Energy Conversion Technologies (Biomass and Coal)

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Lecture 25

Mechanism of trans-esterification and biodiesel production

Good morning everyone.

Welcome to this second lecture of module 6. In this lecture, we will discuss mechanism of transesterification reaction. That is mechanism of acid catalyzed transesterification reaction, mechanism of alkali catalyzed transesterification reaction. Followed by that we will discuss the different parameters that affect the biodiesel yield, purification of biodiesel, fuel characteristics, and at the end we will practice one or two examples on the concept of theoretical biodiesel yield or theoretical glycerol yield. If you recollect our discussion in the previous lecture, we discussed about the esterification process that is also regarded as acid pretreatment step to lower the free fatty acid content followed by transistorification reaction of reduced FFA containing raw material.

Transesterification is a traditional method used for the biodiesel production. And transesterification, it refers to the reaction of triglyceride commonly referred as triacylglycerol with alcohol in presence of catalyst. And the commonly used catalyst for the transesterification reaction includes sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide to produce biodiesel and that is also referred as fatty acid alkyl ester and glycerol.

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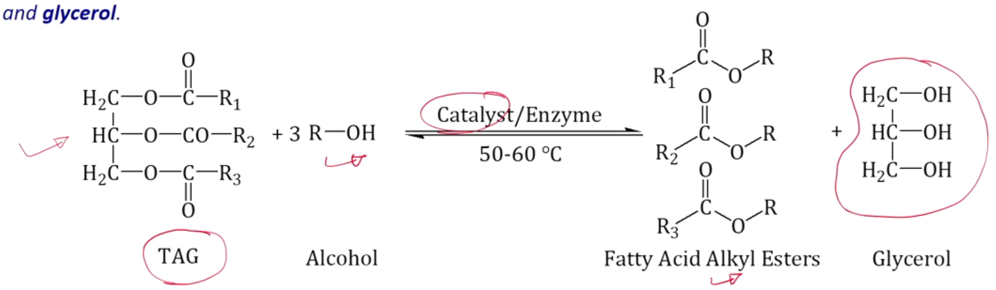
Biodiesel Production – Transesterification

- Traditional method for biodiesel production includes transesterification reaction.
- *Transesterification refers to the reaction of **triglycerides** (triacyl glycerol, TAG) with **alcohol** in the presence of **catalyst** (like NaOH, KOH, sodium methylate, or potassium methylate) to produce **biodiesel** (fatty acid alkyl esters) and **glycerol**.*



- **Catalyst** : It can be a homogeneous or heterogeneous catalyst including acid, base, or enzyme.
- **Alcohol** : Commonly used alcohols are methanol, ethanol, and 2-propanol.

This following reaction it represents the transesterification reaction of triacylglycerol that is TAG which reacts with alcohol in presence of catalyst to produce fatty acid alkyl esters. And along with that this reaction also produces glycerol as a byproduct. And the catalyst used in this process it can be a homogeneous catalyst or heterogeneous catalyst including acid base or enzyme and the commonly used alcohol for this transesterification reaction includes methanol, ethanol and propanol. And this is general scheme for the transesterification reaction.

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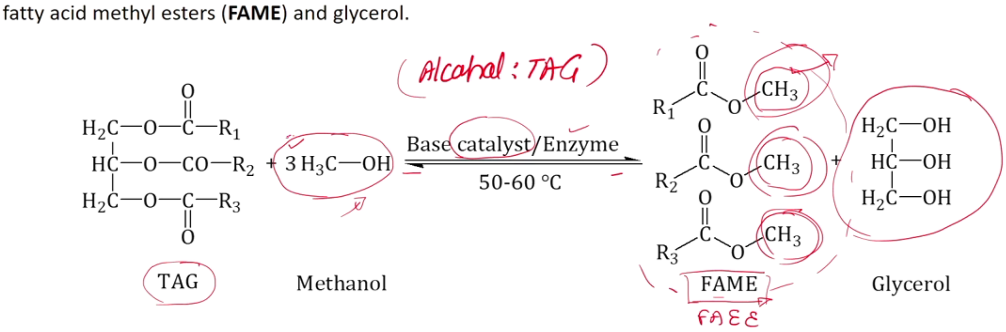
- Transesterification of triglycerides (triacyl glycerol, TAG) with **methanol** in the presence of base catalyst produce fatty acid methyl esters (**FAME**) and glycerol.



- Stoichiometric reaction requires 1 mole of triglyceride and 3 moles of methanol, to produce 3 moles of FAME.
- Transesterification is a reversible reaction and proceeds essentially by mixing the reactants.
- In general, a higher molar ratio (Alcohol:TAG) is employed to keep the equilibrium of the reaction toward the forward direction, for maximum ester production.

However, if this transesterification reaction is carried out with any specific alcohol say for example with methanol then the reaction can be represented as follows. Triacylglycerol it reacts with methanol in presence of base catalyst or enzyme to produce fatty acid methyl ester. And that is commonly termed as biodiesel along with this glycerol.

So, here in this case these methyl groups are replaced here because the methanol is being used as an alcohol for this particular reaction. Similarly, if the reaction is carried out with ethanol, so accordingly this group will get replaced and that will be termed as fatty acid ethyl ester instead of the fatty acid methyl ester. And the stoichiometric reaction here it requires 1 mole of triacylglycerol that is triacylglycerol and 3 moles of alcohol here that is methanol to produce 3 moles of fame. As I mentioned just now, FAME is fatty acid methyl ester and if the ethanol is used as a alcohol then it will be fatty acid ethyl ester because here then here this methyl group will get replaced by the ethyl group.

Along with this it also produces 1 mole of glycerol and this transesterification reaction, as we can see, here it is a reversible reaction and proceeds essentially by mixing the reactant. In general, high molar ratio alcohol to triacylglycerol or triglyceride is employed to keep this equilibrium of the reaction towards the forward direction that means toward formation of this methyl ester. And this is mainly required because as you can see here, this is a reversible reaction so to keep this equilibrium of the reaction towards the forward direction that means toward the formation of the methyl ester, so the alcohol need to be used in the excess quantity during the transesterification reaction.

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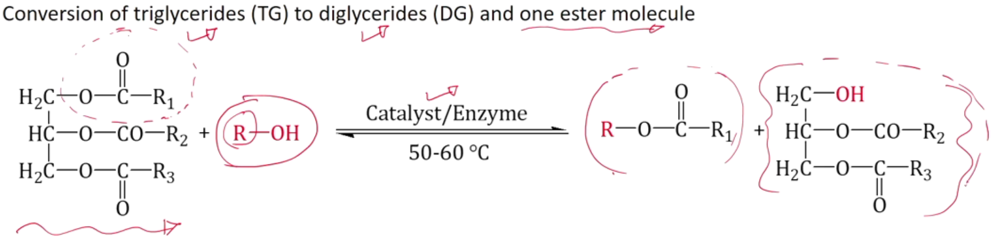
Mechanism of transesterification

- Transesterification mechanism consists of a number of consecutive and reversible reactions.
- The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and then monoglycerides to glycerol, yielding one molecule of methyl ester per mole of glyceride at each step.
- Three step transesterification of triglycerides:

1. Conversion of triglycerides (TG) to diglycerides (DG) and one ester molecule



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So, this mechanism of transesterification reaction as we can see here, it consists of number of consecutive and reversible reaction. And in this transesterification reaction the first step is the conversion of triglyceride to diglyceride followed by the conversion of diglyceride to monoglyceride and then monoglycerides converts into glycerol and during this conversion step it yields 1 molecule of ester per mole of glyceride at each step. And this mechanism of transesterification reaction is a three step process in which, as we discussed earlier, the triglycerides converts to diglyceride and release 1 ester molecule.

Say for example here, this is a triglyceride molecule reacts with alcohol in presence of catalyst to produce 1 molecule of ester and diglyceride. So, in this particular molecule if you see here the ester separates out here and then the methyl group of alcohol is getting attached to this ester molecule forming the fatty acid methyl ester and producing diglyceride molecule.

