Technologies for Clean and Renewable Energy Production
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Lecture - 37
Energy from Biomass and Wastes 2 (Chemical Route)

Hi friends, now we will start discussing on the topic energy production from biomass and waste part 2 and that is chemical route based processes. So in the part 1, we have discussed how the biomass and waste can be converted to energy component through biological routes, basically anaerobic digestion, and some specific type of waste we have seen that are most suitable for that route. Similarly for the chemical route, we will also see that some specific type of waste and biomass components will be more suitable for the energy production.

Some example say some used oil or waste grease or say some oil seeds can also be used for this process. So what we will see some of the biomass can be directly used for chemical conversion in which the glycerol or say lipid content is higher or some feedstock can be used to produce the oil or lipid first then to it can be converted to biodiesel. So basically the chemical route converts the feedstock, particularly the bio-oil or the lipids to biodiesel through transesterification.

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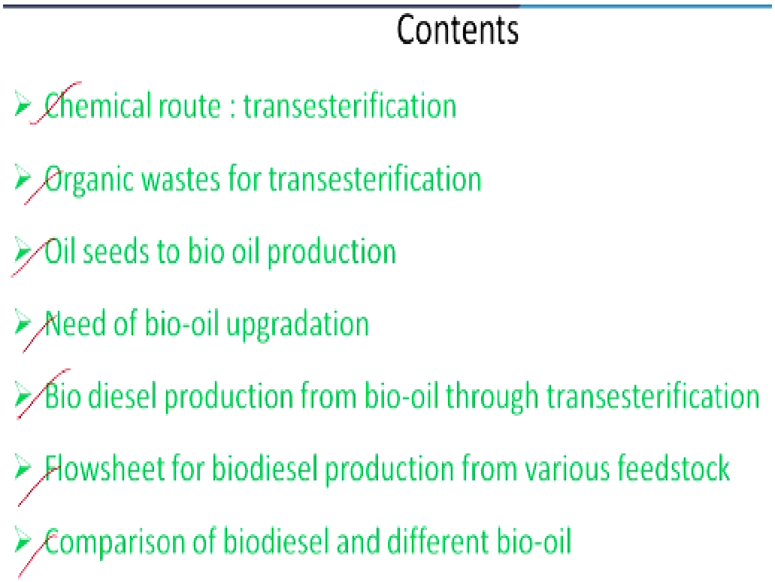

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- Chemical route : transesterification
- Organic wastes for transesterification
- Oil seeds to bio oil production
- Need of bio-oil upgradation
- Bio diesel production from bio-oil through transesterification
- Flowsheet for biodiesel production from various feedstock
- Comparison of biodiesel and different bio-oil

Now we will discuss on this contents that is the chemical route transesterification what is this, then organic waste for transesterification that is what type of waste can be used for transesterification process and oil seeds to oil production, then need of bio-oil upgradation via biodiesel production, why we can't use bio-oil directly that part we will discuss, then biodiesel production from bio-oil through transesterification sort of the routes and the flow sheets and different prospects and concerns we will discuss,

And flow sheet for biodiesel production from various feedstock, and then comparison of biodiesel and different bio-oil to justify the need of the biodiesel production.

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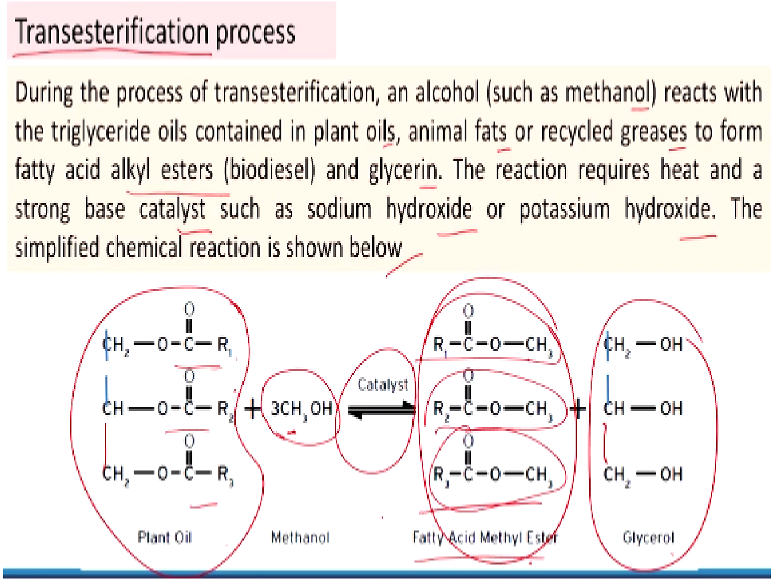

Transesterification process

During the process of transesterification, an alcohol (such as methanol) reacts with the triglyceride oils contained in plant oils, animal fats or recycled greases to form fatty acid alkyl esters (biodiesel) and glycerin. The reaction requires heat and a strong base catalyst such as sodium hydroxide or potassium hydroxide. The simplified chemical reaction is shown below

So now we will see what the transesterification process is. We see the term indicates transesterification, so there will be some esters and the alkyl groups of the esters will be changed in this reaction and one example is the glycerol if we have that is the major component of oil, in the plant oil maybe, say edible and non-edible oil if we have, so it is our oil if we have, this oil we have here CH_2OH and CH_2H that is the glycerol back bone and this OH is replaced by some organic acids.

So 3 different organic acids so that is giving us triglyceride. So this triglyceride is available in the oil and then that has to be converted to this fatty acid methyl ester that is called biodiesel and we will get the glycerol here. So we are getting the glycerol. So triglyceride will be converted to fatty acid methyl esters and glycerol. So this process is called transesterification. So these R_1COOCH_2 this group, we are getting this separated R_1COO and CH_3.

So we are getting here R_1COOCH_3, similarly R_2COOCH3, similarly R_3COOCH3. So, these are the different compounds which we are getting, those are the composition of biodiesel, that is called fatty acid methyl ester and this process is called transesterification process. So, this process will not take place at any condition. So some specific requirement is there for this reaction. So that is we need some catalyst and we need to add methyl alcohol, so methyl alcohol will give us the methyl group and that will be added with R_1COOCH_3 like this type of esters.

So, one esters we had here, we are getting another ester, so that is transesterification and in this case, during the processes of transesterification, an alcohol such as methanol reacts with the triglyceride oils contained in plant oil, animal fats or recycled greases to form fatty acid alkyl esters that is biodiesel and glycerin. The reaction requires heat and a strong base catalyst such as sodium hydroxide or potassium hydroxide and the simplified chemical reaction is as follows as i have explained.

