Biomass Conversion and Biorefinery
Prof. Kaustubha Mohanty
Department of Chemical Engineering
Indian Institute of Technology-Guwahati

Module 08
Lecture-23
Factors Affecting Biooil, Biochar production, Fuel Properties Characterization

Good morning students. This is lecture 2 under module 8. As you know, we have been discussing biooil and biochar. Under this lecture we will be discussing about the various fuel characterization techniques. I will tell you the details about the procedures which will help you immensely later when you try to carry out such analysis for the biofuel that you are going to produce - especially the liquid biofuels. And then today we will also talk about the biooil upgradation technologies. So, let us begin.

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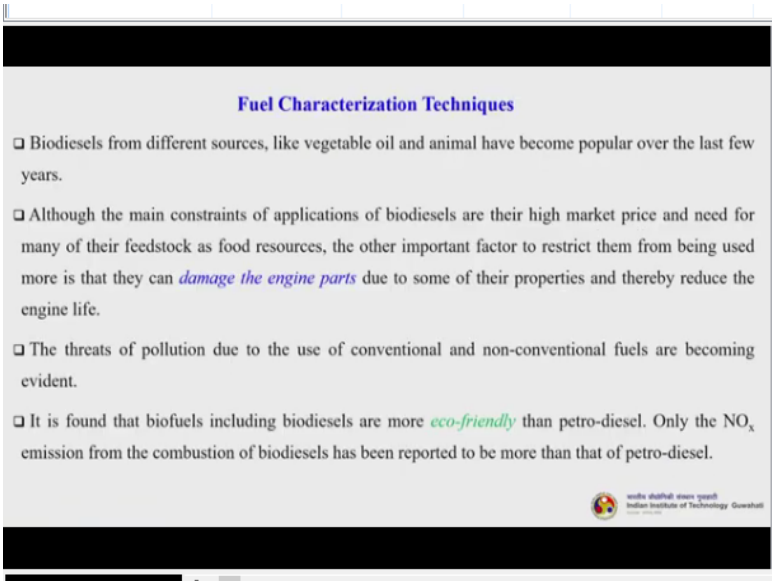

Fuel Characterization Techniques

- Biodiesels from different sources, like vegetable oil and animal have become popular over the last few years.
- Although the main constraints of applications of biodiesels are their high market price and need for many of their feedstock as food resources, the other important factor to restrict them from being used more is that they can *damage the engine parts* due to some of their properties and thereby reduce the engine life.
- The threats of pollution due to the use of conventional and non-conventional fuels are becoming evident.
- It is found that biofuels including biodiesels are more *eco-friendly* than petro-diesel. Only the NO_x emission from the combustion of biodiesels has been reported to be more than that of petro-diesel.

Biodiesels from different sources like vegetable oil and animal have become popular over the last few years. Although the main constraints of applications of biodiesel are their high market price and need for many of their feedstock as food sources, the other important factor to restrict them from being used more is that they can damage the engine parts due to some of their properties and thereby reduce the engine life.

The threats of pollution due to the use of conventional and non conventional fuels are becoming evident. It is found that biofuels including biodiesels are more eco-friendly than petro-diesel. Only the NO_X emissions from the combustion of biodiesels have been reported to be little more than that of the petro-diesel.

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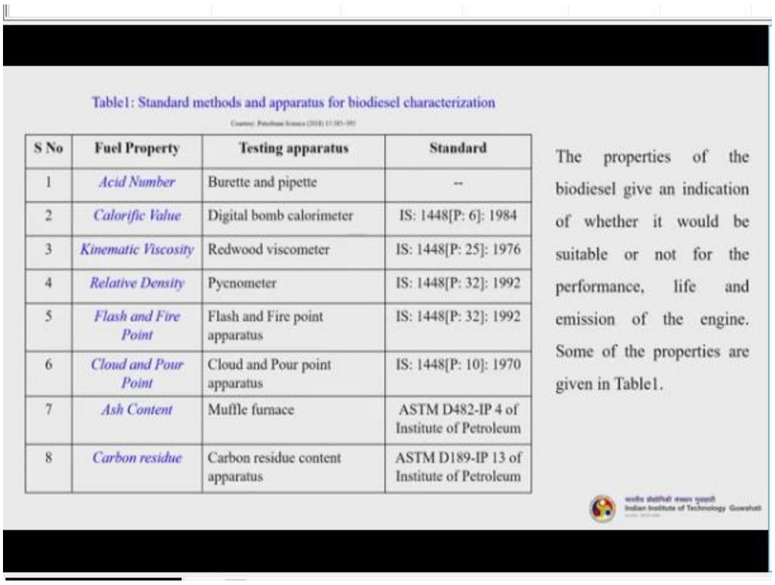

Table1: Standard methods and apparatus for biodiesel characterization

S No	Fuel Property	Testing apparatus	Standard
1	*Acid Number*	Burette and pipette	--
2	*Calorific Value*	Digital bomb calorimeter	IS: 1448[P: 6]: 1984
3	*Kinematic Viscosity*	Redwood viscometer	IS: 1448[P: 25]: 1976
4	*Relative Density*	Pycnometer	IS: 1448[P: 32]: 1992
5	*Flash and Fire Point*	Flash and Fire point apparatus	IS: 1448[P: 32]: 1992
6	*Cloud and Pour Point*	Cloud and Pour point apparatus	IS: 1448[P: 10]: 1970
7	*Ash Content*	Muffle furnace	ASTM D482-IP 4 of Institute of Petroleum
8	*Carbon residue*	Carbon residue content apparatus	ASTM D189-IP 13 of Institute of Petroleum

The properties of the biodiesel give an indication of whether it would be suitable or not for the performance, life and emission of the engine. Some of the properties are given in Table1.

So, this table will tell you the different types of fuel properties, the testing apparatus and the respective standard. Now there are 8 here we have listed which are the standard characterization parameters that needs to be carried out for any biodiesel or biooil that you actually produce. So, the first is acid number, the testing apparatus require is a burette and pipette, it is very simple.

Then next is calorific value, you need a digital bomb calorimeter for that and the plain bomb calorimeter digital or not digital is not an issue actually. So, then kinematic viscosity you need a viscometer. Relative density you can calculate it using pycnometer. Flash and fire point using the respective apparatus. Cloud and pour point using the respective apparatus. Ash content you need a muffle furnace it is a simple thing. Carbon residue, also you can carry out using a carbon residue content apparatus.

You can see the standards are given the international standards ASTMs and all these things. So, the properties of the biodiesel give an indication of whether it would be suitable or not for the performance, life and emission of the engine. Some of the properties we have already discussed under this table.

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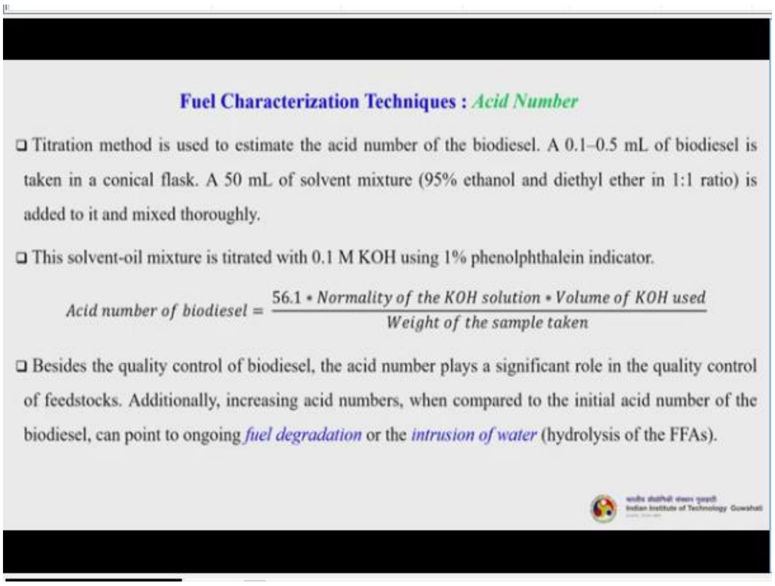

Fuel Characterization Techniques : *Acid Number*

- Titration method is used to estimate the acid number of the biodiesel. A 0.1–0.5 mL of biodiesel is taken in a conical flask. A 50 mL of solvent mixture (95% ethanol and diethyl ether in 1:1 ratio) is added to it and mixed thoroughly.
- This solvent-oil mixture is titrated with 0.1 M KOH using 1% phenolphthalein indicator.

$$\text{Acid number of biodiesel} = \frac{56.1 * \text{Normality of the KOH solution} * \text{Volume of KOH used}}{\text{Weight of the sample taken}}$$

- Besides the quality control of biodiesel, the acid number plays a significant role in the quality control of feedstocks. Additionally, increasing acid numbers, when compared to the initial acid number of the biodiesel, can point to ongoing *fuel degradation* or the *intrusion of water* (hydrolysis of the FFAs).

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So, we will see one by one. The first is acid number. Titration method is used to estimate the acid number of the biodiesel. Usually 0.1 to 0.5 ml of biodiesel is taken in a conical flask. A 50 ml of the solvent mixture which is usually 95% ethanol and diethyl ether in 1 : 1 ratio is added to it and mixed thoroughly. Now this solvent oil mixture is titrated against 0.1 molar KOH using a 1% phenolphthalein indicator.

So, you can find out the acid number from this formula. So, 56.1 into normality of the KOH solution into volume of KOH used divided by weight of the sample taken.

$$\text{Acid number of biodiesel} = \frac{56.1 * \text{Normality of KOH solution} * \text{Volume of KOH used}}{\text{Weight of sample taken}}$$

Now besides the quality control of biodiesel the acid number plays a significant role in the quality control of the feedstock also. Additionally, increasing acid numbers when compared to the initial acid number of the biodiesel can point to ongoing fuel degradation or the intrusion of the water. So, which actually happens by the hydrolysis of the free fatty acids.

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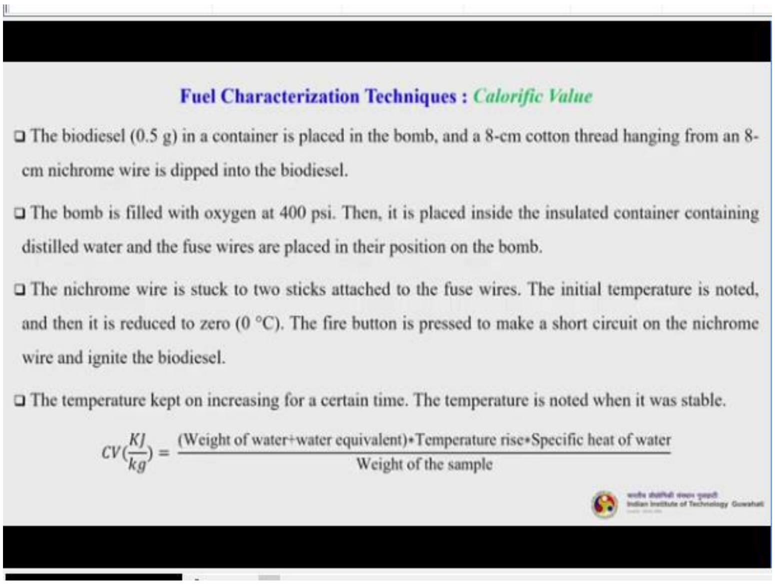

Fuel Characterization Techniques : *Calorific Value*

- ❑ The biodiesel (0.5 g) in a container is placed in the bomb, and a 8-cm cotton thread hanging from an 8-cm nichrome wire is dipped into the biodiesel.
- ❑ The bomb is filled with oxygen at 400 psi. Then, it is placed inside the insulated container containing distilled water and the fuse wires are placed in their position on the bomb.
- ❑ The nichrome wire is stuck to two sticks attached to the fuse wires. The initial temperature is noted, and then it is reduced to zero (0 °C). The fire button is pressed to make a short circuit on the nichrome wire and ignite the biodiesel.
- ❑ The temperature kept on increasing for a certain time. The temperature is noted when it was stable.

$$CV(\frac{KJ}{kg}) = \frac{\text{(Weight of water+water equivalent)*Temperature rise*Specific heat of water}}{\text{Weight of the sample}}$$

Then the next is calorific value. Biodiesel about 0.5 gram in a container is placed in the bomb and the 8 centimeter cotton thread hanging from an 8 centimeter nichrome wire is dipped into the biodiesel. The bomb is then filled with oxygen at 400 psi. Then it is placed inside the insulated container containing distilled water and the fuse wires are placed in their position on the bomb. The nichrome wire is stuck to 2 sticks attached to the fuse wires.