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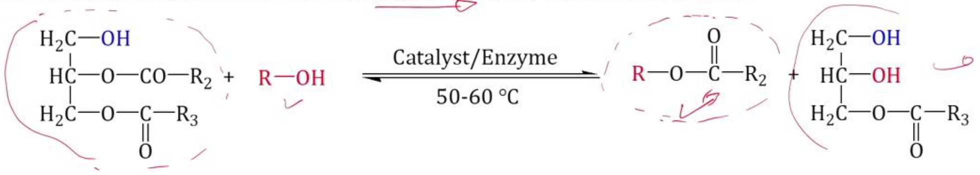
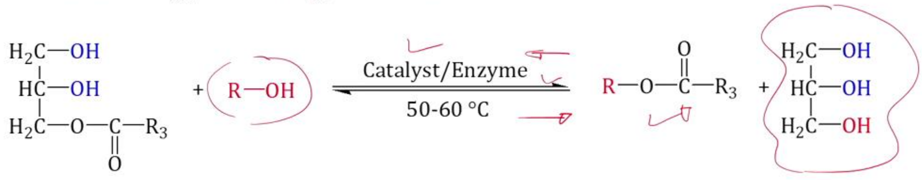
2. Conversion of diglycerides (DG) into monoglycerides (MG) and one ester molecule



3. Conversion of monoglycerides into glycerol and one ester molecule.



- The step wise reactions are reversible, thus use of excess alcohol shifts the equilibrium towards the forward direction i.e. formation of esters.
- In presence of excess alcohol, the foreword reaction is pseudo 1st order and the reverse reaction is 2nd order.

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And the second step involves the conversion of diglyceride to monoglyceride. In this case the diglyceride produced in step 1 reacts with alcohol to produce ester molecule and monoglyceride. Here this monoglyceride converts with alcohol in presence of catalyst to produce 1 ester molecule and glycerol. As we can see here these step-wise reactions are reversible reactions. Thus excess of alcohol is required during this particular reaction, so that this equilibrium shifts toward the forward direction that is formation of the ester. And in the presence of excess alcohol this forward reaction is considered as the pseudo first order and the reversible reaction is second order reaction.

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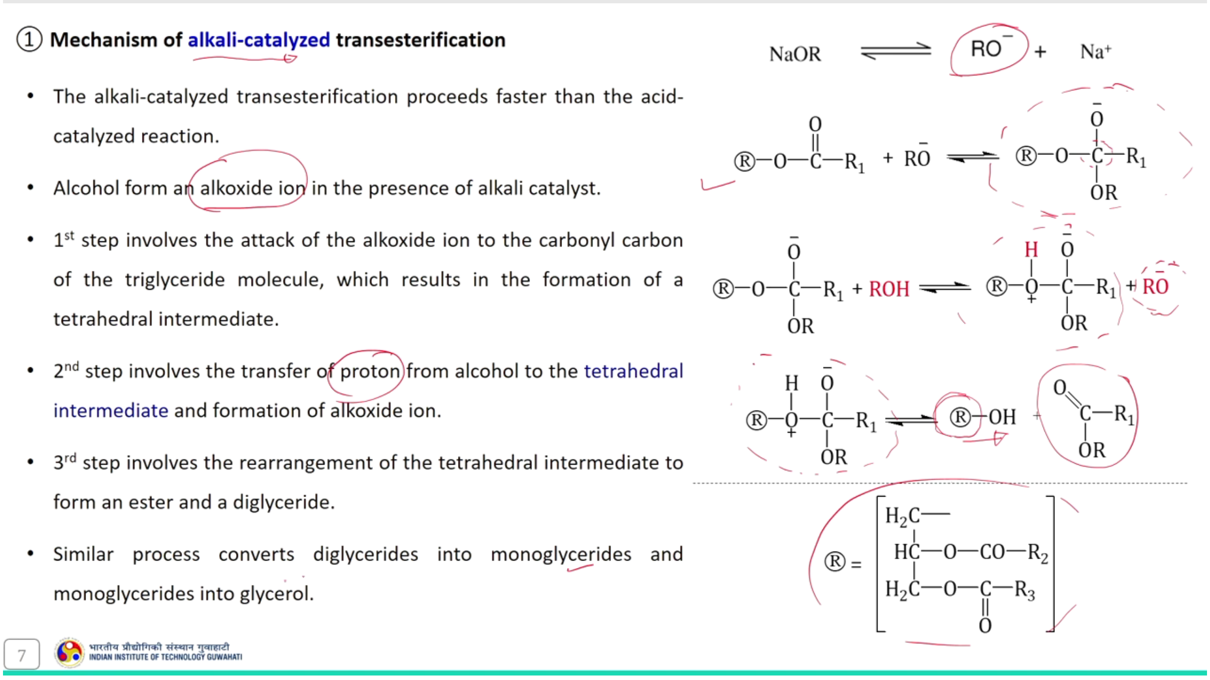

So, after learning this mechanism of transesterification reaction, let us discuss this mechanism of transesterification reaction with alkali catalyst. So, this alkali catalyzed transesterification reaction, it proceeds faster than the acid catalyzed transesterification reaction. And alcohol here forms an alkoxide ion in the presence of alkali catalyst. And in the first step the attack of this alkoxide ion to the carbonyl carbon of the triglyceride molecule results in the formation of tetrahedral intermediate. And the second step it involves the transfer of the proton from alcohol to this tetrahedral intermediate and the formation of this alkoxide ion.

And third step it involves the rearrangement of this tetrahedral intermediate to form an ester and diglyceride and this is represented as a diglyceride molecule. In the similar way the process converts diglyceride to monoglyceride and monoglyceride to glycerol.

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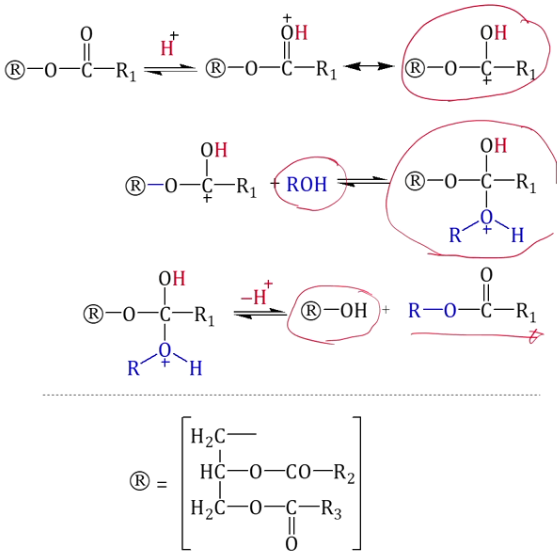
② **Mechanism of acid-catalyzed transesterification**

- Transesterification can be catalyzed by Brownsted acids, preferably by sulfonic and sulfuric acids.
- These catalysts give very high yields of alkyl esters, but this reaction is slow, requiring typically > 3 h of reaction time.
- 1st step: In the presence of acid catalyst, the protonation of carbonyl group of the triglyceride leads to the carbocation.
- 2nd step: Carbocation after a nucleophilic attack of the alcohol produces a tetrahedral intermediate.
- 3rd step: This intermediate eliminates diglyceride to form an ester and regenerate the catalyst.
- This mechanism can be extended to di- and mono-glycerides.



While the mechanism of acid catalyzed transesterification reaction indicates that the transesterification reaction it can be catalyzed by bronsted acids preferably by sulfuric and sulfuric acids. And this catalyst it gives very high yield of alkyl ester. But this reaction is relatively slow compared to that of the alkali catalyst transesterification reaction, and required typically more than 3 hours of the reaction time to complete the transesterification process.

In first step here, the presence of acid catalyzed the protonation of carbonyl group of triglyceride leads to the formation of carbocation. And in the second step the carbocation after a nucleophilic attack of the alcohol produces tetrahedral intermediate in this particular form. And in the third step this intermediates eliminates diglyceride as we have seen in the previous slide to form an ester and regenerate the catalyst. So, in the third step the regeneration of the catalyst takes place in case of the acid catalyst transesterification reaction. And this mechanism, it can be extended in the similar way to diglyceride and monoglyceride followed by conversion of monoglyceride to glycerol and fatty acid alkyl ester.