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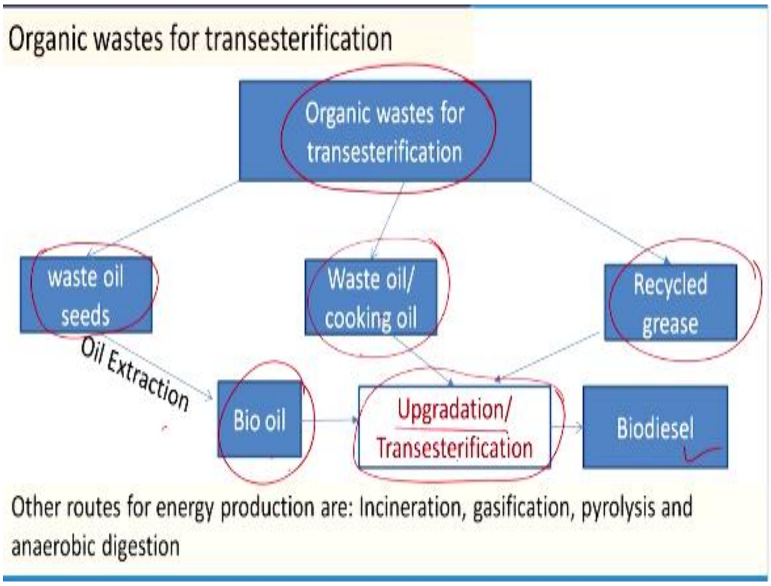

Organic wastes for transesterification

Other routes for energy production are: Incineration, gasification, pyrolysis and anaerobic digestion

Now, what type of feedstocks will be more suitable for this type of conversion processes that part we will see. So, we have some organic waste which can go through this transesterification process, may be of waste oil seed, it may have waster oil or cooking oil or we may have recycled grease. So these 3 major components of the waste which can be processed through this route, and if it is waste oil seed, then we have to get the oil first from the oil seeds, then we will get bio oil by oil extraction.

Then bio oil or this waste oil or cooking oil and recycled grease, all those intermediate products or all the inputs will be converted to biodiesel through the transesterification and this process is called upgradation of the oil. So, these are the different feedstocks which can be used or can be upgraded to biodiesel.

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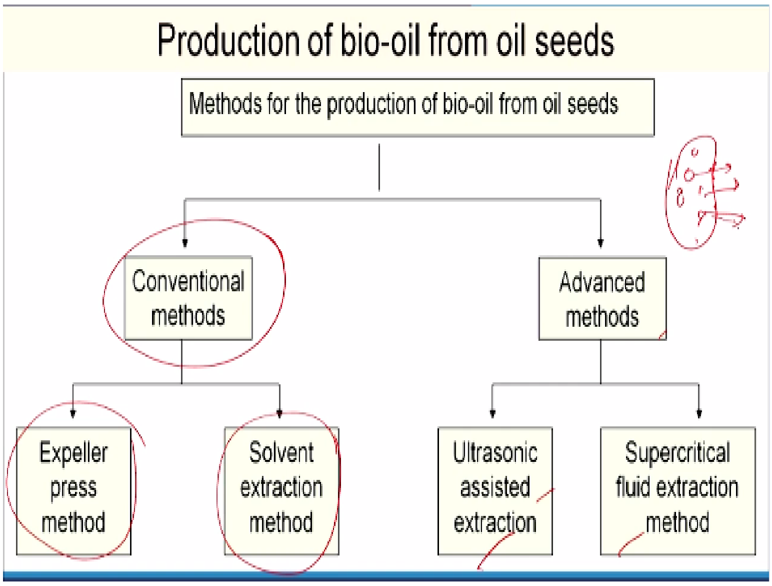

Now, we will see how this bio oil can be produced from the waste oil seeds. So waste oil seeds can be converted to bio oil through different routes. One is your conventional methods that is expeller. Expeller that is based on the pressing on the oil seed and extract the oil from it and then solvent extractions, so you can use some solvent also, the solvent will take the oil part and then the residual part will be as a solid and then also will get the bio oil or some advanced method are there, they are ultrasonic assisted extractions and then supercritical fluid extractions.

So in this solvent extraction, we can use some solvent and then there will be some extraction process with maintaining certain condition, and in this case, if we use ultrasonicator, then that will help the release of oil from the oil seeds. So, if we have oil seed say, inside the oil is there. So these oil molecules has to come out. So that can come out if the surface is dissolved with the solvent or through the pores it made. So then these molecules will come out.

Now if we use ultrasonification, then helps the extractions of this oil and it will come easily, so the extractions becomes easier, that is its called advanced method. Supercritical extraction is also possible by using some carbon dioxide in supercritical phase that can be used to extract the liquid from the outer part of the oil seed to the solvent, that is the supercritical solvent. So, these are different methods, which have been reported to use for the extraction of the oil from the oil seeds.

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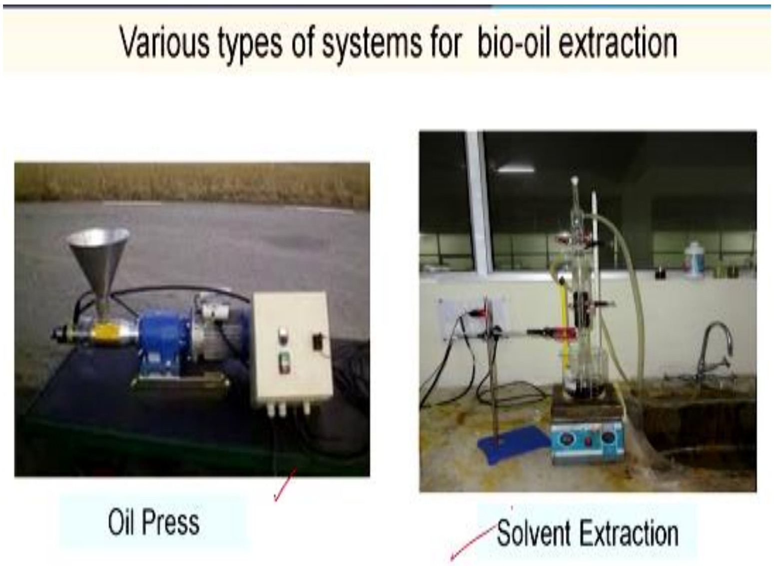

Various types of systems for bio-oil extraction

Oil Press

Solvent Extraction

Now, these are the oil press how it looks like various lab scale and this is your lab scale solvent extraction unit, where the oil is extracted from the oil seeds.

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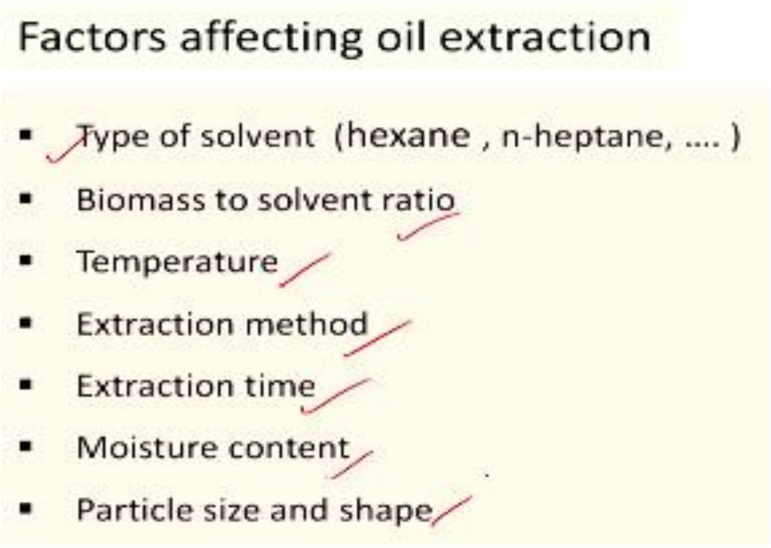

Factors affecting oil extraction

- Type of solvent (hexane , n-heptane, ….)
- Biomass to solvent ratio
- Temperature
- Extraction method
- Extraction time
- Moisture content
- Particle size and shape

What are the factors that influence the extraction of the oil from oil seeds are mentioned here, that is type of solvent, what type of solvent we are using, that solvent has to be good interaction with the or the mixing capacity with the lipid part or that is the oil part or the oil seed. Then we have to biomass to solvent ratio, obviously, we have to use more solvent, more will be gradient for the transfer of mass, so more extraction we will get. Then temperature also influence, the temperature should not be very high.