The initial temperature is noted and then it is reduced to 0 degree centigrade. The fire button is pressed to make a short circuit on the nichrome wire and ignite the biodiesel. The temperature kept on increasing for a certain time. The temperature is noted when it was stable. So, the calorific value in kilo joules per kilogram can be calculated by this equation. So, weight of the water plus water equivalent into temperature rise into specific heat of water divided by weight of the sample.

$$CV\left(\frac{KJ}{kg}\right) = \frac{(Weight\ of\ water + Water\ equivalent) * Temperature\ rise * Specific\ heat\ of\ water}{Weight\ of\ the\ sample}$$

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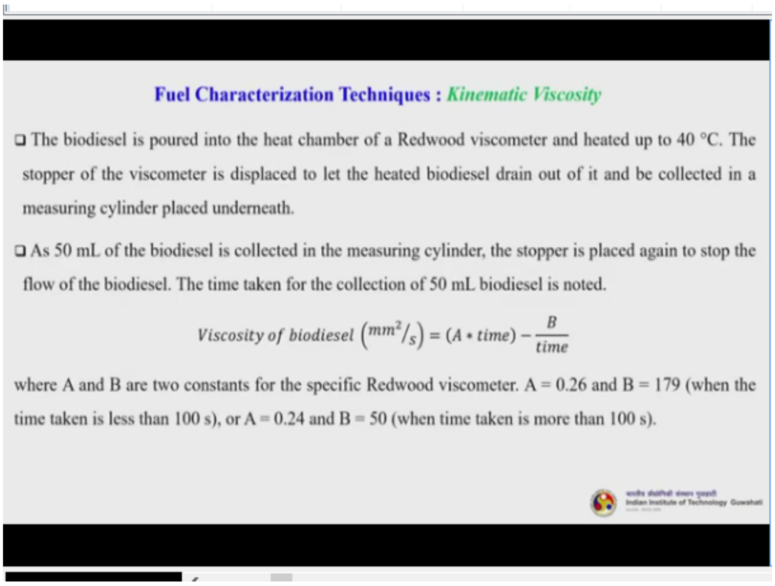

Fuel Characterization Techniques : *Kinematic Viscosity*

- The biodiesel is poured into the heat chamber of a Redwood viscometer and heated up to 40 °C. The stopper of the viscometer is displaced to let the heated biodiesel drain out of it and be collected in a measuring cylinder placed underneath.
- As 50 mL of the biodiesel is collected in the measuring cylinder, the stopper is placed again to stop the flow of the biodiesel. The time taken for the collection of 50 mL biodiesel is noted.

$$Viscosity\ of\ biodiesel\ \left({mm^2}/{s}\right) = (A * time) - \frac{B}{time}$$

where A and B are two constants for the specific Redwood viscometer. A = 0.26 and B = 179 (when the time taken is less than 100 s), or A = 0.24 and B = 50 (when time taken is more than 100 s).

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Then kinematic viscosity: The biodiesel is poured into the heat chamber of a Redwood viscometer and heated up to 40 degree centigrade. The stopper of the viscometer is displaced to let the heater biodiesel drain out of it and be collected in a measuring cylinder placed underneath. As 50 ml of the biodiesel is collected in the measuring cylinder the stopper is placed again to stop the flow of the biodiesel.

The time taken for the collection of 50 ml biodiesel is noted. So, you can calculate the viscosity using this equation A into time - B by time. So, here A and B are 2 constants for the specific redwood viscometer A = 0.26 and B = 179, when the time taken is less than 100 second and A becomes 0.24 and B becomes 50 when the time taken is more than 100 second.

$$Viscosity\ of\ biodiesel\ \left({mm^2}/{s}\right) = (A * time) - \frac{B}{time}$$

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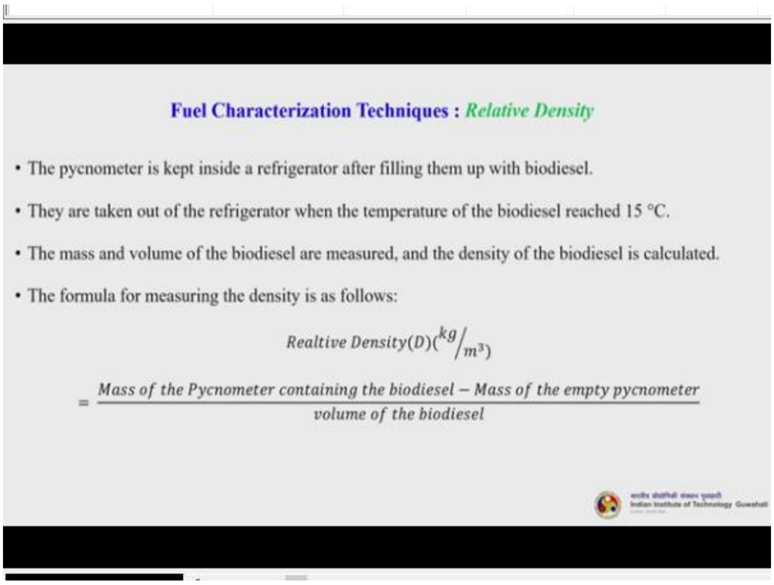

Fuel Characterization Techniques : *Relative Density*

- The pycnometer is kept inside a refrigerator after filling them up with biodiesel.
- They are taken out of the refrigerator when the temperature of the biodiesel reached 15 °C.
- The mass and volume of the biodiesel are measured, and the density of the biodiesel is calculated.
- The formula for measuring the density is as follows:

$$Realtive\ Density(D)\left(^{kg}/_{m^3}\right) = \frac{Mass\ of\ the\ Pycnometer\ containing\ the\ biodiesel - Mass\ of\ the\ empty\ pycnometer}{volume\ of\ the\ biodiesel}$$

So, the next is relative density. The pycnometer is kept inside a refrigerator after filling them up with biodiesel. They are taken out of the refrigerator when the temperature of the biodiesel reached 15 degrees centigrade. The mass and volume of the biodiesel are measured and the density of the biodiesel is calculated. The formula for measuring the density is as follows. So, the relative density in kilograms per meter cube equals to mass of the pycnometer containing the biodiesel minus mass of the empty pycnometer divided by the volume of the biodiesel.

$$Relative\ Density\ (D)\left(^{kg}/_{m^3}\right) = \frac{Mass\ of\ Pycnometer\ containing\ biodiesel - Mass\ of\ Pycnometer}{volume\ of\ biodiesel}$$

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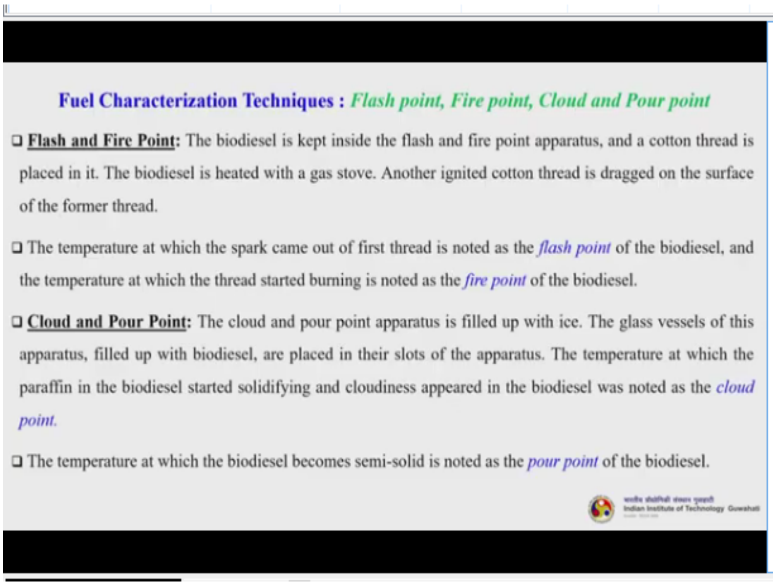

Fuel Characterization Techniques : *Flash point, Fire point, Cloud and Pour point*

❑ **Flash and Fire Point:** The biodiesel is kept inside the flash and fire point apparatus, and a cotton thread is placed in it. The biodiesel is heated with a gas stove. Another ignited cotton thread is dragged on the surface of the former thread.

❑ The temperature at which the spark came out of first thread is noted as the *flash point* of the biodiesel, and the temperature at which the thread started burning is noted as the *fire point* of the biodiesel.

❑ **Cloud and Pour Point:** The cloud and pour point apparatus is filled up with ice. The glass vessels of this apparatus, filled up with biodiesel, are placed in their slots of the apparatus. The temperature at which the paraffin in the biodiesel started solidifying and cloudiness appeared in the biodiesel was noted as the *cloud point*.

❑ The temperature at which the biodiesel becomes semi-solid is noted as the *pour point* of the biodiesel.

So, then we will talk about the flash point, fire point, cloud and pour point. These are very important properties for any liquid fuels. So, flash and fire point: the biodiesel is kept inside the flash and fire point apparatus and a cotton thread is placed in it. The biodiesel is heated with a gas stove; another ignited cotton thread is dragged on the surface of the former thread. The temperature at which the spark came out of the first thread is noted as the flash point of the biodiesel. And the temperature at which the thread started burning is noted as the fire point of the biodiesel. These are very simple experiments.

Then similarly cloud and pour point: the cloud and pour point apparatus is filled up with ice, the glass vessels of these apparatus filled up with biodiesel are placed in their slots of the apparatus. The temperature at which the paraffin in the biodiesel started solidifying and cloudiness appeared in the biodiesel was noted as the cloud point. The temperature at which the biodiesel becomes semi-solid is noted as the pour point of the biodiesel.

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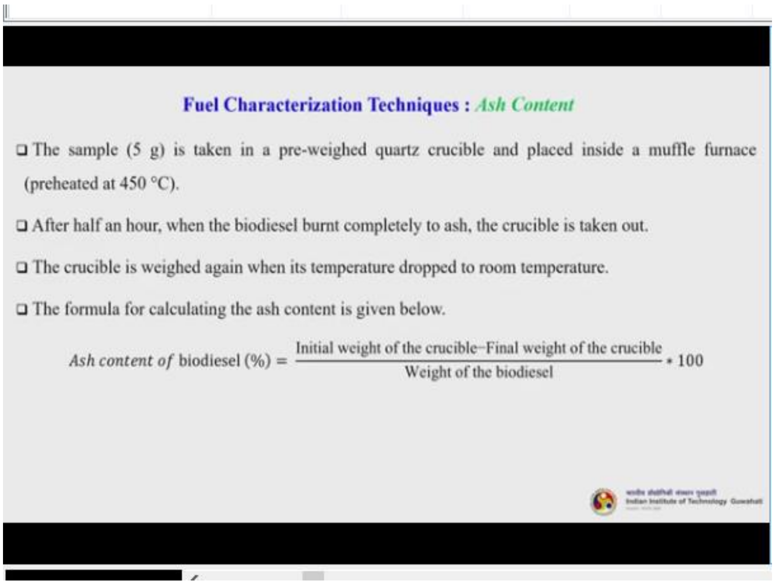

Fuel Characterization Techniques : *Ash Content*

- ❑ The sample (5 g) is taken in a pre-weighed quartz crucible and placed inside a muffle furnace (preheated at 450 °C).
- ❑ After half an hour, when the biodiesel burnt completely to ash, the crucible is taken out.
- ❑ The crucible is weighed again when its temperature dropped to room temperature.
- ❑ The formula for calculating the ash content is given below.

$$Ash\ content\ of\ \text{biodiesel}\ (\%) = \frac{\text{Initial weight of the crucible} - \text{Final weight of the crucible}}{\text{Weight of the biodiesel}} * 100$$

Then ash content: The sample (5 gram) is taken in a pre-weight quartz crucible and placed inside a muffle furnace usually at 450 degrees centigrade preheated. After half an hour when the biodiesel burnt completely to ash the crucible is taken out. The crucible is weighed again when its temperature drops to room temperature. So, you basically keep it in a desiccator. The formula for calculating the ash content is given below. Ash content of biodiesel in percentage equals to initial weight of the crucible minus final weight of the crucible divided by weight of the biodiesel into 100.

$$Ash\ content\ of\ the\ biodiesel\ (\%) = \frac{Initail\ weight\ of\ the\ crucible - Final\ weight\ of\ the\ crucible}{Weight\ of\ the\ biodiesel} * 100$$

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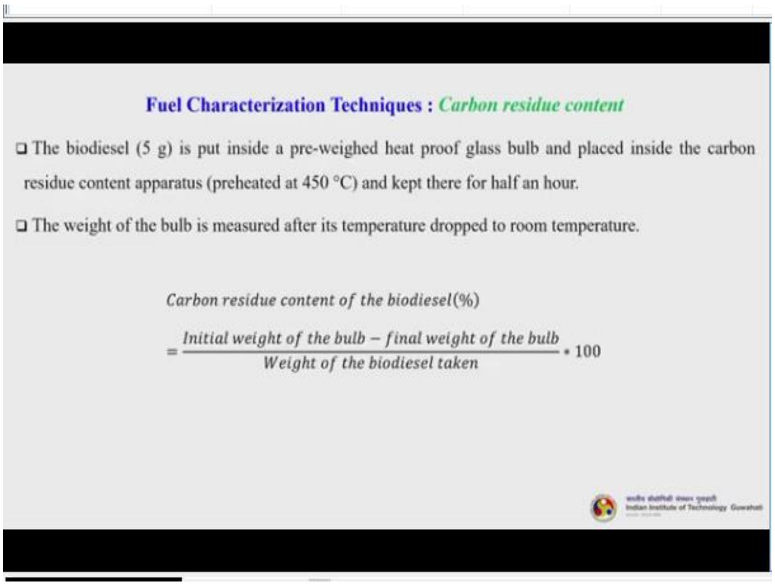

Fuel Characterization Techniques : *Carbon residue content*

- The biodiesel (5 g) is put inside a pre-weighed heat proof glass bulb and placed inside the carbon residue content apparatus (preheated at 450 °C) and kept there for half an hour.
- The weight of the bulb is measured after its temperature dropped to room temperature.

