Food Oils and Fats: Chemistry & Technology

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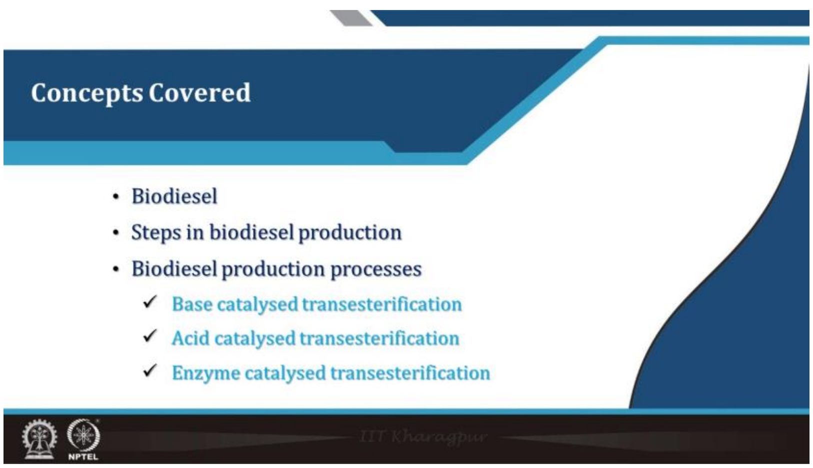
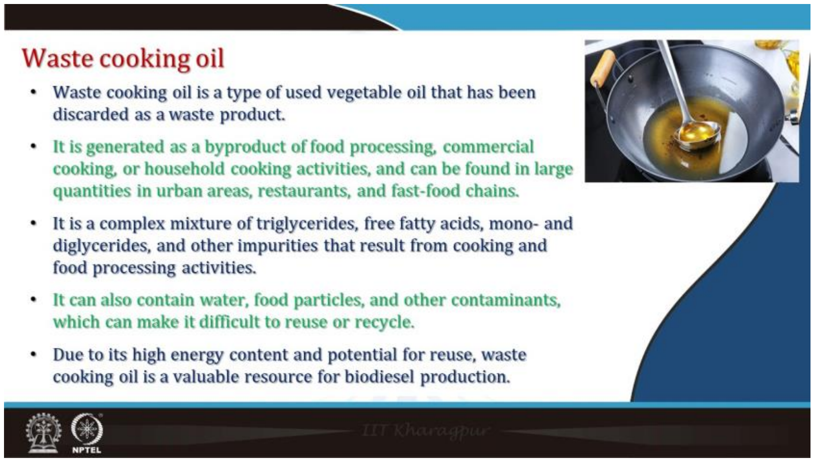
Module 11: By-products Utilisation & Valorisation of Oil Milling Industry Waste

Lecture 55: Biodiesel Production from Waste Cooking Oil

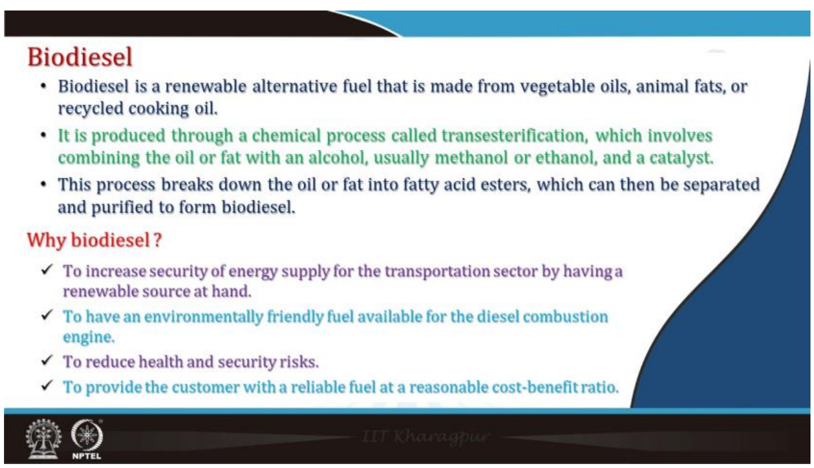
Hello everybody. Namaskar. Now, we are in lecture 55.



In this lecture, in the next half an hour or so, we will talk about another very important aspect of the by-product utilization and valorization of oil milling industry waste. We will talk about biodiesel production from waste cooking oil. The topics which we cover today is biodiesel, what are the steps in biodiesel production and biodiesel production processes like base catalyzed transesterification, acid catalyzed transesterification, and enzyme catalyzed transesterification processes.

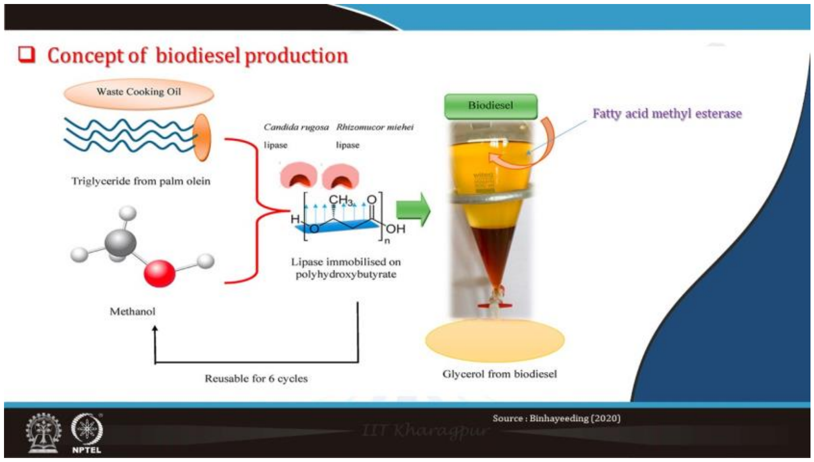


So, let us talk about waste cooking oil. It is a type of used vegetable oil that has been discarded as a waste product. Many times, it has because when the oil is heated, then it goes to polymerization and other various reactions and it develops very dark colour and it is not useful. Rather many times there are some undesirable or toxic compounds etc. may form in the polymerized products, may be toxic. It is a waste cooking oil as I told you generated by the byproduct of food processing, commercial cooking, or household cooking activities and can be found in large quantities in urban areas, restaurants, and fast-food chains. So, it is a complex mixture of triglyceride that is the waste cooking oil or hot polymerized cooking oil; heated oil contains triglyceride, free fatty acids, mono- and di-glycerides, other impurities that result from cooking and food processing activities. It can also contain water, food particles, and other contaminants, which can make it difficult to reuse or even recycle. Due to its high energy content and potential for reuse, waste cooking oil is a valuable resource for biodiesel production.

