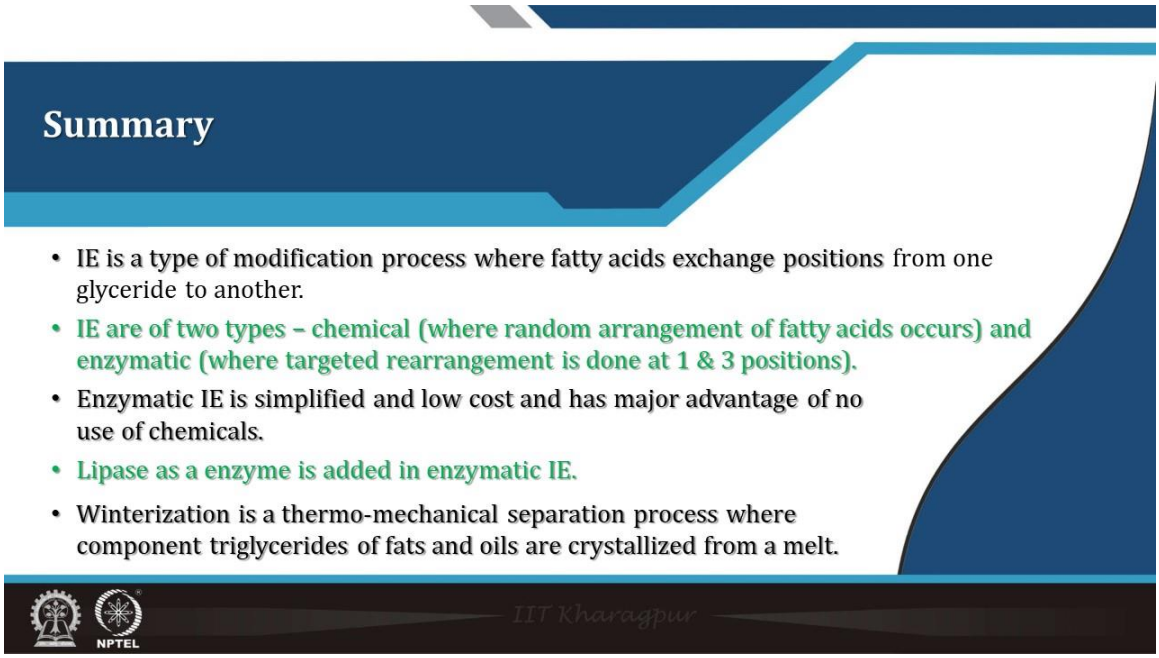
Apparently this crystallization or winterization process looks very simple, but in practice this physical process is complicated by the fact that the formation of nuclei depends upon the presence of any foreign particles that is if there is any more foreign particles present in the oil more number of nuclei will be formed. Even the proper agitation of the oil, the proper temperature, the triglyceride composition and the type of pretreatment followed by that is given to the oil or fat. Even the triglyceride composition that is other it is a mixture of triglyceride with the fatty acids, nature of the fatty acid, long chain fatty acids, short chain fatty acid, unsaturated fatty acid, saturated all these combinations and permutations will influence the crystal nucleus formation, and the crystal growth also and even at the sub cellular level the molecular packing of these crystals is very important. The processes are commercially done for winterization, process are properly controlled crystallization process tempering that is to remove the heat of crystallization at a proper level to get the proper size, fat etcetera for a specialty uses like margarine etcetera are produced by this winterization and crystallization process. That is application of this crystallization process. Historically winterization has always been associated with the cottonseed oil. Liquid oils that contain fractions that solidify when chilled must be winterized or fractionated to remain clear at cool temperatures. Winterized cottonseed oil was the standard salad oil. Winterized soybean oil was rejected earlier due to flavour

problems which can be eliminated using partial hydrogenation and then used. Even sometime if you keep oil at the low temperature then solid impurity settle at the bottom and this is also used for the clarification, this winterization or this further you go that is the fractionation crystallization, which is a fractionation separation process as well.



As I was telling that even when you crystallized oil, depending upon the nucleus formation and then further conditions like controlled removal of the latent heat of the crystallization it will result in formation of the different polymers with various crystals packing at the cellular level. And depending upon that different forms like alpha forms, beta forms and beta prime forms, that is having different melting curve points like alpha form has a melting point of 54 degree Celsius, beta crystals have melting point of 64, alpha crystals have melting point of 54 degree Celsius, beta crystals they have melting point of 50, 64 degree Celsius and beta prime has melting point of 73 degree Celsius can be formed. And even all these beta prime has a more suitability in the use of the bakery fats etcetera because of their property they helps in incorporation of more amount of air with smaller bubbles and it gives a good textural characteristics in the baked products. So, that is the benefits of the proper crystallization, winterization we can get the fats or polymers specific polymers for a specific uses. So, you see here how the liquid is there transition pathways that is exothermic transition and endothermic transition, proper control if you do, then it give that is the alpha form. It is a hexagonal form where hydrocarbons are self-packing. And the polymorphic characteristics of the alpha form leads to unstable lifetime typically short. Then this beta form is a more stable it is a triclinic form. Beta-prime is a common ortho forming orthorhombic form you can see, the circular crystal packing how it is there. So, it has a meta stable lifetime and ranges from short to infinity that is the beta prime. If proper controlled crystallization is done,

you will get either alpha form, beta prime form or beta prime and then it gives the polymers suitable for particularly specific operations as in margarine or in the bakery product or confectionery product.



So, with this now I will summarize this lecture that inter esterification is a type of modification process where fatty acids exchange positions from one glyceride to another. IE are of two types – chemical (where random arrangement of fatty acids occurs) and enzymatic (where targeted rearrangement is done at 1 & 3 positions). Enzymatic IE is simplified and low cost and has major advantage of no use of chemicals. Lipase as an enzyme is added in enzymatic IE.

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