$$Carbon\ residue\ content\ of\ the\ biodiesel(\%) = \frac{Initial\ weight\ of\ the\ bulb - final\ weight\ of\ the\ bulb}{Weight\ of\ the\ biodiesel\ taken} * 100$$

Then the another one is the carbon residue content. So, what you do is that you take 5 gram of biodiesel and put it inside a pre-weighed heat proof glass bulb and place inside the carbon residue apparatus, preheated at 450 degree centigrade and kept there for half an hour. The weight of the bulb is measured after its temperature drop to room temperature. So, the carbon residue content of the biodiesel in percentage can be calculated by this equation: Initial weight of the bulb minus final weight of the bulb divided by weight of the biodiesel taken into 100.

$$Carbon\ residue\ content\ of\ the\ biodiesel\ (\%) = \frac{Initial\ weight\ of\ the\ bulb - final\ weight\ of\ the\ bulb}{Weight\ of\ the\ biodiesel\ taken} * 100$$

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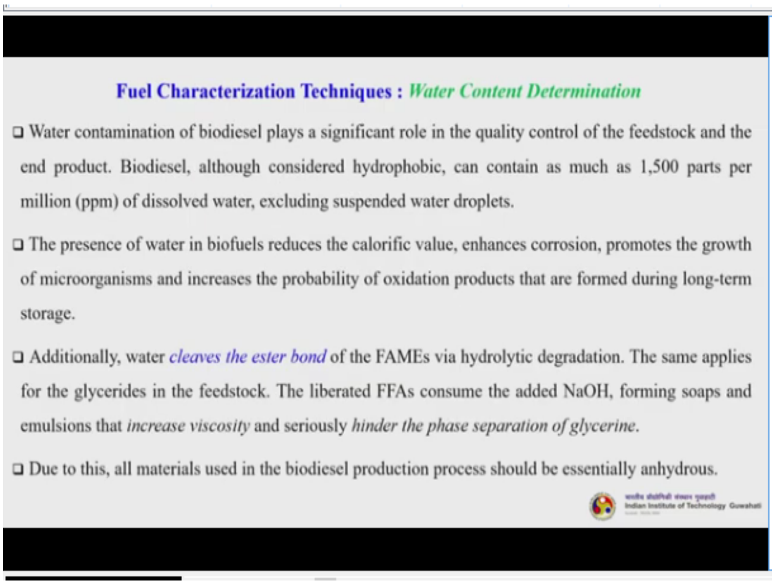

Fuel Characterization Techniques : *Water Content Determination*

- Water contamination of biodiesel plays a significant role in the quality control of the feedstock and the end product. Biodiesel, although considered hydrophobic, can contain as much as 1,500 parts per million (ppm) of dissolved water, excluding suspended water droplets.
- The presence of water in biofuels reduces the calorific value, enhances corrosion, promotes the growth of microorganisms and increases the probability of oxidation products that are formed during long-term storage.
- Additionally, water *cleaves the ester bond* of the FAMEs via hydrolytic degradation. The same applies for the glycerides in the feedstock. The liberated FFAs consume the added NaOH, forming soaps and emulsions that *increase viscosity* and seriously *hinder the phase separation of glycerine*.
- Due to this, all materials used in the biodiesel production process should be essentially anhydrous.

So, another very important parameter for any liquid fuel is the water content determination. Water contamination of biodiesel plays a significant role in the quality control of the feedstock and the end product. Biodiesel although considered hydrophobic, can contain as much as 1500 parts per million (ppm) of dissolved water excluding that of the suspended water droplets.

Now the presence of water in biofuels reduces the calorific value, enhances corrosion, promotes the growth of microorganisms and also increases the probability of oxidation products that are formed during long term storage. Additionally, water cleaves the ester bond of the FAMEs via hydrolytic degradation. The same applies for the glycerides in the feedstock also.

The liberated free fatty acids consume the added sodium hydroxide thereby forming soaps and emulsions that increase viscosity and seriously hinder the phase separation of the glycerine. But due to these all materials used in the biodiesel production process should be essentially anhydrous.

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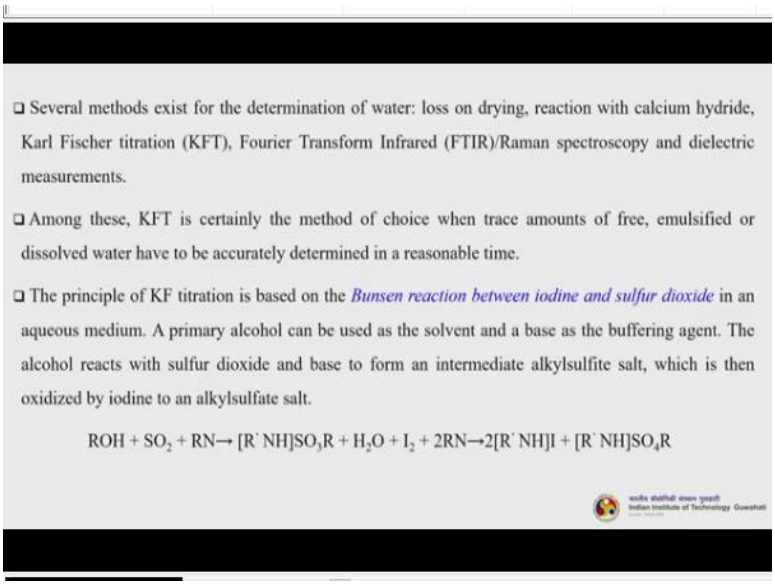

- ❑ Several methods exist for the determination of water: loss on drying, reaction with calcium hydride, Karl Fischer titration (KFT), Fourier Transform Infrared (FTIR)/Raman spectroscopy and dielectric measurements.
- ❑ Among these, KFT is certainly the method of choice when trace amounts of free, emulsified or dissolved water have to be accurately determined in a reasonable time.
- ❑ The principle of KF titration is based on the *Bunsen reaction between iodine and sulfur dioxide* in an aqueous medium. A primary alcohol can be used as the solvent and a base as the buffering agent. The alcohol reacts with sulfur dioxide and base to form an intermediate alkylsulfite salt, which is then oxidized by iodine to an alkylsulfate salt.

$$ROH + SO_2 + RN \rightarrow [R'NH]SO_3R + H_2O + I_2 + 2RN \rightarrow 2[R'NH]I + [R'NH]SO_4R$$

Several methods exist for the determination of water, so like loss on drying, reaction with calcium hydride, Karl Fischer titration which is the most adapted one, then Fourier transform infrared or Raman spectroscopy and dielectric measurements. Now among these the KFT or the Karl Fischer titration is certainly the method of choice when trace amounts of free emulsified or dissolved water have to be accurately determined in a reasonable time.

The principle of KF titration is based on the Bunsen reaction between the iodine and sulfur dioxide in an aqueous medium. A primary alcohol can be used as the solvent and a base as the buffering agent. The alcohol reacts with sulfur dioxide and base to form an intermediate alkyl sulphide salt which is then oxidized by iodine to an alkyl sulfate salt. So, this is the reaction.

$$ROH + SO_2 + RN \rightarrow [R'NH]SO_3R + H_2O + I_2 + 2RN \rightarrow 2[R'NH]I + [R'NH]SO_4R$$

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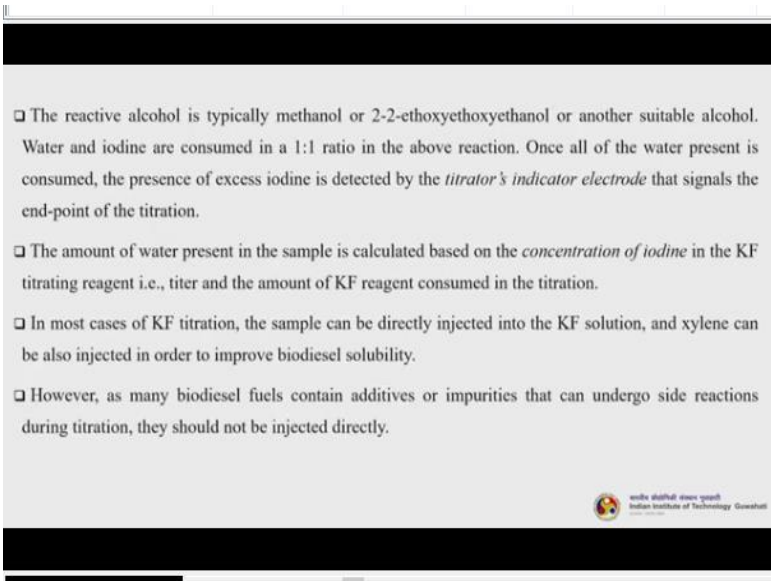

- The reactive alcohol is typically methanol or 2-2-ethoxyethoxyethanol or another suitable alcohol. Water and iodine are consumed in a 1:1 ratio in the above reaction. Once all of the water present is consumed, the presence of excess iodine is detected by the *titrator's indicator electrode* that signals the end-point of the titration.
- The amount of water present in the sample is calculated based on the *concentration of iodine* in the KF titrating reagent i.e., titer and the amount of KF reagent consumed in the titration.
- In most cases of KF titration, the sample can be directly injected into the KF solution, and xylene can be also injected in order to improve biodiesel solubility.
- However, as many biodiesel fuels contain additives or impurities that can undergo side reactions during titration, they should not be injected directly.

The reactive alcohol is typically methanol or 2-2 ethoxyethoxyethanol or another suitable alcohol. Water and iodine are consumed in a 1 : 1 ratio in the above reaction. Once all of the water present in consumed the presence of excess iodine is detected by the titrators indicator electrode that signals the end point of the titration. The amount of water present in the sample is calculated based on the concentration of iodine in the KF titrating reagent that is titre and the amount of KF reagent consumed in the titration.

In most cases of the KF titration the sample can be directly injected into the KF solution and xylene can also be injected in order to improve biodiesel solubility. However, as many biodiesel fuels contain additives or impurities that can undergo side reactions during titration they should not be injected directly.

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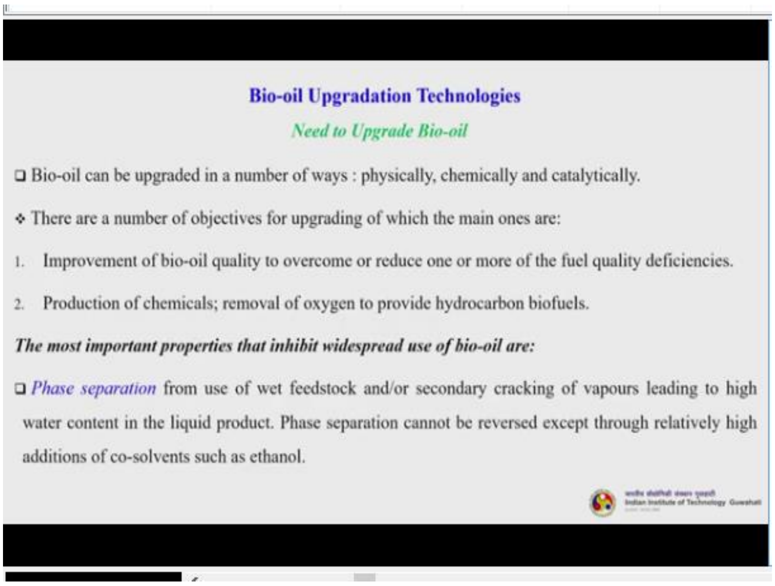

Bio-oil Upgradation Technologies

Need to Upgrade Bio-oil

❑ Bio-oil can be upgraded in a number of ways : physically, chemically and catalytically.

❖ There are a number of objectives for upgrading of which the main ones are:

1. Improvement of bio-oil quality to overcome or reduce one or more of the fuel quality deficiencies.
2. Production of chemicals; removal of oxygen to provide hydrocarbon biofuels.

The most important properties that inhibit widespread use of bio-oil are:

❑ *Phase separation* from use of wet feedstock and/or secondary cracking of vapours leading to high water content in the liquid product. Phase separation cannot be reversed except through relatively high additions of co-solvents such as ethanol.

So, now we understand the different types of the fuel properties that needs to be actually characterized for a biodiesel or biooil. Now we will talk about the biooil which is the major product from the pyrolysis of biomass and as we have discussed many times that biooil suffers so many different types of drawbacks like high water content, high oxygen content, higher viscosity, there are many other things also we will discuss now.

So, there is a need to upgrade the biooil. So, now we will discuss the different biooil upgradation techniques and how they can be performed. So, why there is a need to upgrade the biooil? Now biooil can be upgraded in a number of ways, so we can do it either physically or chemically or catalytically. So, there are number of objectives for upgrading of which the main ones are: first one is the most important of course the improvement of the biooil quality to overcome or reduce one or more of the fuel quality deficiencies.

And the second is, towards the production of chemicals and if you remove oxygen then you can produce hydrocarbon biofuels. So, the most important properties that inhibit the widespread use of biooil are - first is the phase separation. So, phase separation from use of wet feedstock and or secondary cracking of vapours leading to high water content in the liquid product. Phase separation cannot be reversed except though relatively high additions of co-solvents such as ethanol.