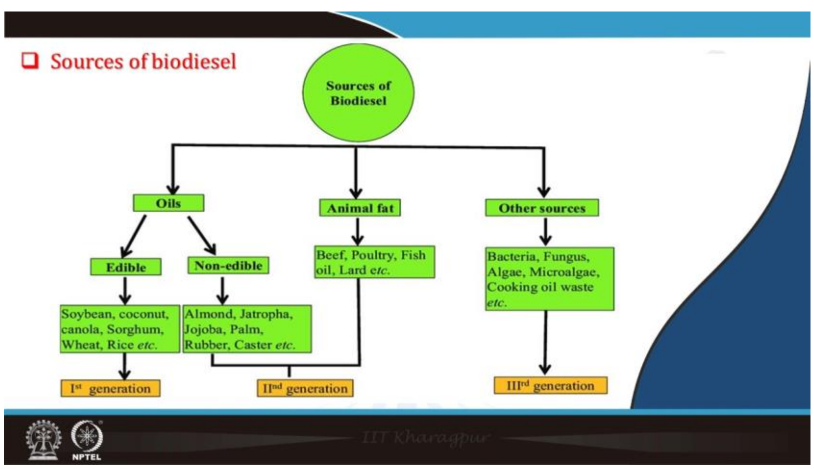


Biodiesel is a renewable alternative fuel that is made from vegetable oils, animal fats or recycled cooking oil. It is produced through a chemical process called transesterification, which involves combining oil or fat with an alcohol usually methanol or ethanol as a catalyst. This process breaks down the oil or fat into fatty acid esters, which can then be separated and purified to form biodiesel.

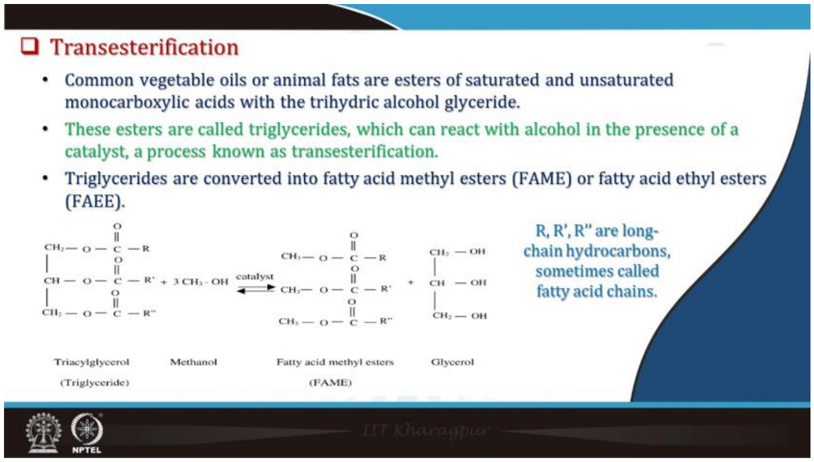
Now why biodiesel? This biodiesel increases security of energy supply for the transportation sector by having a renewable source at hand. It gives an environmentally friendly fuel available for the diesel combustion engine. It is used to reduce health and security risks as well as to provide the customer with a reliable fuel at a reasonable cost-benefit ratio.



So, this is the concept of biodiesel production. I told you that is the waste cooking oil which has various triglycerides, palm olein and other compounds, and this triglyceride may be example palm olein etc., then it is treated with methanol which is reusable for 6 cycles methanol and then you can see lipase these enzymes. So, this, lipase immobilized on the polyhydroxybutyrate and then it is into the reaction mixture it is broken into fatty acid methyl esterase enzymes is there. So, it gives biodiesel as well as glycerol is recovered from the biodiesel. So, this is the concept that is the triglyceride it is treated with methanol, methanol act as a catalyst and then it gives the fatty acid methyl ester that is, it breaks the methyl fatty ester is formed and it gives the biodiesel as well as glycerol.

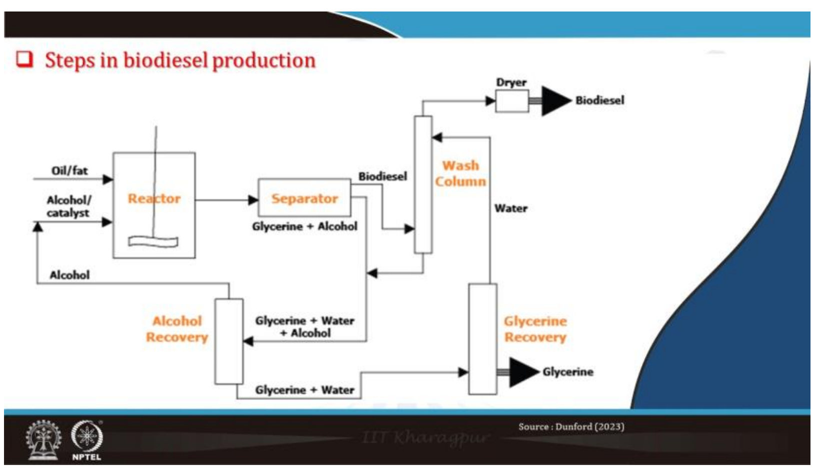


Sources of biodiesel include that is oils, animal fats, or other sources. In the oils, it may be edible oil like soybean, coconut, canola, sorghum, etc., they are considered the first-generation oil sources. Whereas, the second-generation oils include non-edible oils like almond, jatropha, jojoba, palm, rubber, castor or even beef, poultry, fish oil, lard etc., they are the second-generation sources. The third-generation sources of biodiesel include the bacteria, fungus, algae, microalgae, or cooking oil waste etc.

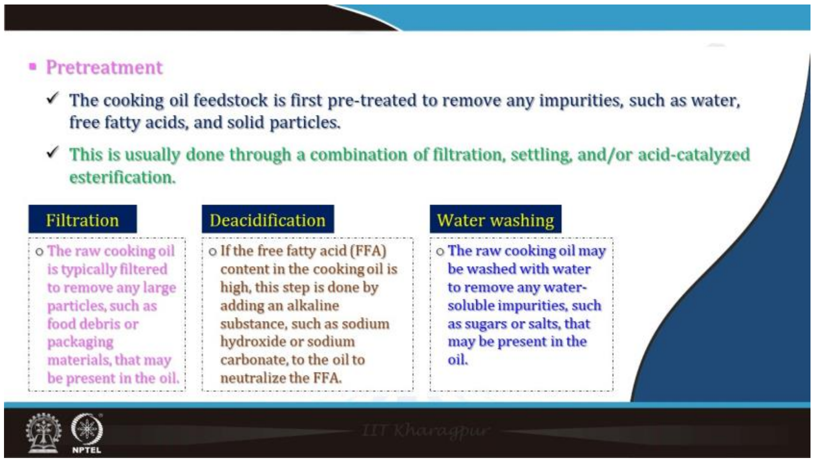


Then the transesterification process. The transesterification basically is the process which gives the biodiesel. So, it is common vegetable oils or animal fats or esters of saturated and unsaturated monocarboxylic acid with trihydric alcohol glyceride that we discussed earlier also several times. So, these esters are called triglycerides, which can react with alcohol in the presence of a catalyst, which is the process known as a transesterification.