If it is very high, then the solvent can be vaporized, or if it is very less, then also the extraction may not be that efficient. Then extraction method, what type of extraction method we are using, whether it is mechanical method like expeller or chemical or we are going for a extraction method using some solvent. So all those things will influence the efficiency. The extraction time, how much time we are allowing that also influence what amount of oil is coming, more we get the time, it expected that more oil will come out, and then moisture content and there may be some optimum value for the extraction time also.

The moisture content that also influences the oil extraction method. The particular size and shape, obviously that will also provide the surface area for the oil molecules to come out from it. So, smaller the particles, obviously more will be the extraction. So, these are the factors which influences the overall extraction processes.

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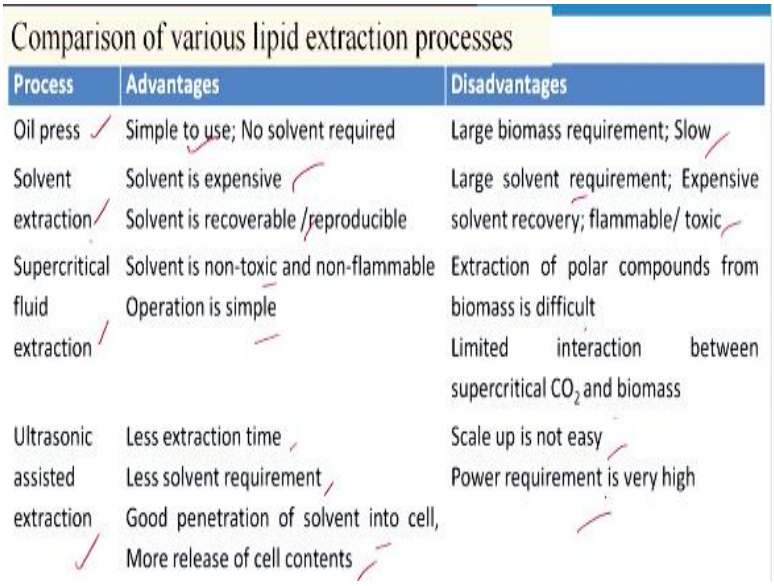

Comparison of various lipid extraction processes

Process	Advantages	Disadvantages
Oil press	Simple to use; No solvent required	Large biomass requirement; Slow
Solvent extraction	Solvent is expensive Solvent is recoverable /reproducible	Large solvent requirement; Expensive solvent recovery; flammable/ toxic
Supercritical fluid extraction	Solvent is non-toxic and non-flammable Operation is simple	Extraction of polar compounds from biomass is difficult Limited interaction between supercritical CO_2 and biomass
Ultrasonic assisted extraction	Less extraction time Less solvent requirement Good penetration of solvent into cell, More release of cell contents	Scale up is not easy Power requirement is very high

So now we will compare the different extraction process, which have been used for the production of bio oil from the oil seeds. So we have oil press, then solvent extraction, then supercritical fluid extraction, and then ultrasonic assisted extraction. So, all these have some advantage and disadvantage as given here. Then it is very simple to use and no solvent is required, that is the great advantage, but what is the disadvantage large biomass requirements, slow, that means its complete recovery may not be possible, some amount of oil can still be available and it is a slow process.

Then solvent extraction process, solvent is required which may be expensive, let us say hexanes, as we have mentioned here the hexanes, n-heptane, etc., so those are expensive solvent can be required. Solvent is recoverable and reproducible, although we are using the expensive solvent we can recover it, but disadvantage is that large volume of solvent is required and expensive solvent recovery. If we want to recover the solvent, then that recovery also require some amount of money.

So, that is also flammable and toxics, we have to be careful for handling of the solvent. Then is supercritical, then solvent is nontoxic and non flammable, and operation in simple. So that way we are getting advantage replacing the solvent like hexane, n-heptane by the supercritical carbon dioxide. This also has a limitation that is the extraction of polar compounds from biomass is difficult and the limited interaction between supercritical carbon dioxide and biomass. So, these are the disadvantage of this process.

The next is ultrasonic assisted. So then less extraction time as it helps to rupture the wall of the seeds and helps to release the oil molecules from the inner side to the outer side and to the solvent. So less solvent requirement for that reason and good penetration of solvent into cell and more release of cell contents. So, these are the advantage when we use the ultrasonic assisted extraction method. This has some difficulty, that they scale up is not very easy and power requirement is also very high. So these are the advantage and disadvantage of different types of oil extraction methods from the oil seed.

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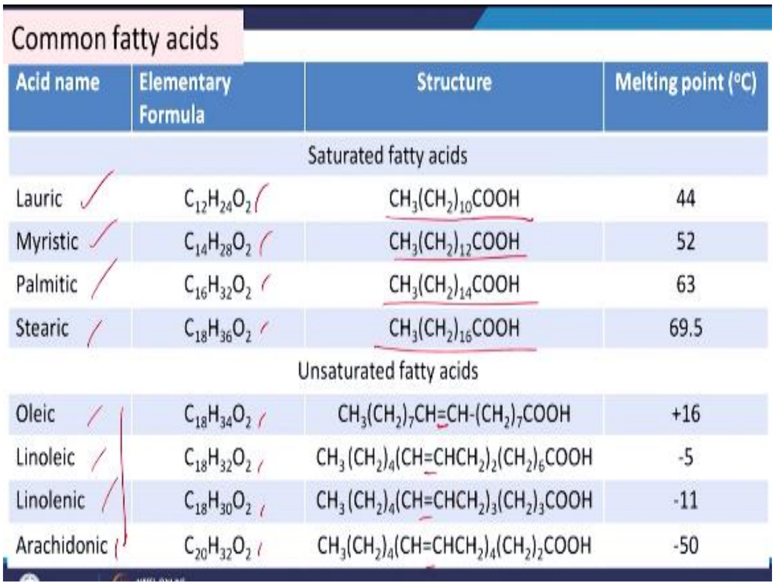

Common fatty acids

Acid name	Elementary Formula	Structure	Melting point (°C)
		Saturated fatty acids	
Lauric	$C_{12}H_{24}O_2$	$CH_3(CH_2)_{10}COOH$	44
Myristic	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{12}COOH$	52
Palmitic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$	63
Stearic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$	69.5
		Unsaturated fatty acids	
Oleic	$C_{18}H_{34}O_2$	$CH_3(CH_2)_7CH{=}CH\text{-}(CH_2)_7COOH$	+16
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	-5
Linolenic	$C_{18}H_{30}O_2$	$CH_3(CH_2)_4(CH{=}CHCH_2)_3(CH_2)_3COOH$	-11
Arachidonic	$C_{20}H_{32}O_2$	$CH_3(CH_2)_4(CH{=}CHCH_2)_4(CH_2)_2COOH$	-50

After this extraction of oil, what oil we are getting that contains different types of lipids as mentioned here, the different types of say lauric acid, myristic acid, palmitic acid, stearic acid, folic acid, linoleic acid, linolenic acid, and arachidonic acid. So, these are the seeds which are normally available in the bio oil, which is produced from the oil seeds and these are the elementary formula and from these formula if we see, most structure of this compound, so that it $C_{12}H_{24}O_2$, so $CH_3(CH_2)_{10}COOH$, so there is no unsaturation.