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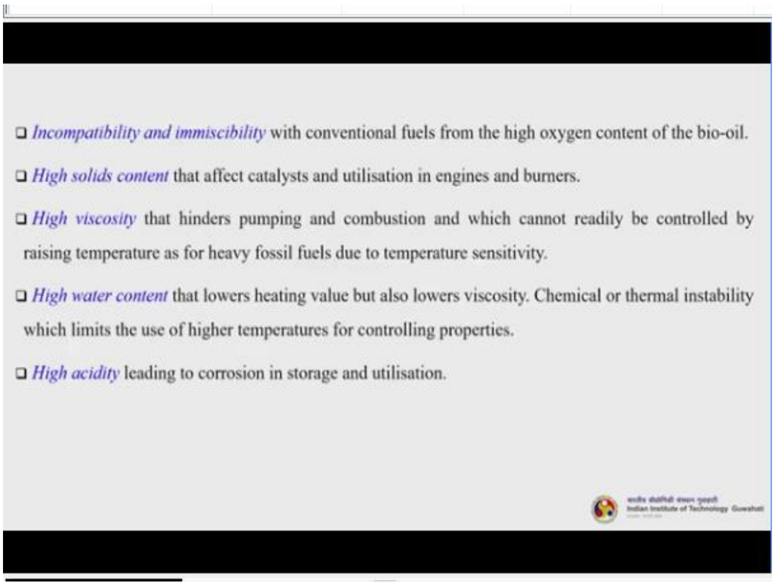

- *Incompatibility and immiscibility* with conventional fuels from the high oxygen content of the bio-oil.
- *High solids content* that affect catalysts and utilisation in engines and burners.
- *High viscosity* that hinders pumping and combustion and which cannot readily be controlled by raising temperature as for heavy fossil fuels due to temperature sensitivity.
- *High water content* that lowers heating value but also lowers viscosity. Chemical or thermal instability which limits the use of higher temperatures for controlling properties.
- *High acidity* leading to corrosion in storage and utilisation.

Then incompatibility and immiscibility with conventional fuels from the high oxygen content of the bio-oil. So, if you cannot do that then the problem is that you cannot blend it with the petrol fuels. And then high solids content that affect the catalyst and utilization in engines and burners. High viscosity that hinders pumping and combustion and which cannot readily be controlled by raising temperature as for heavy fossil fuels due to the temperature sensitivity.

Now high water content that lowers heating value but also lowers viscosity. Chemical or thermal instability which limits the use of the higher temperatures for controlling properties. And again another one is the high acidity which actually leads to corrosion in storage and utilization. So, as you understand from these so many drawbacks you have to understand what is the intention?

So, the intention of producing biodiesel and upgrade it to a certain quality so that its fuel properties matches to that of the petrol-diesel, if it matches then only you can blend it or you can directly use it in the engines which were used to burn actually the petro-diesel. So, to achieve that there are various upgradation technologies available, so we will discuss one by one.

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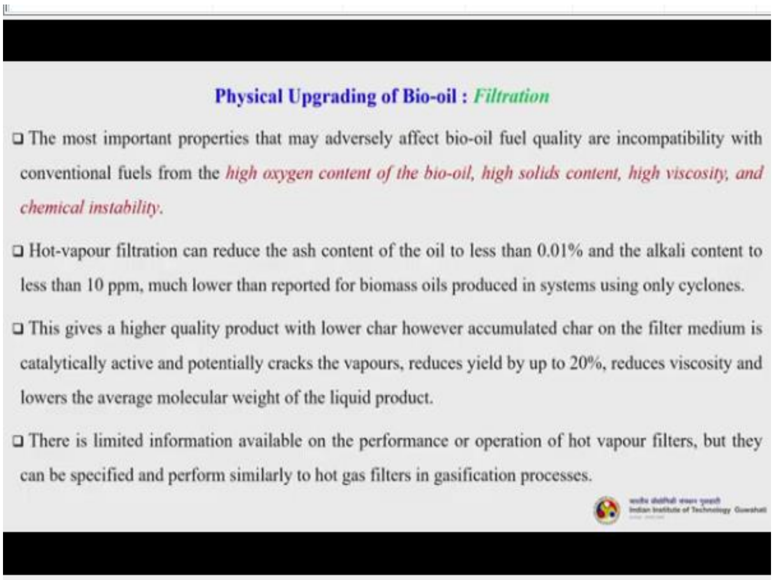

Physical Upgrading of Bio-oil : *Filtration*

- The most important properties that may adversely affect bio-oil fuel quality are incompatibility with conventional fuels from the *high oxygen content of the bio-oil, high solids content, high viscosity, and chemical instability.*
- Hot-vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm, much lower than reported for biomass oils produced in systems using only cyclones.
- This gives a higher quality product with lower char however accumulated char on the filter medium is catalytically active and potentially cracks the vapours, reduces yield by up to 20%, reduces viscosity and lowers the average molecular weight of the liquid product.
- There is limited information available on the performance or operation of hot vapour filters, but they can be specified and perform similarly to hot gas filters in gasification processes.

So, the first one physical upgradation of the biooil using the simple filtration mechanism. Now the most important properties that may adversely affect biooil fuel quality are incompatibility with the conventional fuels, from the high oxygen content of the biooil, high solids content, high viscosity and chemical instability. Now hot vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm much lower than reported for biomass oils produced in systems using only cyclones.

Now this gives a higher quality product with lower char however accumulated char on the filter medium is catalytically active and potentially cracks the vapours, reduces yield by up to 20%, reduces viscosity and lowers the average molecular weight of the liquid product. Now there is limited information available on the performance or operation of hot vapour filters but they can be specified and perform similarly to hot gas filters in gasification processes.

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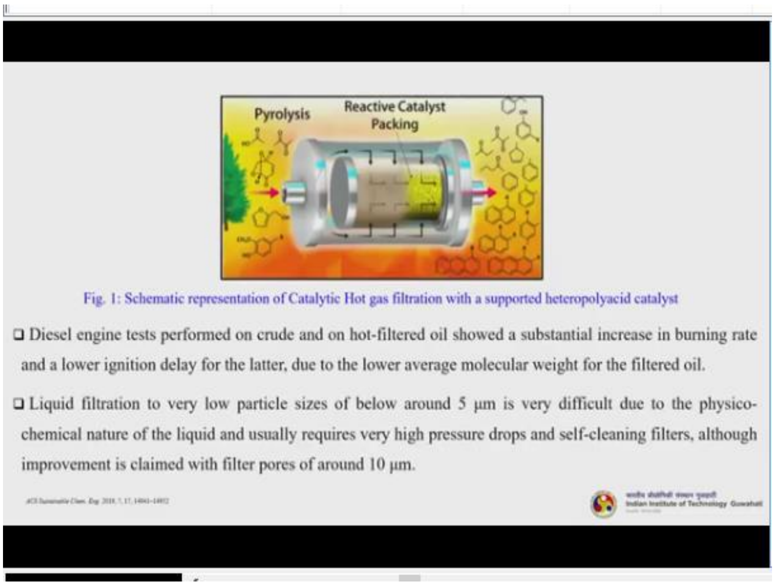

Fig. 1: Schematic representation of Catalytic Hot gas filtration with a supported heteropolyacid catalyst

- ❑ Diesel engine tests performed on crude and on hot-filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter, due to the lower average molecular weight for the filtered oil.
- ❑ Liquid filtration to very low particle sizes of below around 5 µm is very difficult due to the physico-chemical nature of the liquid and usually requires very high pressure drops and self-cleaning filters, although improvement is claimed with filter pores of around 10 µm.

ACS Sustainable Chem. Eng. 2018, 7, 17, 14941-14952

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So, this is a classical study. In the below you can see that the reference is given. So, it is ACS sustainable chemistry and engineering and it is a nice work, what they have done here? They have performed the catalytic hot gas filtration with a supported heteropolyacid acid catalyst. So, the diesel engine test performed on crude and hot filtered oil showed a substantial increase in burning rate and a lower ignition delay for the latter due to the lower average molecular weight of the filter oil.

Liquid filtration to very low particle sizes of below around let us say 5 microns is very difficult due to the physicochemical nature of the liquid and usually requires very high pressure drops and self cleaning filters. Although improvement is claimed with filter pores of around 10 micron.

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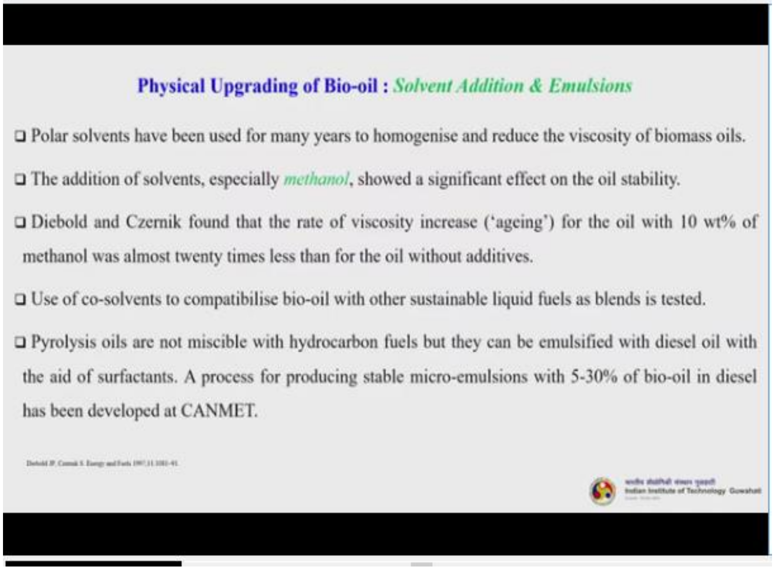

Physical Upgrading of Bio-oil : *Solvent Addition & Emulsions*

- ❑ Polar solvents have been used for many years to homogenise and reduce the viscosity of biomass oils.
- ❑ The addition of solvents, especially *methanol*, showed a significant effect on the oil stability.
- ❑ Diebold and Czernik found that the rate of viscosity increase ('ageing') for the oil with 10 wt% of methanol was almost twenty times less than for the oil without additives.
- ❑ Use of co-solvents to compatibilise bio-oil with other sustainable liquid fuels as blends is tested.
- ❑ Pyrolysis oils are not miscible with hydrocarbon fuels but they can be emulsified with diesel oil with the aid of surfactants. A process for producing stable micro-emulsions with 5-30% of bio-oil in diesel has been developed at CANMET.

Diebold JP, Czernik S. Energy and Fuels 1997,11,1081-91.

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So, the next physical upgradation is solvent addition and emulsions. Polar solvents have been used for many years to homogenize and reduce the viscosity of biomass oils. The addition of solvent especially methanol showed a significant effect on the oil stability. Diebold and Czernik found that the rate of viscosity increase or we can say that due to the ageing actually for the oil with 10 weight percent of methanol was almost 20 times less than that of the oil without additive.

Now use of co-solvents to compatibilize biooil with other sustainable liquid fuels as blends is tested. Pyrolysis oils or biooils are not miscible with hydrocarbon fuels but they can be emulsified with diesel oil with the aid of surfactants. A process for producing stable micro emulsion with 5 to 30% of the biooil in diesel has been developed at CANMET. So, the reference is given below.

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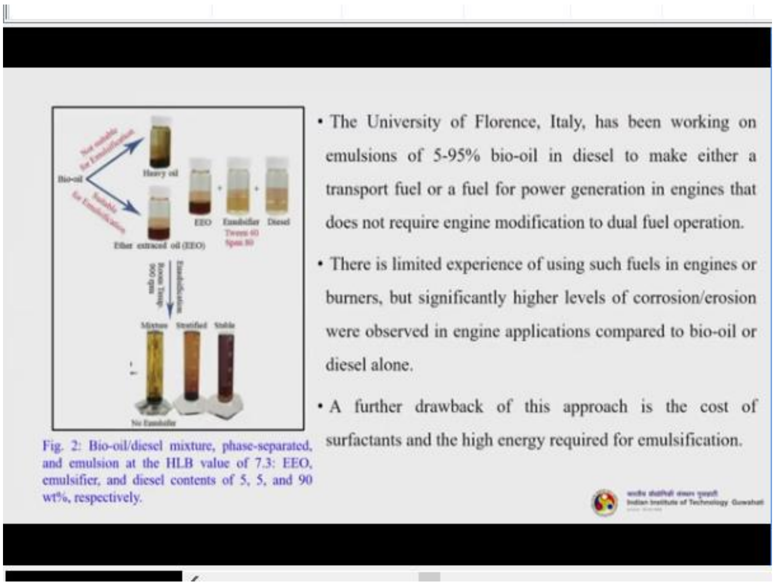

Fig. 2: Bio-oil/diesel mixture, phase-separated, and emulsion at the HLB value of 7.3: EEO, emulsifier, and diesel contents of 5, 5, and 90 wt%, respectively.

- The University of Florence, Italy, has been working on emulsions of 5-95% bio-oil in diesel to make either a transport fuel or a fuel for power generation in engines that does not require engine modification to dual fuel operation.
- There is limited experience of using such fuels in engines or burners, but significantly higher levels of corrosion/erosion were observed in engine applications compared to bio-oil or diesel alone.
- A further drawback of this approach is the cost of surfactants and the high energy required for emulsification.

So, this is what they have done actually. This was done at the University of Florence, Italy. So, they have been working on emulsions of 5 to 95% biooil in diesel to make either a transport fuel or a fuel for power generation in engines that does not require engine modification to dual fuel operation. Now there is limited experience of using such fuels in engines or burners but significantly higher levels of corrosion erosion were observed in engine applications compared to biooil or diesel alone.