The reaction between triglyceride and alcohol in the presence of a catalyst. So, triglycerides are converted into fatty acid methyl esters (FAME) or fatty acid ethyl ester depending upon whatever the alcohol is. So, you can see the reaction triglyceride plus methanol it gives fatty acid methyl ester and plus glycerol is liberated.

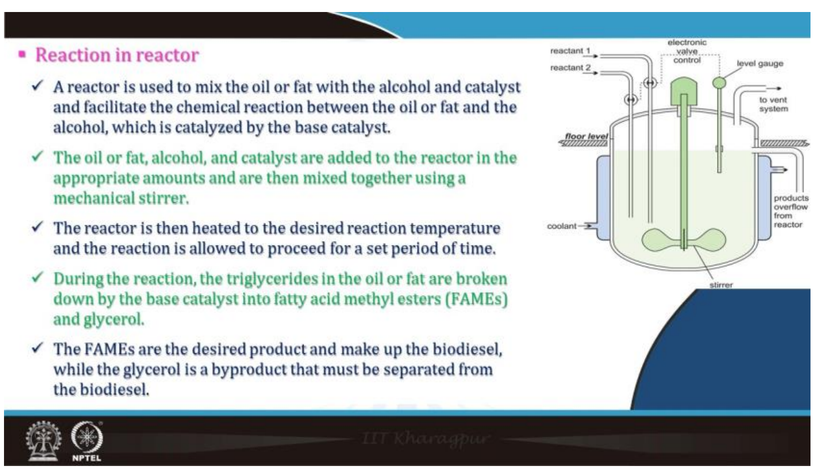


Steps in biodiesel production. It was reported by Dunford in 2023 recently, that is, the oil and fat it is fed into the reactor and then alcohol as a catalyst they are fed into the reactor and here the reaction takes place, fatty acid methyl ester is formed then they are passed through the separator where glycerine and alcohol are separated. The glycerine portion may come contain some water plus alcohol as well. So, this is sent for alcohol recovery and the alcohol goes further recycle further reaction and some glycerine plus water, it goes to the glycerine recovery and water which is evaporated goes through wash column and again recycled. From the separator, where glycerine plus alcohol and the biodiesel goes into where it is sent to the wash column, dryer and biodiesel is obtained. So, this gives a simplified step for production process of the biodiesel.



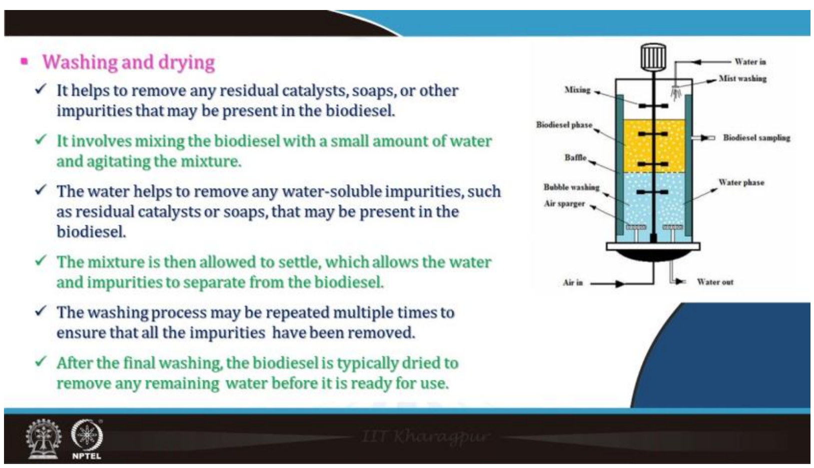
So, the pretreatment here, the cooking oil feedstock is first pretreated to remove any impurities such as water, free fatty acids, solid particles, etc. This is usually done through a combination of filtering, settling, and/or acid-catalyzed esterification process.

In filtration, the raw cooking oil is typically filtered to remove any large particles, such as food debris or packaging materials, that may be present in the oil. Then it is passed through deacidification, in the deacidification, if the free fatty acid content in the cooking oil is high. This step is done by adding an alkaline substance, such as sodium hydroxide or sodium carbonate, etc. to the oil to neutralize the free fatty acid and then water washing. The raw cooking oil may be washed with the water to remove the water-soluble impurities such as sugar, salts that may be present in the oil.

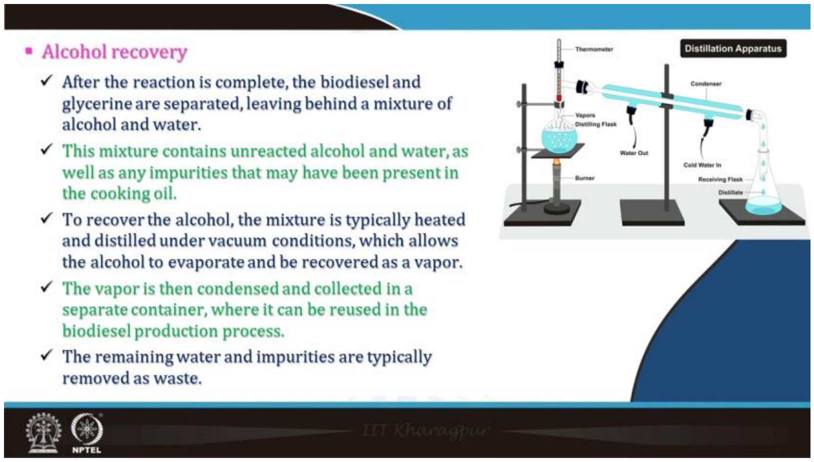


Then in the reactor which you have seen, that is, where alcohol and these reactants they are used. So, the reactor is used to mix the oil or fat with the alcohol and the catalyst to facilitate the chemical reaction between the oil or fat and the alcohol, which is catalyzed by the base catalyst. The oil or fat, alcohol, and catalyst are added to the reactor in the appropriate amounts and are then mixed together using a mechanically stirrer. You can see here. This reactor is then heated to the desired reaction temperature and the reaction is allowed to proceed for the desired period of time. During the reaction, the triglycerides in the oil and fat are broken down by the base catalyst into the fatty acid methyl ester and glycerol. The fatty acid methyl esters are desired product and make the biodiesel, while the glycerol is a byproduct that must be separated from the biodiesel.