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Major factors affecting the biodiesel

The major factors affecting the biodiesel yield via esterification and transesterification reactions are :

1. Free fatty acid (FFA)
2. Water/moisture Content
3. Catalyst type and concentration,
4. Molar ratio of alcohol,
5. Reaction temperature,
6. Reaction time,
7. Mixing Rate

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So, after understanding about the mechanism of transesterification process with alkali and the acid catalyst, let us discuss about the factors affecting the biodiesel process, which includes free fatty acid content of the raw material, water or we can say the moisture content of the feed material, catalyst type and concentration, molar ratio of alcohol, reaction temperature, reaction time and mixing rate.

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① Free fatty acid (FFA) and water content

- Transesterification reaction is affected to a great extent due to FFA and water content.
- In case of higher FFA content (> 1%) requirement for base catalyst increases for neutralizing FFA.
- Triglycerides may undergo hydrolysis in presence of water to form free fatty acids (FFAs).
- Water also hinders the reaction by frothing and soap formation that results in increase in viscosity.
- Soap consumes the catalyst and reduces its efficiency, whereas foaming make the glycerol separation difficult.

- For best conversion efficiency in the alkali-catalyzed transesterification reaction:
  - ↦ The oil should have acid value of <1 mg KOH/g (or FFA below 0.5%). (Ingle, 2021; Mathew et al., 2021)
  - ↦ All other reactants should be anhydrous, and water content should be maintained below 0.06% w/w.

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The process of transesterification of the oily feedstock material is affected to a great extent due to FFA and the water content. In case if the feedstock material has high FFA content then requirement of the base catalyst increases to neutralize the FFA. FFA is nothing but the free fatty acid content in the feedstock material.

Even in this transesterification process the triglyceride may undergo hydrolysis in presence of water the excess water which is present in the feed material to form free fatty acid. So, this is also one of the reactions which may occur in the transesterification process. If the water content is high then this triglyceride may undergo hydrolysis process to form free fatty acids. Water also hinders the reaction by frothing and soap formation that results in increase in the viscosity of the reaction mixture. And the soap form in this particular process consumes the catalyst and reduces its efficiency, whereas the foam makes the glycerol separation difficult from the rest of the reaction mixture.

Therefore for the base conversion efficiency in alkali catalyzed reaction the oil should have acid value of less than 1 milligram KOH per gram of oil sample or we can say the FFA should be below 0.5% and all other reactant which are used during the transesterification process should be unaddressed reactant and the water content should be maintained below 0.06% that is weight percent. So, these are some important point which needs to be taken into consideration while conducting alkali catalyst transesterification reaction.

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② **Catalyst type and concentration**

- In transesterification reactions different types of heterogeneous and homogeneous catalyst (alkali, acid, or enzyme) are used for attaining maximum biodiesel yield.

- Alkali-catalyzed reactions are faster than the acid-catalyzed (Mathew et al. 2021).
- Acid catalyst give very high yields of alkyl esters, but reaction is slow, typically > 3 h of reaction time.
- Acid catalyst work better with high FFA feedstocks, while base catalyst used for low FFA feedstocks.

Overall, among all these catalysts, alkali catalysts, like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are the most effective for biodiesel production (Meher et al., 2006).

So, another important factor is catalyst type and its concentration. In transesterification reaction different types of catalyst that is homogeneous and heterogeneous catalyst are used for attaining the maximum biodiesel yield and the catalyst used during this transesterification reaction includes alkali catalyst acid or enzyme. And as we discussed earlier the alkali catalyst transesterification reaction are faster than the acid catalyzed transesterification reaction. And although we know the acid catalyst reaction can give very high yield of alkyl ester but the reaction rate is slow with acid catalyzed reaction and it typically takes more than 3 hours of reaction time to reach to completion.

Acid catalyst works better with high FFA feedstock while base catalyst used for low FFA feedstock material. So, among all these catalyst alkali catalyst like sodium hydroxide, sodium methoxide, potassium hydroxide or potassium methoxide are the most effective catalysts for the biodiesel production.

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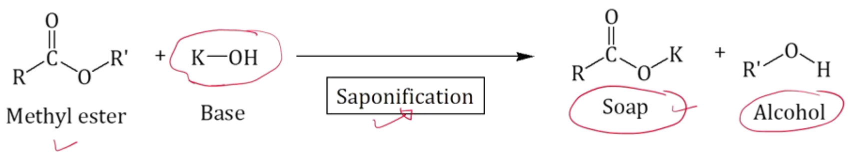
- **Catalyst concentration** is among the most influential parameters which affect the biodiesel yield.
- Optimum catalyst concentrations should be determined experimentally for attaining desirable biodiesel yield.

e.g. If the alkali-catalyst concentration exceeds the optimum range, it increases soap formation that ultimately lowers the final yield of methyl esters.



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Apart from the catalyst type the catalyst concentration or we normally term it as a catalyst loading is among the most influential parameter which affects the biodiesel yield. Therefore the optimum catalyst concentration should be determined experimentally for attaining the maximum biodiesel yield. And in case if the alkali catalyst concentration exceeds the optimum range then it increases the soap formation and that ultimately lowers the yield of methyl ester.

As represented in the following reaction the methyl ester reacts with excess alkali present in the reaction mixture and produces soap and alcohol as product and this reaction commonly referred as saponification reaction or saponification process. For that reason the optimum catalyst concentration need to be used during the alkali catalyzed transesterification process for attaining the maximum biodiesel yield.

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Catalyst Type	Examples	Advantage	Disadvantage
Acid catalyst (Homogenous)	H_2SO_4, HCl, Phosphoric acid, Organic sulfonic acid, etc.	Improved catalysis	Corrosion of reactor, Slower reaction rate.
(Heterogenous)	Bronsted and Lewis acids.	Reusable and easy separation	Expensive catalyst preparation, Harsh reaction conditions.
Base catalyst (Homogenous)	NaOH, NaH, sodium amide ($NaNH_2$), CH_3ONa, KOH, KH, CH_3OK, etc.	High rate of catalysis, Noncorrosive, Easily available	Saponification at high FFA, Non-reusable.
(Heterogenous)	Zeolites, hydrotalcites, metal oxides and carbonates like CaO, $CaCO_3$, etc.	Reusable and easy separation, Less waste generation	Costly, Leaching of active sites.
Heterogenous Nanocatalyst	Nanoparticles of ZnO, CaO, MgO, TiO_2, nanohydrotalcites, nanozeolites, etc.	Reusable and easy recovery, Non-toxic and cost effective.	Lengthy catalyst synthesis.
Enzymes	Free lipase (from bacteria, yeast/fungi)	Higher biodiesel yield.	Low catalytic activity, Difficult recovery of glycerol.
	Immobilized lipase (commercial)	Higher biodiesel yield, Easy recovery of glycerol.	Low catalytic activity.

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Courtesy: Mathew et al. Science of the Total Environment, 2021, 794, 148751.

And this table here it depicts the comparative analysis of different homogeneous and heterogeneous catalyst that are used for the transesterification process. So, let us first compare the acid catalyst that is homogeneous acid catalyst that includes sulphuric acid, hydrochloric acid, phosphoric acid, organic sulphonic acid, etc. And the advantage of using this catalyst for the transesterification reaction is improved catalysis process. However the limitation associated with the use of this catalyst include corrosion of reactor and slower reaction rate.

And this point we already discussed in one of the slide, that the acid catalyzed reactions are relatively slow compared to that of the alkali catalyzed transesterification reaction. However the heterogeneous acid catalyst includes Bronsted and Lewis acids. The advantage is easy separation of this catalyst from the reaction mixture and reusable. However the limitation associated with the use of this catalyst includes expensive catalyst preparation procedure and also it required harsh reaction condition to achieve the maximum biodiesel yield. Compared to acid catalyst the base catalyst transesterification reactions are more preferred in that the homogeneous base catalyst reactions are commonly being used for the biodiesel synthesis process which includes sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide and other catalyst as well.