A further drawback of this approach is the cost of surfactants and the high energy required for the emulsification. So, what they have done? It is a simple experiment. So, the biooil if it is not suitable for emulsification basically the heavier fraction whatever the lighter fractions are, can be emulsified, will be mixed with different emulsifying agents like these surfactants - tween 60, span 80 and all these things and diesel in different proportions.

So, once that is done so you can get something like this is the mixture, this is the stratified one, this is the stable one. So at different proportions or you can say the different blends using different surfactants so different mixtures were prepared, their stability is tested and their engine performance is also carried out. So, a further drawback of this approach is the cost of the surfactants and the high energy required for the emulsification.

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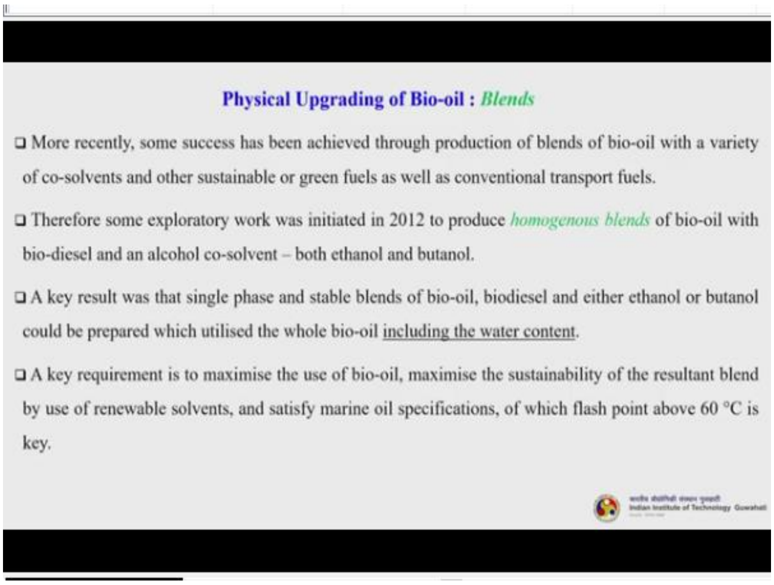

Physical Upgrading of Bio-oil : ***Blends***

- More recently, some success has been achieved through production of blends of bio-oil with a variety of co-solvents and other sustainable or green fuels as well as conventional transport fuels.
- Therefore some exploratory work was initiated in 2012 to produce *homogenous blends* of bio-oil with bio-diesel and an alcohol co-solvent – both ethanol and butanol.
- A key result was that single phase and stable blends of bio-oil, biodiesel and either ethanol or butanol could be prepared which utilised the whole bio-oil including the water content.
- A key requirement is to maximise the use of bio-oil, maximise the sustainability of the resultant blend by use of renewable solvents, and satisfy marine oil specifications, of which flash point above 60 °C is key.

So, the next one is physical upgradation using the blends. So, more recently some success has been achieved through production of blends of biooil with a variety of co-solvents and other sustainable or green fuels as well as conventional transport fuels. Therefore some exploratory work was initiated in 2012 to produce homogeneous blends of biooil with biodiesel and an alcohol co-solvent.

So, both ethanol and butanol were tried. A key result was that single phase and stable blends of biooil, biodiesel and either ethanol or butanol could be prepared which utilize the whole biooil including the water content. So, this is one of the best things regarding this blending actually. So, use the entire biooil that is coming out of the pyrolysis reactor including that of the water part or aqueous part.

So, a key requirement is to maximize the use of biooil, maximize the sustainability of the resultant blend by use of renewable solvents and satisfy marine oil specifications of which flash point above 60 degree centigrade is the key.

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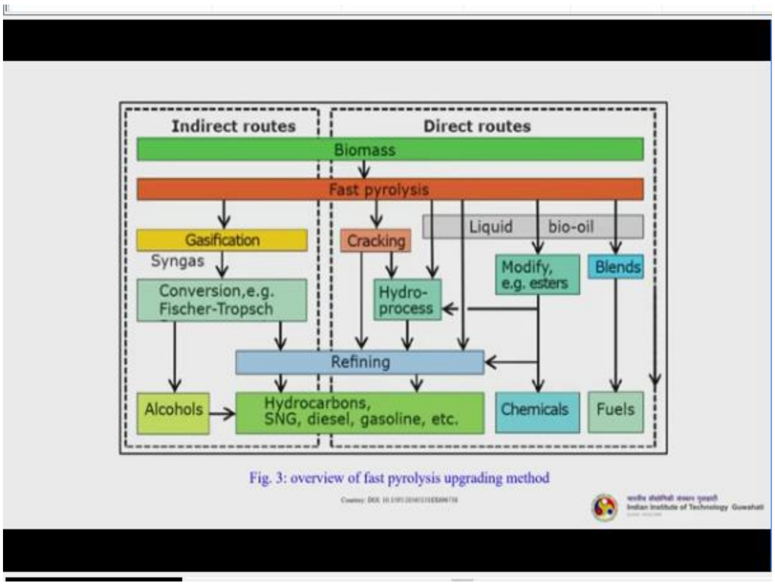

Indirect routes
Direct routes
Biomass
Fast pyrolysis
Gasification
Syngas
Conversion,e.g. Fischer-Tropsch
Cracking
Liquid bio-oil
Hydro-process
Modify, e.g. esters
Blends
Refining
Alcohols
Hydrocarbons, SNG, diesel, gasoline, etc.
Chemicals
Fuels

Fig. 3: overview of fast pyrolysis upgrading method

So, this is the overview of the fast pyrolysis upgrading technologies. So, another important upgradation method. So, this is the direct route of the fast pyrolysis and this is indirect route. So, under the direct route biomass undergoes the fast pyrolysis so the cracking is happening, so part of that directly goes to refining and part of that again further processed using the hydro processing. And you then refined and you get these hydrocarbons, SNG, diesel, gasoline etcetera or various different fractions.

The liquid biooil part can be modified as for example to esters and can be used as chemicals and also part of that can be refined to get the biofuels. And you can prepare directly the blends and use as fuels. Under the indirect routes you can use the gasification that means the syngas and then convert it using the Fischer Tropsch synthesis to different types of alcohols and then you can get another fuel platform here or from here the FT synthesis directly goes to the refining platform and you get the different types of biofuels.

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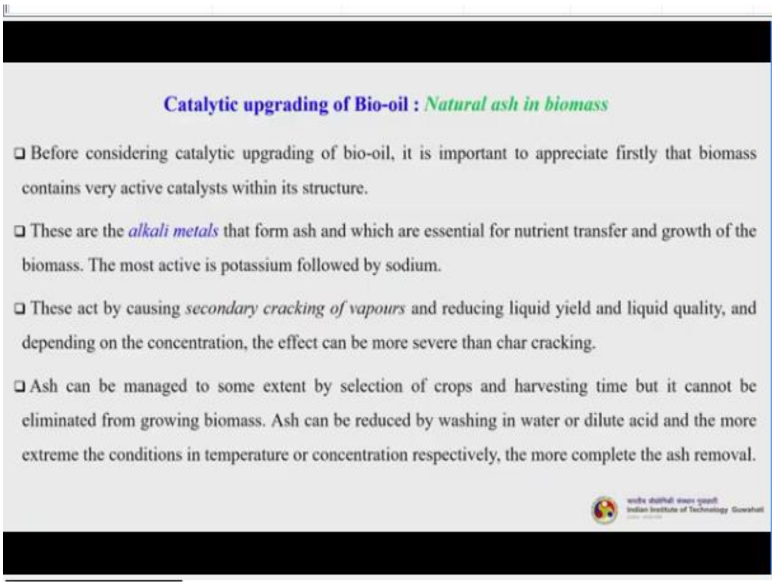

Catalytic upgrading of Bio-oil : *Natural ash in biomass*

- ❑ Before considering catalytic upgrading of bio-oil, it is important to appreciate firstly that biomass contains very active catalysts within its structure.
- ❑ These are the *alkali metals* that form ash and which are essential for nutrient transfer and growth of the biomass. The most active is potassium followed by sodium.
- ❑ These act by causing *secondary cracking of vapours* and reducing liquid yield and liquid quality, and depending on the concentration, the effect can be more severe than char cracking.
- ❑ Ash can be managed to some extent by selection of crops and harvesting time but it cannot be eliminated from growing biomass. Ash can be reduced by washing in water or dilute acid and the more extreme the conditions in temperature or concentration respectively, the more complete the ash removal.

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Then catalytic upgradation of the biooil so natural ash in biomass. Before considering catalytic upgradation of biooil it is important to appreciate firstly that biomass contains very active catalyst within its structures. So, these are called the alkali metals that form ash and which are essential for nutrient transfer and growth of the biomass. The most active is of course potassium followed by sodium.

Now these act by causing secondary cracking of vapours and reducing liquid yield and liquid quality and depending on the concentration the effect can be more severe than even the char cracking. Ash can be managed to some extent by selection of the crops and harvesting time but it cannot be eliminated from growing biomass. Ash can be reduced by washing in water or dilute acid and the more extreme the conditions in temperature or concentration respectively the more complete removal of the ash will happen.

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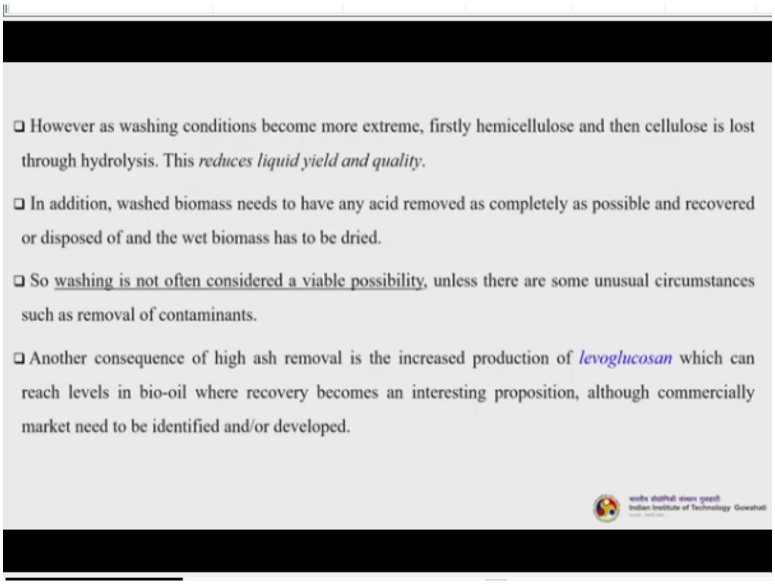

- However as washing conditions become more extreme, firstly hemicellulose and then cellulose is lost through hydrolysis. This *reduces liquid yield and quality*.
- In addition, washed biomass needs to have any acid removed as completely as possible and recovered or disposed of and the wet biomass has to be dried.
- So washing is not often considered a viable possibility, unless there are some unusual circumstances such as removal of contaminants.
- Another consequence of high ash removal is the increased production of *levoglucosan* which can reach levels in bio-oil where recovery becomes an interesting proposition, although commercially market need to be identified and/or developed.

However as washing conditions becomes more extreme, firstly hemicellulose and then cellulose is lost through hydrolysis. Now this reduces the liquid yield as well as the quality. In addition, washed biomass needs to have an acid removed as completely as possible and recovered or disposed of and the wet biomass has to be dried again. So washing is therefore not considered as a viable possibility, unless there are some unusual circumstances such as removal of the contaminants.

Another consequence of high ash removal is the increased production of levoglucosan which can reach levels in biooil where recovery becomes an interesting proposition. Although commercially market needs to be identified and/or developed. You know levoglucosan is one of the most important chemical that forms during pyrolysis directly as a decomposition product from the carbohydrates starch and other things cellulose and hemicellulose whatever it is.

Now levoglucosan is also an important chemical it has various widespread application - one of the most important application is its use as a tracer. So, there are many other applications also.

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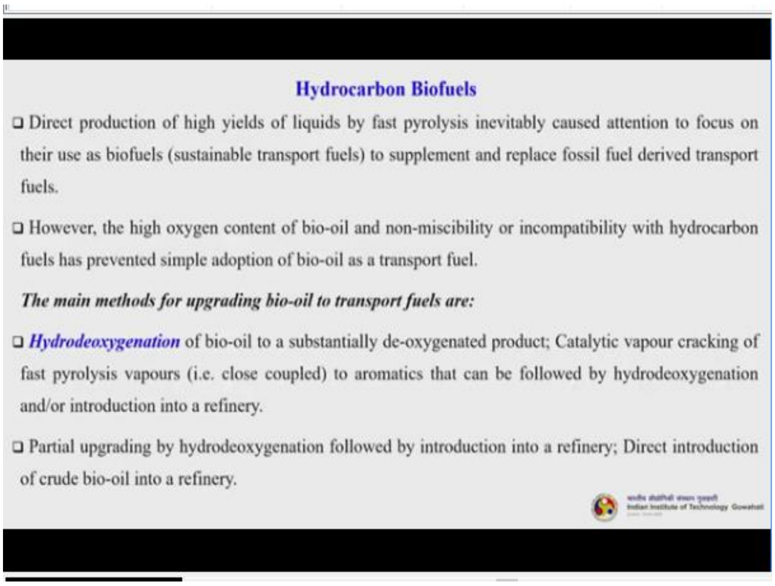

Hydrocarbon Biofuels

- Direct production of high yields of liquids by fast pyrolysis inevitably caused attention to focus on their use as biofuels (sustainable transport fuels) to supplement and replace fossil fuel derived transport fuels.
- However, the high oxygen content of bio-oil and non-miscibility or incompatibility with hydrocarbon fuels has prevented simple adoption of bio-oil as a transport fuel.

