Biomass Conversion and Biorefinery

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Module-07
Lecture-20
Transesterification FT Process, Catalysts

Good morning students, this is lecture 2 under module 7. As you know that we are discussing biodiesel under this particular module. Today we will discuss about transesterification reaction in detail, the various reaction mechanisms basically. As well as the Fischer-Tropsch process and we also discuss about the catalyst and the reactors which are required to carry out such reactions. So, let us begin.

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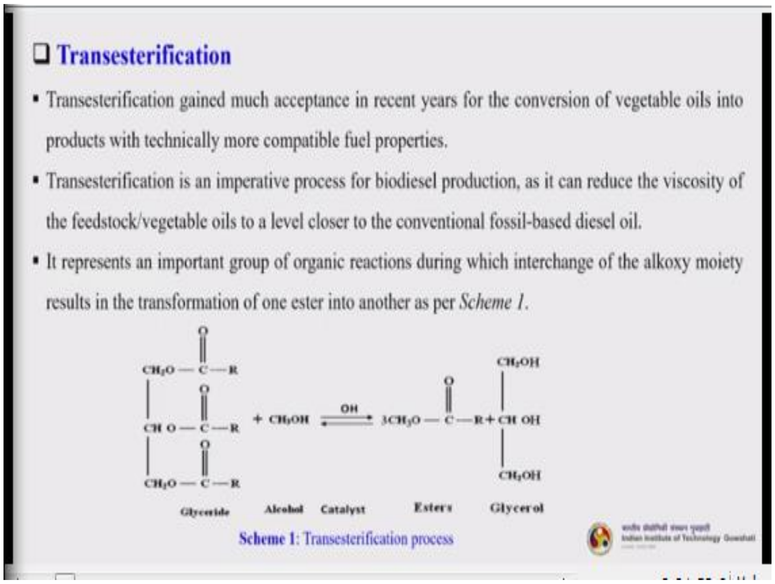


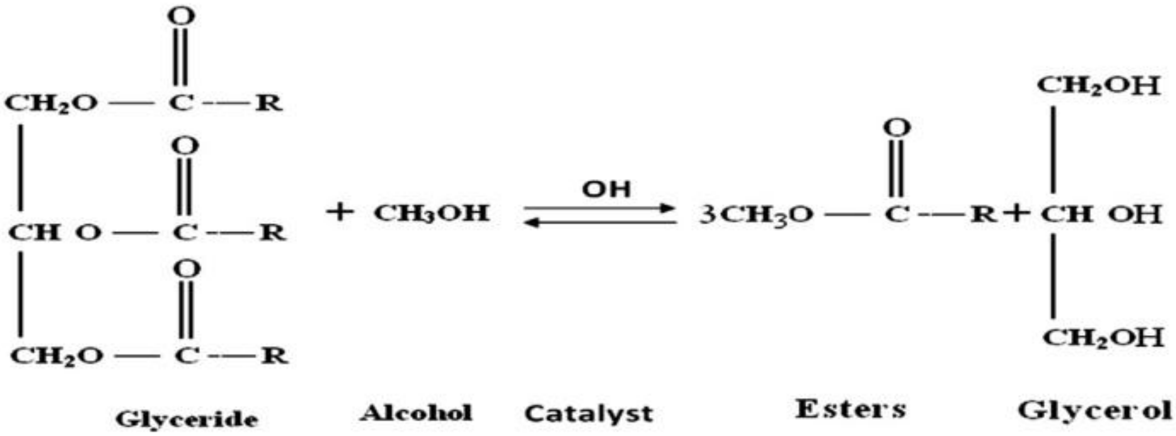
❑ Transesterification

- Transesterification gained much acceptance in recent years for the conversion of vegetable oils into products with technically more compatible fuel properties.
- Transesterification is an imperative process for biodiesel production, as it can reduce the viscosity of the feedstock/vegetable oils to a level closer to the conventional fossil-based diesel oil.
- It represents an important group of organic reactions during which interchange of the alkoxy moiety results in the transformation of one ester into another as per *Scheme 1*.

Scheme 1: Transesterification process

So, transesterification gained much acceptance in recent years for the conversion of the vegetable oils into products with technically more compatible fuel properties. Transesterification is an imperative process for biodiesel production, as it can reduce the viscosity of the feedstock vegetable oils to a level closer to the conventional fossil based diesel oil. It represents an important group of organic reactions during which interchange of the alkoxy moiety results in the transformation of one ester to another as per this particular scheme.

You can see this, this is the simplest reaction glyceride + alcohol with a presence of a catalyst, it can be any acid type catalyst, basic type catalyst or homogeneous, heterogeneous anything. So, it will result us ester + glycerol, this is the general reaction scheme. So, we will learn about the detailed mechanism later.



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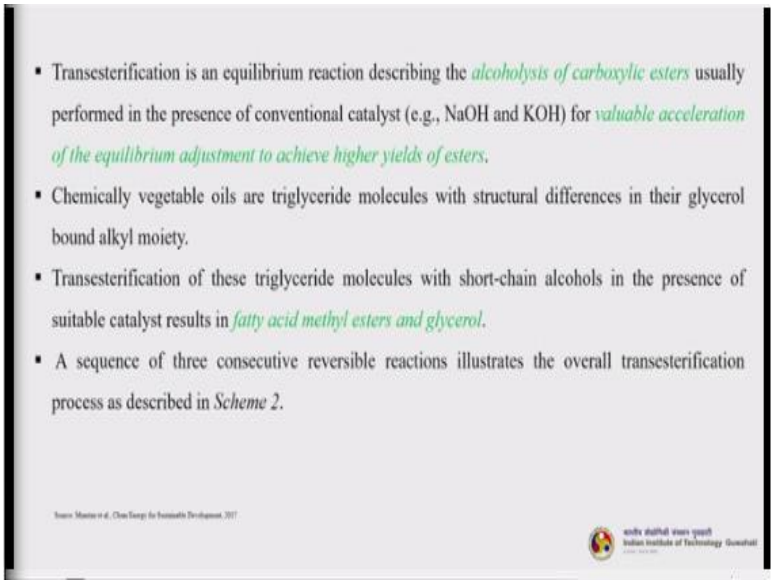

- Transesterification is an equilibrium reaction describing the *alcoholysis of carboxylic esters* usually performed in the presence of conventional catalyst (e.g., NaOH and KOH) for *valuable acceleration of the equilibrium adjustment to achieve higher yields of esters*.
- Chemically vegetable oils are triglyceride molecules with structural differences in their glycerol bound alkyl moiety.
- Transesterification of these triglyceride molecules with short-chain alcohols in the presence of suitable catalyst results in *fatty acid methyl esters and glycerol*.
- A sequence of three consecutive reversible reactions illustrates the overall transesterification process as described in *Scheme 2*.

So, transesterification is an equilibrium reaction describing the alcoholysis of carboxylic esters usually performed in the presence of a conventional catalyst (sodium hydroxide, potassium hydroxide) for valuable acceleration of the equilibrium adjustment to achieve a higher yield of esters. Chemically vegetable oils are triglyceride molecules with structural differences in their glycerol bound alkyl moiety.

Now transesterification of these triglyceride molecules with short chain alcohols in the presence of suitable catalyst results in fatty acid methyl esters and glycerol. Now these fatty acids (FAME) are your biodiesel. Now a sequence of 3 consecutive reverse reactions illustrates the overall transesterification process.

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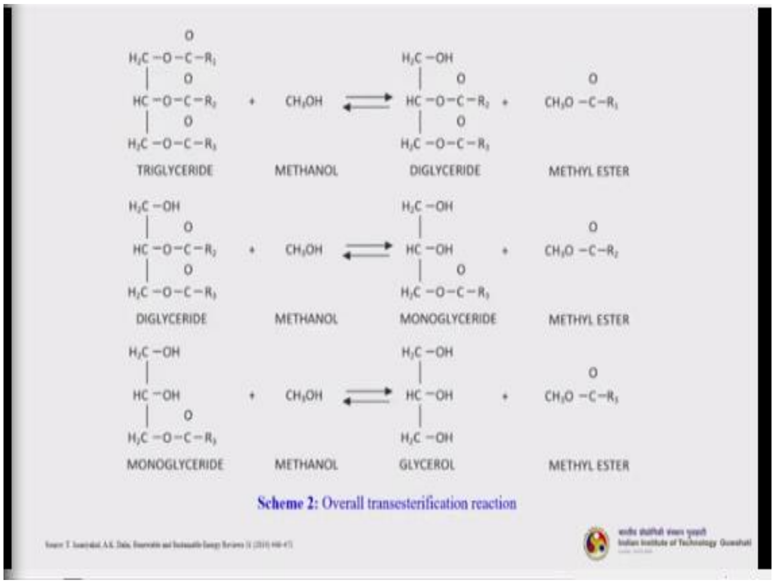
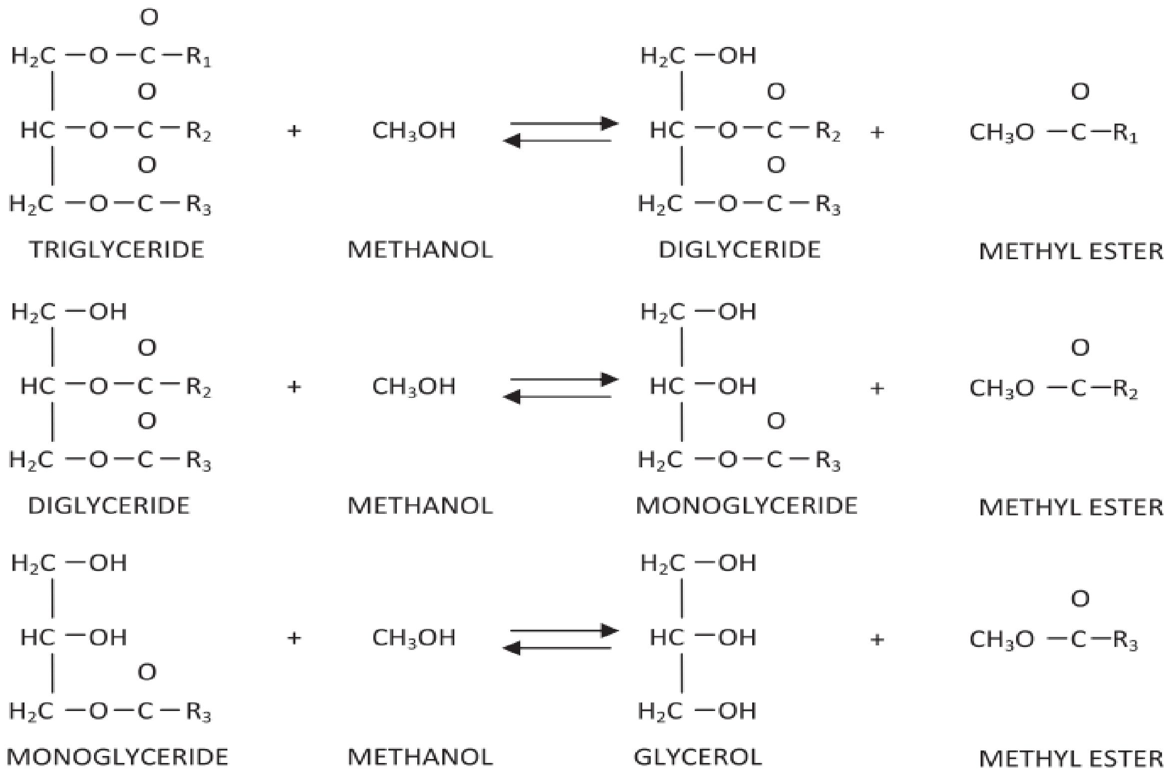


Scheme 2: Overall transesterification reaction

So, this is how it happens actually, this is the overall reaction mechanism of a biodiesel formation. Now we have a triglyceride that reacts with methanol to give us diglyceride and one methyl ester. Now what you see that, we are getting series of methyl ester R 1, R 2, R 3 different R groups and a series of methyl esters. So, these reactions are happening simultaneously.



Now that diglyceride is again reacting with another methanol molecule to give us a monoglyceride and another methyl ester. This monoglyceride is further reacting with methanol to give as another methyl ester and glycerol. So, glycerol is the final byproduct of transesterification reaction.

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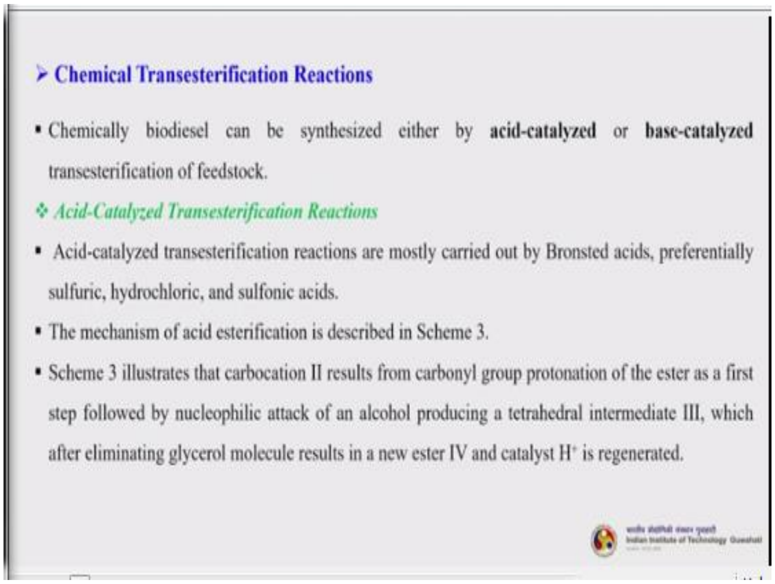

➢ Chemical Transesterification Reactions

- Chemically biodiesel can be synthesized either by **acid-catalyzed** or **base-catalyzed** transesterification of feedstock.