So, advantage of using this catalyst includes higher rate of catalysis non-corrosive in nature and easily available. However the limitation of this catalyst as we discussed earlier, the use of this catalyst may result into the saponification reaction with high FFA containing feedstock and also it is non reusable. However the heterogeneous catalyst includes zeolites, hydrodilzides, metal oxides, and carbonates like calcium oxide and calcium carbonate. And the advantage associated with the use of this heterogeneous base catalyst includes easy separation from the reaction mixture. Hence it can be reused for the transesterification process and because of this reusability the waste generation would be minimal.

However the limitation or the disadvantages associated with the use of this catalyst include costly process to synthesize this kind of catalyst as well as the leaching of active sites during the transesterification process. And the new class of catalyst which are being used for the transesterification reaction includes the heterogeneous nano catalyst including nanoparticles of zinc oxide, calcium oxide, magnesium oxide and titanium dioxide as well as the nano hydrotalcite and nanozeolites. The advantage of this heterogeneous nano catalyst includes the easy separation as well as easy recovery and its reusability, non-toxic and even cost effective. However, the limitation includes the lengthy catalyst synthesis process and this is the major limitation of use of this particular catalyst for the transesterification process. And the next class of catalyst is enzymes which includes the free lipase and immobilized lipase.

In case of free lipase the advantage is like it gives higher biodiesel yield however it has low catalytic activity and difficult recovery of the glycerol. While in case of immobilized lipase it gives higher biodiesel yield even easy recovery of glycerol but lower catalytic activity. Considering all these limitations of the homogeneous and the heterogeneous catalyst, base catalyst that is alkali catalyst process are still widely being used for the biodiesel synthesis.

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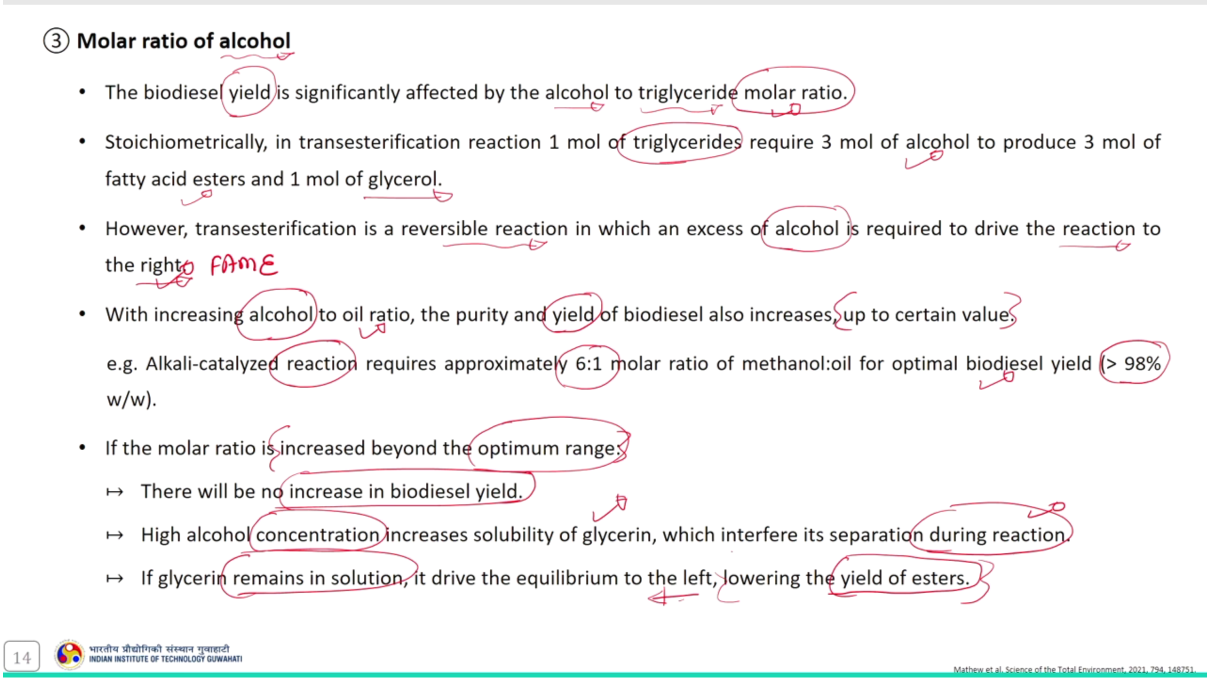

Another important factor for the biodiesel synthesis includes the molar ratio of alcohol and this biodiesel yield is significantly affected by the alcohol to triglyceride molar ratio as we discussed in the previous slide as well. The molar ratio of alcohol to triglyceride is a crucial parameter in optimizing the biodiesel yield. Stoichiometrically as we know in transesterification reaction 1 mole of triglycerides required 3 mole of alcohol to produce 3 moles of fatty acid esters and 1 mole of glycerol.

However as we know the transesterification reaction is a reversible reaction, so in which excess alcohol is required to drive this transesterification reaction to forward direction that is to the right that is toward the formation of fatty acid methyl ester. With increasing this alcohol to oil ratio the purity and the yield of biodiesel also increases but up to certain level. For example if alkali catalyst reaction requires approximately 6 to 1 molar ratio of methanol to oil for optimal biodiesel yield that is close to 98%. Now if this molar ratio is increased beyond say the optimum range then there will be no further increase in the biodiesel yield.

However this high alcohol concentration it may increase the solubility of the glycerin which interfere its separation during the reaction. Because as we know this glycerin is soluble in the alcohol so with increasing concentration of alcohol it increases the solubility of the glycerin and then it interfere its separation during the reaction. Moreover if the glycerin remains in the solution it drives this equilibrium to the left and lowers the yield of ester. So, rather than driving this equilibrium towards the right this excess alcohol concentration, because of this increasing solubility of the glycerin, will drive this equilibrium towards the left and it eventually results in lowering the yield of the esters. For that reason the optimum range of alcohol to triglyceride molar ratio need to be maintained in the transesterification process.

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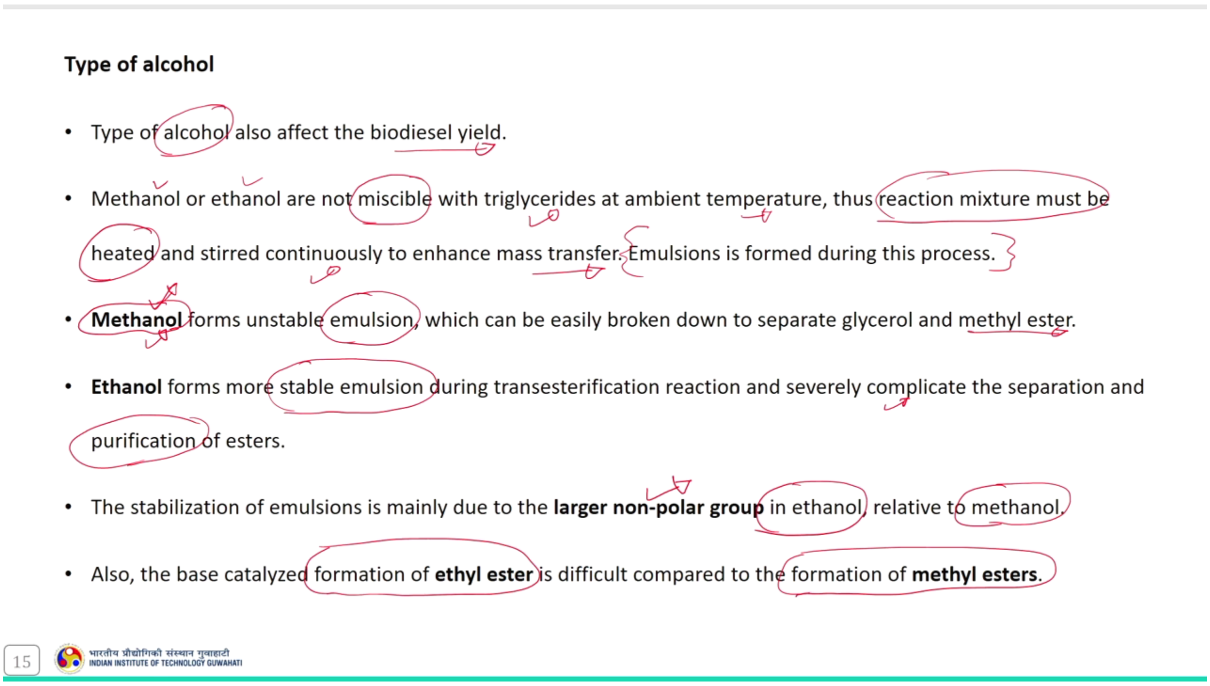

Even this type of alcohol it also affects the biodiesel yield, because this methanol and ethanol are not miscible with triglyceride at ambient temperature. And because of that the reaction mixture need to be heated and stirred continuously to enhance the mass transfer between these two phases and even the emulsions are formed during this particular process. As we know the methanol forms unstable emulsion which can easily be broken down to separate the glycerol from methyl ester. However in case of the ethanol it forms more stable emulsion during the transesterification reaction then it severely complicates the separation and purification of esters.