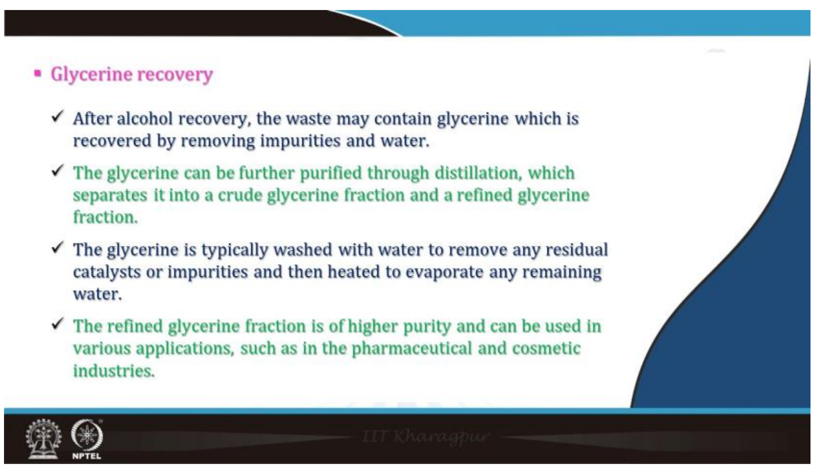
Then after the reactor, it is passed through the separators to separate the biodiesel from the glycerine. There are several types of separators that can be used for this purpose including settling tanks, centrifuges, or the decanters.



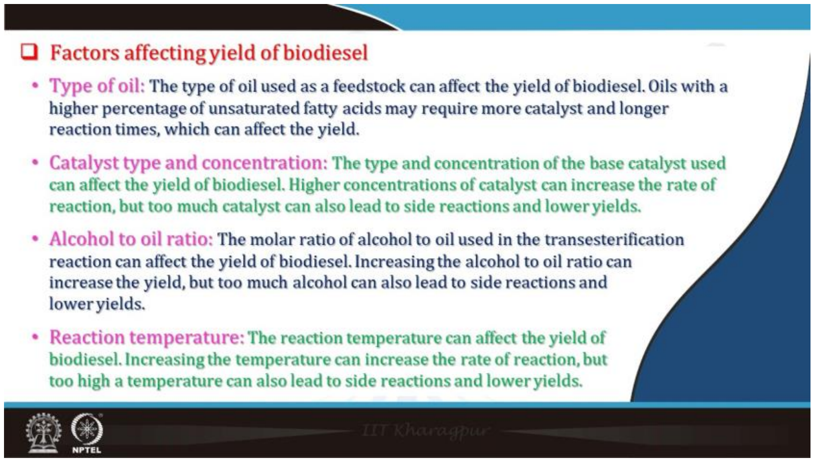
Then after that, it goes to the drying. Washing and drying helps to remove any residual catalysts, soaps, or other impurities that may be present into the biodiesel. It involves mixing the biodiesel with a small amount of water and agitating the mixture in the reactor. The water helps to remove any water-soluble impurities such as residual catalysts or soaps that may be present in the biodiesel. The mixture is then allowed to settle which allows the water and impurities to separate from the biodiesel. The washing process may be repeated multiple times to ensure that all the impurities have been removed. After the final washing, the biodiesel is a typically dried to remove any remaining water before it is ready for use.



Then alcohol recovery. After the reaction is complete, the biodiesel and glycerine are separated, leaving behind a mixture of alcohol plus water. The mixture contains unreacted alcohol and water, as well as any impurities that may have been present in the cooking oil. So, to recover the alcohol, the mixture is typically heated and distilled under vacuum conditions which allows the alcohol to evaporate and recovered as a vapour. The vapour is then condensed and collected in a separate container, where it can be reused in the biodiesel production process. The remaining water and impurities are typically removed as a waste.

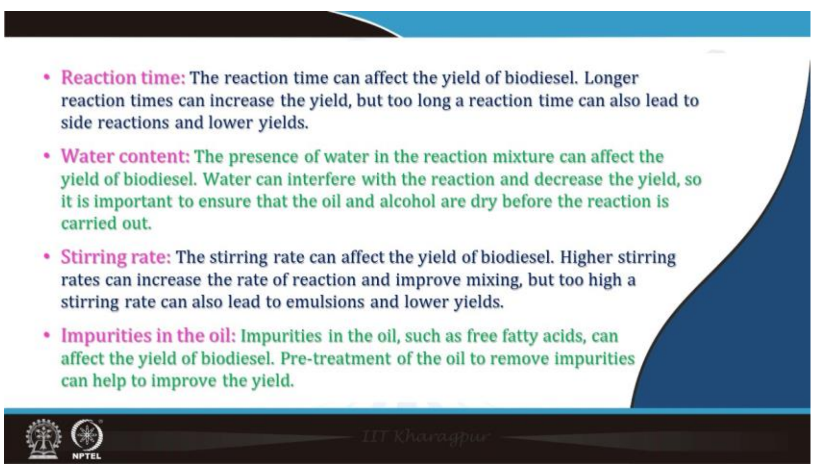


Then glycerine recovery, that is after alcohol recovery the waste may contain glycerine, which is recovered by removing impurities and water. The glycerine can be further purified through distillation, which separates it into a crude glycerine fraction and refined glycerine fraction. The glycerine is typically washed with water to remove any residual catalysts or impurities and then heated to evaporate any remaining water. The refined glycerine fraction is of higher purity and can be used in various applications such as in the pharmaceutical as well as in the cosmetic industry.



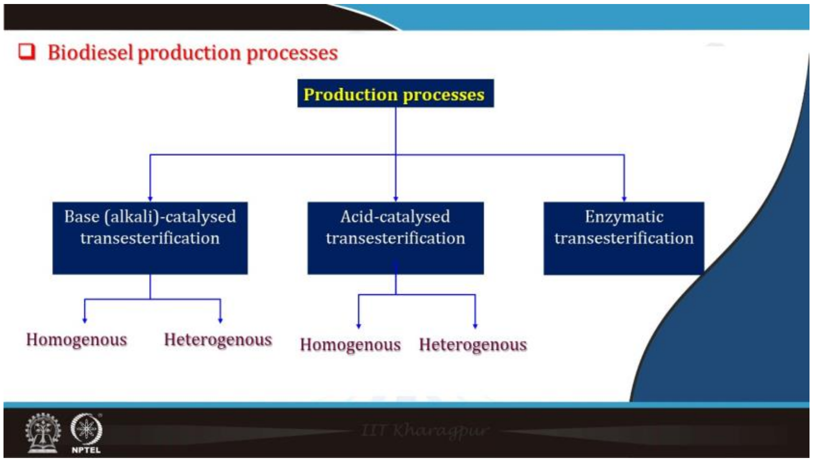
The factors affecting yield of biodiesel, that is, one is the type of oil. Oil used as a feedstock can affect the yield of biodiesel. Oils with a higher percentage of unsaturated fatty acids may require more catalyst and larger reaction time which can affect the yield. The type and concentration of the base catalyst used can affect the yield of biodiesel. Higher concentration of catalyst can increase the rate of reaction, but too much catalyst can also lead to side reactions and it may lower the yield.