❖ *Acid-Catalyzed Transesterification Reactions*

- Acid-catalyzed transesterification reactions are mostly carried out by Bronsted acids, preferentially sulfuric, hydrochloric, and sulfonic acids.
- The mechanism of acid esterification is described in Scheme 3.
- Scheme 3 illustrates that carbocation II results from carbonyl group protonation of the ester as a first step followed by nucleophilic attack of an alcohol producing a tetrahedral intermediate III, which after eliminating glycerol molecule results in a new ester IV and catalyst H^+ is regenerated.

So, let us understand the chemical transesterification reactions. Chemically biodiesel can be synthesized either by acid catalyzed or base catalyzed transesterification of the feedstock. Now we will discuss both. So, acid catalyzed transesterification reactions: acid catalyzed transesterification reactions are mostly carried out by Bronsted acids, preferentially sulfuric, hydrochloric and sulfonic acids.

So, this name bronsted acid, bronsted base many times you will come across in such type of reactions. So, bronsted acid is something which actually is ready to give a proton, and bronsted base is one which is ready to accept a proton. So, this is the general understanding of bronsted acid and base**.** So, the mechanism of acid esterification is described in scheme 3, so in the next slide it is there.

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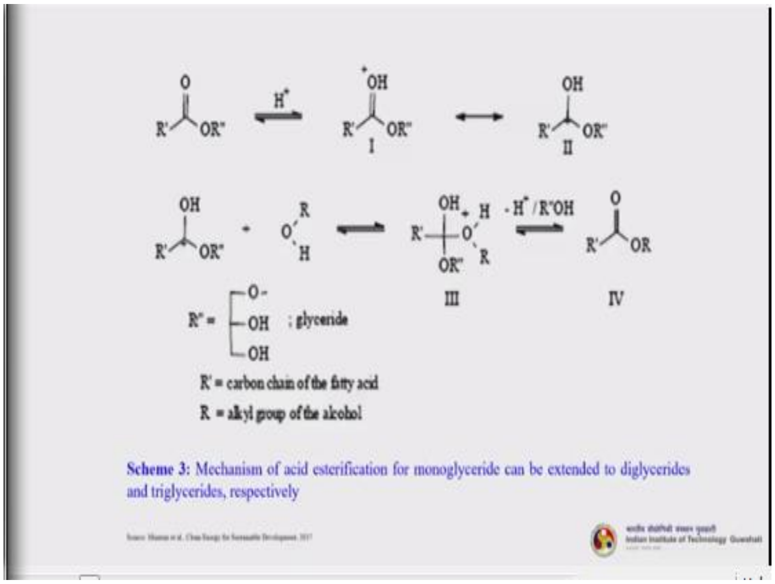

R" = –O- / –OH / –OH ; glyceride

R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 3: Mechanism of acid esterification for monoglyceride can be extended to diglycerides and triglycerides, respectively

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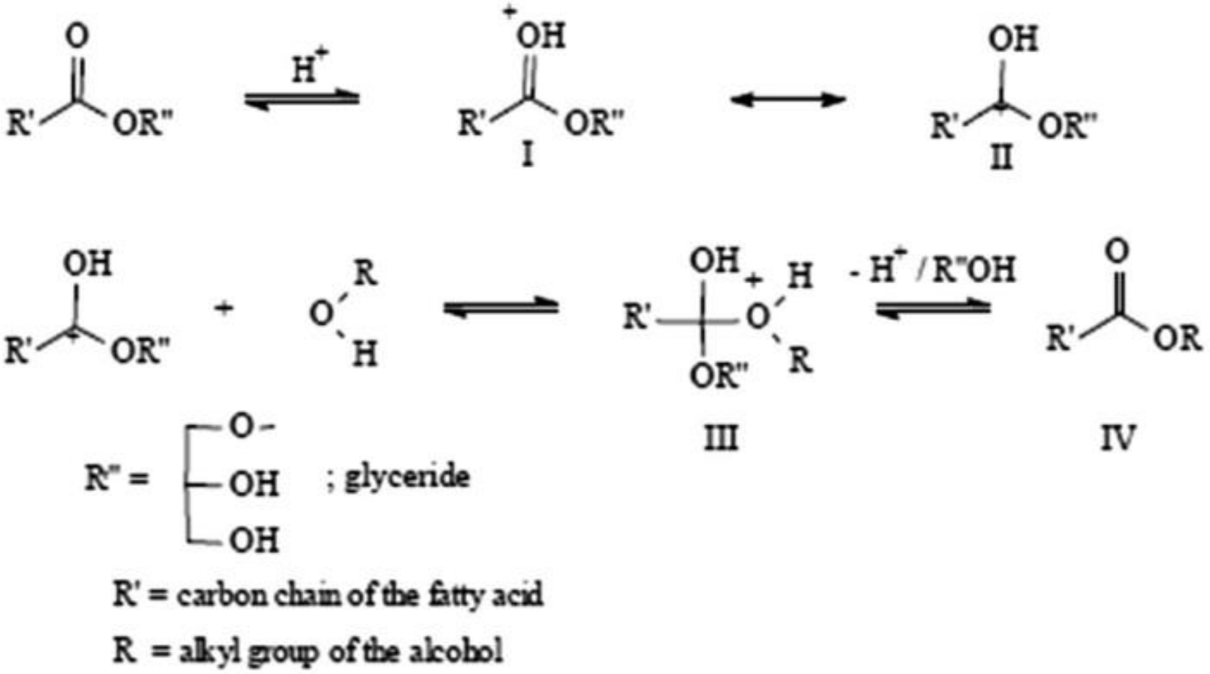
So, let us see what is this reaction, I will try to make you understand. So, here you can see there is one catalyst is there, so H+ is a protonated catalyst. So, here carbocation reaction II results from the carbonyl group protonation of the ester as a first step followed by a nucleophilic attack of an alcohol producing a tetrahedral intermediate. So, let me make you understand this reaction mechanism.



So, here this is first getting protonated, now this protonated is going to make as a carbocation molecule. Now what is a carbocation molecule? So, this is a carbocation molecule. So a carbocation molecule is something in which the carbon atom is positively charged. So, it is a carbon cation basically. The carbon atom here is positively charged, and it has 3 bonds, you can see 1, 2, 3. Now this carbocation group is reacting with the alcohol to give as an intermediate complex.

Now this intermediate complex, when we remove glycerol molecule from this intermediate complex, then we will get the methyl ester. And the catalyst will be again further deprotonated. So the deprotonated catalyst will have more active surface areas to further carryout the reaction. So, this is an overall simplified understanding of how the esterification of the monoglyceride can be extended to diglyceride and triglycerides, so this is a series of reactions.

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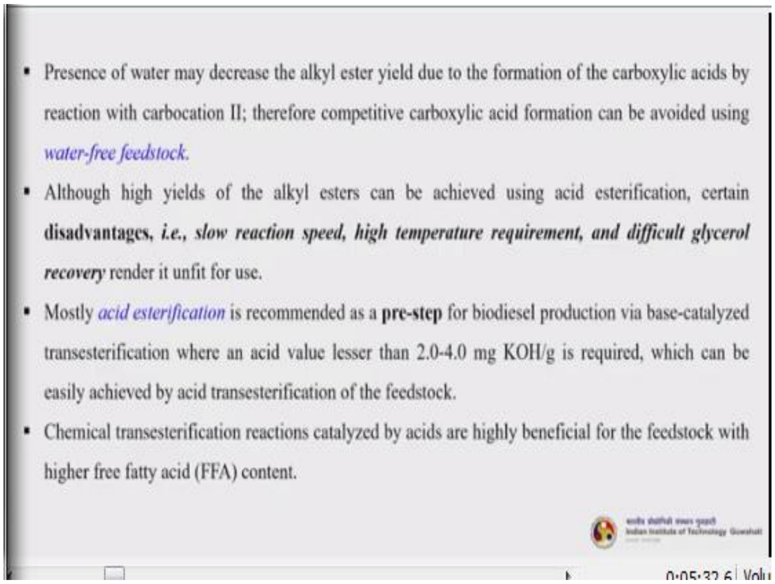

- Presence of water may decrease the alkyl ester yield due to the formation of the carboxylic acids by reaction with carbocation II; therefore competitive carboxylic acid formation can be avoided using *water-free feedstock.*
- Although high yields of the alkyl esters can be achieved using acid esterification, certain **disadvantages,** ***i.e., slow reaction speed, high temperature requirement, and difficult glycerol recovery*** render it unfit for use.
- Mostly *acid esterification* is recommended as a **pre-step** for biodiesel production via base-catalyzed transesterification where an acid value lesser than 2.0-4.0 mg KOH/g is required, which can be easily achieved by acid transesterification of the feedstock.
- Chemical transesterification reactions catalyzed by acids are highly beneficial for the feedstock with higher free fatty acid (FFA) content.

Now, the presence of water may decrease the alkyl ester yield due to the formation of the carboxylic acids by reaction with carbocation II; therefore, competitive carboxylic acid formation can be avoided using water free feedstock. Although high yields of alkyl esters can be achieved using acid esterification, certain disadvantages, that is slow reaction speed, high temperature requirement and difficult glycerol recovery render it unfit for use.

Mostly acid esterification is recommended as a pre step for biodiesel production via base catalyzed transesterification where an acid value lesser than 2 to 4 milligrams potassium hydroxide per gram is required which can be easily achieved by acid transesterification of the feedstock. Now chemical transesterification reactions catalyzed by acids are highly beneficial for the feedstock with higher free fatty acid content. So, those, feedstock which have a very high free FFA content they can go for the acid catalyzed reaction.

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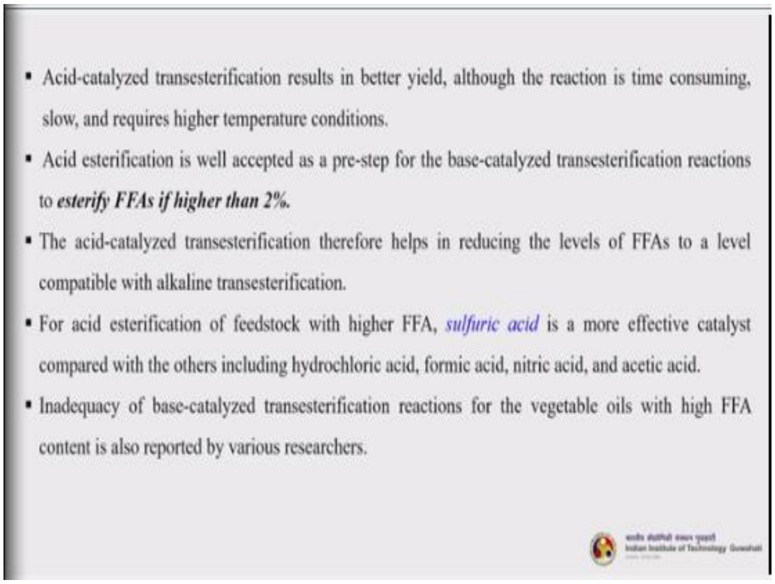

- Acid-catalyzed transesterification results in better yield, although the reaction is time consuming, slow, and requires higher temperature conditions.
- Acid esterification is well accepted as a pre-step for the base-catalyzed transesterification reactions to ***esterify FFAs if higher than 2%.***
- The acid-catalyzed transesterification therefore helps in reducing the levels of FFAs to a level compatible with alkaline transesterification.
- For acid esterification of feedstock with higher FFA, *sulfuric acid* is a more effective catalyst compared with the others including hydrochloric acid, formic acid, nitric acid, and acetic acid.
- Inadequacy of base-catalyzed transesterification reactions for the vegetable oils with high FFA content is also reported by various researchers.

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So, acid catalyzed reaction results in better yield, although the reaction is time consuming, slow and requires higher temperature conditions. Acid esterification is well accepted as a pre step for the base catalyzed transesterification reactions to esterify free fatty acids if higher than 2%, if they are present higher than 2%. The acid catalyzed transesterification therefore helps in reducing the levels of the free fatty acids to a level compatible with alkaline transesterification.

For acid esterification of feedstock with higher free fatty acids, sulfuric acid is a more effective catalyst compared with others including hydrochloric acid, formic acid, nitric acid and acetic acid. Inadequacy of base catalyzed transesterification reactions for the vegetable oils with high free fatty acid content is also reported by various researchers.

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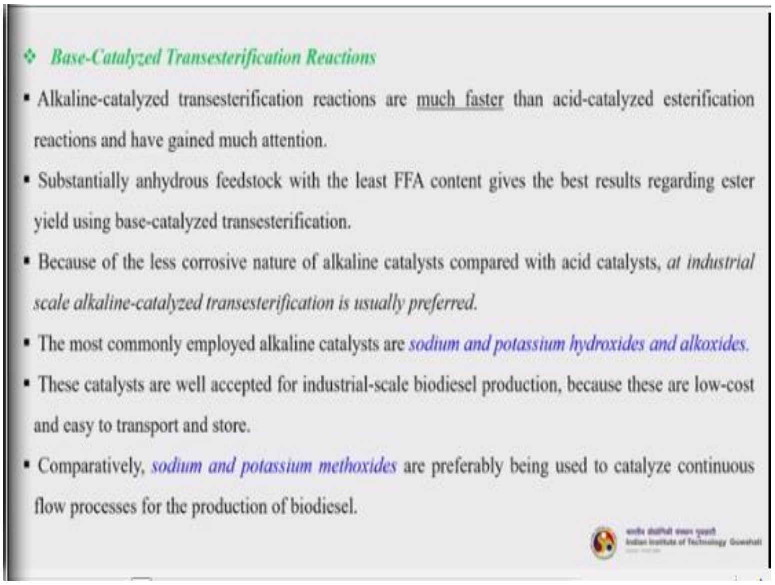

❖ *Base-Catalyzed Transesterification Reactions*

- Alkaline-catalyzed transesterification reactions are much faster than acid-catalyzed esterification reactions and have gained much attention.
- Substantially anhydrous feedstock with the least FFA content gives the best results regarding ester yield using base-catalyzed transesterification.
- Because of the less corrosive nature of alkaline catalysts compared with acid catalysts, *at industrial scale alkaline-catalyzed transesterification is usually preferred.*
- The most commonly employed alkaline catalysts are *sodium and potassium hydroxides and alkoxides.*
- These catalysts are well accepted for industrial-scale biodiesel production, because these are low-cost and easy to transport and store.
- Comparatively, *sodium and potassium methoxides* are preferably being used to catalyze continuous flow processes for the production of biodiesel.