And this stabilization of emulsion in case of ethanol is mainly due to the large non-polar group in ethanol relative to methanol. And also the base catalyzed formation of ethyl ester is quite difficult compared to the formation of the methyl ester. And because of this reason the methanol is the most widely used alcohol or we can say the most preferred alcohol for the transesterification reaction.

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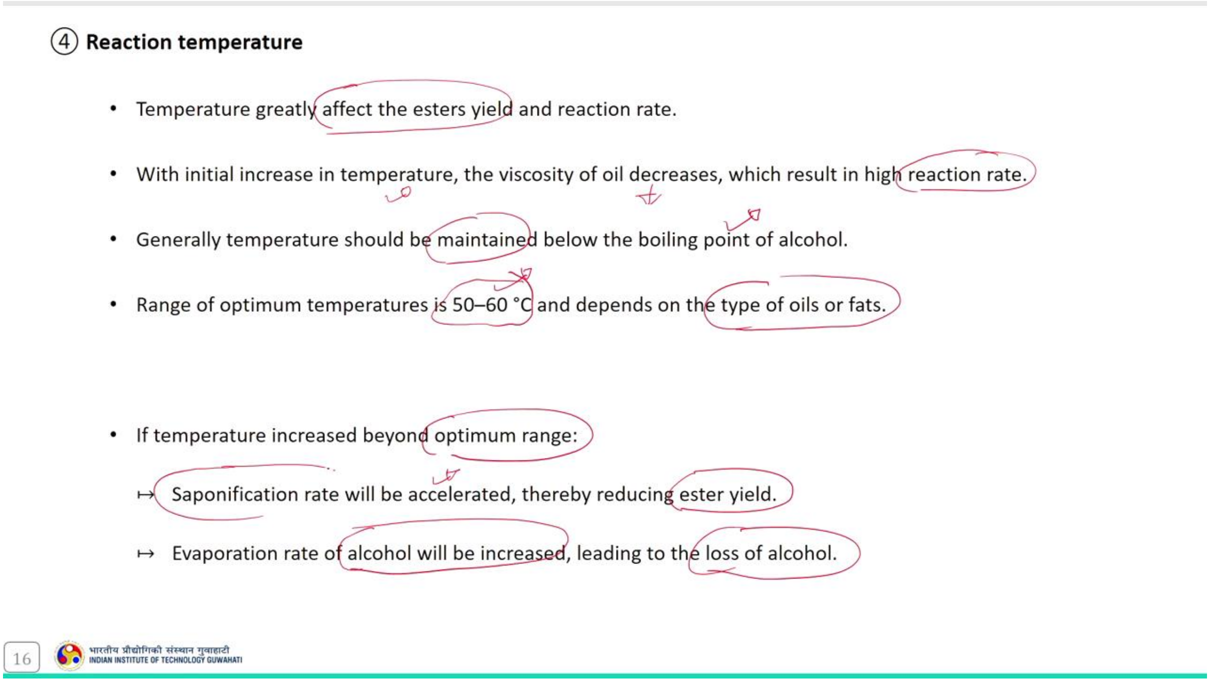

Similarly this reaction temperature also it greatly affect the ester yield and the reaction rate with increasing the temperature the viscosity of the oil decreases which results in the higher reaction rate. Similarly the temperature it should be maintained below the boiling point of the alcohol which is being used for the transesterification process. And the range of optimum temperature is 50 to 60 °C and it also depends on the type of oils and the fats being used for the transesterification process.

In case, if the temperature increases beyond this optimum range then the saponification rate will be accelerated and thereby reducing the ester yield. Moreover, the evaporation rate of the alcohol will be increased and leading to the loss of alcohol and because of this reason the optimum temperature range of 50 to 60 degree Celsius need to be maintained during the transesterification process to avoid the loss of alcohol as well as to reduce the chances of saponification reaction.

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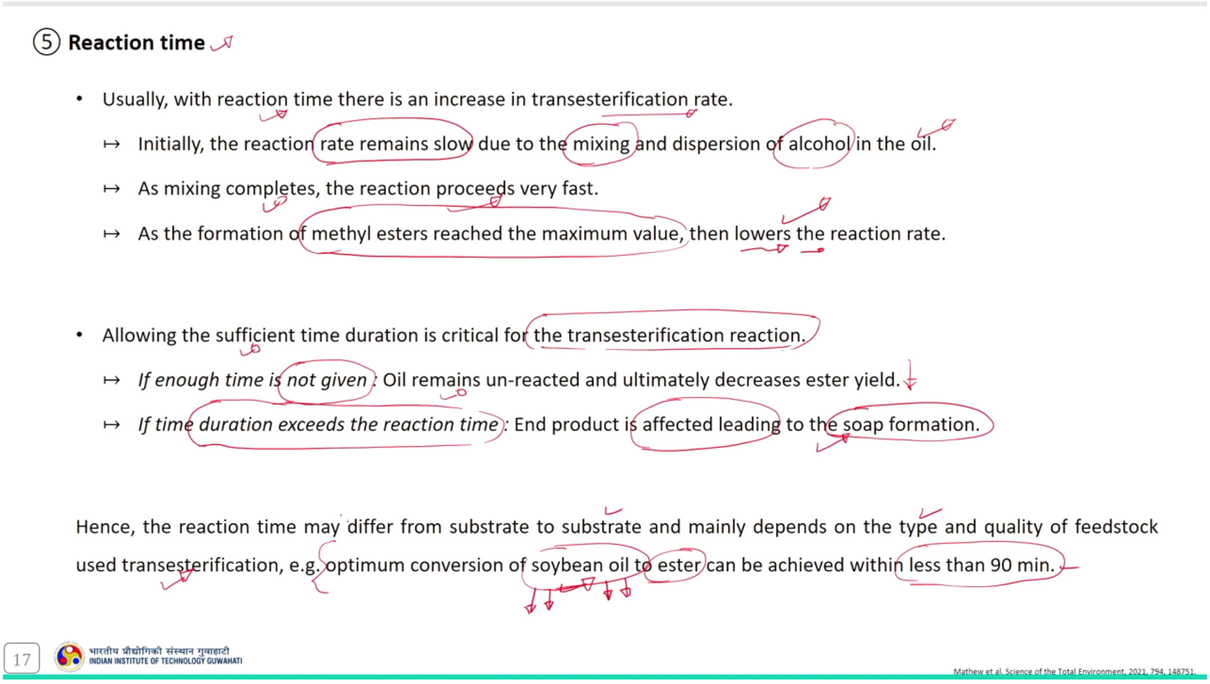

Similarly the reaction time is also one of the crucial factors during this transesterification reaction. Usually with reaction time there is an increase in the transesterification rate. Initially the reaction rate remains slow and that is mainly due to the mixing and the dispersion of alcohol in the oil phase. And as the mixing completes then the reaction proceed very fast. However, as the formation of the methyl ester reach the maximum level or value then it lowers the reaction rate. Therefore allowing this sufficient time duration is a critical step for the transesterification reaction. If enough time is not given then what will happen is like the oil remains unreacted and ultimately decreases the ester yield.