The main methods for upgrading bio-oil to transport fuels are:

- ***Hydrodeoxygenation*** of bio-oil to a substantially de-oxygenated product; Catalytic vapour cracking of fast pyrolysis vapours (i.e. close coupled) to aromatics that can be followed by hydrodeoxygenation and/or introduction into a refinery.
- Partial upgrading by hydrodeoxygenation followed by introduction into a refinery; Direct introduction of crude bio-oil into a refinery.

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The next is hydrocarbon biofuels. Now direct production of high yields of liquids by fast pyrolysis inevitably caused attention to focus on their use as biofuels (basically looking towards the sustainable transport fuels) to supplement and replace fossil fuel derived transport fuels. However, the high oxygen content of biooil and the non miscibility or incompatibility with hydrocarbon fuels have prevented simple adoption of biooil as a transport fuel at least as a blend.

Now the main methods for upgrading biooil to transport fuels are the first one is hydrodeoxygenation. So, hydrodeoxygenation of biooil to a substantially deoxygenated product, then catalytic vapour cracking of fast pyrolysis vapours in a closed coupled atmosphere to aromatics that can be followed by hydrodeoxygenation and/or introduction into a refinery for further processing basically. So, partial upgrading by hydrodeoxygenation followed by introduction into a refinery direct introduction of crude biooil into a refinery.

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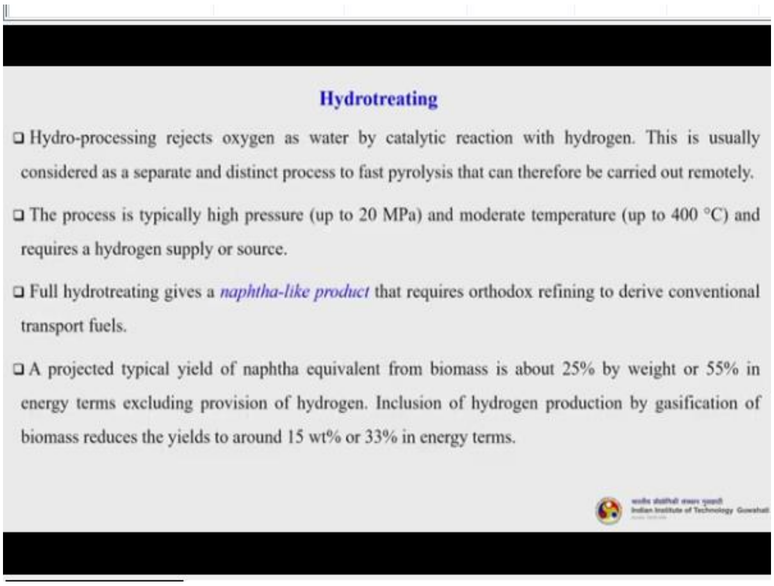

Hydrotreating

- Hydro-processing rejects oxygen as water by catalytic reaction with hydrogen. This is usually considered as a separate and distinct process to fast pyrolysis that can therefore be carried out remotely.
- The process is typically high pressure (up to 20 MPa) and moderate temperature (up to 400 °C) and requires a hydrogen supply or source.
- Full hydrotreating gives a *naphtha-like product* that requires orthodox refining to derive conventional transport fuels.
- A projected typical yield of naphtha equivalent from biomass is about 25% by weight or 55% in energy terms excluding provision of hydrogen. Inclusion of hydrogen production by gasification of biomass reduces the yields to around 15 wt% or 33% in energy terms.

So, hydrotreating is another option actually for upgradation. So, hydro-processing rejects oxygen as water by catalytic reaction with hydrogen. This is usually considered as a separate and distinct process to fast pyrolysis that can therefore be carried out remotely. The process is typically high pressure up to 20 mega pascal and moderate temperature up to 400 degree centigrade and requires a hydrogen supply or source.

Full hydrotreating gives a naphtha-like product that requires orthodox refining to derive conventional transport fuels. So, you basically distilled it to different cuts. So, a projected typical yield of naphtha equivalent from biomass is about 25% weight or 55% in energy terms excluding the provision of the hydrogen. Inclusion of hydrogen production by gasification of biomass reduces the yields to around 15 weight percent or 33% in terms of energy.

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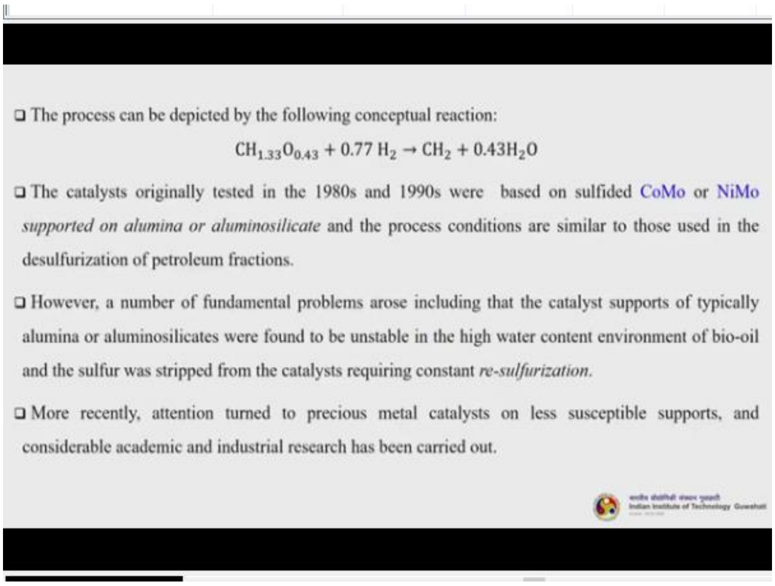

- The process can be depicted by the following conceptual reaction:

$$CH_{1.33}O_{0.43} + 0.77\ H_2 \rightarrow CH_2 + 0.43H_2O$$

- The catalysts originally tested in the 1980s and 1990s were based on sulfided CoMo or NiMo *supported on alumina or aluminosilicate* and the process conditions are similar to those used in the desulfurization of petroleum fractions.
- However, a number of fundamental problems arose including that the catalyst supports of typically alumina or aluminosilicates were found to be unstable in the high water content environment of bio-oil and the sulfur was stripped from the catalysts requiring constant *re-sulfurization*.
- More recently, attention turned to precious metal catalysts on less susceptible supports, and considerable academic and industrial research has been carried out.

The process can be depicted by the following conceptual reaction. So, CHO + 0.77 hydrogen gives CH 2 + 0.43 water.

$$CH_{1.33}O_{0.43} + 0.77H_2 \rightarrow CH_2 + 0.43H_2O$$

The catalyst originally tested in 1980s and 1990s were based on sulfided CoMo or NiMo. So, cobalt molybdenum or nickel molybdenum supported on alumina and aluminosilicate and the process conditions are much similar to those used in the desulphurization process.

Now you know this CoMo, NiMo catalysts are the desulphurization catalyst which are used in the petroleum industries. However, a number of fundamental problems arose including that the catalyst supports of typically alumina or aluminosilicates were found to be unstable in the high water content environment of biooil and the sulfur was stripped up from the catalyst requiring constant re-sulfurization.

So, this is a big problem. More recently attention turned to precious metal catalyst on less susceptible supports and considerable academic and industrial research has been carried out. One of the most important aspect of this type of catalyst is that how the catalyst is supported on the base material? In this case alumina aluminosilicates, they should not come out when the processing is happening.

When the water content is higher so there is a huge chance that though the catalyst will be dug up. So, that is why there is a need to look out for the proper doping methods as well as there should be a proper susceptible supports which will take care of this problem.

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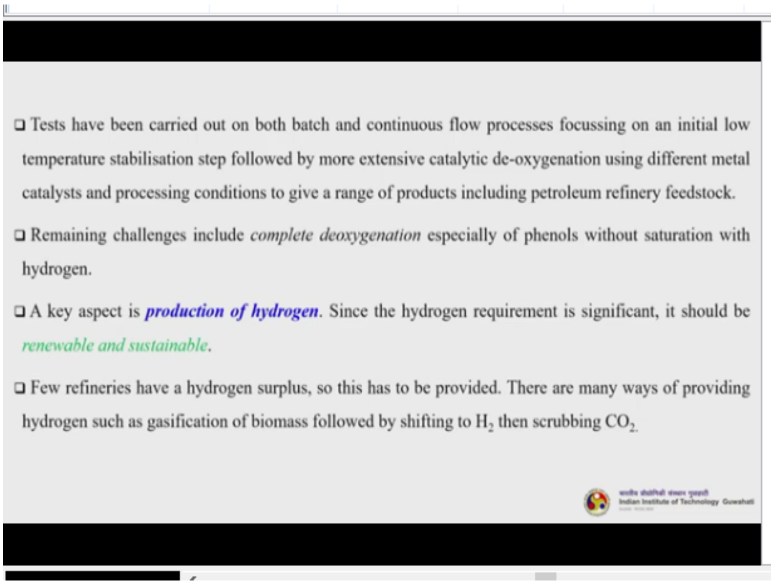

- ❑ Tests have been carried out on both batch and continuous flow processes focussing on an initial low temperature stabilisation step followed by more extensive catalytic de-oxygenation using different metal catalysts and processing conditions to give a range of products including petroleum refinery feedstock.
- ❑ Remaining challenges include *complete deoxygenation* especially of phenols without saturation with hydrogen.
- ❑ A key aspect is ***production of hydrogen***. Since the hydrogen requirement is significant, it should be *renewable and sustainable*.
- ❑ Few refineries have a hydrogen surplus, so this has to be provided. There are many ways of providing hydrogen such as gasification of biomass followed by shifting to H_2 then scrubbing CO_2.

Tests have been carried out on both batch and continuous flow processes focusing on an initial low temperature stabilization step followed by more extensive catalytic deoxygenation using different metal catalyst and processing conditions to give a range of products including that of the petroleum refinery feedstock. Now remaining challenges include complete deoxygenation especially of phenols without saturation with the hydrogen.

A key aspect is of course the production of hydrogen very important. Since the hydrogen requirement is significant it should be renewable and sustainable. Having said that the meaning of renewable and sustainable it is a complex you can say some sort of biorefinery concept, where the requirement of hydrogen whatever it is should be made from in-house hydrogen production, you cannot buy hydrogen from outside its very costly and transportation also makes it not feasible.

So, few refineries have a hydrogen surplus, so this has to be provided. There are many ways of providing hydrogen such as gasification of biomass followed by shifting to hydrogen, then scrubbing the carbon dioxide.

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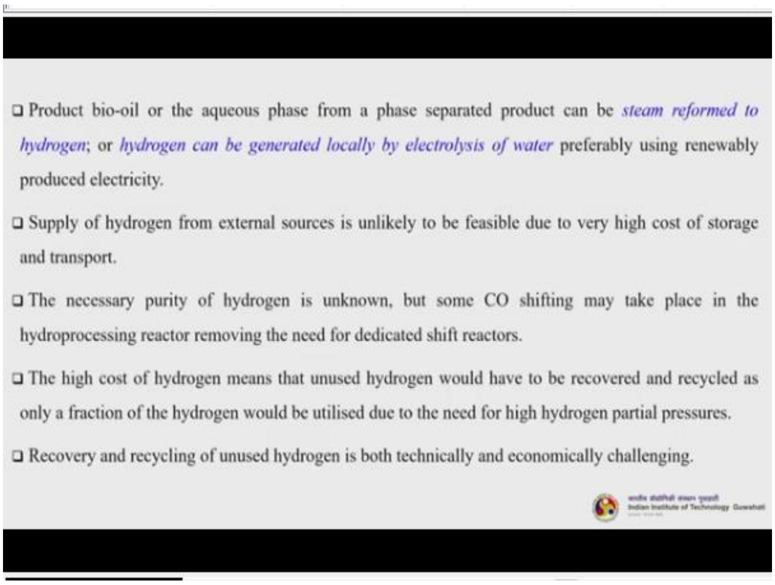

- ❑ Product bio-oil or the aqueous phase from a phase separated product can be *steam reformed to hydrogen*; or *hydrogen can be generated locally by electrolysis of water* preferably using renewably produced electricity.
- ❑ Supply of hydrogen from external sources is unlikely to be feasible due to very high cost of storage and transport.
- ❑ The necessary purity of hydrogen is unknown, but some CO shifting may take place in the hydroprocessing reactor removing the need for dedicated shift reactors.
- ❑ The high cost of hydrogen means that unused hydrogen would have to be recovered and recycled as only a fraction of the hydrogen would be utilised due to the need for high hydrogen partial pressures.
- ❑ Recovery and recycling of unused hydrogen is both technically and economically challenging.

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Product biooil or the aqueous phase from the phase separated product can be steam reformed to hydrogen or hydrogen can also be generated locally by the electrolysis of water preferably using the renewably produced electricity. Again we are talking about the renewable electricity because the electricity has to be generated in house so as to meet the energy requirement as well as the make the entire process sustainable.