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Now we will discuss about the base catalyzed transesterification reaction. So, alkaline catalyzed transesterification reactions are much faster than acid catalyzed esterification reactions and have gained much attention. Substantially anhydrous feedstock with the least free fatty acid content gives the best results regarding ester yield using base catalyzed transesterification. Now because of the less corrosive nature of the alkaline catalyst compared with acid catalyst, at industrial scale alkaline catalyzed transesterification is usually preferred, because it is anyway a faster reaction. Now the most commonly employed alkaline catalyst are sodium and potassium hydroxides and alkoxides. These catalysts are well accepted for industrial scale biodiesel production, because these are low cost and easy to transport and store. Comparatively, sodium and potassium methoxides are preferably being used to catalyze continuous flow processes for the production of the biodiesel.

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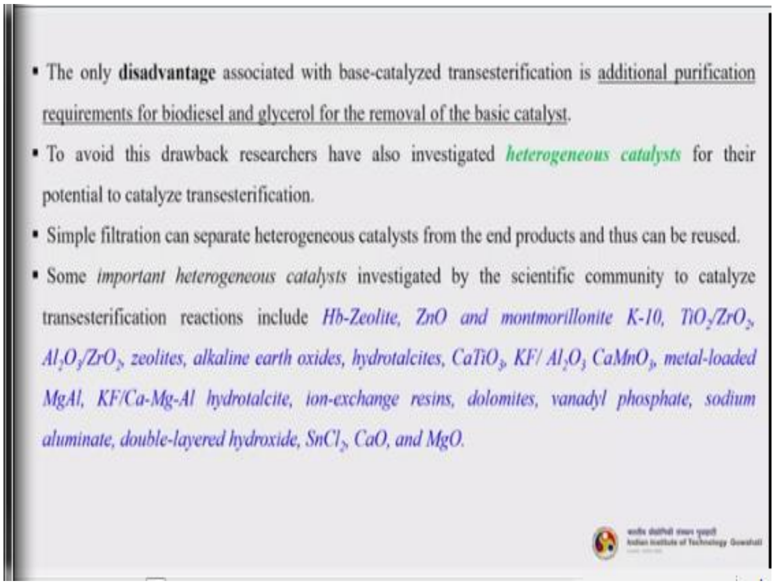

- The only **disadvantage** associated with base-catalyzed transesterification is additional purification requirements for biodiesel and glycerol for the removal of the basic catalyst.
- To avoid this drawback researchers have also investigated *heterogeneous catalysts* for their potential to catalyze transesterification.
- Simple filtration can separate heterogeneous catalysts from the end products and thus can be reused.
- Some *important heterogeneous catalysts* investigated by the scientific community to catalyze transesterification reactions include *Hb-Zeolite, ZnO and montmorillonite K-10,* TiO_2/ZrO_2, Al_2O_3/ZrO_2, *zeolites, alkaline earth oxides, hydrotalcites,* $CaTiO_3$, KF/Al_2O_3 $CaMnO_3$, *metal-loaded MgAl, KF/Ca-Mg-Al hydrotalcite, ion-exchange resins, dolomites, vanadyl phosphate, sodium aluminate, double-layered hydroxide,* $SnCl_2$, *CaO, and MgO.*

The only disadvantage associated with the base catalyzed transesterification is the additional purification requirements of biodiesel and glycerol for the removal of the base catalyst. To avoid this drawback, researchers have investigated heterogeneous catalyst for their potential to catalyze transesterification. Simple filtration can separate heterogeneous catalyst from the end products and thus can be reused.

Now some important heterogeneous catalyst investigated by scientific community to catalyze transesterification reactions include Hb-zeolite, zinc oxide, titanium dioxide, zirconium dioxide, zeolites, alkaline earth oxides, then ion exchange resins, dolomites, sodium aluminate, then calcium oxide and magnesium oxide. So, there are many more; I have just listed a few. More or less these are tested, gave high selectivity and also readily available and many of them are also low cost.

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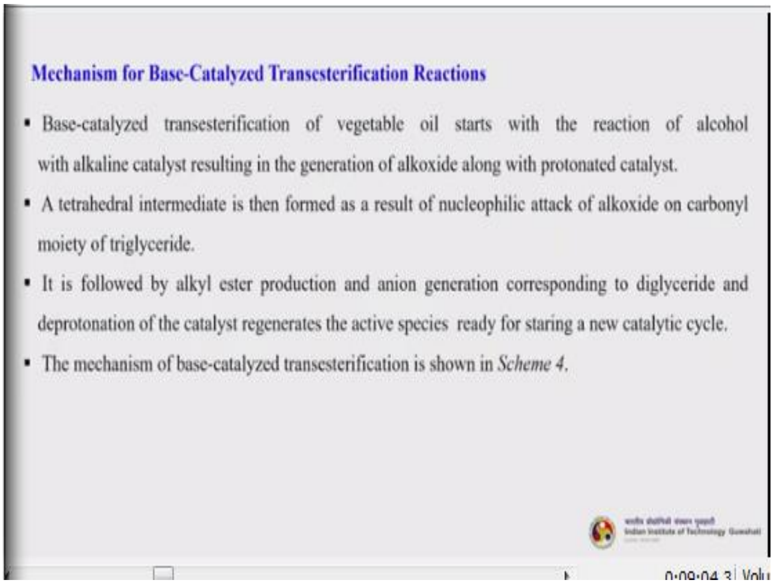

Mechanism for Base-Catalyzed Transesterification Reactions

- Base-catalyzed transesterification of vegetable oil starts with the reaction of alcohol with alkaline catalyst resulting in the generation of alkoxide along with protonated catalyst.
- A tetrahedral intermediate is then formed as a result of nucleophilic attack of alkoxide on carbonyl moiety of triglyceride.
- It is followed by alkyl ester production and anion generation corresponding to diglyceride and deprotonation of the catalyst regenerates the active species ready for staring a new catalytic cycle.
- The mechanism of base-catalyzed transesterification is shown in *Scheme 4*.

So, now let us understand the mechanism for the base catalyzed transesterification reactions. Now, base catalyzed transesterification of vegetable oil starts with the reaction of alcohol with alkaline catalyst resulting in the generation of alkoxide along with the protonated catalyst. A tetrahedral intermediate is then formed as a result of nucleophilic attack of alkoxide on carbonyl moiety of the triglyceride. Let us see how; actually in the next slide it is there.

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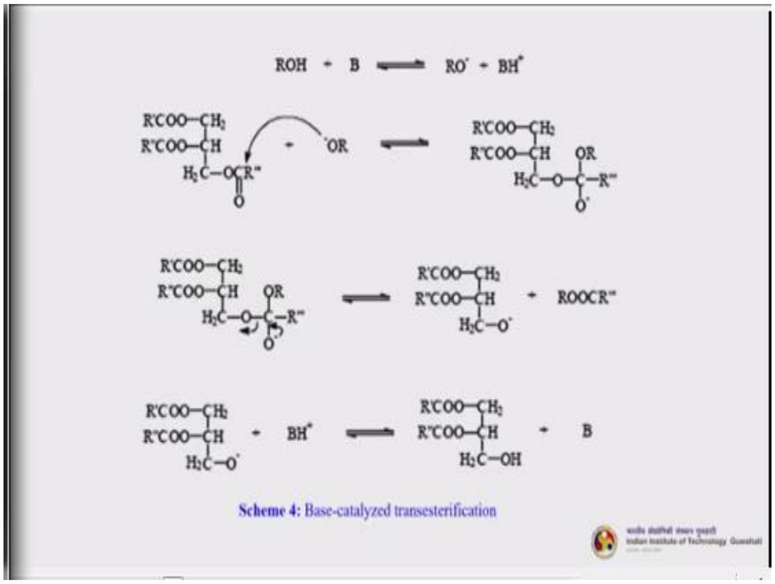
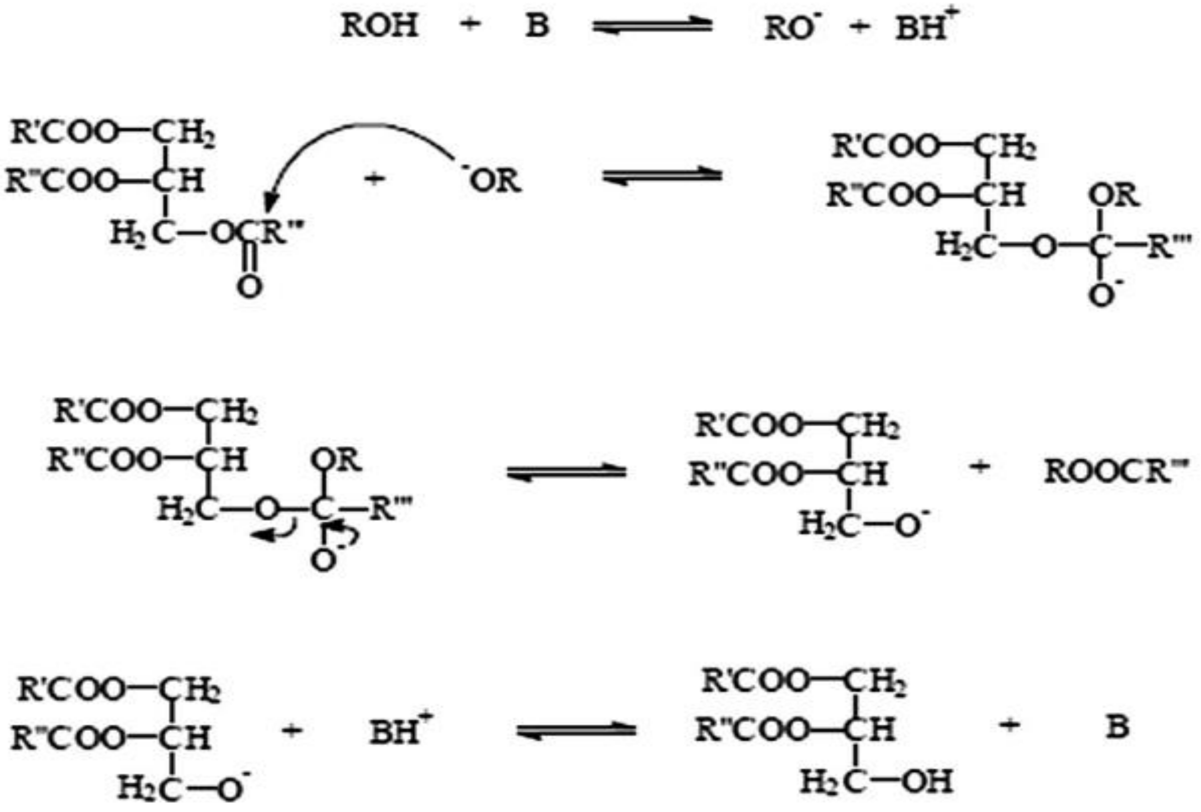


Scheme 4: Base-catalyzed transesterification

So, there are 4 steps being shown here. The first one, the alcohol is reacting with the catalyst, B is the catalyst. So, the B is getting protonated, so BH and we will get a carbonyl moiety of the triglyceride. So, here you can get a carbonyl moiety, so when it is again reacted, so we get another intermediate product. Now that intermediate product is again decomposed into 1 anion, this is 1 anionic group and plus here ester**.** Now this anionic group is further reacted with the protonated catalyst to give as a methyl ester and deprotonated catalyst. Now this deprotonated catalyst is having free or active more surface area which can carry out further reactions, so simple reaction mechanism.



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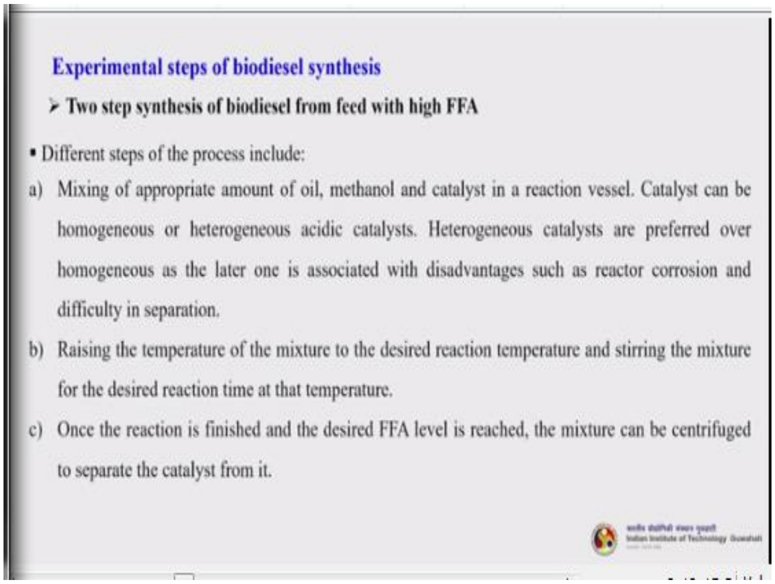

Experimental steps of biodiesel synthesis

➢ Two step synthesis of biodiesel from feed with high FFA

- Different steps of the process include:

a) Mixing of appropriate amount of oil, methanol and catalyst in a reaction vessel. Catalyst can be homogeneous or heterogeneous acidic catalysts. Heterogeneous catalysts are preferred over homogeneous as the later one is associated with disadvantages such as reactor corrosion and difficulty in separation.

b) Raising the temperature of the mixture to the desired reaction temperature and stirring the mixture for the desired reaction time at that temperature.

c) Once the reaction is finished and the desired FFA level is reached, the mixture can be centrifuged to separate the catalyst from it.