In case if the time duration exceeds the reaction time then the end product is affected leading to the soap formation as we discuss this formation of soap with increasing the temperature in the previous slide as well. Similarly with increase in the reaction time the end product will get affected and may lead to the formation of the soap. Hence the reaction time may differ from substrate to substrate and it mainly depends on the type and the quality of the feedstock which is used for the transesterification process. For example in case of soybean oil the optimum conversion of soybean oil to ester can be achieved within less than 90 minutes. However, in some cases if the oil contains high amount of FFA as well as the impurities then the duration of the reaction may get extended.

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⑥ **Agitation/mixing**

- Oils or fats are immiscible with catalyst-alcohol solution (e.g. sodium hydroxide–methanol solution).
- Therefore, for transesterification reaction agitation or mixing is mandatory.
- Once the two phases are mixed and the reaction is started, the effect of stirring is insignificant.

- Agitation/mixing speed also has an important role for end product formation.
  - ↦ Lower stirring speed cause less ester yield.
  - ↦ Higher stirring speed leads soap formation.
  - ↦ Beyond the optimum speed, the reaction time is the controlling factor in determining the ester yield.

Similarly, the agitation and the mixing of the reaction mixture, since oils and fats are immiscible with catalyst and alcohol solution say for example if the catalyst use is sodium hydroxide and the alcohol use is methanol, then oil or fats are immiscible with this sodium hydroxide methanol solution. Therefore for transesterification reaction agitation or mixing is mandatory. And once these two phases are mixed and the reaction is started then the effect of stirring is insignificant.

Apart from that the agitation and the mixing speed also has an important role for the end product formation that is biodiesel formation. Lower stirring speed causes lower stir yield and higher stirring speed leads to the soap formation. In case of the stirring speed beyond the optimum range the reaction time is the controlling factor in determining the ester yield.

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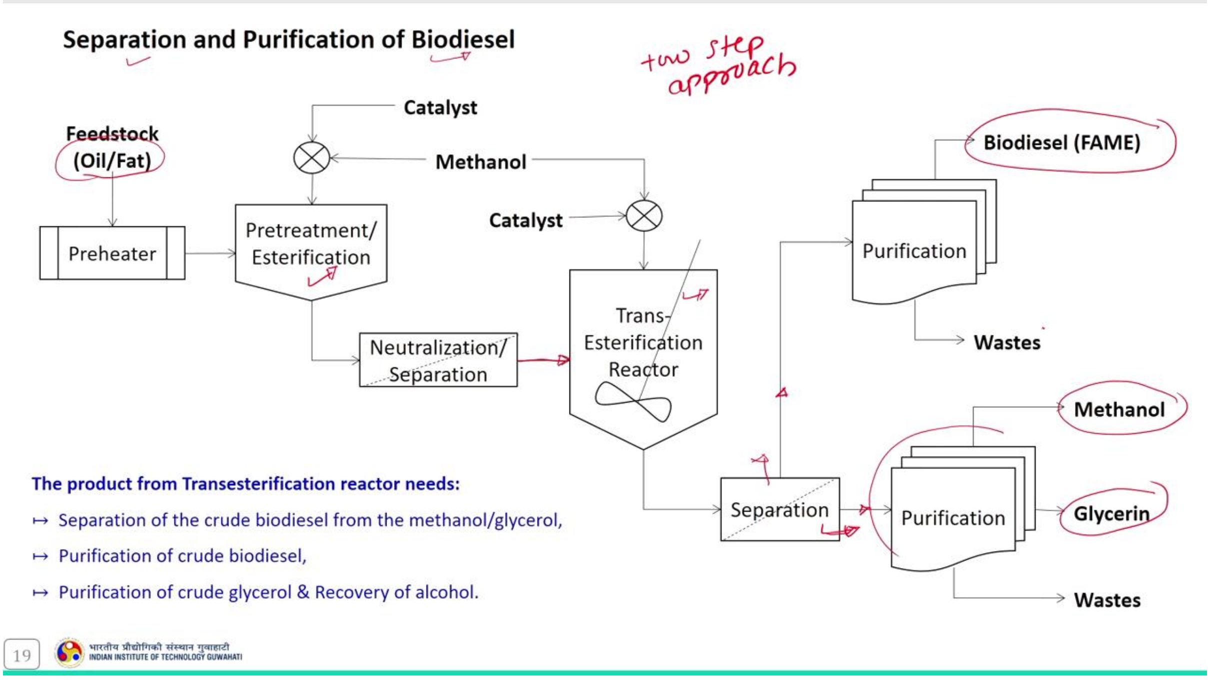

So, the next important topic is the separation and the purification of the prepared biodiesel. So, this schematic here it represent the process arrangement of biodiesel production using two-step approach which includes acid catalyze pre-esterification followed by the base catalyze transesterification reaction to convert the FFA and triacylglycerol into esters.

In the end of the esterification process the product is purified by removing the water and the other impurities and the resultant mixture is transesterified to convert into the ester. And the product mixture is allowed to separate crude biodiesel from the methanol and glycerol phase followed by its purification. So, the glycerol which is obtained at the bottom can be purified to obtain methanol and pure glycerin and the crude biodiesel that is the top layer in the separation vessel can be purified to produce biodiesel and waste.

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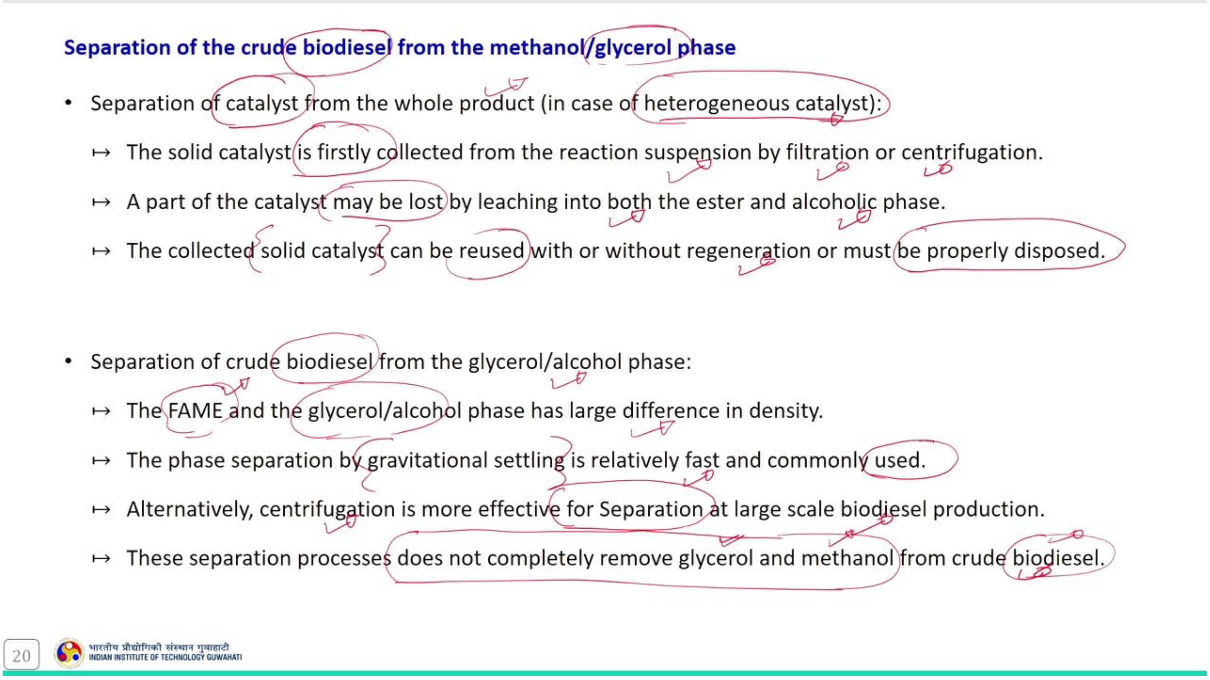

Using the separation of the crude biodiesel from the methanol and the glycerol phase the separation of the catalyst from the whole product is important because the solid catalyst first need to be collected from the reaction suspension by filtration or the centrifugation technique. A part of the catalyst may lost by leaching into the both ester and alcoholic phase. And this collected solid catalyst can be reused with or without regeneration or may be disposed properly.