Alcohol to oil ratio is another important factor. The molar ratio of alcohol to oil used in the transesterification process can affect the yield. Increasing the alcohol to oil ratio can increase the yield, but too much alcohol can also lead to side reactions and lower yields. Reaction temperature can affect the yield of biodiesel. Increasing the temperature can increase the rate of reaction, but too high a temperature can also lead to side reactions and which may lower the yield.

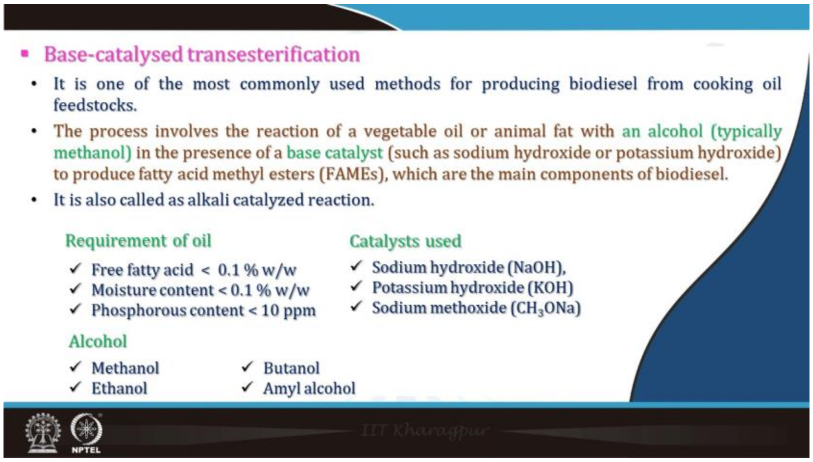


Reaction time can increase the yield, but too long a reaction time can also lead to side reactions and lower yields. The presence of water in the reaction mixture can affect the yield of biodiesel. Water can interfere with the reaction and decrease the yield. So, it is important to ensure that the oil and alcohol are dry before the reaction is carried out.

The stirring rate can affect the yield of biodiesel. Higher stirring rates can increase the rate of reaction and improve mixing, but too high a stirring can also lead to the emulsion and lower yields. Then impurities in the oil such as free fatty acids, can affect the yield of biodiesel. Pre-treatment of the oil to remove impurities can help to improve the yield.

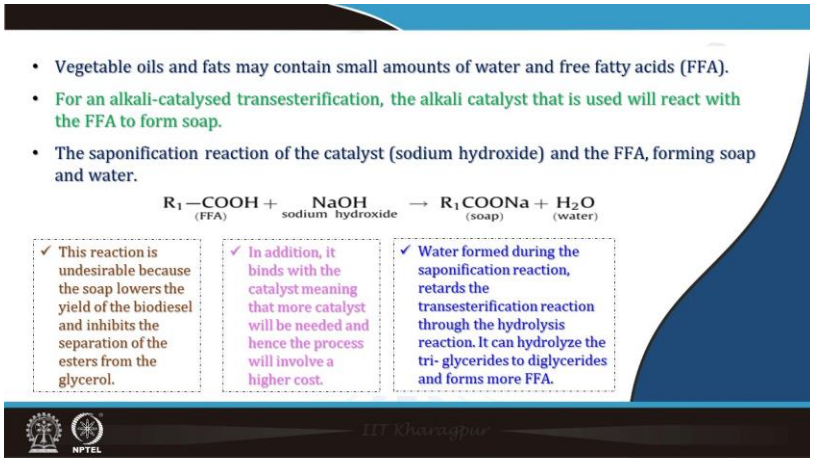


Then biodiesel production processes are base (alkali)-catalyzed transesterification, acid-catalyzed transesterification, or enzymatic transesterification. Both acid and alkali catalyzed transesterification can be homogeneous or heterogeneous.



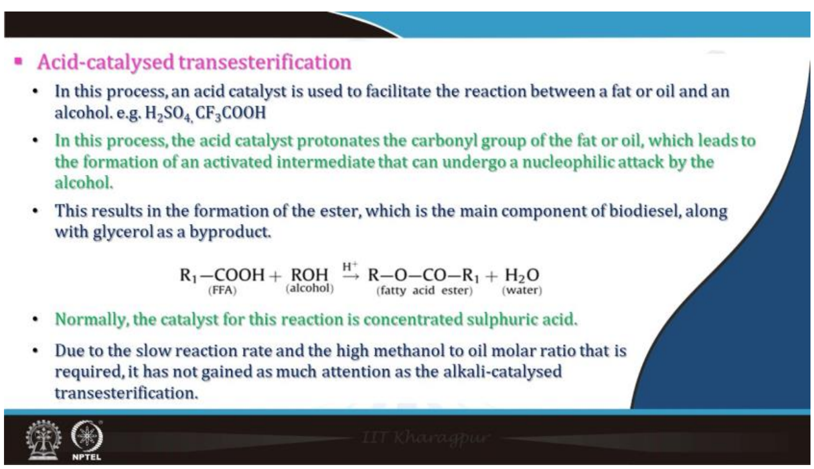
Base-catalyzed transesterification is the most commonly used method for producing biodiesel from cooking oil feedstocks. The process involves the reaction of a vegetable oil or animal fat with an alcohol typically methyl alcohol in the presence of a base catalyst such as sodium hydroxide or potassium hydroxide to improve fatty acid methyl esters, which is the main component of the biodiesel. It is also called as alkali catalyzed reaction.

So, requirement of the oil, there it should be free fatty acid less than 0.1 percent weight by weight, moisture content it should be less than 0.1 percent weight by weight and phosphorus content less than 10 ppm. The other catalysts which are used are sodium hydroxide, potassium hydroxide, or sodium methoxide. The alcohols can be used are methanol, ethanol, butanol, or amyl alcohol.