So, we will try to understand the experimental steps for biodiesel synthesis. Two step synthesis of biodiesel from feed with high free fatty acid. Different steps of the process include: First is that mixing of appropriate amount of oil, methanol and catalyst in a reaction vessel. Catalyst can be homogeneous or heterogeneous acidic catalyst. Heterogeneous catalysts are preferred over homogeneous as the later one is associated with disadvantage such as reactor corrosion and difficulty in separation.

Now second, raising the temperature of the reaction mixture to the desired reaction temperature and stirring the mixture for the desired reaction time at that temperature. Once the reaction is finished and the desired free fatty acid level is reached, the mixture can be centrifuged to separate the catalyst from it. That is why you can use the heterogeneous catalyst, so you can remove is using centrifugation and filtration.

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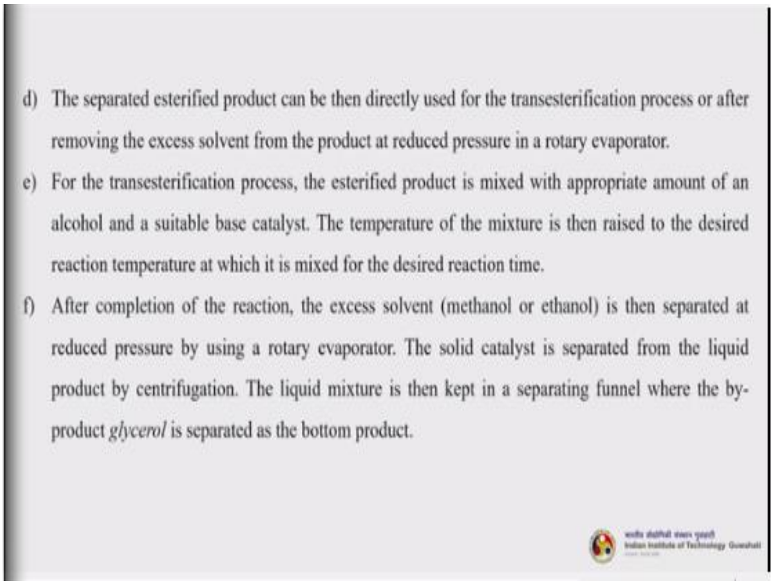

d) The separated esterified product can be then directly used for the transesterification process or after removing the excess solvent from the product at reduced pressure in a rotary evaporator.

e) For the transesterification process, the esterified product is mixed with appropriate amount of an alcohol and a suitable base catalyst. The temperature of the mixture is then raised to the desired reaction temperature at which it is mixed for the desired reaction time.

f) After completion of the reaction, the excess solvent (methanol or ethanol) is then separated at reduced pressure by using a rotary evaporator. The solid catalyst is separated from the liquid product by centrifugation. The liquid mixture is then kept in a separating funnel where the by-product *glycerol* is separated as the bottom product.

The separated esterified product can then be directly used for the transesterification process or after removing the excess solvent from the product at reduced pressure in a rotary evaporator. For the transesterification process the esterified product is mixed with appropriate amount of an alcohol and a suitable base catalyst. The temperature of the mixture is then raised to the desired reaction temperature at which it is mixed for the desired reaction time.

After completion of the reaction the excess solvent either methanol or ethanol is then separated at reduced pressure by using a rotary evaporator. The solid catalyst is separated from liquid product by centrifugation. The liquid mixture is then kept in a separating funnel where the byproduct glycerol is separated as the bottom product. So, I hope you understand and I have listed entirely the experimental procedure how to produce biodiesel.

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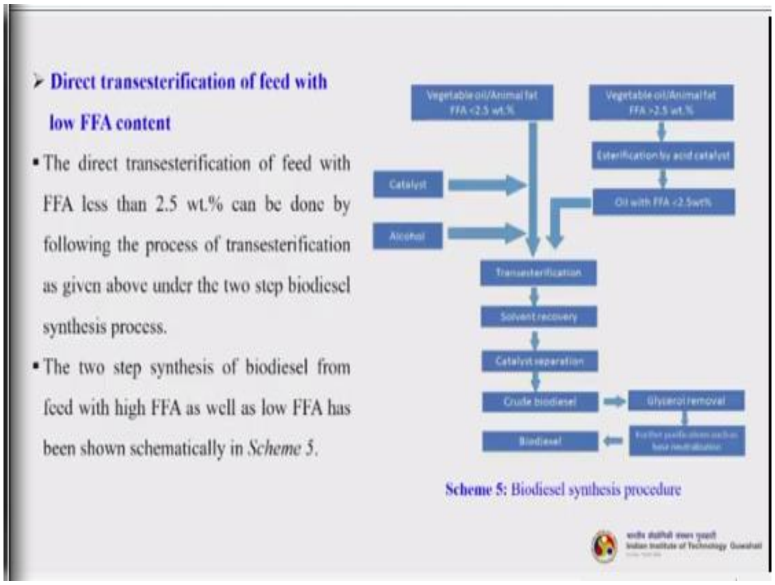

- **Direct transesterification of feed with low FFA content**
  - The direct transesterification of feed with FFA less than 2.5 wt.% can be done by following the process of transesterification as given above under the two step biodiesel synthesis process.
  - The two step synthesis of biodiesel from feed with high FFA as well as low FFA has been shown schematically in *Scheme 5*.

Scheme 5: Biodiesel synthesis procedure

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So, this is the direct transesterification of the feed with low free fatty acid content. So, we can see that, so vegetable oil or animal fat less than 2.5% free fatty acid, so you can add catalyst and alcohol, so you can go for the transesterification. Here the vegetable oil and animal fat which are having greater than 2.5 weight percent of free fatty acid will be esterified first.

So, try to understand the two different processes. Here if the free fatty acid content is less than 2.5 weight percent then you can directly add a catalyst and alcohol and you go for the transesterification. Now if the free fatty acid content is higher than if you remember we have just discussed that when the free fatty acid content is higher we usually go by the acid catalyzed reaction. So, that is a pre step before the base catalyzed reaction so then you are just going to do that.

So, esterification by the acid catalyst, then you get oil with free fatty acid content which is less than 2.5 weight percent then you go for the usual transesterification route**.** Then you go for the solvent recovery, catalyst separation, crude biodiesel and remove the glycerol. So, glycerol can be further purified by base neutralization and you get the biodiesel. So, this is the schematic or flow chart you can say of the biodiesel production**.**

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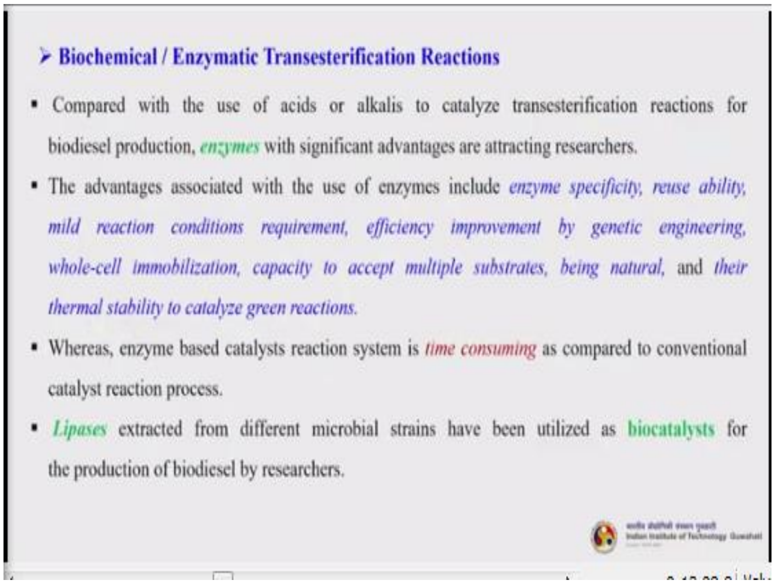

➢ **Biochemical / Enzymatic Transesterification Reactions**

- Compared with the use of acids or alkalis to catalyze transesterification reactions for biodiesel production, *enzymes* with significant advantages are attracting researchers.
- The advantages associated with the use of enzymes include *enzyme specificity, reuse ability, mild reaction conditions requirement, efficiency improvement by genetic engineering, whole-cell immobilization, capacity to accept multiple substrates, being natural,* and *their thermal stability to catalyze green reactions.*
- Whereas, enzyme based catalysts reaction system is *time consuming* as compared to conventional catalyst reaction process.
- *Lipases* extracted from different microbial strains have been utilized as biocatalysts for the production of biodiesel by researchers.

Then we will try to also understand the biochemical or enzymatic transesterification reactions. So much of work has already been done and reported (you can see the literature) on enzymatic transesterification reactions. Now compared with the use of acids or alkalis to catalyze transesterification reactions for biodiesel production, enzymes with significant advantages are attracting the researchers.

The advantages associated with enzymes are: they have huge specificity, reuse ability, mild reaction conditions requirement, and efficiency improvement by genetic engineering, whole cell immobilization, capacity to accept multiple substrates, they are natural and their thermal stability to catalyze green reactions. Now enzyme based catalyst reaction system is time consuming as compared to the conventional catalyst reaction process.

We have learnt that basic catalyzed reactions are extremely fast, so they are industrially being adapted**.** So, lipases extracted from different microbial strains have been utilized as biocatalyst for the production of biodiesel by researchers.

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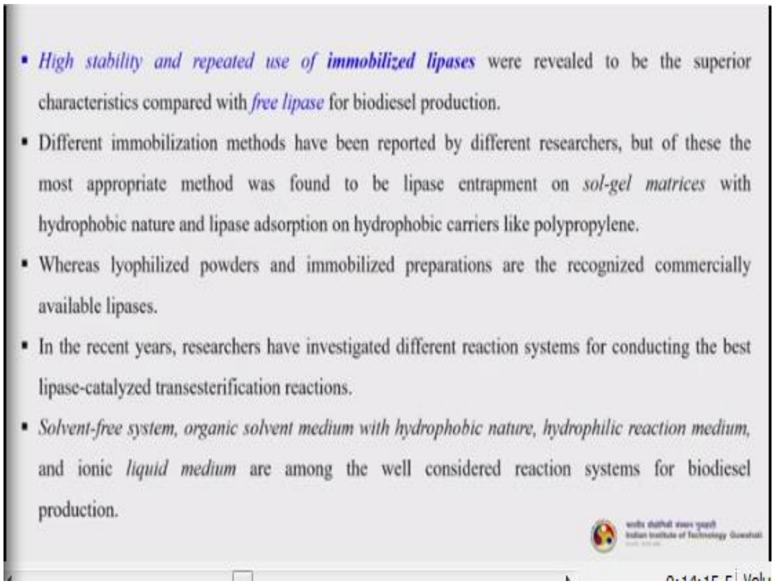

- *High stability and repeated use of* ***immobilized lipases*** were revealed to be the superior characteristics compared with *free lipase* for biodiesel production.
- Different immobilization methods have been reported by different researchers, but of these the most appropriate method was found to be lipase entrapment on *sol-gel matrices* with hydrophobic nature and lipase adsorption on hydrophobic carriers like polypropylene.
- Whereas lyophilized powders and immobilized preparations are the recognized commercially available lipases.
- In the recent years, researchers have investigated different reaction systems for conducting the best lipase-catalyzed transesterification reactions.
- *Solvent-free system, organic solvent medium with hydrophobic nature, hydrophilic reaction medium,* and ionic *liquid medium* are among the well considered reaction systems for biodiesel production.

High stability and repeated use of immobilized lipases were revealed to be the superior characteristics compared to the free lipase for biodiesel production. Anyway in one class we have discussed about the importance of immobilization**.** So, immobilized lipases can be reused for many times rather than free lipases, and they have other advantages also. So, different immobilization methods have been reported by different researchers but of these the most appropriate method was found to be lipase entrapment on sol-gel matrices with hydrophobic nature and lipase adsorption on hydrophobic carriers such as polypropylene.

Whereas lyophilized powders and immobilized preparations are the recognized commercially available lipases. In the recent years, researchers have investigated different reaction systems for conducting the best lipase catalyzed transesterification reactions. Solvent free system, organic solvent medium with hydrophobic nature, hydrophilic reaction medium and ionic liquid medium are among the well considered reaction systems for biodiesel productions.

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Process flow schematic for biodiesel production from vegetable oils

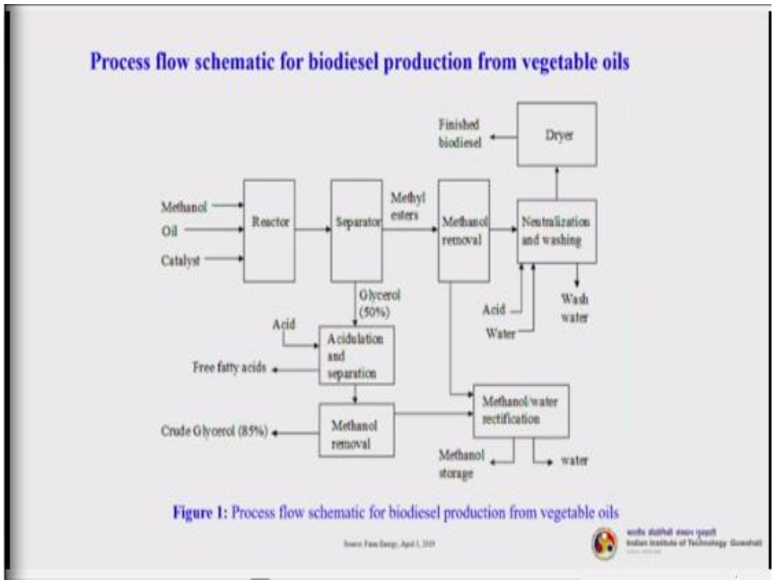

Figure 1: Process flow schematic for biodiesel production from vegetable oils

So much of work has already been reported and some of them are fantastic works**.** So, this is I am trying to show you the process flow schematic for the biodiesel production from the vegetable oils**.** So, what you are going to do is that, you are adding methanol and catalyst to the vegetable oil feed to the reactor**.** So, here the reaction is happening then you go for the separator, so here you remove basically the glycerol.