And this separation of catalyst from the whole product is part of the discussion when the heterogeneous catalyst is used during the transesterification process. Followed by the separation of crude biodiesel from glycerol alcohol phase the fatty acid methyl ester and glycerol alcohol phase has a large density difference. And thus this phase separation by gravitational settling is relatively fast and most commonly used technique to separate the fatty acid methyl ester from glycerol alcohol phase. Alternatively centrifuge is used more effectively for the separation at large scale biodiesel production. However, the limitation of this separation technique is this separation process does not completely remove glycerol and methanol from the crude biodiesel and some fraction of glycerol and methanol may be observed in the biodiesel.

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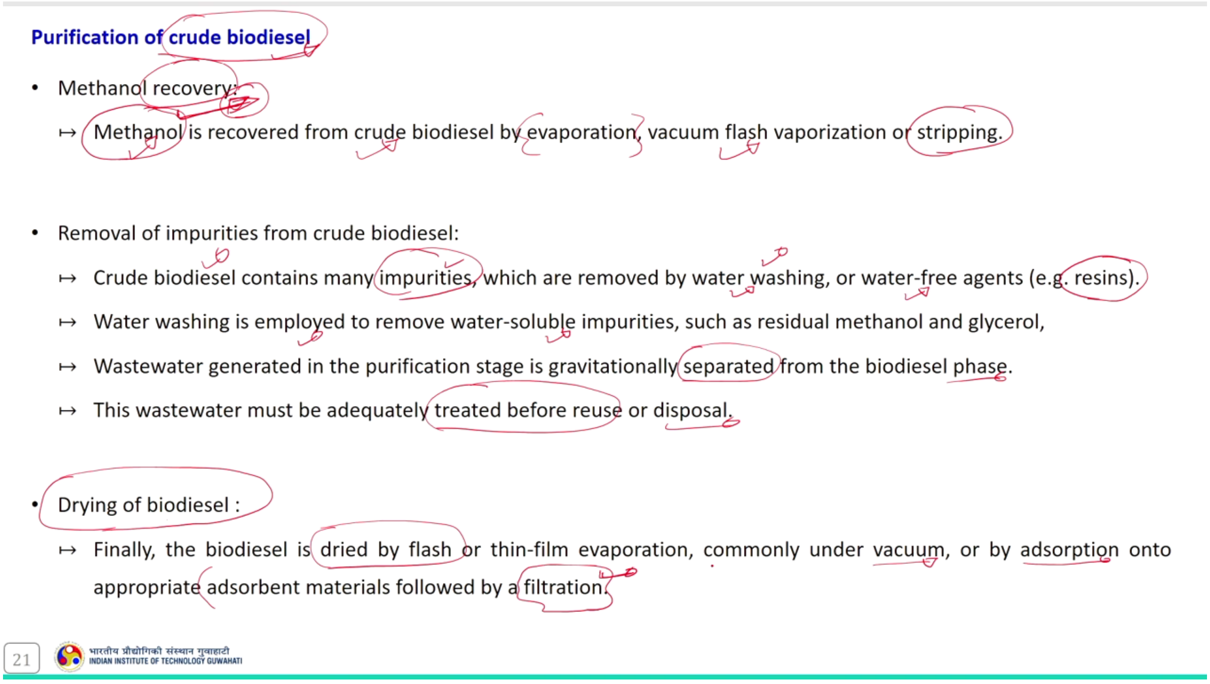

Followed by that is the recovery of the methanol. So, this methanol is recovered from the crude biodiesel by evaporation, vacuum flash vaporization or stripping operation. So, the removal of the ethanol is most crucial and the important step in the purification of the biodiesel since excess amount of the alcohol is used during the transesterification process. So, the excess alcohol need to be removed from the crude biodiesel so that it can be reused in the transesterification process, followed by the removal of impurities from the crude biodiesel. Since crude biodiesel contains many impurities which are removed by the water washing or water free agent example resins. So, sometime these resins are used to remove impurities present in the crude biodiesel to avoid the water washing step.

Water washing is employed to remove water soluble impurities such as residual methanol and glycerol. And the waste water generated during this purification step is gravitationally separated from the biodiesel and this water must be adequately treated before reuse or may be disposed of following the waste water treatment process. And the last operation in the purification of the biodiesel is a drying of biodiesel. Finally the biodiesel is dried by flash or the thin film evaporation commonly under vacuum or by absorption onto appropriate adsorbent material followed by the filtration, so that the trace amount of the impurities remains in the biodiesel can be separated out during this filtration operation.

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Fuel Characteristics of Biodiesel (ASTM D6751)

(B5)

Fuel Characteristic	**Unit**	**B100**	**B6 to B20**
Kinematic viscosity at 40 °C	(mm^2/s)	1.9-6.0	1.9-4.1
Flash point (closed cup)	(°C)	93	52
Oxidation stability	(h)	3	6
Cetane number	-	47	40
Acid number	(mg KOH/g)	0.5	0.3
Ramsbottom carbon residue	(% by wt)	0.05	0.35
Ca+ Mg	(μg/g or ppm)	5	-
K+ Na	(μg/g or ppm)	5	-
Sulfur Content	(μg/g or ppm)	15	15
Ash content	(% by wt)	0.02	0.01
Water and sediment	(% by vol)	0.05	0.05
Distillation temperature (90% recovery)	(°C)	360	343

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And this table here it depicts the fuel characteristics of different biodiesel blends as per the standard specified by ASTM. This biodiesel it can be blended and used in many different concentrations. And the most common is B5 that is up to 5% biodiesel and B20 that is 6 to 20% biodiesel. And this B100 that is termed as a pure biodiesel is typically used as a blend stock to produce lower percentages blends and is rarely used as a transportation fuel. And this table here it provides the fuel characteristics of these different blends along with its ranges.

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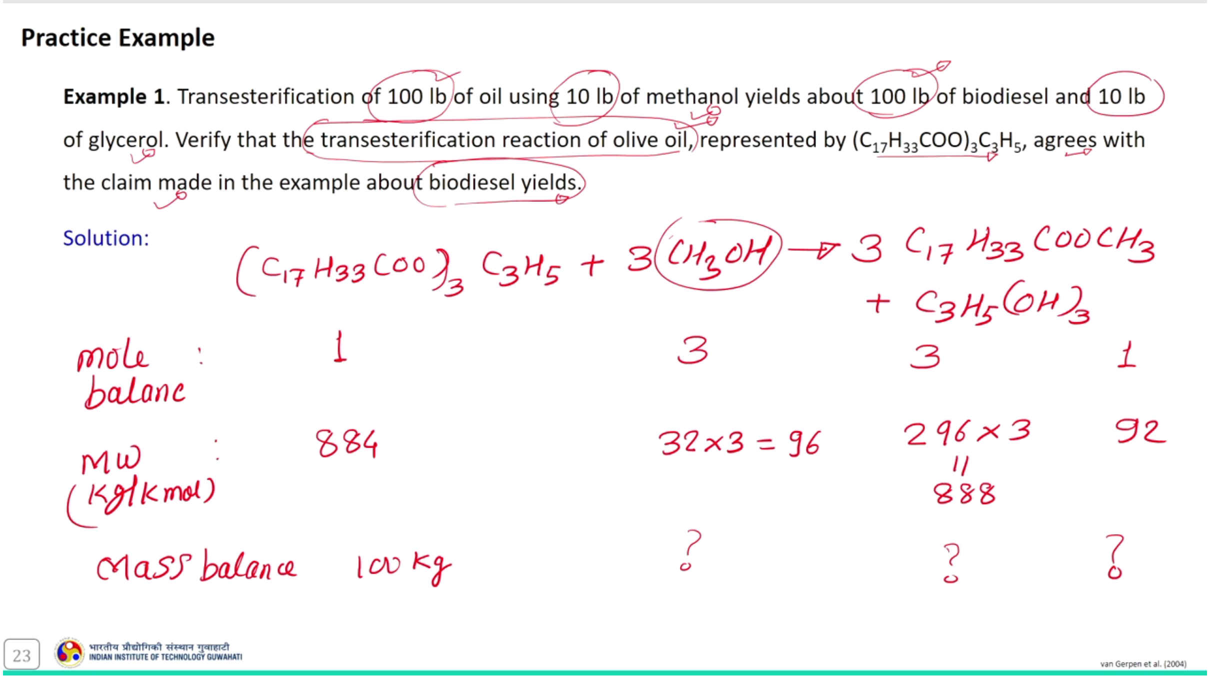

So, after learning about this transesterification process and its mechanism as well as the parameters which affect the transesterification process, let us try to solve one example to calculate the maximum biodiesel yield. So, in this example the transesterification of 100 pound of oil using 10 pound of methanol yields about 100 pound of biodiesel and 10 pound of glycerol. So, we need to verify this transesterification reaction of olive oil which is represented by this formula here and we have to also verify that it agrees with the claim made in this example about the biodiesel yield. As it is mentioned here 100 pound of oil gives around 100 pound of biodiesel. So, this claim needs to be verified with the help of transesterification of the olive oil.