Supply of the hydrogen from external sources is unlikely to be feasible due to the very high cost of storage and transport. The necessary purity of hydrogen is unknown but some carbon monoxide shifting may take place in the hydroprocessing reactor removing the need for dedicated shift reactors. The high cost of hydrogen means that unused hydrogen would have to be recovered and recycled as only a fraction of the hydrogen would be utilized due to the need for high hydrogen partial pressures.

Recovery and recycling of unused hydrogen is both technically and economically very, very challenging and lot of work has been going on this particular aspect.

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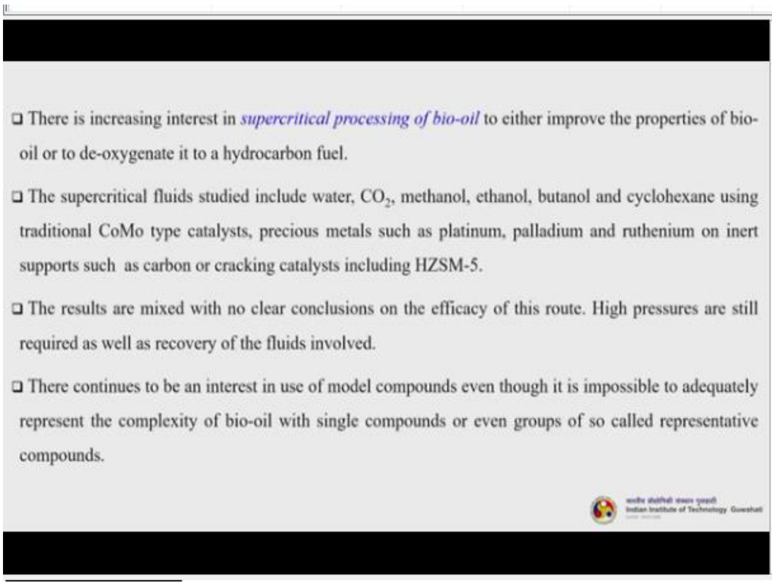

- ❑ There is increasing interest in *supercritical processing of bio-oil* to either improve the properties of bio-oil or to de-oxygenate it to a hydrocarbon fuel.
- ❑ The supercritical fluids studied include water, CO_2, methanol, ethanol, butanol and cyclohexane using traditional CoMo type catalysts, precious metals such as platinum, palladium and ruthenium on inert supports such as carbon or cracking catalysts including HZSM-5.
- ❑ The results are mixed with no clear conclusions on the efficacy of this route. High pressures are still required as well as recovery of the fluids involved.
- ❑ There continues to be an interest in use of model compounds even though it is impossible to adequately represent the complexity of bio-oil with single compounds or even groups of so called representative compounds.

There is increasing interest in supercritical processing of biooil, another important study has been done, to either improve the properties of the biooil or to deoxygenate into a hydrocarbon fuel. The supercritical fluid studied included water, carbon dioxide, methanol, ethanol, butanol and cyclohexane using traditional CoMo type catalyst**,** precious metals such as platinum, palladium and ruthenium on inert support such as carbon or cracking catalyst including the HZSM-5.

Now the results are mixed with no clear conclusions on the efficacy of this route. High pressures are still required as well as the recovery of the fluids involved. There continues to be an interest in use of model compounds even though it is impossible to adequately represent the complexity of biooil with single compounds or even groups of so called representative compounds.

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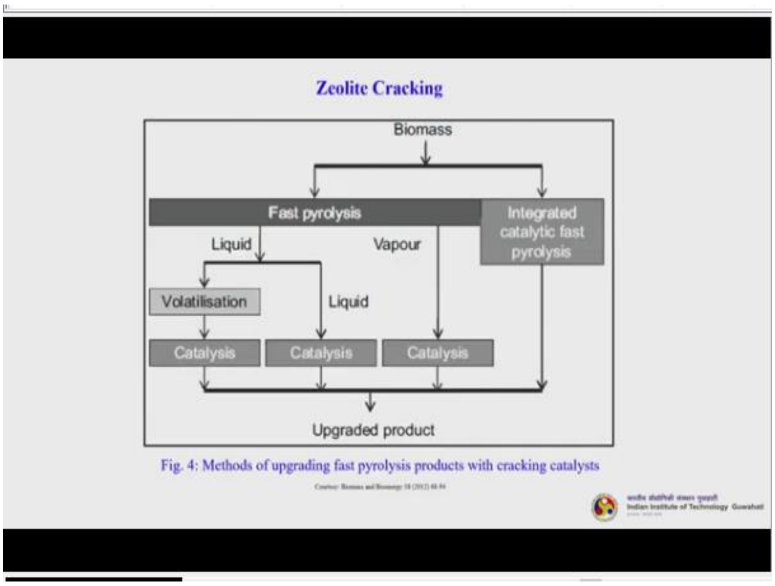

Zeolite Cracking

Fig. 4: Methods of upgrading fast pyrolysis products with cracking catalysts

The next important one is of course using the zeolite catalyst to crack the biooil. So, you have biomass. So use the fast pyrolysis process you get liquid then it comes to 2 different fractions - of course liquid directly goes to catalysis and you get the upgraded product. You go for the volatilization, again catalysis and you get upgraded product. Vapour can be directly catalyzed. The vapour catalytic cracking, you get upgraded product or you can have an integrated catalytic fast pyrolysis approach also which is now more recently been adopted in many of the industries.

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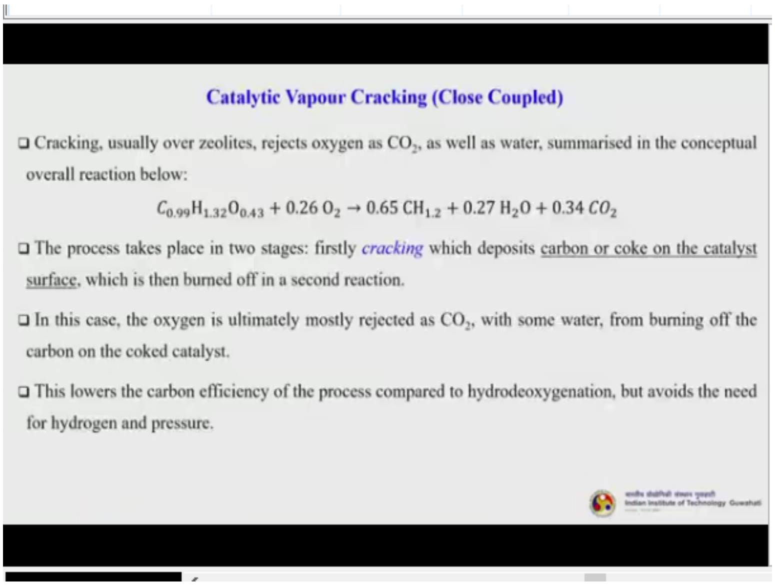

Catalytic Vapour Cracking (Close Coupled)

- Cracking, usually over zeolites, rejects oxygen as CO_2, as well as water, summarised in the conceptual overall reaction below:

$$C_{0.99}H_{1.32}O_{0.43} + 0.26\ O_2 \rightarrow 0.65\ CH_{1.2} + 0.27\ H_2O + 0.34\ CO_2$$

- The process takes place in two stages: firstly *cracking* which deposits carbon or coke on the catalyst surface, which is then burned off in a second reaction.
- In this case, the oxygen is ultimately mostly rejected as CO_2, with some water, from burning off the carbon on the coked catalyst.
- This lowers the carbon efficiency of the process compared to hydrodeoxygenation, but avoids the need for hydrogen and pressure.

So, we will discuss about the catalytic vapour cracking in a closed loop scenario. Cracking usually over zeolites, rejects oxygen as carbon dioxide as well as water, summarized in the conceptual overall reaction below. So, this CHO + 0.26 oxygen gives 0.65 CH + 0.27 water + 0.34 carbon dioxide.

$$C_{0.99}H_{1.32}O_{0.43} + 0.26O_2 \rightarrow 0.65CH_{1.2} + 0.27H_2O + 0.34CO_2$$

The process takes place in 2 stages. Firstly, cracking which deposits carbon or coke on the catalyst surface which is then burned up in the second reaction.

This deposition of coke on the surface of catalyst is a very bad phenomenon but however it has been noticed that the amount that get deposited on the surface of the catalyst is actually very low. So, in this case the oxygen is ultimately mostly rejected as carbon dioxide with some water from burning of the carbon on the coked catalyst. Now this lowers the carbon efficiency of the process compared to the hydro deoxygenation but avoids the need for hydrogen and pressure. So, there is a good thing about that. That you do not need hydrogen at higher pressure.

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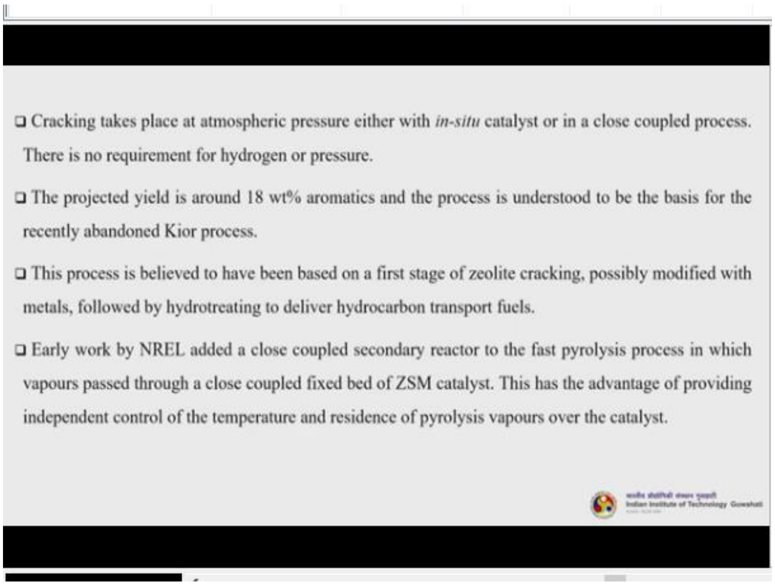

- ❑ Cracking takes place at atmospheric pressure either with *in-situ* catalyst or in a close coupled process. There is no requirement for hydrogen or pressure.
- ❑ The projected yield is around 18 wt% aromatics and the process is understood to be the basis for the recently abandoned Kior process.
- ❑ This process is believed to have been based on a first stage of zeolite cracking, possibly modified with metals, followed by hydrotreating to deliver hydrocarbon transport fuels.
- ❑ Early work by NREL added a close coupled secondary reactor to the fast pyrolysis process in which vapours passed through a close coupled fixed bed of ZSM catalyst. This has the advantage of providing independent control of the temperature and residence of pyrolysis vapours over the catalyst.

So, cracking takes place at atmospheric pressure either with in-situ catalyst or in a closed coupled process. There is no requirement of hydrogen or pressure. So, the projected yield is around 18 weight percent aromatics and the process is understood to be the basis for the recently abandoned Kior process. Now this process is believed to have been based on the first stage of zeolite cracking, possibly modified with metals followed by hydrotreating to deliver hydrocarbon transport fuels.

Early work by NREL added a closed to secondary reactor to the fast pyrolysis process in which vapours pass through a closed coupled fixed bed of ZSM catalyst, this has the advantage of providing independent control of the temperature and residences of pyrolysis vapours over the catalyst.

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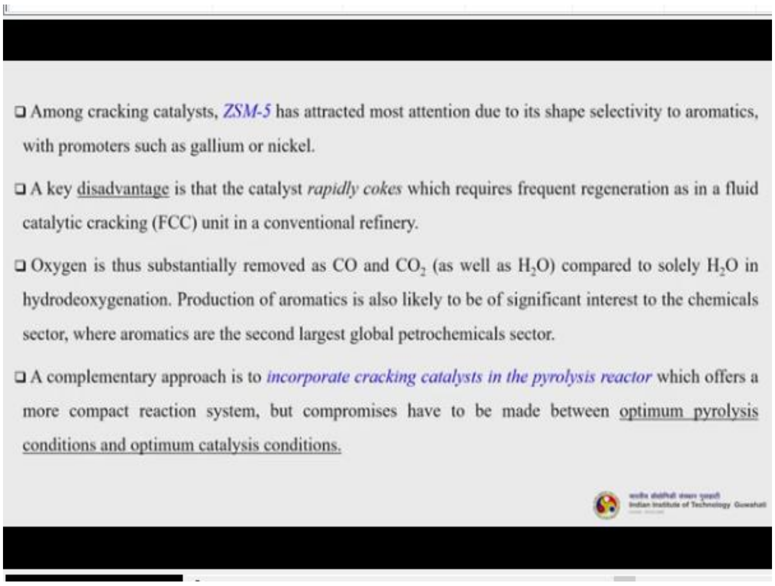

- Among cracking catalysts, *ZSM-5* has attracted most attention due to its shape selectivity to aromatics, with promoters such as gallium or nickel.
- A key disadvantage is that the catalyst *rapidly cokes* which requires frequent regeneration as in a fluid catalytic cracking (FCC) unit in a conventional refinery.
- Oxygen is thus substantially removed as CO and CO_2 (as well as H_2O) compared to solely H_2O in hydrodeoxygenation. Production of aromatics is also likely to be of significant interest to the chemicals sector, where aromatics are the second largest global petrochemicals sector.
- A complementary approach is to *incorporate cracking catalysts in the pyrolysis reactor* which offers a more compact reaction system, but compromises have to be made between optimum pyrolysis conditions and optimum catalysis conditions.