So, almost close to 50% yield. So then you go for acidulation and separation, you are just adding acid**.** So, you get the free fatty acid whatever unconverted free fatty acids here, then again you go for your methanol removal here, so you get the methanol removal method, so you get the crude glycerol which is almost 85% yield**.** So, the methanol can also be recovered and goes to the methanol water rectification unit, so you can basically recover the methanol**.**

So, from here the methyl ester, your biodiesel part, goes to the methanol removal part, here methanol is removed and again fed back to the rectification unit**.** Then it goes to the neutralization and washing step which are just the finishing steps. So, you go for drying then you get the finished biodiesel. So, you may need acid, water and all these things to do that in this process.

So, please understand that this is the simplified schematic representation of the biodiesel production from vegetable oils. There are many small unit operations and many small operations are there which are not being shown here in industrial scale what is being required actually**.**

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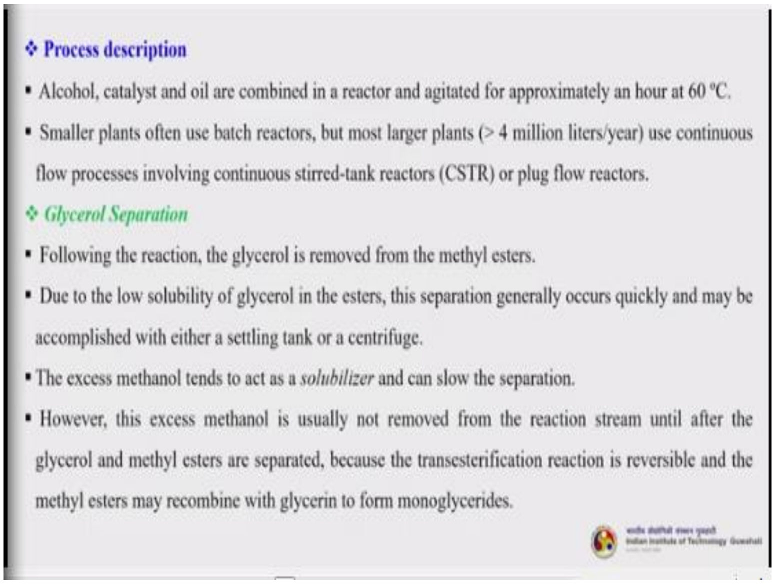

❖ **Process description**

- Alcohol, catalyst and oil are combined in a reactor and agitated for approximately an hour at 60 °C.
- Smaller plants often use batch reactors, but most larger plants (> 4 million liters/year) use continuous flow processes involving continuous stirred-tank reactors (CSTR) or plug flow reactors.

❖ *Glycerol Separation*

- Following the reaction, the glycerol is removed from the methyl esters.
- Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge.
- The excess methanol tends to act as a *solubilizer* and can slow the separation.
- However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated, because the transesterification reaction is reversible and the methyl esters may recombine with glycerin to form monoglycerides.

So, let us understand the process; alcohol catalyst and oil are combined in the reactor and agitated for approximately an hour at 60 degree centigrade. Smaller plants often use batch reactors but most, larger plants greater than 4 more million liters per year production, use continuous flow processes involving continuous stirred tank reactors CSTR or plug flow reactors.

Now let us understand the glycerol separation; following the reaction glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters this separation generally occurs quickly and maybe accomplished with either a settling tank or a centrifuge. So, when you talk about a huge amount of feedstock you are dealing with that, you cannot go for a centrifuge**,** so you have to go for settling tank.

Now the excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated because the transesterification reaction is reversible and the methyl esters may recombine with glycerin to form the monoglycerides. So, that is one of the biggest disadvantage and you have to take care of that.

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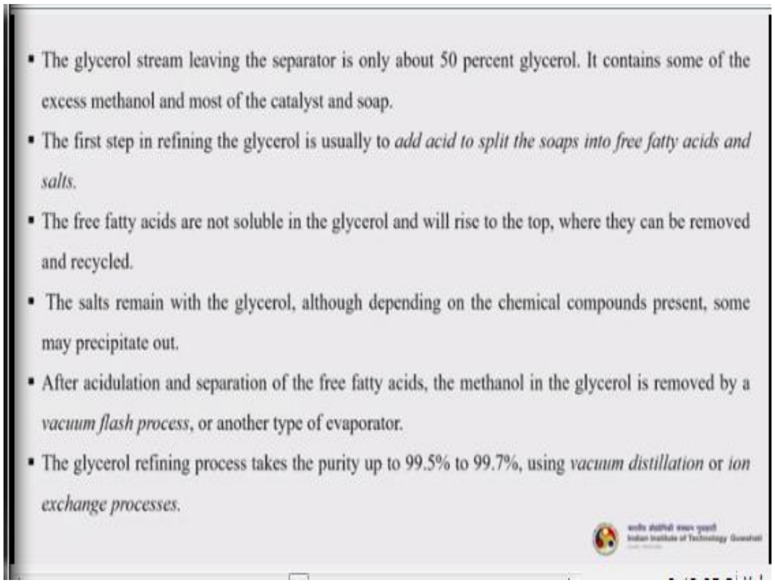

- The glycerol stream leaving the separator is only about 50 percent glycerol. It contains some of the excess methanol and most of the catalyst and soap.
- The first step in refining the glycerol is usually to *add acid to split the soaps into free fatty acids and salts.*
- The free fatty acids are not soluble in the glycerol and will rise to the top, where they can be removed and recycled.
- The salts remain with the glycerol, although depending on the chemical compounds present, some may precipitate out.
- After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a *vacuum flash process*, or another type of evaporator.
- The glycerol refining process takes the purity up to 99.5% to 99.7%, using *vacuum distillation* or *ion exchange processes.*

So, the glycerol stream leaving the separator is only about 50% glycerol, it contains some of the excess methanol and most of the catalyst and soap. The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acid and salts. The free fatty acids are not soluble in the glycerol and will rise to the top and where they can be removed and recycled. The salts remain with the glycerol although depending upon the chemical compounds present some may precipitate out.

After acidulation and separation of the free fatty acids the methanol in the glycerol is removed by a vacuum flash process or another type of evaporator. The glycerol refining process takes the purity up to 99.5% to 99.7% using vacuum distillation or ion exchange processes.

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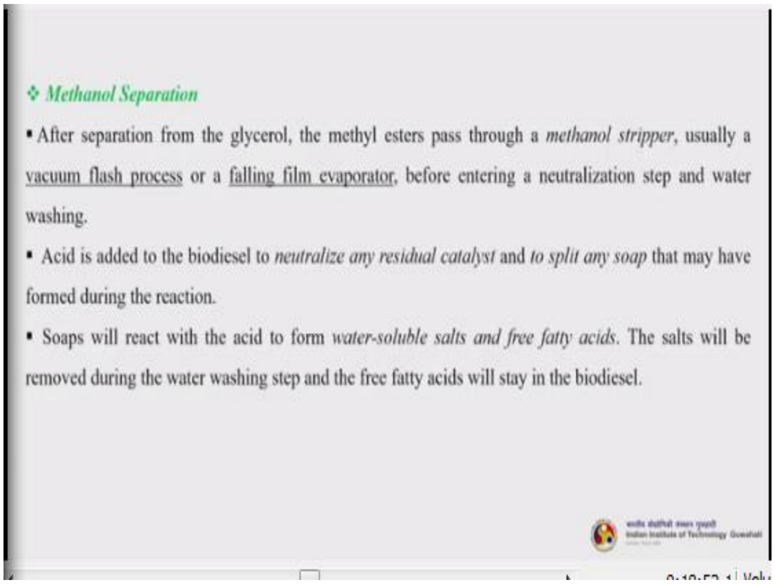

❖ *Methanol Separation*

- After separation from the glycerol, the methyl esters pass through a *methanol stripper*, usually a vacuum flash process or a falling film evaporator, before entering a neutralization step and water washing.
- Acid is added to the biodiesel to *neutralize any residual catalyst* and *to split any soap* that may have formed during the reaction.
- Soaps will react with the acid to form *water-soluble salts and free fatty acids*. The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel.

Then methanol separation; after separation from the glycerol the methyl esters pass through a methanol stripper usually a vacuum flash process or a falling film evaporator before entering the neutralization step and water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids. The salts will be removed during the water washing step and the free fatty acids will stay in the biodiesel.

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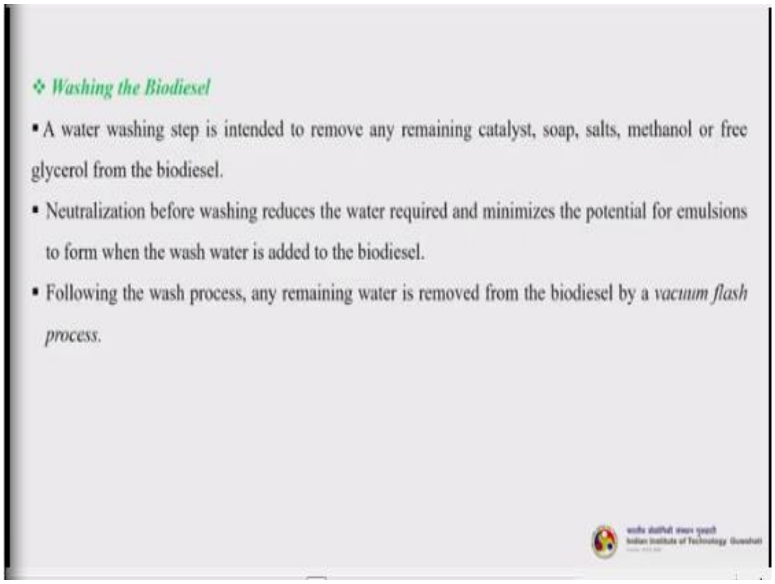

❖ *Washing the Biodiesel*

- A water washing step is intended to remove any remaining catalyst, soap, salts, methanol or free glycerol from the biodiesel.
- Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel.
- Following the wash process, any remaining water is removed from the biodiesel by a *vacuum flash process*.

Then washing the biodiesel; a water washing step is intended to remove any remaining catalyst, soap, salts, methanol or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. Following the wash process, any remaining water is removed from the biodiesel by a vacuum flash process.

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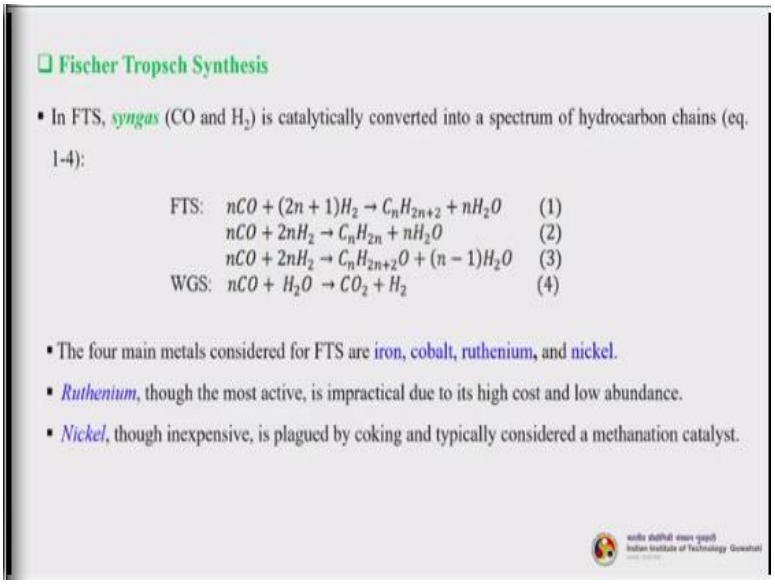

❑ **Fischer Tropsch Synthesis**

- In FTS, *syngas* (CO and H_2) is catalytically converted into a spectrum of hydrocarbon chains (eq. 1-4):

$$\begin{aligned}
\text{FTS:}\quad & nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O && (1)\\
& nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O && (2)\\
& nCO + 2nH_2 \rightarrow C_nH_{2n+2}O + (n-1)H_2O && (3)\\
\text{WGS:}\quad & nCO + H_2O \rightarrow CO_2 + H_2 && (4)
\end{aligned}$$

- The four main metals considered for FTS are iron, cobalt, ruthenium, and nickel.
- *Ruthenium*, though the most active, is impractical due to its high cost and low abundance.
- *Nickel*, though inexpensive, is plagued by coking and typically considered a methanation catalyst.

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Now let us understand the FT synthesis**,** the Fischer Tropsch synthesis, though we have discussed about Fischer Tropsch earlier also. We will again see the reactions and other process conditions and reactors in detail. So, in FTS syngas, that is carbon monoxide and hydrogen is catalytically converted into a spectrum of hydrocarbon chains, so this is the reaction, this we have already discussed earlier.

But again to maintain the reading properly, so I have again given these reactions**.** So, the 4 main metals considered for Fischer Tropsch synthesis are iron, cobalt, ruthenium and nickel. Ruthenium the most active is impractical due to it is high cost and low abundance, it is a very costly metal. Nickel although inexpensive is plagued by coking and typically considered a methanation catalyst.