For the second myristic also there is no unsaturation, here also no unsaturation, here also no unsaturation. So if we go for these fatty acids, then we are getting unsaturation here. Here so maybe one unsaturation in this case, somewhere it maybe 2 unsaturation also. So that way saturated and unsaturated both type of acids are available in the bio oil. So these type of fatty acids will also influence the quality of bio diesel.

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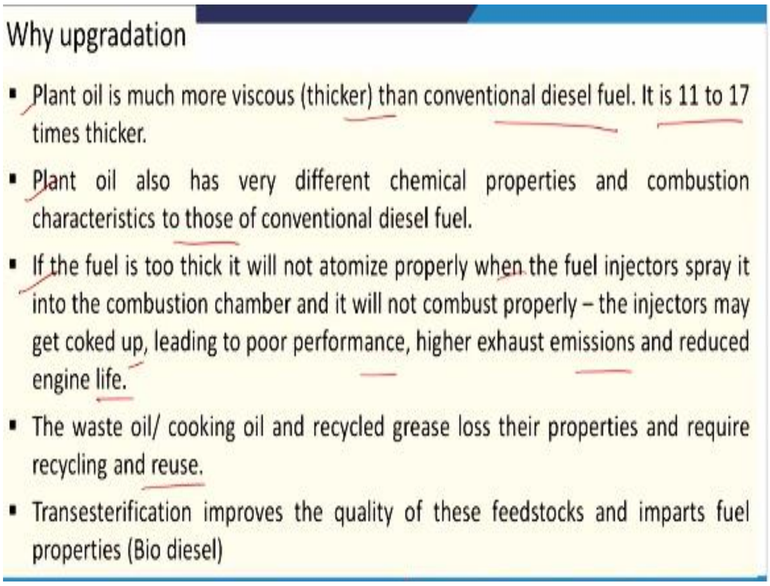

Why upgradation

- Plant oil is much more viscous (thicker) than conventional diesel fuel. It is 11 to 17 times thicker.
- Plant oil also has very different chemical properties and combustion characteristics to those of conventional diesel fuel.
- If the fuel is too thick it will not atomize properly when the fuel injectors spray it into the combustion chamber and it will not combust properly – the injectors may get coked up, leading to poor performance, higher exhaust emissions and reduced engine life.
- The waste oil/ cooking oil and recycled grease loss their properties and require recycling and reuse.
- Transesterification improves the quality of these feedstocks and imparts fuel properties (Bio diesel)

So then what is the need of this bio oil? Bio oil we are getting just simply extracting the oil part or lipid part from the oil seed, but what is the need of its upgradation, because of its inferior quality. If we see the viscosity of this bio oil is higher, and we need to reduce it for its applications in the engine and the plant oil is much more viscous than its conventional diesel fuel that is 11 to 17 times thicker than the conventional diesel oil. So, we have to break the viscosity, we have to reduce the viscosity of this.

Then plant oil has also very different chemical properties and combustion characteristics to those of the conventional diesel fuel, so we have to change those properties by the conversion. Then if the fuel is too thick, it will not automize properly. So it will be difficult to use in the engine or the injectors may get coked up and leading to poor performance, higher exhaust emissions and reduced engine life.

In the waste oil or cooking oil or recycle grease, those waste materials lose their fuel properties basically and we require the recycling and reuse and then conversation is required. Transesterification process basically improves all those qualities and gives an improved quality to the upgraded product that is called biodiesel. So that is the need of the upgradation of the bio oil and that is done through the transesterification process.

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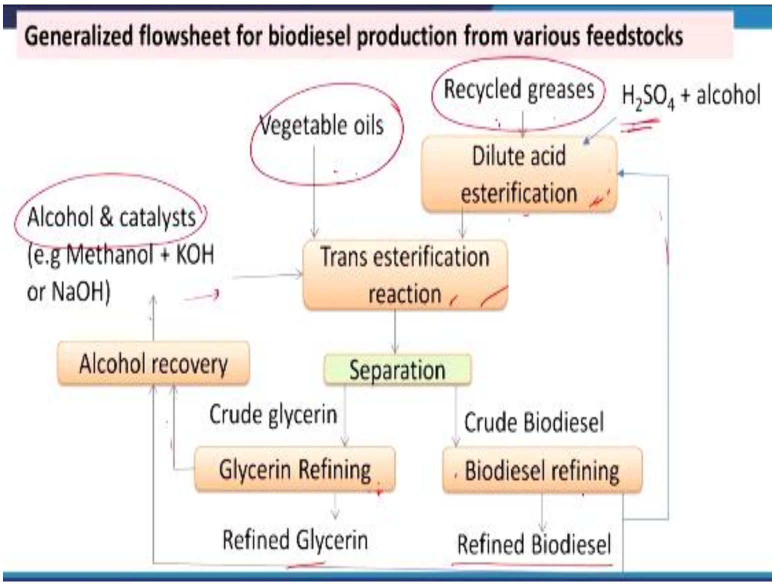

Generalized flowsheet for biodiesel production from various feedstocks

Now depending upon the feedstocks also, the process maybe to some extent different, so that part we are going to discuss and here are the generalized flow sheet for biodiesel production from various feedstocks. So generalized process if we see, we have some plant oil or so that is vegetable oil we have say or we have say recycle grease. So what is the basic difference between these 2. So if we think about the vegetable oils, then free fatty acids in these case is less, but we think about the recycle grease, we are having higher free fatty acid.

So when free fatty acid is available in the feedstock, then if we go for transesterification process, then free fatty acid, they will help to the production of soap, so we have to remove the free fatty acid first. So how will do, we will have to use some alcohol and then that will be the H_2SO_4 will be consumed by that process and then we will go for the transesterification reaction. So if we take the vegetable oils first, then vegetable oil that is containing triglycerides, we need one catalyst and we need some alcohol.

So alcohol and catalyst, methanol plus KOH or NaOH that is mixed with this vegetable oils. So then maybe vegetable oil or maybe say recycled oil, if recycled oil, then we have to separate this acid free fatty acids we have to get it free from the free fatty acids in the free state and then that is called dilute acid esterification step, then the product from this dilute acid esterification step will come to the transesterification reaction and then this is after that it is very common to both type of feedstock, but up to this, these two processes are different.

When free fatty acids is less, we do not need any dilute acid esterification, but when the free fatty acid is high, then we need this process. Then when starting from this transesterification reaction, then we will be getting the product of it, then those products will be having obviously glycerol, unconverted alcohol, and water also, separation has to be done. So, we will get biodiesel part and another we will get glycerin part, so biodiesel and glycerin part will separate and biodiesel will also contain alcohol, so will be biodiesel refining.

So what alcohol we are getting, it is going back to this and then refined biodiesel will get. Similarly what glycerin we are getting here that crude glycerin. So crude glycerin will also contain some soap, some alcohol, water, etc., so that refining of the crude glycerin is also required. So after refining we will get refined glycerin and alcohol part which is being recovered that will go to this alcohol recovery sections and will be recycled back, can be used in the transesterification reaction.

So, this is the overall flow sheet for the transesterification of vegetable oils or recycled grease.