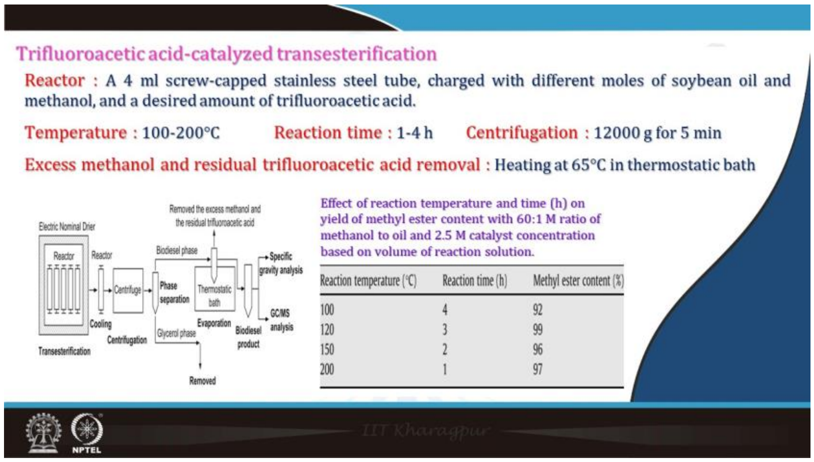


Vegetable oils and fats may contain a small amount of water and free fatty acids. For an alkali catalyzed transesterification, the alkali catalyst that is used will react with FFA to form the soap. The saponification reaction of the catalyst and the FFA form the soap and water.

The reaction is undesirable because the soap lowers the yield of biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve higher cost. Water formed during the saponification reaction, retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more free fatty acids.



Acid-catalyzed reaction is used in sulphuric acid or trifluoroaceticacids. In this process, the acid catalysts protonates the carbonyl group of the fat or oil, which leads to the formation of an activated intermediate that can undergo a nucleophilic attack by the alcohol. This results in the formation of ester, which is the main component of biodiesel along with the glycerol as a byproduct. That is the fatty acid ester is formed. Fatty acid plus alcohol gives fatty acid ester plus water. Normally the catalyst for this reaction is concentrated sulphuric acid. Due to slow reaction rate and the high methanol to oil molar ratio that is required, it has not gained as much attention as the alkali catalyzed transesterification.

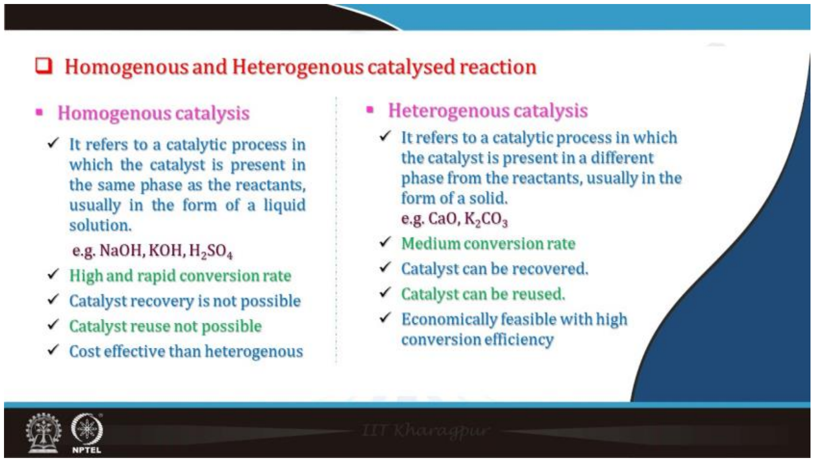


Trifluoroacetic acid-catalyzed transesterification, here a 4 ml screw-capped stainless-steel tube is charged with the different moles of soybean oil and methanol, and a desired amount of trifluoroacetic acid. Temperature is generally 100 to 200 degree Celsius. Reaction time may be 1 to 4 hours. Centrifugation is given to 12000 g for 5 minutes and excess methanol and residual trifluoroacetic acids removed by heating at 65 degree Celsius in thermostatic baths.

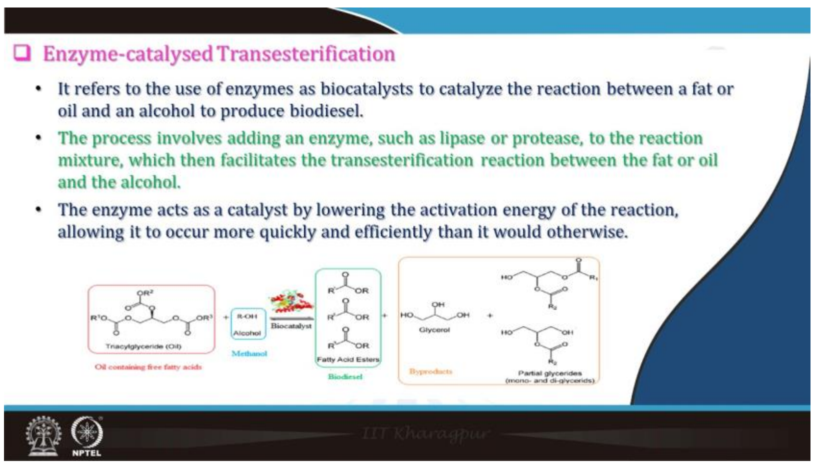
The figure shows here that is transesterification after that this is the cooled, it goes to the centrifugation and phase separation and you get the biodiesel phase as well as the other evaporators you get biodiesel product.

The effect of reaction temperature and time on the yield of methyl ester is 60:1 M ratio of methanol to oil and 2.5 M catalyst concentration bound on oil. The reaction time is given here in the table. You can see that, at 100 degree Celsius, reaction time is 4 hours it gives around 92 percent methyl ester; at 120 degree Celsius, 3 hours reaction time, it gives 99 percent methyl ester. So, if the temperature is increasing obviously, reaction time will reduce and you get more methyl ester content.

Homogeneous and heterogeneous catalyzed reactions, that is homogeneous catalysis, it refers to a catalytic process in which the catalyst is present in the same phase as the reactants, usually in the form of a liquid solution like sodium hydroxide, potassium hydroxide, sulphuric acid etc. It has high and rapid conversion rate, the catalyst recovery is not possible, in this case, catalyst reuse not possible therefore, and it is a cost effective then heterogeneous formation.