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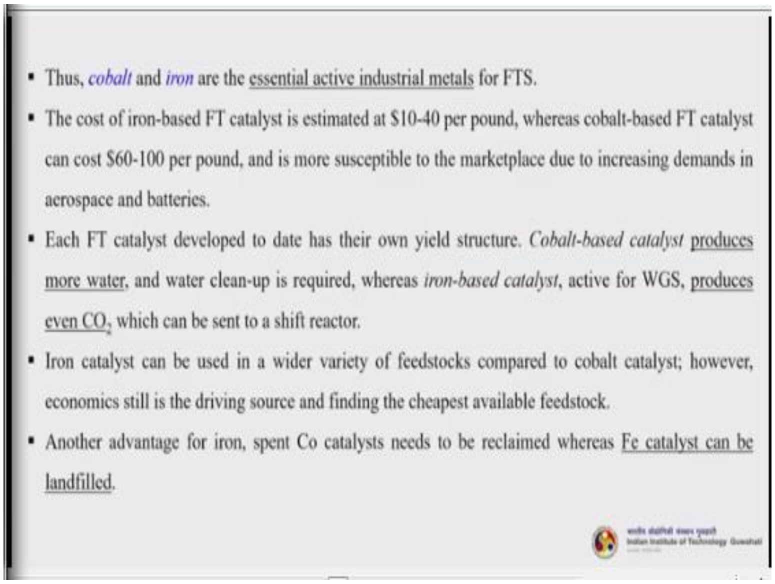

- Thus, *cobalt* and *iron* are the essential active industrial metals for FTS.
- The cost of iron-based FT catalyst is estimated at $10-40 per pound, whereas cobalt-based FT catalyst can cost $60-100 per pound, and is more susceptible to the marketplace due to increasing demands in aerospace and batteries.
- Each FT catalyst developed to date has their own yield structure. *Cobalt-based catalyst* produces more water, and water clean-up is required, whereas *iron-based catalyst*, active for WGS, produces even CO_2 which can be sent to a shift reactor.
- Iron catalyst can be used in a wider variety of feedstocks compared to cobalt catalyst; however, economics still is the driving source and finding the cheapest available feedstock.
- Another advantage for iron, spent Co catalysts needs to be reclaimed whereas Fe catalyst can be landfilled.

Thus cobalt and iron are the essential active industrial metals for the Fischer Tropsch synthesis. The cost of iron based FT catalyst is estimated to be 10 to 40 dollar per pound, whereas cobalt based FT catalyst can cost about 60 to 100 dollar per pound. And are more susceptible to the; marketplace due to increasing demands in the aerospace and batteries. Each FT catalyst developed to date has their, own yield structure.

Cobalt based catalyst produces more water and water cleanup is required whereas iron based catalyst active for the WGS produces even carbon dioxide which can be sent to a **(**WGS is the water gas shift reaction) shift reactor**.** So, iron catalyst can be used in a wider variety of feedstocks compared to cobalt catalyst, however, economics still is the driving source and finding the cheapest available feedstock. Another advantage of iron, spent cobalt catalyst needs to be reclaimed whereas iron catalyst can be land filled.

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Figure 2: Sources of synthesis gas for Fischer-Tropsch synthesis

This is just a schematic understanding of the sources for the synthesis gas for the Fischer Tropsch synthesis process**.** So, it can be coal, it can be biomass, it can be natural gas, now those can be converted to syngas, carbon monoxide and hydrogen and further go for the Fischer Tropsch process and you get your fuel. Similarly, carbon dioxide from the atmosphere or from the flue gas and electricity also can help to produce carbon dioxide and hydrogen**.** And this also can be further processed by the Fischer Tropsch process to generate fuel**.**

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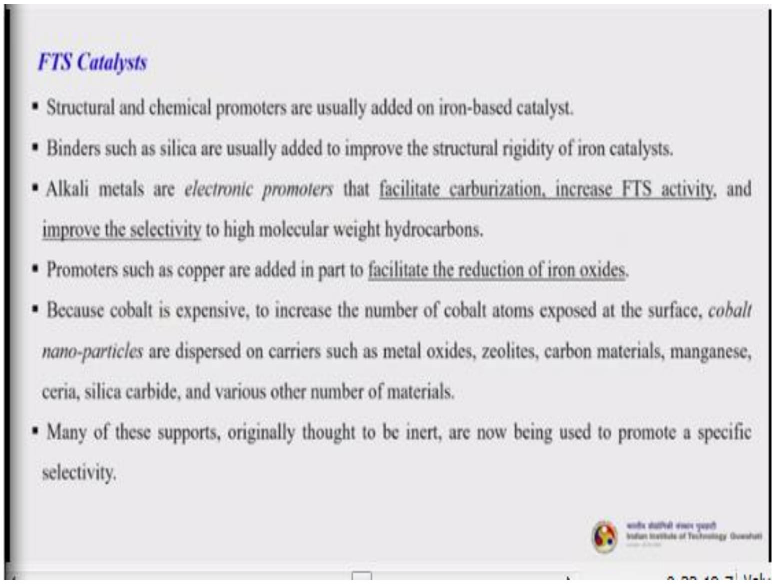

FTS Catalysts

- Structural and chemical promoters are usually added on iron-based catalyst.
- Binders such as silica are usually added to improve the structural rigidity of iron catalysts.
- Alkali metals are *electronic promoters* that facilitate carburization, increase FTS activity, and improve the selectivity to high molecular weight hydrocarbons.
- Promoters such as copper are added in part to facilitate the reduction of iron oxides.
- Because cobalt is expensive, to increase the number of cobalt atoms exposed at the surface, *cobalt nano-particles* are dispersed on carriers such as metal oxides, zeolites, carbon materials, manganese, ceria, silica carbide, and various other number of materials.
- Many of these supports, originally thought to be inert, are now being used to promote a specific selectivity.

Now let us understand little more about the FTS catalysts. Structural and chemical promoters are usually added on iron based catalyst. Binders such as silica are usually added to improve the structural rigidity of iron catalyst. Alkali metals are electronic promoters that facilitate carburization, increase the FTS activity and improve the selectivity to high molecular weight hydrocarbons.

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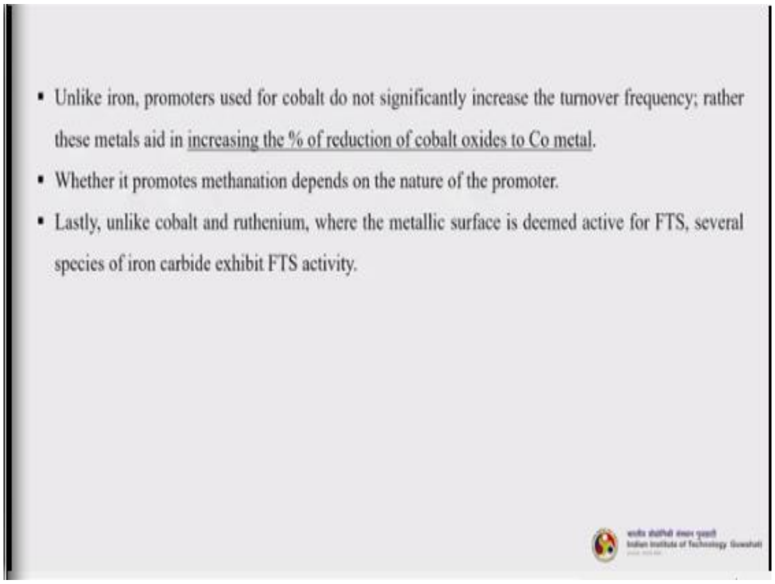

- Unlike iron, promoters used for cobalt do not significantly increase the turnover frequency; rather these metals aid in increasing the % of reduction of cobalt oxides to Co metal.
- Whether it promotes methanation depends on the nature of the promoter.
- Lastly, unlike cobalt and ruthenium, where the metallic surface is deemed active for FTS, several species of iron carbide exhibit FTS activity.

Unlike iron, promoters used for cobalt do not significantly increase the turnover frequency; rather these metals aid in increasing the percentage of reduction of cobalt oxides to cobalt metal. Whether it promotes methanation depends on the nature of the promoter. Lastly, unlike cobalt and ruthenium where the metallic surface is deemed active for the Fischer Tropsch synthesis, several species of iron carbide exhibit Fischer Tropsch synthesis activity.

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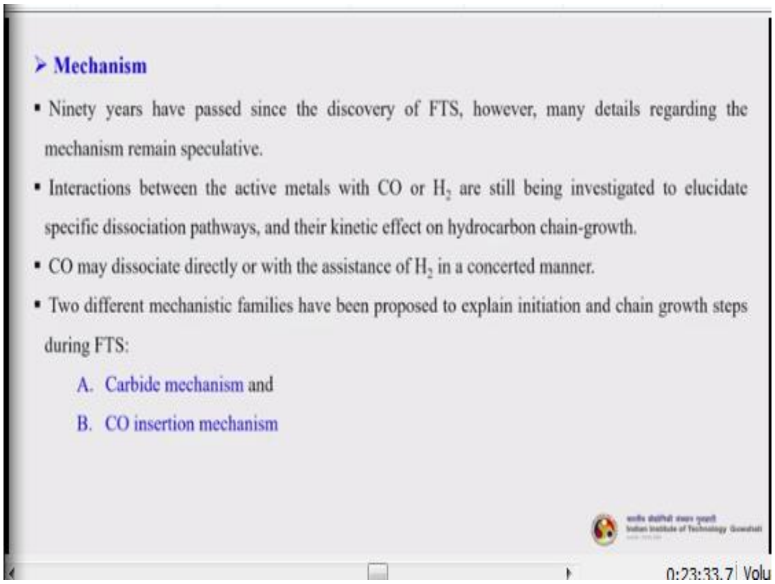

➢ **Mechanism**

- Ninety years have passed since the discovery of FTS, however, many details regarding the mechanism remain speculative.
- Interactions between the active metals with CO or H_2 are still being investigated to elucidate specific dissociation pathways, and their kinetic effect on hydrocarbon chain-growth.
- CO may dissociate directly or with the assistance of H_2 in a concerted manner.
- Two different mechanistic families have been proposed to explain initiation and chain growth steps during FTS:
  - A. Carbide mechanism and
  - B. CO insertion mechanism

So, we will try to understand the mechanism now. So, ninety years have passed since discovery of the Fischer Tropsch synthesis process. However, many details regarding the mechanism remains speculative. Interactions between the active metals with carbon monoxide or hydrogen are still being investigated to elucidate specific dissociation pathways, and their kinetic effect on hydrocarbon chain growth.

Carbon monoxide may dissociate directly or with assistance of hydrogen in a concerted manner. Two different mechanistic families have been proposed to explain initiation and chain growth steps during the Fischer Tropsch synthesis, first is carbide mechanism, second is carbon monoxide insertion mechanism.

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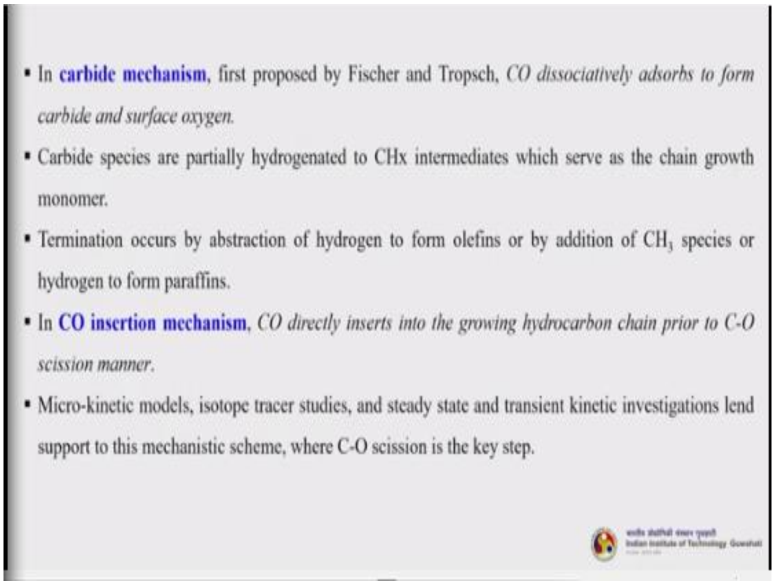

- In **carbide mechanism**, first proposed by Fischer and Tropsch, *CO dissociatively adsorbs to form carbide and surface oxygen.*
- Carbide species are partially hydrogenated to CHx intermediates which serve as the chain growth monomer.
- Termination occurs by abstraction of hydrogen to form olefins or by addition of CH_3 species or hydrogen to form paraffins.
- In **CO insertion mechanism**, *CO directly inserts into the growing hydrocarbon chain prior to C-O scission manner.*
- Micro-kinetic models, isotope tracer studies, and steady state and transient kinetic investigations lend support to this mechanistic scheme, where C-O scission is the key step.

So, in carbide mechanism first proposed by Fischer and Tropsch, carbon monoxide dissociatively adsorbs to form carbide and surface oxygen. Carbide species are partially hydrogenated to CHx intermediates which serve as a chain growth monomer. Termination occurs by abstraction of hydrogen to form olefins or by addition of CH_3 species or hydrogen to form paraffins. Whereas in carbon monoxide insertion mechanism; carbon monoxide directly inserts into the growing hydrocarbon chain prior to carbon oxygen scission manner.

Micro kinetic models, isotope tracer studies and steady state and transient kinetic investigations lend support to this mechanistic scheme, where C-O scission is the key step.