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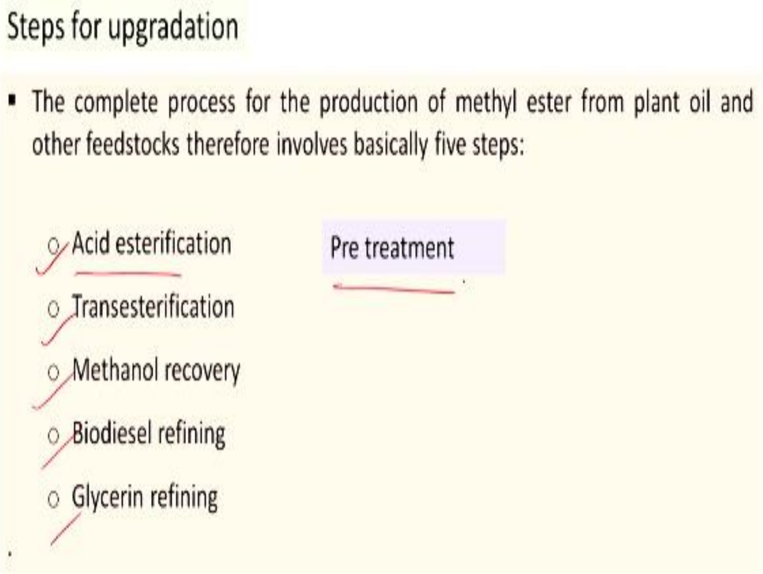

Steps for upgradation

- The complete process for the production of methyl ester from plant oil and other feedstocks therefore involves basically five steps:
  - ○ Acid esterification
  - ○ Transesterification
  - ○ Methanol recovery
  - ○ Biodiesel refining
  - ○ Glycerin refining

Pre treatment

Now, from this flow sheet, it is very clear to us that it had basic 5 steps. One is acid esterification, then transesterification, methanol recovery, biodiesel refining, and glycerin refining. This acid esterification is also called as pretreatment and this is required basically when the free acid content in the feedstock is higher.

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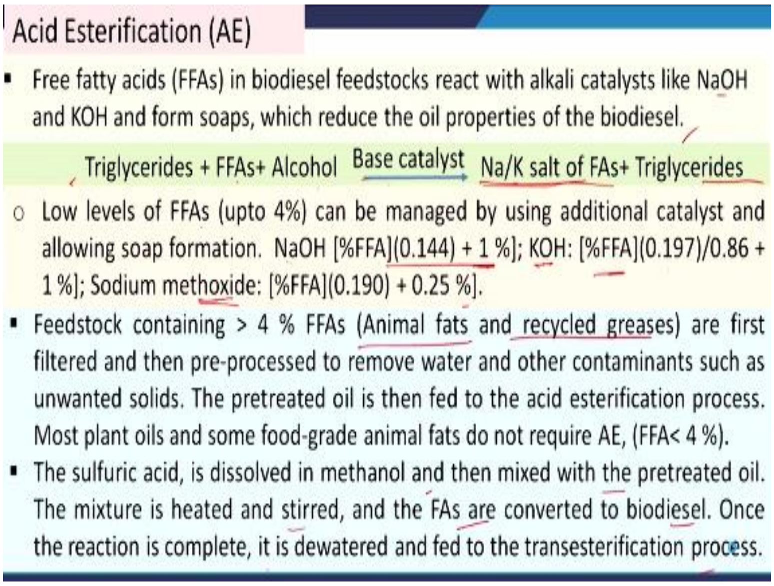

Acid Esterification (AE)

- Free fatty acids (FFAs) in biodiesel feedstocks react with alkali catalysts like NaOH and KOH and form soaps, which reduce the oil properties of the biodiesel.

Triglycerides + FFAs+ Alcohol $\xrightarrow{\text{Base catalyst}}$ Na/K salt of FAs+ Triglycerides

  - Low levels of FFAs (upto 4%) can be managed by using additional catalyst and allowing soap formation. NaOH [%FFA](0.144) + 1 %]; KOH: [%FFA](0.197)/0.86 + 1 %]; Sodium methoxide: [%FFA](0.190) + 0.25 %].
- Feedstock containing > 4 % FFAs (Animal fats and recycled greases) are first filtered and then pre-processed to remove water and other contaminants such as unwanted solids. The pretreated oil is then fed to the acid esterification process. Most plant oils and some food-grade animal fats do not require AE, (FFA< 4 %).
- The sulfuric acid, is dissolved in methanol and then mixed with the pretreated oil. The mixture is heated and stirred, and the FAs are converted to biodiesel. Once the reaction is complete, it is dewatered and fed to the transesterification process.

Then what is the acid esterification and how we will do it. So, free fatty acids in biodiesel feedstock react with alkali catalyst like a NaOH and KOH and from soaps, so which reduce the oil properties of the biodiesel. So, that is the major disadvantage. If free fatty acid is available, then free fatty acid will react with NaOH and it will form soap, which is not desirable in the biodiesel product. So, triglyceride + free fatty acids + alcohol if we take base catalyst, we will get sodium plus potassium salt or free fatty acids + triglycerides.

So, this will be the initial step because the free fatty acids reacts earlier quickly then the triglyceride. So free fatty acids reacts quickly than the triglycerides, that is also formations will take place very easily. Then low levels of free fatty acids if available, then this can be managed, say around 4% can be managed. How it can be managed, initially we will add some additional NaOH, additional NaOH if it is added, then these reactions will take fast and the soap formation will not be that very high as the free fatty acids is less.

So that can be manageable to some extent. What will be the alkali content in case of three fatty acids, there are some formula. So, these catalyst concentration we have to add in excess amount and that excess amount is presented here. If we use NaOH, then that will be percentage of free fatty acids x 0.144 + 1%. If it is KOH, then it will be percentage of free fatty acids x 0.197/0.86 + 1%. If it is sodium methoxide, then percent of free fatty acid x 0.190 + 0.25%.

So, these are the some formula which are available and that can be used for the removal of those free fatty acids by these catalyst itself. But when it will be higher than 4%, then we have to remove the free fatty acids first as the pretreatment state and basically in case of animal fats and recycle grease, we get more than 4% free fatty acids and it requires pretreatment. So the sulfuric acid is dissolved in methanol and then mixed with the pretreated oil.

The mixer is heated and stirred and the free fatty acids are converted to biodiesel. That means, fatty acid is converted to biodiesel first through the acid catalysis reactions. So, fatty acid is not available as free fatty acids, it is now into glyceride form. So, once the reaction is complete, it is dewatered and fed to the transesterification process, then it is going for the transesterification process as shown in this step.

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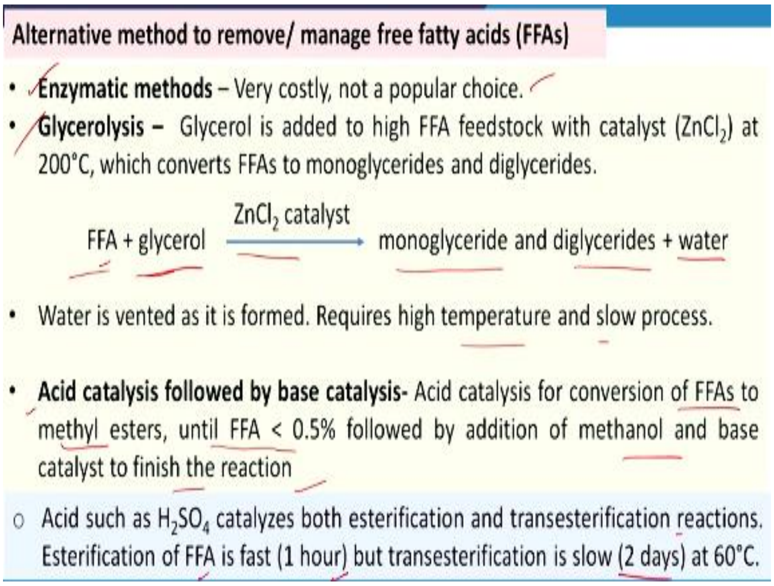

Alternative method to remove/ manage free fatty acids (FFAs)

- **Enzymatic methods** – Very costly, not a popular choice.
- **Glycerolysis –** Glycerol is added to high FFA feedstock with catalyst ($ZnCl_2$) at 200°C, which converts FFAs to monoglycerides and diglycerides.

$$\text{FFA + glycerol} \xrightarrow{ZnCl_2 \text{ catalyst}} \text{monoglyceride and diglycerides + water}$$

- Water is vented as it is formed. Requires high temperature and slow process.
- **Acid catalysis followed by base catalysis-** Acid catalysis for conversion of FFAs to methyl esters, until FFA < 0.5% followed by addition of methanol and base catalyst to finish the reaction
  - Acid such as H_2SO_4 catalyzes both esterification and transesterification reactions. Esterification of FFA is fast (1 hour) but transesterification is slow (2 days) at 60°C.