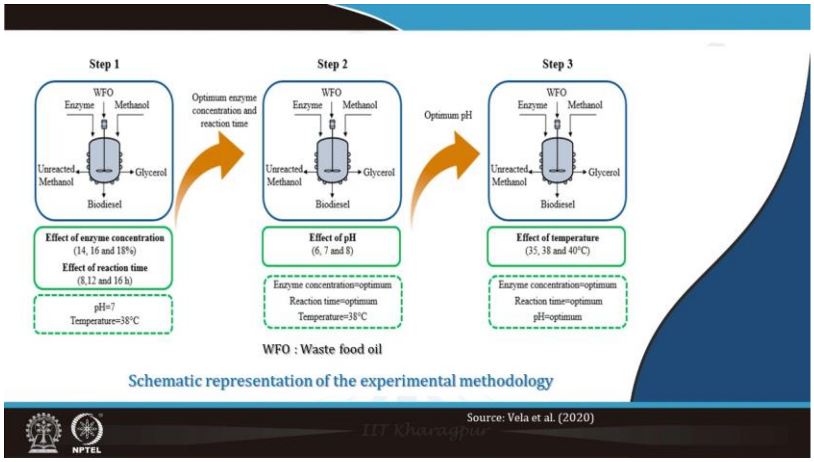


Heterogeneous catalysis, it refers to a catalytic process in which the catalyst is present in a different phase than that of the reactants and usually it is in the solid phase like calcium oxide, potassium carbonate etc. It has a medium conversion rate, catalyst can be recovered here. However, catalyst accordingly therefore, catalyst can be reused and it is an economically feasible with high conversion efficiency.



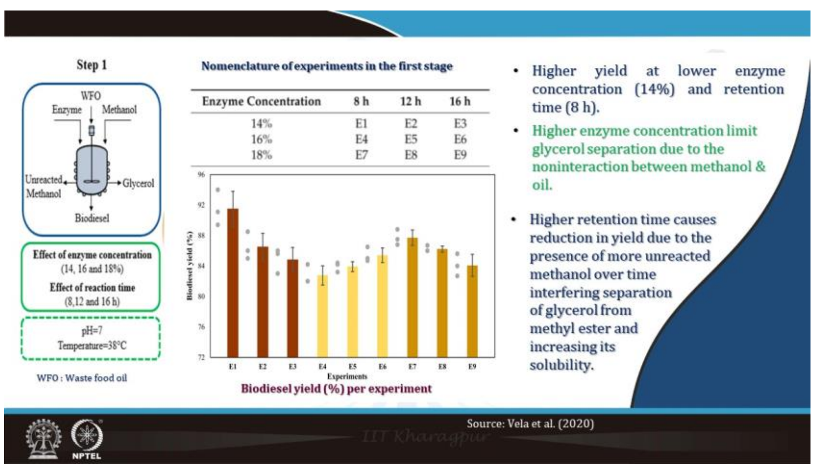
Enzyme-catalyzed transesterification process. It refers to the use of enzymes as biocatalysts to catalyze the reaction between a fat or oil and an alcohol to produce biodiesel. The process involves adding an enzyme such as lipase or protease, to the reaction mixture, which then facilitates the transesterification reaction between the fat or the oil and the alcohol. The enzyme acts as a catalyst by lowering the activation energy of the reaction, allowing it to occur more quickly and efficiently than it would have been otherwise.

So, you can see here, oil containing free fatty acids and methanol biocatalyst is given. So, it is biodiesel form and byproducts like glycerol and the partial glycerides etcetera and enzymes that is it is there.

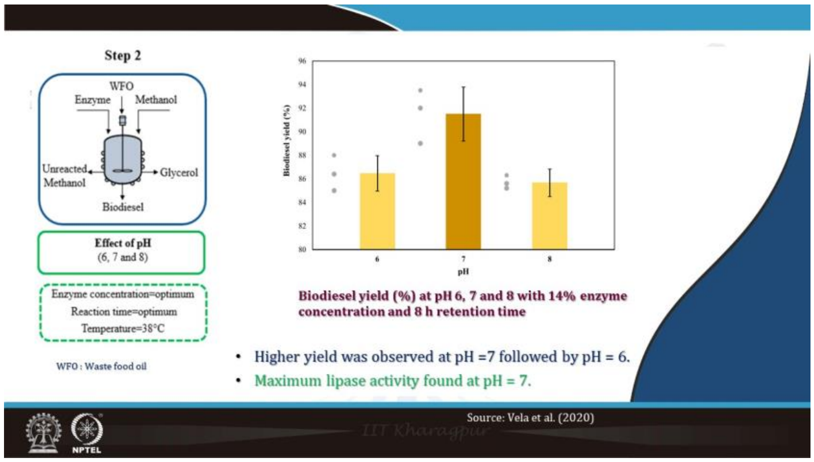


There are three step processes given by Veda et al. in 2020. They gave schematic representation of the experimental methodology to have this process and they studied the effect of enzyme concentration like 14, 16 and 18 percent concentration, effects of reaction time in step 1, pH was 7 and temperature 38 degree Celsius.

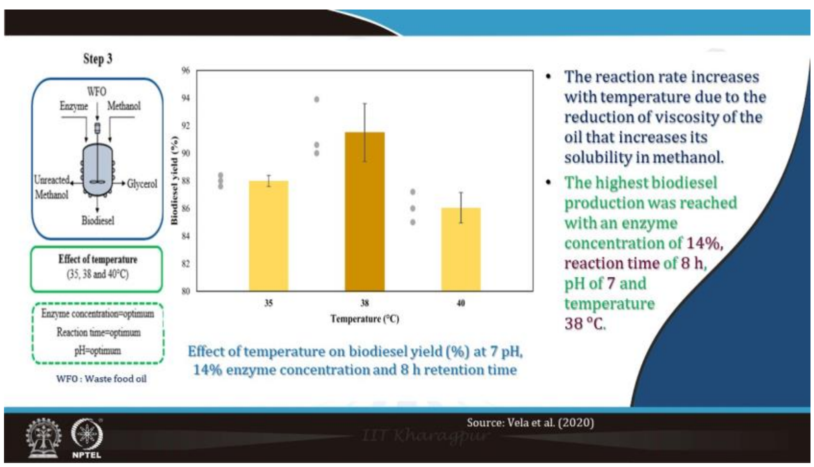
In the second step, the optimum conditions of this were used and effect of pH i.e. 6, 7, 8 was seen. Enzyme concentration and reaction time was optimum and temperature 38 degree. And in the third step, that is the effect of temperature 35, 38 and 40 degree Celsius and they got enzyme concentration optimum, reaction time and pH optimum. So, in this process in three steps, they optimized the enzyme concentration, reaction time, and pH etcetera to give the better biodiesel yield.