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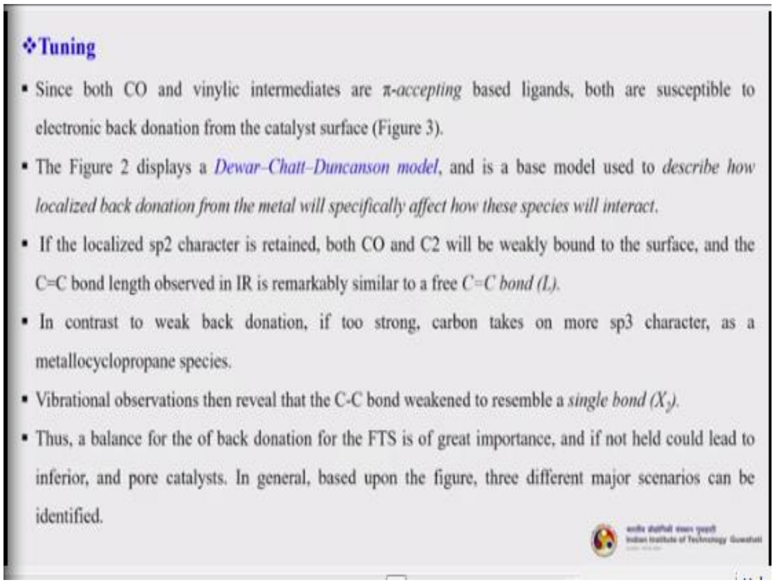

❖**Tuning**

- Since both CO and vinylic intermediates are *π-accepting* based ligands, both are susceptible to electronic back donation from the catalyst surface (Figure 3).
- The Figure 2 displays a *Dewar–Chatt–Duncanson model*, and is a base model used to *describe how localized back donation from the metal will specifically affect how these species will interact.*
- If the localized sp2 character is retained, both CO and C2 will be weakly bound to the surface, and the C=C bond length observed in IR is remarkably similar to a free *C=C bond (L).*
- In contrast to weak back donation, if too strong, carbon takes on more sp3 character, as a metallocyclopropane species.
- Vibrational observations then reveal that the C-C bond weakened to resemble a *single bond* (X_3).
- Thus, a balance for the of back donation for the FTS is of great importance, and if not held could lead to inferior, and pore catalysts. In general, based upon the figure, three different major scenarios can be identified.

So, tuning; since both carbon monoxide and vinylic intermediates are π-accepting based ligands, both are susceptible to electronic back donation from the catalyst surface**.**

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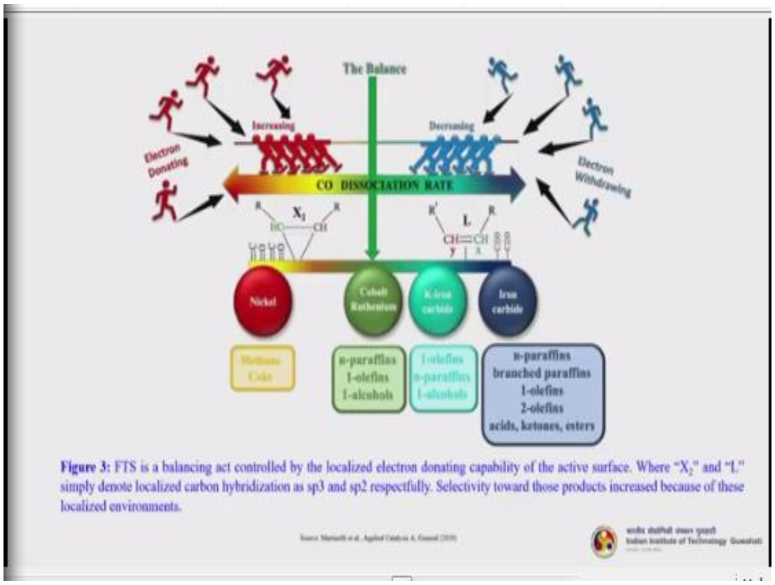

Figure 3: FTS is a balancing act controlled by the localized electron donating capability of the active surface. Where "X_2" and "L" simply denote localized carbon hybridization as sp3 and sp2 respectfully. Selectivity toward those products increased because of these localized environments.

So, we will see a mechanism here. So, this is FTS mechanism**,** it is a balancing act controlled by the localized electron donating capability of the active surface. So, you can see this, you can see that carbon monoxide dissociation rate. Here this side it is decreasing where the electrons are withdrawing, here it is increasing where the electrons are donating. Various catalyst like nickel, cobalt, ruthenium, iron carbide, iron, all these are being used.

And different catalyst depending upon the different dissociation rate and what is the active surface and what type of bonding is happening, you will get different types of products. Let us go back; so this, whatever I have shown, is a Dewar-Chatt-Duncanson model and is a base model used to describe how localized back donation from the metal will specifically affect how these species will interact**.**

So, if the localized sp2 character is retained, both carbon monoxide and C2 will be weakly bound to the surface and the C = C will be observed in the IR is remarkably similar to the free C = C**.** So, it is specifically talking about this and the position is also very important. Now in contrast to weak back donation, if too strong carbon takes one more sp3 character as a metallocyclopropane species.

Vibrational observations then reveal that C-C bond weakened to resemble a single bond X_2, this one. So, you can see here it is a double bond, here the bond is weakened, it is a single bond here. So, vibrational observations reveal that C-C bond we can to resemble a single bond marked by the X_2 in the image. Thus, a balance for the back donation of FTS is of great importance and if not held could lead to inferior and pore catalyst.

Now in general based upon the figure 3, different major scenarios can be identified. So, we will discuss what are the 3 different scenarios that can happen while this carbon monoxide dissociation is happening?

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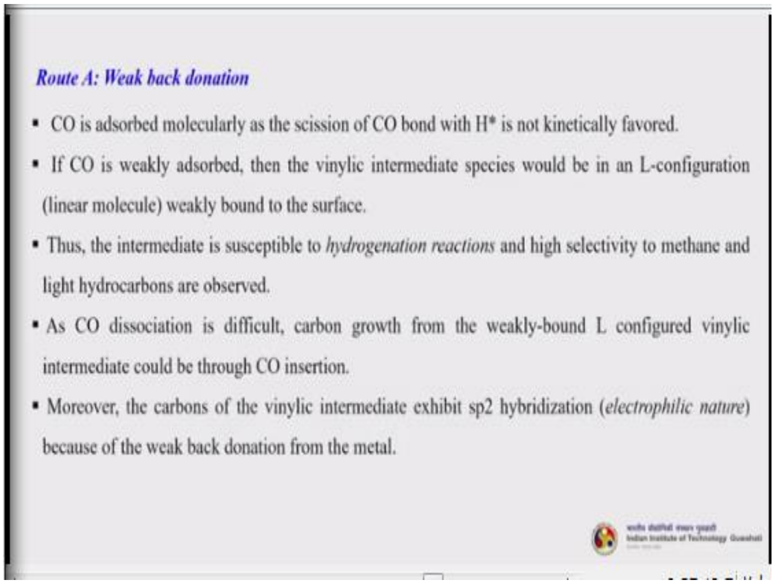

Route A: Weak back donation

- CO is adsorbed molecularly as the scission of CO bond with H* is not kinetically favored.
- If CO is weakly adsorbed, then the vinylic intermediate species would be in an L-configuration (linear molecule) weakly bound to the surface.
- Thus, the intermediate is susceptible to *hydrogenation reactions* and high selectivity to methane and light hydrocarbons are observed.
- As CO dissociation is difficult, carbon growth from the weakly-bound L configured vinylic intermediate could be through CO insertion.
- Moreover, the carbons of the vinylic intermediate exhibit sp2 hybridization (*electrophilic nature*) because of the weak back donation from the metal.

The first one is route A, weak back donation. So, carbon monoxide is adsorbed molecularly as the scission of carbon bond with H+ is not kinetically favored. If carbon monoxide is weakly adsorbed then the vinylic intermediate species will be an L configuration weakly bound to the surface, this one. They will be in this type of configuration L configuration.

Thus the intermediate is susceptible to hydrogenation reactions and high selectivity to methane and light hydrocarbons are observed. As carbon monoxide dissociation is difficult, carbon growth from the weakly bound L configured vinylic intermediate could be through the carbon monoxide insertion. Moreover, the carbons of the vinylic intermediate exhibit sp2 hybridization, that is electrophilic in nature because of the weak back donation from the metal.

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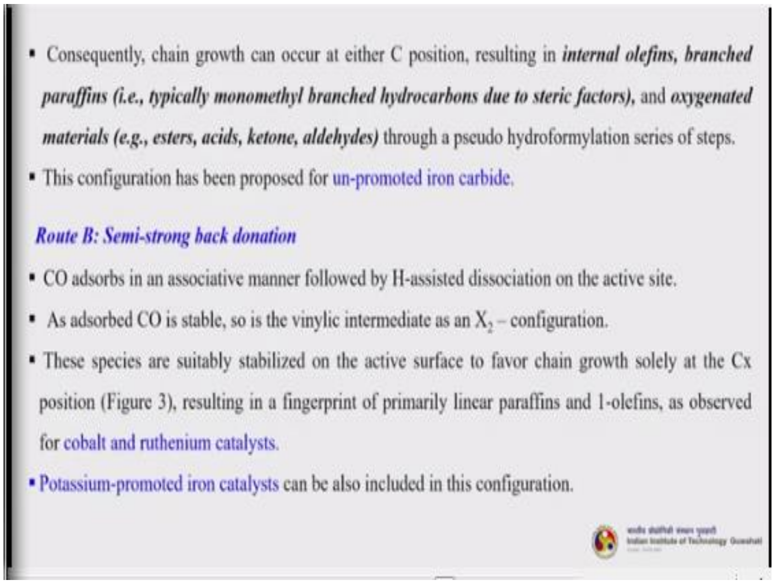

- Consequently, chain growth can occur at either C position, resulting in ***internal olefins, branched paraffins (i.e., typically monomethyl branched hydrocarbons due to steric factors)***, and ***oxygenated materials (e.g., esters, acids, ketone, aldehydes)*** through a pseudo hydroformylation series of steps.
- This configuration has been proposed for un-promoted iron carbide.

Route B: Semi-strong back donation

- CO adsorbs in an associative manner followed by H-assisted dissociation on the active site.
- As adsorbed CO is stable, so is the vinylic intermediate as an X_2 – configuration.
- These species are suitably stabilized on the active surface to favor chain growth solely at the Cx position (Figure 3), resulting in a fingerprint of primarily linear paraffins and 1-olefins, as observed for cobalt and ruthenium catalysts.
- Potassium-promoted iron catalysts can be also included in this configuration.

Now consequently, chain growth can occur at either C position, resulting in internal olefins, branched paraffins, and oxygenated materials through a pseudo hydroformylation series of steps. This configuration has been proposed for the un-promoted iron carbide. So, basically we discussed about this**,** we can see the n-paraffins, branched olefins, 1-olefin, 2-olefin, acids, ketones and esters all these things will be produced in this route weak back donation.

Now route B is the semi strong back donation. Now carbon monoxide adsorbs in an associative manner followed by H dissociation on the active side. As adsorbed carbon monoxide is stable, so is the vinylic intermediate as an X_2 configuration. Now we are talking about this configuration, we can call this as a semi strong back donation happening here, thus this is the metallic surface of the catalyst**.**

So, these species are suitably stabilized on the active surface to favor chain growth solely at the Cx position, resulting in a fingerprint of primarily linear paraffins and 1-olefins as observed for cobalt and ruthenium catalyst, usually cobalt and ruthenium based catalyst are being used. Potassium promoted iron catalyst can also be included in this configuration.

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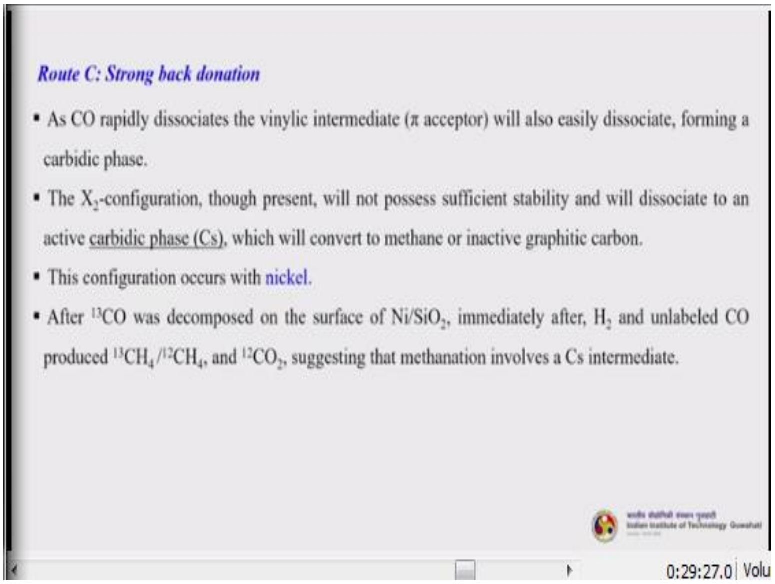

Route C: Strong back donation

- As CO rapidly dissociates the vinylic intermediate (π acceptor) will also easily dissociate, forming a carbidic phase.
- The X_2-configuration, though present, will not possess sufficient stability and will dissociate to an active carbidic phase (Cs), which will convert to methane or inactive graphitic carbon.
- This configuration occurs with nickel.
- After ^{13}CO was decomposed on the surface of Ni/SiO_2, immediately after, H_2 and unlabeled CO produced $^{13}CH_4/^{12}CH_4$, and $^{12}CO_2$, suggesting that methanation involves a Cs intermediate.

Now route C, the last one is the strong back donation. Now as carbon monoxide rapidly dissociates the vinylic intermediate, that is the π-acceptor, will also easily dissociate forming a carbidic phase. The X_2 configuration though present will not possess sufficient stability and will dissociate to an active carbidic phase which will convert to methane or inactive graphite carbon.