So, what are the alternative methods to remove the free fatty acids or manage the free fatty acids. One we have discussed that we can use some more amount of alkali if it is less than 4%, free fatty acid is les s than 4%. Otherwise you can use some enzymatic method okay, enzymatic method can convert the free fatty acids into glyceride and then but this is very costly and not popular choice.

So glycerolysis, in this process, glycerol is added, some amount of glycerol is added and then free fatty acid and glycerol reacts in presence of $ZnCl_2$ catalyst and it is converted, FFA is converted to monoglyceride and diglycerides plus water. So, this is one method which can be followed to convert the free fatty acids to monoglyceride or diglycerides and then water is vented off and it requires high temperature and it is also slow process. Then acid catalysis followed by base catalysis.

So, if we can use some acid catalyst, then if we use base catalytic reactions for transesterification, then also it can be very good solution. If we use sulfuric acid, then it catalyzes both esterification and transesterification reactions and esterification of free fatty acid that is within 1 hour this reaction takes place, but for transesterification it takes 2 days at 60 degrees centigrade. So, this property we can exploit it. So, within 1 hour the FFA is converted to esters whereas the triglyceride is converted to esters with 2 days of reactions.

So, if we have free fatty acids, at the initial stage you can add acid sulfuric acid, so the free fatty acid should be converted to esters. So when we will be going for transesterification process and use alkali catalyst, then the production of soap will be reduced, the chance of the soap production will be reduced. So, that is the concept.

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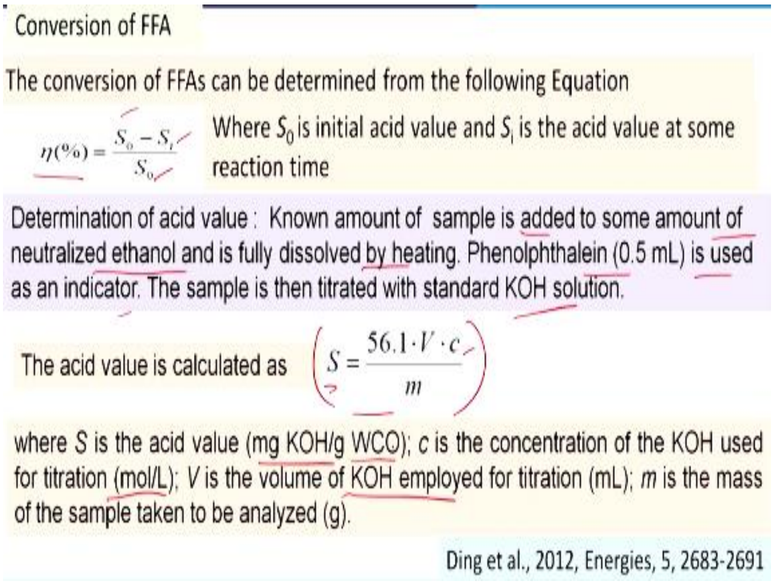

Conversion of FFA

The conversion of FFAs can be determined from the following Equation

$$\eta(\%) = \frac{S_0 - S_t}{S_0}$$

Where S_0 is initial acid value and S_t is the acid value at some reaction time

Determination of acid value : Known amount of sample is added to some amount of neutralized ethanol and is fully dissolved by heating. Phenolphthalein (0.5 mL) is used as an indicator. The sample is then titrated with standard KOH solution.

The acid value is calculated as $S = \frac{56.1 \cdot V \cdot c}{m}$

where S is the acid value (mg KOH/g WCO); c is the concentration of the KOH used for titration (mol/L); V is the volume of KOH employed for titration (mL); m is the mass of the sample taken to be analyzed (g).

Ding et al., 2012, Energies, 5, 2683-2691

Then how we know that free fatty acid is available or not or what would be conversion of free fatty acids, how we will determine. So, conversion of free fatty acid is your obviously the initial minus final, so initial - final acid value/initial acid value, so that we can measure. If we can measure avid value, then you can get the conversion of free fatty acids. So acid value we have to measure. So, how we can measure acid value, that can be measured by this expression.

So, what we have to do, known amount of sample is added to some amount of neutralized ethanol and is fully dissolved by heating. Then phenolphthalein is used as indicator and the sample is titrated with standard alkali solution, then how much alkali solution is taking and what is the strength of the alkali solution that will be used to calculate the acid value as per this expressions.

So S = 56.1 x V x c/m where V is the volume of KOH employed for the titration in mL and then c is concentration of any solution which we have used in mole/L unit and then S which we are getting here that is the mg KOH per gram waste cooking oil. So that way we can determine the free fatty acids.

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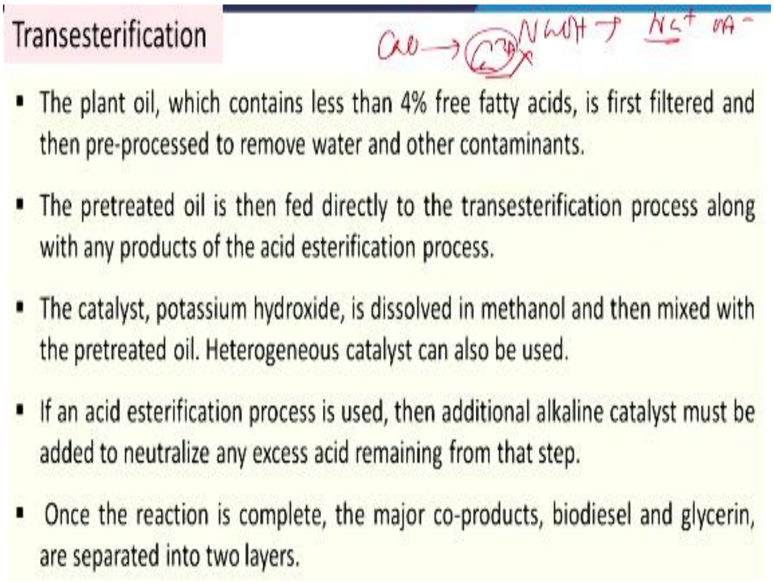

Transesterification

Oil → [illegible] NaOH → Na^+ OA^-

- The plant oil, which contains less than 4% free fatty acids, is first filtered and then pre-processed to remove water and other contaminants.
- The pretreated oil is then fed directly to the transesterification process along with any products of the acid esterification process.
- The catalyst, potassium hydroxide, is dissolved in methanol and then mixed with the pretreated oil. Heterogeneous catalyst can also be used.
- If an acid esterification process is used, then additional alkaline catalyst must be added to neutralize any excess acid remaining from that step.
- Once the reaction is complete, the major co-products, biodiesel and glycerin, are separated into two layers.