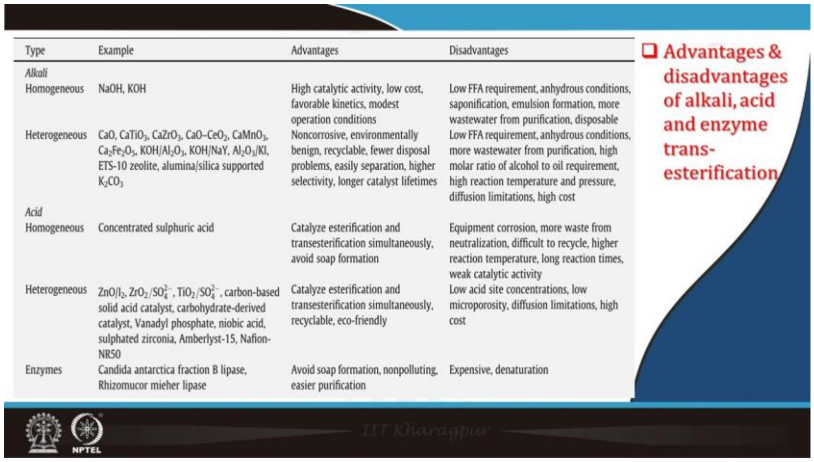
So, in the step 1, you can see here, it is biodiesel yield percent all right. Biodiesel yield vs experiments E1, E2, E3, E5, etc. E1 means that is 14 percent concentration for 8 hours, E2 is the 14 percent for 12 hours, and E3 is 14 percent for 16 hours and accordingly. So, you can see here that, higher yield at lower enzyme concentration and retention time of 8 hour like E1. E1 here, it gives around 92 percent biodiesel yield and E1 is at 14 percent enzyme concentration and 8 hour reaction time. And as the enzyme concentration increased that is E4, E7 etc. i.e. 16, 18 percent; 16 percent is E4, E5 and E6. You see may be little at E6 there is a little more in comparison to E4 and E5, but definitely the yield is less than the E1. So, the higher enzyme concentration limit glycerol separation due to the non-interaction between methanol and oil. Higher retention time causes a reduction in yield due to the presence of more unreacted methanol over time interfering the separation of glycerol from the methyl ester and increasing its solubility.



Similarly, that is you see, the higher yield was obtained at pH 7. When the effect of pH 6, pH 7, and it was at pH 7, the highest yield was obtained in comparison to pH 6 and pH 8. So, maximum lipase activity was found at pH 7.



Then in third step, there is the effect of temperature 35, 38 and 40 degree Celsius and you can see here the reaction rate increases with temperature due to the reduction of viscosity of the oil that increases its solubility in methanol. The highest biodiesel production was reached with an enzyme concentration of 14 percent, reaction time of 8 hours, pH 7, and temperature 38 degree Celsius that gives around 90 percent biodiesel yield.



Type	Example	Advantages	Disadvantages
Alkali			
Homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable
Heterogeneous	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite, alumina/silica supported K_2CO_3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid			
Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Heterogeneous	ZnO/I_2, ZrO_2/SO_4^{2-}, TiO_2/SO_4^{2-}, carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulphated zirconia, Amberlyst-15, Nafion-NR50	Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly	Low acid site concentrations, low microporosity, diffusion limitations, high cost
Enzymes	Candida antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

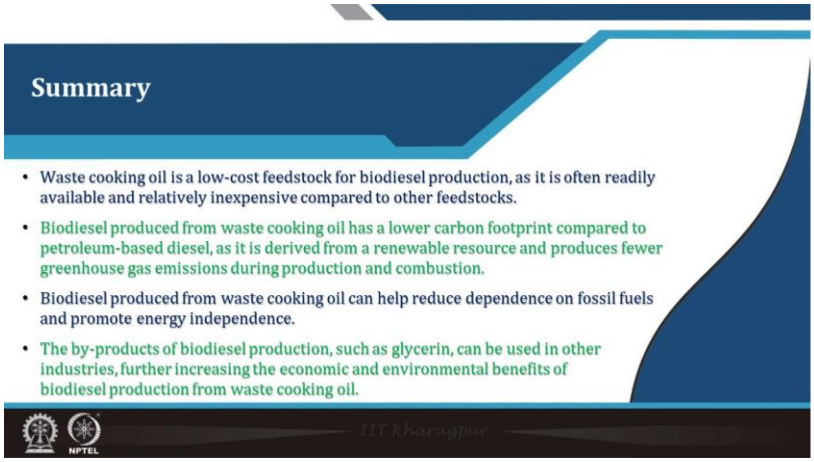
This are the some of the examples of different types of alkali-catalyst, homogeneous and heterogeneous, acid-catalyst and enzymes. So, you have seen that is, advantages of the homogeneous alkali-catalyst include high catalytic activity, low cost, favorable kinetics, and modest operation conditions. Disadvantages are low free fatty acid requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification etcetera.

Then heterogeneous alkali, it has calcium oxides, aluminum oxides etcetera that is an alumina/silica supported K_2CO_3. These are the types of the reactant which are used as a catalyst. Then advantages here, it is non-corrosive, environmentally benign, recyclable, fewer disposal problems, and easy separation. Whereas, the disadvantage includes low free fatty acid requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol to oil requirement, and so on. It is also required high reaction temperature and pressure.

Then if you see acid catalyst, that in homogeneous acid catalyst, concentrated sulfuric acid is generally used. Here, advantages include catalyzed esterification and transesterification simultaneously and it avoid soap formation, but it has a problem, that is equipment corrosion, more waste from neutralization, difficult to recycle and so on.

Heterogeneous acid catalyzation that carbon based solid catalyst activists, carbohydrate derived catalyst etc. Advantages include catalyzed esterification and transesterification simultaneously, recyclable as these are eco-friendly. However, disadvantages are low acid site concentration, low microscopy, diffusion limitations, or high cost are some of the disadvantages.

Enzymes that is normally *Candida antarctica* fraction B lipase, and *Rhizomucor mieher* lipase is used. Advantages are they avoid soap formation, non-polluting, easier purification, whereas expensive and denaturation are the disadvantages of this.



Finally, I will summarize this lecture by saying that the waste cooking oil is a low-cost feedstock for biodiesel production as it is often readily available and relatively inexpensive compared to other feedstocks. Biodiesel produced from waste cooking oil has a lower carbon footprint compared to petroleum-based biodiesel as it is derived from a renewable resource and produces fewer greenhouse gas emissions during the production and consumption. Biodiesel produced from waste cooking oil can help reduce dependence on fossil fuels and promote energy independence. The byproducts of biodiesel production such as glycerine can be used in other industries, further increasing the economic and environmental benefits of biodiesel production from the waste cooking oil, that is they are given that is the if the byproducts like glycerine etc. can also be used. This further improve the economics and the cost of the biodiesel etc. will be lower and finally, it will add to the value to the oil miller.

These are the references you did during this class with this.

Thank you very much for your presentation. Thank you.