Now this usually happens with nickel catalyst**.** So, you can see that the same X_2 configuration, with the nickel catalyst will result as methane and coke formation will happen**,** so due to the strong back donation scheme. After carbon monoxide was decomposed on further surface of the nickel or silicon dioxide immediately after hydrogen and unlabeled carbon monoxide produced methane and carbon dioxide, suggesting that methanation involves a Cs intermediate, which basically happens due to the strong back donation.

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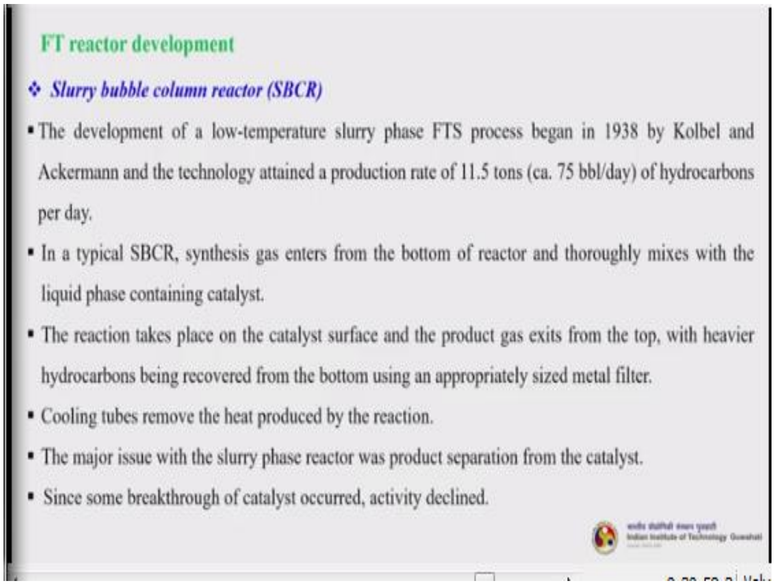

FT reactor development

❖ ***Slurry bubble column reactor (SBCR)***

- The development of a low-temperature slurry phase FTS process began in 1938 by Kolbel and Ackermann and the technology attained a production rate of 11.5 tons (ca. 75 bbl/day) of hydrocarbons per day.
- In a typical SBCR, synthesis gas enters from the bottom of reactor and thoroughly mixes with the liquid phase containing catalyst.
- The reaction takes place on the catalyst surface and the product gas exits from the top, with heavier hydrocarbons being recovered from the bottom using an appropriately sized metal filter.
- Cooling tubes remove the heat produced by the reaction.
- The major issue with the slurry phase reactor was product separation from the catalyst.
- Since some breakthrough of catalyst occurred, activity declined.

So, we will try to understand now and learn about the different reactors that are essential for the FT synthesis reaction. So, slurry bubble column reactor, the SBCR. The development of a low temperature slurry phase FTS process began in 1938 by Kolbel and Ackermann and the technology attained a production rate of 11.5 tons of hydrocarbons per day. In a typical slurry bubble column reactor synthesis gas enters from the bottom of the reactor and thoroughly mixes with the liquid phase containing the catalyst.

The reaction takes place on the catalyst surface and the product gas exits from the top with heavier hydrocarbons being recovered from the bottom using an appropriately sized metal filter. Cooling tubes remove the heat produced by the reaction; the major issue with the slurry phase reactor was product separation from the catalyst. Since some breakthrough of the catalyst occurs activity declined.

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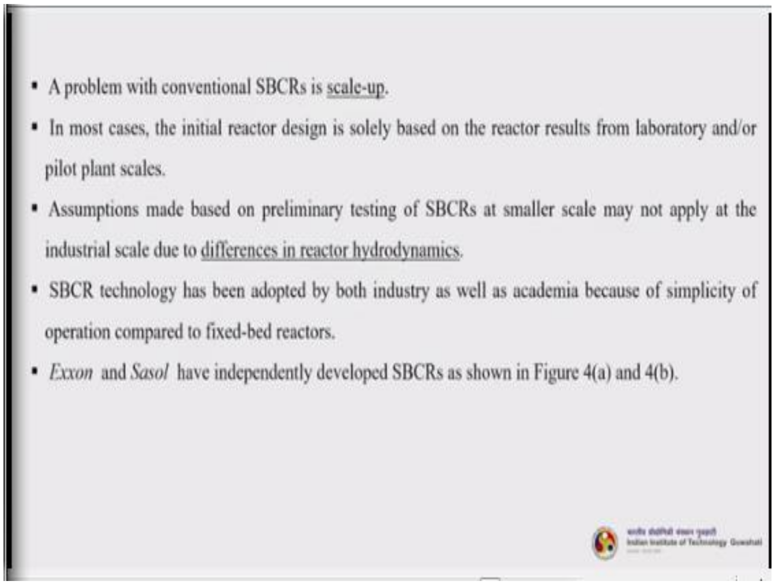

- A problem with conventional SBCRs is scale-up.
- In most cases, the initial reactor design is solely based on the reactor results from laboratory and/or pilot plant scales.
- Assumptions made based on preliminary testing of SBCRs at smaller scale may not apply at the industrial scale due to differences in reactor hydrodynamics.
- SBCR technology has been adopted by both industry as well as academia because of simplicity of operation compared to fixed-bed reactors.
- *Exxon* and *Sasol* have independently developed SBCRs as shown in Figure 4(a) and 4(b).

A problem with the conventional SBCRs is the scale up. In most cases the initial reactor design is solely based on the reactor results from the laboratory and/or pilots plant scale studies. Assumptions made based on preliminary testing of the slurry bubble column reactors at small scale may not apply at the industrial scale due to the differences in the reactor hydrodynamics. So, SBCR technology has been adopted by both industry as well as academia because of the simplicity of the operation compared to the fixed bed reactors. Exxon and Sasol have independently developed SBCRs as shown in figure 4 a and 4 b.

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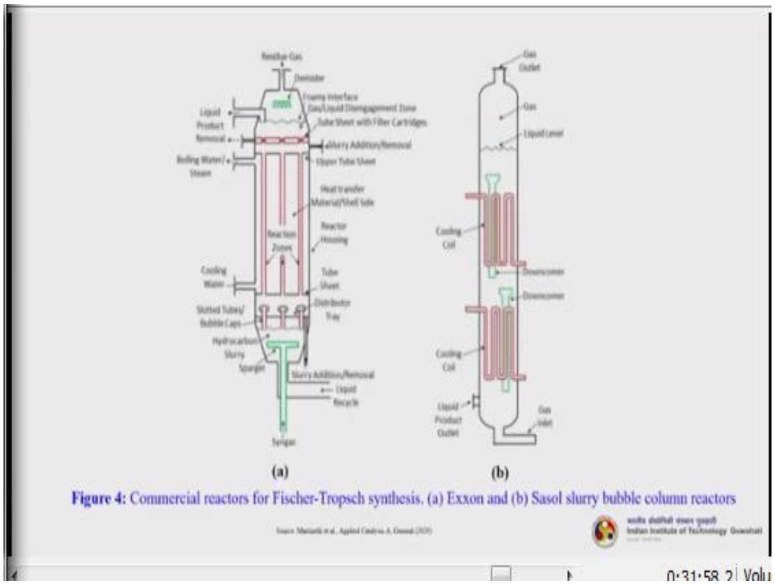

Figure 4: Commercial reactors for Fischer-Tropsch synthesis. (a) Exxon and (b) Sasol slurry bubble column reactors

We will see these 2 reactors**.** So, the A design is done by the Exxon company and B design is by the Sasol**.** So, you can see that there is little difference between the design. So basically you can see that in the B you have cooling coils that is inserted inside the reactors**.** So, that the cooling can be done very fast, if you have it outside the reactor, so it will take time and cooling effect may not be so good.

But if you put it inside the reaction, but there are problems also maintenance and all these things is a big issue, so but the cooling can be faster**.** So, here you can see the reaction, this is the main reaction zone and there are integrities given here. Mostly both the designs have been well adapted by industrial sector, and are still in practice**.**

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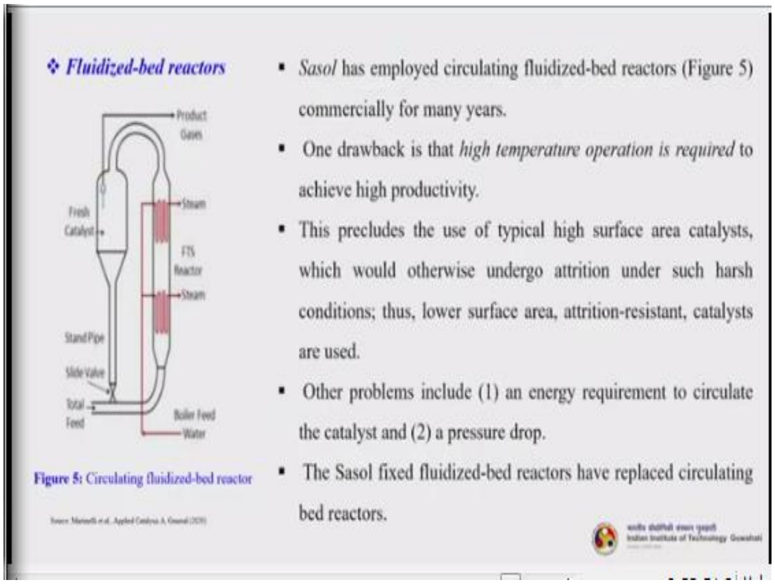

❖ ***Fluidized-bed reactors***

Figure 5: Circulating fluidized-bed reactor

- *Sasol* has employed circulating fluidized-bed reactors (Figure 5) commercially for many years.
- One drawback is that *high temperature operation is required* to achieve high productivity.
- This precludes the use of typical high surface area catalysts, which would otherwise undergo attrition under such harsh conditions; thus, lower surface area, attrition-resistant, catalysts are used.
- Other problems include (1) an energy requirement to circulate the catalyst and (2) a pressure drop.
- The Sasol fixed fluidized-bed reactors have replaced circulating bed reactors.

Then is the fluidized bed reactors which are also very common. Sasol has employed circulating fluidized bed reactors commercially for many years. One drawback is that high temperature operation is required to achieve high productivity. Now this precludes the use of typical high surface area catalyst which would otherwise undergo attrition under such harsh conditions, thus lower surface area, attrition resistance, catalysts are used.

Other problems include an energy requirement to circulate the catalyst and the pressure drop. The Sasol fixed fluidized bed reactors have replaced circulating based reactors. So, this is a typical circulating fluidized bed reactor**.**

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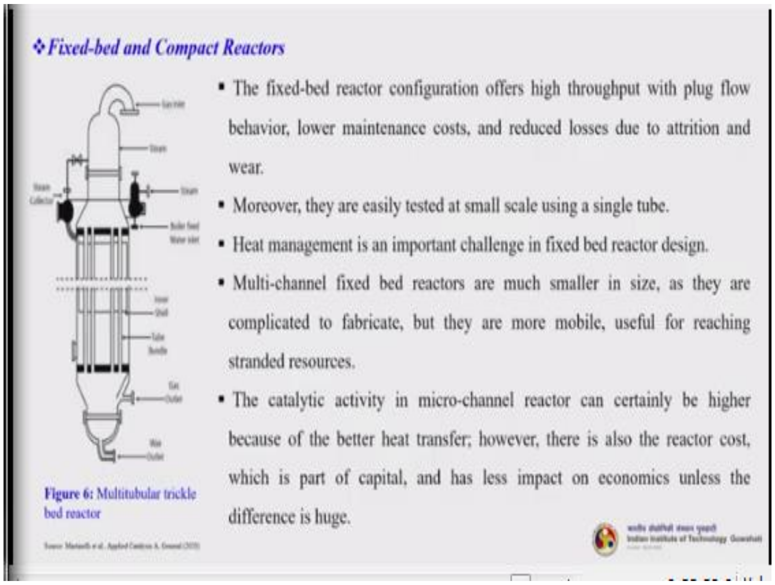

❖ *Fixed-bed and Compact Reactors*

- The fixed-bed reactor configuration offers high throughput with plug flow behavior, lower maintenance costs, and reduced losses due to attrition and wear.
- Moreover, they are easily tested at small scale using a single tube.
- Heat management is an important challenge in fixed bed reactor design.
- Multi-channel fixed bed reactors are much smaller in size, as they are complicated to fabricate, but they are more mobile, useful for reaching stranded resources.
- The catalytic activity in micro-channel reactor can certainly be higher because of the better heat transfer; however, there is also the reactor cost, which is part of capital, and has less impact on economics unless the difference is huge.

Figure 6: Multitubular trickle bed reactor

So, then we will discuss about the fixed bed and compact bed reactors. Now the fixed bed reactor configuration offers high throughput with plug flow behavior, lower maintenance cost and reduced losses due to attrition and wear. Moreover, they are easily tested at small scale using a single tube. So, you can see that there are many tubular tubes are here, so you can have single tube, you can have multiple tubes.

It is basically a design how much feed you are processing, that is very important**.** So, multi-channel fixed bed reactors are much smaller in size as they are complicated to fabricate, but they are more mobile useful for reaching standard resources. You can carry it them and install it any other places**.** So, the catalytic activity in micro channel reactor can certainly be higher because of the better heat transfer. However, there is also the reactor cost which is part of the capital cost and has less impact on the economics unless the difference is huge.

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(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
07	Biodiesel	03	Biodiesel purification, fuel properties

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

So, with this I wind up today's lecture. So, in the next lecture which is again under module 7 lecture 3 under biodiesel, we will discuss about the techniques to purify biodiesel and we will also discuss about the biodiesel fuel properties. So, thank you very much, in case you have any query, please register, it on the swayam portal or you can drop a mail to me at kmohanty@iitg.ac.in.