Then we are coming to transesterification. So after free fatty acids removal or with conversion into esters, we are going for the transesterification reaction, and transesterification reactions we have explained what reaction is and we see we need some catalyst and base catalyst is used. So if homogeneous catalyst is used like NaOH or KOH, then it will convert the triglyceride to methyl esters and then the glycerol, and at the same time if we have some additional catalyst and even in the stoichiometric ratio also some amount of soap formation will also take place.

So, soap, what is soap, sodium and potassium salt of fatty acids, so, fatty acids which will be generated during the process can also react with sodium hydroxide and can be converted to sodium salt or potassium salt that is called soap. So, efforts are on to replace this homogeneous catalyst by a heterogeneous one. For example, say if we have sodium hydroxide, so then sodium hydroxide what it will do, in the immediate it will give sodium plus and OH minus ion.

So, this sodium plus is available to be attached with the acid group and then converted to soap, but if we use calcium oxide as a heterogeneous catalyst, so then it will provide site for the reaction, but it will not give any calcium two plus ion, it will provide site for the reactions for the conversion of the glyceride to methyl esters, but it will not give Ca two plus, this is not available. So, the salt of fatty acid productions is not possible. So heterogeneous catalyst will be having some advantage that it will not produce soap in the product which is not desirable, soap is not desirable, it will decrease the quality of the biodiesel.

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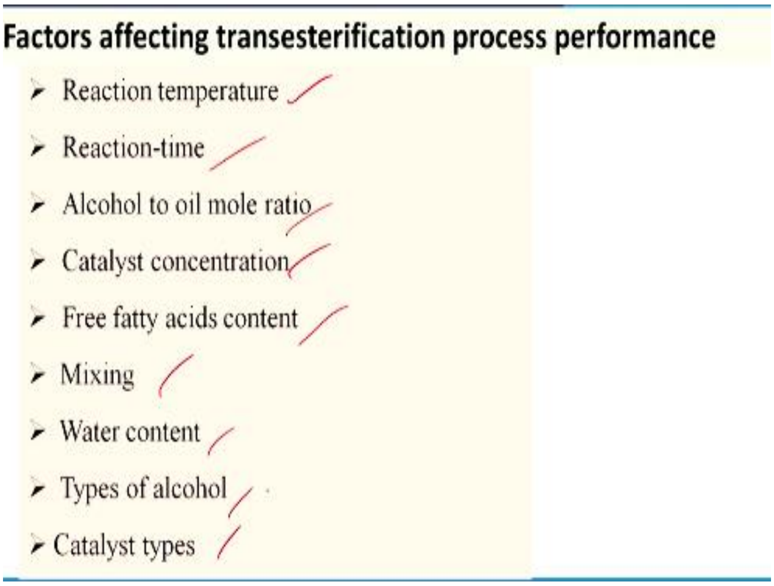

Factors affecting transesterification process performance

- Reaction temperature
- Reaction-time
- Alcohol to oil mole ratio
- Catalyst concentration
- Free fatty acids content
- Mixing
- Water content
- Types of alcohol
- Catalyst types

Now there are many factors which influence the biodiesel production or the performance of the transesterification process likes the reaction temperature, the reaction time, alcohol to oil mole ratio, how much alcohol we are using that influence it, catalyst concentration, type of catalyst, free fatty acids content, mixing, types of alcohol, water content and catalyst types. So these are the factors which influence the performance of the transesterification process.

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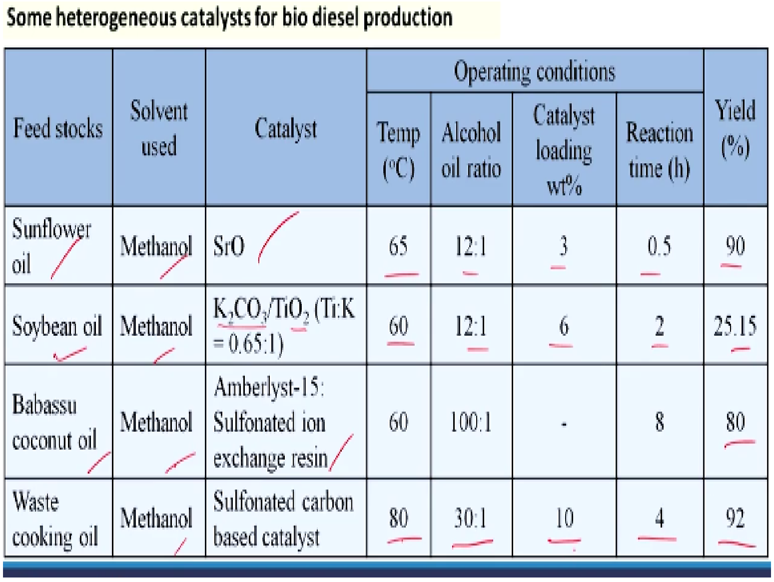

Some heterogeneous catalysts for bio diesel production

Feed stocks	Solvent used	Catalyst	Operating conditions				Yield (%)
			Temp (°C)	Alcohol oil ratio	Catalyst loading wt%	Reaction time (h)	
Sunflower oil	Methanol	SrO	65	12:1	3	0.5	90
Soybean oil	Methanol	K_2CO_3/TiO_2 (Ti:K = 0.65:1)	60	12:1	6	2	25.15
Babassu coconut oil	Methanol	Amberlyst-15: Sulfonated ion exchange resin	60	100:1	-	8	80
Waste cooking oil	Methanol	Sulfonated carbon based catalyst	80	30:1	10	4	92

Here we will see some example of heterogeneous catalyst. Here we see sunflower, this is your feedstock, then solvent methanol used, then we got some catalyst that is strontium oxide, then these are the operating conditions and these are the percentage yield. For soybean oil, methanol, K_2CO_3/TiO_2 that was the catalyst, and then under these operating conditions, we got this percent of 25.15% of yield, biodiesel yield.

Babassu coconut oil, again this is the solvent methanol, for all the cases were having methanol solvent, and this is another heterogeneous catalyst, again it is having 80% of yield. Waste cooking oil, here also having 92% of yield. So here we see the temperature is different, alcohol to oil ratio is different, catalyst loading is different, and reaction time is different. So all those parameter influence the performance of the process for the yield of biodiesel production. But in this case, when we use the heterogeneous catalyst, the quality of the biodiesel improves, it does not have any soap in it.