So, let us begin with the solution. So, the olive oil is represented as $(C_{17}H_{33}COO)_3C_3H_5$ plus methanol undergoes transesterification process to produce 3 moles of ester that is methyl ester since methanol is used as a alcohol for the transesterification process and produces 1 mole of glycerol. So, as per the mole balance 1 mole of triglyceride reacts with 3 moles of alcohol that is methanol produces 3 moles of ester and 1 mole of glycerol. So, the molecular weight of this molecule it is 884 molecular weight of this molecule as for olive oil it is 884 for methanol that is 96 as 3 moles of methanol are used and 296 into 3 moles of ester gives and the glycerol is 92. So, the mass balance for 100 kg of oil, so we need to find out the amount of alcohol ester and the glycerol produced during this process.

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Given: $m_{oil} = 100\ kg$

$$m_{FAME} = \frac{888}{884} \times (100) = 100.45\ kg$$

$$m_{MeOH} = \frac{96}{884} \times (100) = 10.86\ kg$$

$$m_{Gly} = \frac{92}{884} \times (100) = 10.41\ kg$$

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Given in this example is mass of oil is 100 kg. Now, if we need to calculate the mass of fatty acid methyl ester, so it is simply by 884 into 100 kg oil sample so it gives so the methyl ester produced during this reaction is around 100.45 kg. Similarly, methanol is equals to 10.86 kg and glycerol equals to 10.41 kg. And these values indicate that the claim made in this example is substantially correct since 100 kg of oil is giving 100.45 kg biodiesel and 10.41 kg glycerol. And that was the claim made in this example also that 100 pound of oil using 10 pound of methanol yields 100 pound of biodiesel and 10 pound of glycerol.

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Example 2: kg of oil sample having 93% triglyceride (TAG) is transesterified using methanol and KOH catalyst. Calculate theoretical amount of biodiesel and glycerol produced, considering the TAG as Tristearin ($C_{57}H_{110}O_6$, MW = 891.5 g/mol)

Solution:

Given:- 1 kg = (1000 g) of oil sample having 93% (TAG)

Thus, Tristearin = 93% of 1000 g of oil

$= 0.93 \times 1000 = 930\ g$

moles of tristearin $= \dfrac{\text{given mass}}{\text{molar mass}} = \dfrac{930\ gm}{891.5\ g/mol} = 1.043\ mol$

So, let us try to solve another example where we need to calculate the theoretical amount of biodiesel and the glycerol produced during the transesterification process and considering the triacylglycerol as tristearin. So, in this case the kg of oil sample having 93% triglyceride and is transesterified using methanol and KOH as catalyst. So, with the help of this given information we have to just calculate the theoretical amount of the biodiesel and the glycerol produced during this transesterification of tristearin.

So, here given data is 1 kg that is 1000 gram of oil sample having 93% triglyceride that is triacylglycerol. Because, tristearin 93% of 1000 gram of oil gives 0.93 into 1000 that is equal to 930 gram. So, now the moles of tristearin equal to given mass by molar mass. So, here it is 930 gram divided by 891.5 gram per mole that comes out to be around 1.043 moles.

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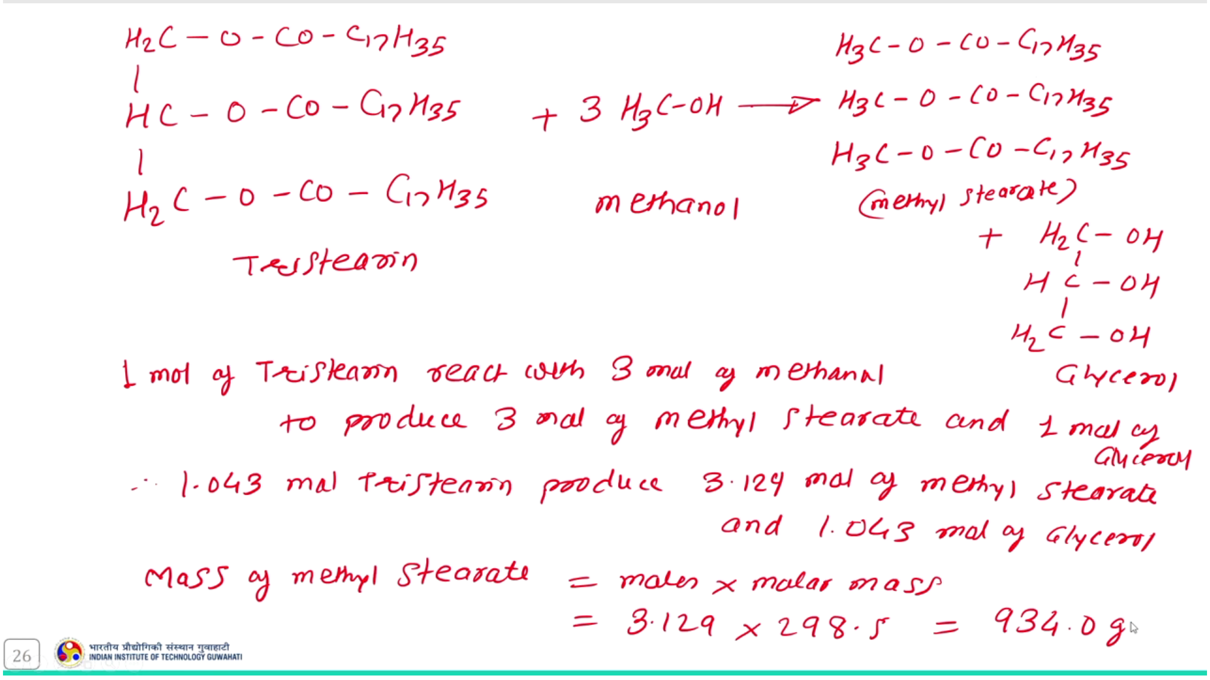

Now suppose this tristearin reacts with 3 moles of methanol produces 3 moles of ester. So, methanol and glycerol. So, this is tristearin, methanol and this is methyl stearate and this is glycerol. So, from this stoichiometry now 1 mole of tristearin react with 3 mole of methanol to produce 3 mole of methyl stearate and 1 mole of glycerol. So therefore, 1.043 mole of tristearin produce around 3.129 mole of methyl stearate and 1.043 mole of glycerine or glycerol. Now suppose, if you have to calculate this mass of methyl stearate then it will be moles into molar mass that is 3.129 into 298.5 and it comes out to be around 934.0 gram.

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mass of Glycerol produced = moles × molar mass

= 1.043 g × 92.1 g/mole = 96.1 g

Therefore 1 kg of oil containing 93 % of tristearin produce 934 g of biodiesel and 96.1 g of Glycerol

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Similarly mass of glycerol produce equal to moles into molar mass that is 1.043 into 92.1 that is gram by mole and this is in gram. So, it comes out to be around 96.1 gram. Therefore 1 kg of oil containing 93 percent of trasterine produces around 934 gram of biodiesel and 96.1 gram of glycerol and this is stoichiometric or you can say the theoretical yield of biodiesel.

This is all about the biodiesel process or we can say the trans-esterification process and you can refer to these references for the additional information. So, in the next lecture that is third lecture of the module 6, we will discuss green diesel synthesis from the bio-based feedstock and their application.

Thank you.