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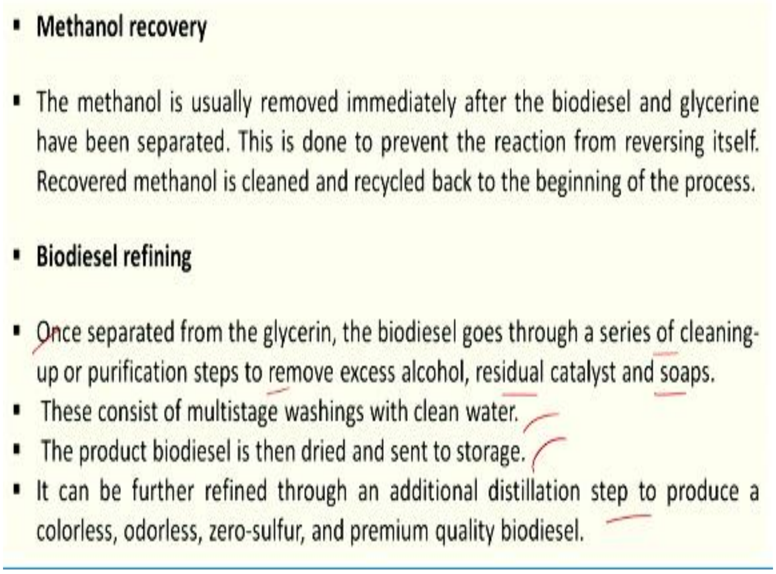

- **Methanol recovery**
- The methanol is usually removed immediately after the biodiesel and glycerine have been separated. This is done to prevent the reaction from reversing itself. Recovered methanol is cleaned and recycled back to the beginning of the process.
- **Biodiesel refining**
- Once separated from the glycerin, the biodiesel goes through a series of cleaning-up or purification steps to remove excess alcohol, residual catalyst and soaps.
- These consist of multistage washings with clean water.
- The product biodiesel is then dried and sent to storage.
- It can be further refined through an additional distillation step to produce a colorless, odorless, zero-sulfur, and premium quality biodiesel.

Then methanol recovery, so after the transesterification, we are having say one biodiesel stream and another glycerol stream. So from both the stream, we will be getting methanol, just application of heat we will get the methanol early, it will be vaporized fast and by condensation we will get the methanol recovered. Then biodiesel refining. So once this separated from the glycerin, the biodiesel goes through a series of cleaning up or purification step to remove excess alcohol, residual catalyst and soaps.

These consist of multistage washing with clean water and the product biodiesel is then dried and sent for the storage. It can be further purified through an additional distillation step to produce a more purified product.

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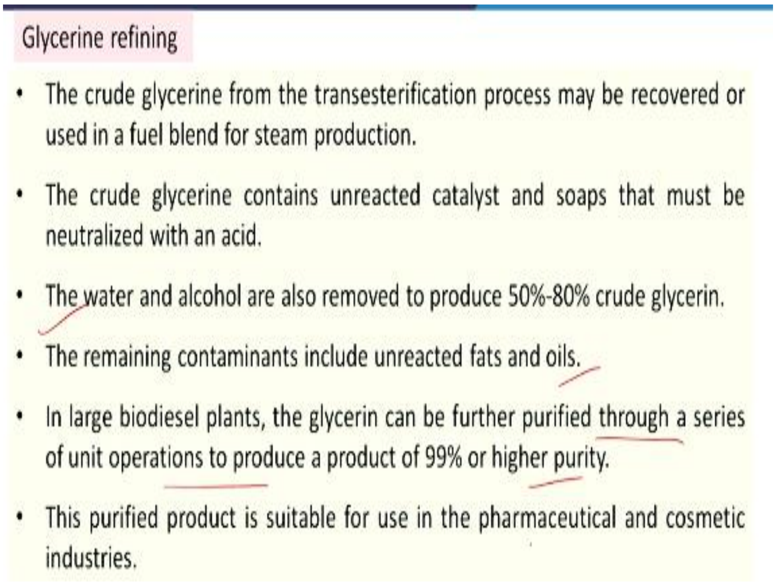

Glycerine refining

- The crude glycerine from the transesterification process may be recovered or used in a fuel blend for steam production.
- The crude glycerine contains unreacted catalyst and soaps that must be neutralized with an acid.
- The water and alcohol are also removed to produce 50%-80% crude glycerin.
- The remaining contaminants include unreacted fats and oils.
- In large biodiesel plants, the glycerin can be further purified through a series of unit operations to produce a product of 99% or higher purity.
- This purified product is suitable for use in the pharmaceutical and cosmetic industries.

Glycerin refining. The glycerin will also have some soap, some catalyst, some water and some alcohol. So, there will be a series of preparation steps or the cleaning steps. So the water and alcohol are also removed to produce 50 to 80% crude glycerin. The remaining constituents include untreated fat and oils. In the large biodiesel plants, glycerin can be further purified through a series of unit operations to produce product of 99% purity and the purified product is suitable for use in pharmaceuticals and cosmetic use and many other applications also.

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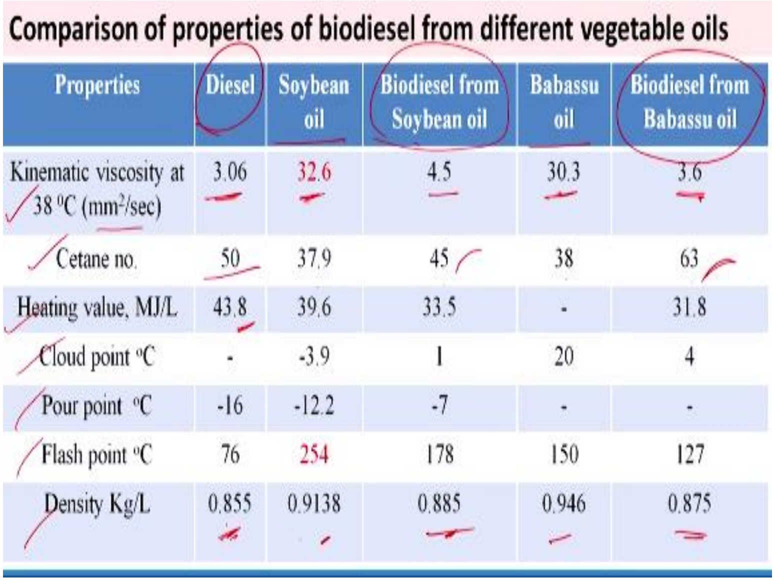

Comparison of properties of biodiesel from different vegetable oils

Properties	Diesel	Soybean oil	Biodiesel from Soybean oil	Babassu oil	Biodiesel from Babassu oil
Kinematic viscosity at 38 °C (mm^2/sec)	3.06	32.6	4.5	30.3	3.6
Cetane no.	50	37.9	45	38	63
Heating value, MJ/L	43.8	39.6	33.5	-	31.8
Cloud point °C	-	-3.9	1	20	4
Pour point °C	-16	-12.2	-7	-	-
Flash point °C	76	254	178	150	127
Density Kg/L	0.855	0.9138	0.885	0.946	0.875

Now, we will see the comparison of these biodiesel which is produced from the bio oil through this transesterification route with some bio oil, so here the properties kinematic viscosity, cetane number, heating value, cloud point, pour point, flash point, density all are fuel properties. We see here this is the standard diesel, this is the biodiesel from Babassu soil and this is Babassu oil, this is your soybean oil and biodiesel from soybean oil.

So, if we have 32.6 millimeter square per second kinematic viscosity, it is reduced to 4.5 for this case, here 30.3 to 3.6, at the diesel is having 3.06. So by this conversion, we are able to make the oil to biodiesel with almost similar viscosity or slightly higher viscosity while the other case in the original bio oil the viscosity was very very high. Similarly, the cetane number is also increased for these biodiesel productions, here 37 to 40 and 30 to 63 and these values are very comparable to 50.

Heating value also, this is a high but heating values all these biodiesel is not high, because you know we have high content of oxygen in these biodiesel with respect to petrol diesel. So the heating value is less. Other properties are also very comparable. So, here also the density also you see, the density of biodiesel this much, so soybean oil is having high density, after this conversions, the density reduced, here also density reduced and this density and this density are very near to the biodiesel.

So that way, the bio oil quality is improved and can be used as a biodiesel. So this is the chemical route through which waste and biomass can be converted to 2 different fuel components. So thank you very much for patience.