Among cracking catalyst ZSM-5 has attracted most attention due to its shape selectivity to aromatics with promoters such as gallium or nickel. A key disadvantage is that catalyst rapidly cokes which requires frequent regeneration as in a fluid catalytic cracking unit in a conventional refinery, the FCC unit. Oxygen is thus substantially removed as carbon monoxide and carbon dioxide even as well as water also a minor fraction compared to solely water in hydrodeoxygenation.

Production of aromatics is also likely to be of significant interest to the chemical sector where aromatics are the second largest global petrochemical sector. A complementary approach is to incorporate catalyst cracking in the pyrolysis reactor which offers a more compact reaction system, but there is a catch. So, you have to compromise between the 2 things. First is the optimum pyrolysis condition and there is also an optimum catalysis conduction.

So, anyway somewhere you have to make a compromise so by optimizing both the process parameters simultaneously and to see that you are getting a moderate yield.

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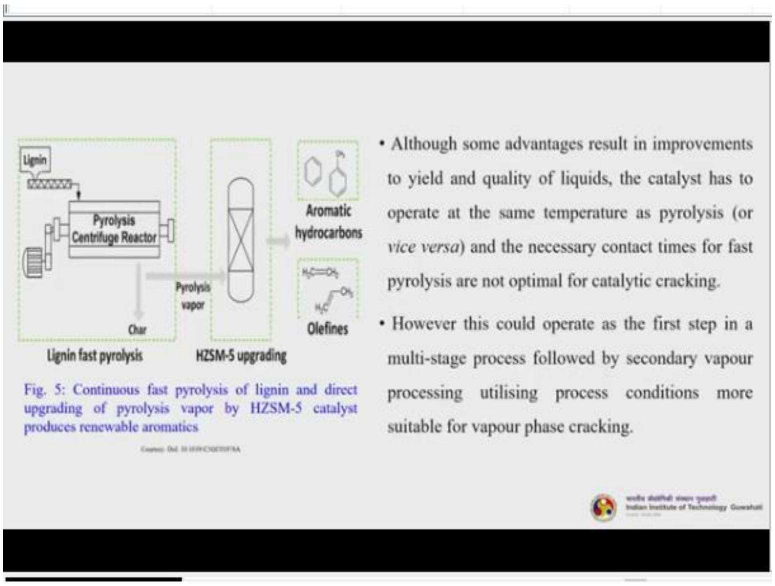

Fig. 5: Continuous fast pyrolysis of lignin and direct upgrading of pyrolysis vapor by HZSM-5 catalyst produces renewable aromatics

- Although some advantages result in improvements to yield and quality of liquids, the catalyst has to operate at the same temperature as pyrolysis (or *vice versa*) and the necessary contact times for fast pyrolysis are not optimal for catalytic cracking.
- However this could operate as the first step in a multi-stage process followed by secondary vapour processing utilising process conditions more suitable for vapour phase cracking.

So, this is one of the continuous fast pyrolysis process, that was developed for the lignin actually and a direct upgradation of pyrolysis vapour by the HZSM-5 catalyst which **is** by producing the renewable aromatics. So, you can see this is a screw feeder where the lignin is being fed to the pyrolysis centrifuge reactor, the pyrolysis has been happening in a separate one and the vapour whatever it is coming from the pyrolysis reactor, it is getting cracked in a separate reactor where the catalyst in the fixed bed system are being provided.

So, the bed is made up of the HZSM-5 catalyst, then you get the aromatic hydrocarbons olefins and all these things. So, although some advantages result in improvements to yield and quality of the liquids the catalyst has to operate at the same temperature as pyrolysis or vice versa and the necessary contact time for the fast pyrolysis are not optimal for catalytic cracking.

So, there is a catch, this is what I was just mentioning you that, kindly understand that the optimized process parameter for pyrolysis, lignin pyrolysis or biomass pyrolysis is quite different than the optimized process parameters for the vapour catalytic cracking. Now if both you want to have in the single reactor then you have to compromise on the optimized parameter for one, either you go for this or you go for that. Then you can further see that what type of yield and the quality of fuel, quality of the product you are achieving or getting.

Now however this could operate as the first step in a multi stage process followed by secondary vapour process utilizing process conditions more suitable for the vapour phase cracking. So, whatever has been done here - if you do that then the question of putting them together in a single reactor in which both your pyrolysis as well as vapour catalytic cracking will be carried out is not required. So, you can have 2 different stages.

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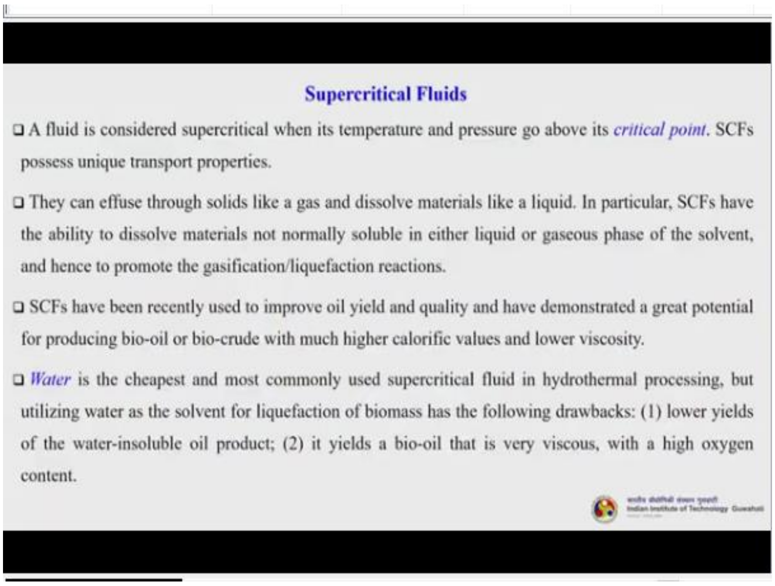

Supercritical Fluids

- A fluid is considered supercritical when its temperature and pressure go above its *critical point*. SCFs possess unique transport properties.
- They can effuse through solids like a gas and dissolve materials like a liquid. In particular, SCFs have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions.
- SCFs have been recently used to improve oil yield and quality and have demonstrated a great potential for producing bio-oil or bio-crude with much higher calorific values and lower viscosity.
- *Water* is the cheapest and most commonly used supercritical fluid in hydrothermal processing, but utilizing water as the solvent for liquefaction of biomass has the following drawbacks: (1) lower yields of the water-insoluble oil product; (2) it yields a bio-oil that is very viscous, with a high oxygen content.

Then we will talk about supercritical fluid, we have just touched that supercritical fluids; we will discuss in detail. So, a fluid is considered supercritical when its temperature and pressure go above its critical point. Supercritical fluids possess unique transport properties. So, they have properties of both gases as well as liquids. So, they can effuse through solids like a gas and diesel materials like a liquid.

That is what I was telling that the supercritical fluid possesses the properties of both gas and liquid. In particular, supercritical fluids have the ability to diesel materials not normally soluble in either liquid or gaseous phase of the solvent and hence to promote the gasification or liquefaction reactions. Supercritical fluids have been recently used to improve oil yield and quality and have demonstrated a great potential for producing biooil or biocrude with much higher calorific values and lower viscosity.

Water is the cheapest and most commonly used supercritical fluid in hydrothermal processing but utilizing water as the solvent for liquefaction of biomass has the following drawbacks. The first is that lower yields of the water insoluble oil product, second is that it yields a biooil that is very viscous with a high oxygen content.

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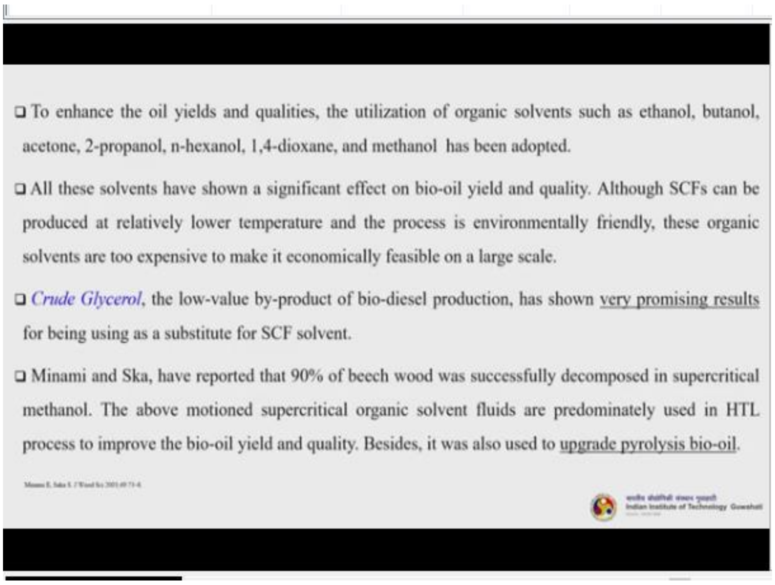

- To enhance the oil yields and qualities, the utilization of organic solvents such as ethanol, butanol, acetone, 2-propanol, n-hexanol, 1,4-dioxane, and methanol has been adopted.
- All these solvents have shown a significant effect on bio-oil yield and quality. Although SCFs can be produced at relatively lower temperature and the process is environmentally friendly, these organic solvents are too expensive to make it economically feasible on a large scale.
- *Crude Glycerol*, the low-value by-product of bio-diesel production, has shown very promising results for being using as a substitute for SCF solvent.
- Minami and Ska, have reported that 90% of beech wood was successfully decomposed in supercritical methanol. The above motioned supercritical organic solvent fluids are predominately used in HTL process to improve the bio-oil yield and quality. Besides, it was also used to upgrade pyrolysis bio-oil.

To enhance the oil yield and qualities the utilization of organic solvents such as ethanol, butanol, acetone, 2-propanol, n-hexanol, 1,4-dioxane, and methanol has been adopted. Now all these solvents have shown a significant effect on biooil yield and quality although super critical fluids can be produced at relatively lower temperature and the process is environmentally friendly these organic solvents are too expensive to make it economically feasible on a large scale.

In a significant work - the reference has been given below - crude glycerol, the low value product of the biodiesel production has also shown very promising results for being used as a substitute for the supercritical solvents, traditional organic solvents. Minami and Ska have reported that 90% of beech wood was successfully decomposed in supercritical methanol. The above mentioned supercritical organic solvent fluids are predominantly used in HTL process to improve the biooil yield and quality. Besides, it was also used to upgrade the pyrolysis biooil.

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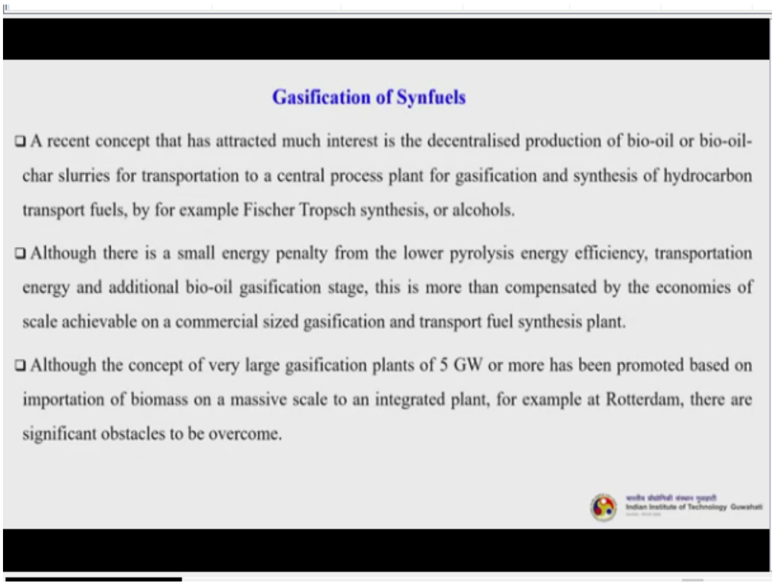

Gasification of Synfuels

- A recent concept that has attracted much interest is the decentralised production of bio-oil or bio-oil-char slurries for transportation to a central process plant for gasification and synthesis of hydrocarbon transport fuels, by for example Fischer Tropsch synthesis, or alcohols.
- Although there is a small energy penalty from the lower pyrolysis energy efficiency, transportation energy and additional bio-oil gasification stage, this is more than compensated by the economies of scale achievable on a commercial sized gasification and transport fuel synthesis plant.
- Although the concept of very large gasification plants of 5 GW or more has been promoted based on importation of biomass on a massive scale to an integrated plant, for example at Rotterdam, there are significant obstacles to be overcome.

Next is gasification of synfuels. A recent concept that has attracted much interest is the decentralized production of biooil or biooil char slurries for transportation to a central process plant for gasification and synthesis of hydrocarbon transport fluids, by for example the FT processing, FT synthesis or alcohols. Although there is a small energy penalty from the lower pyrolysis energy efficiency, transportation energy and additional biooil gasification stage, this is more than compensated by the economies of the scale achievable on a commercial sized gasification and transport fuel synthesis plant. Now although the concept of very large gasification plants of 5 gigawatt or more has been promoted based on the importation of biomass on a massive scale to an integrated plant, for example that was already established at Rotterdam, there are significant obstacles to be overcome.

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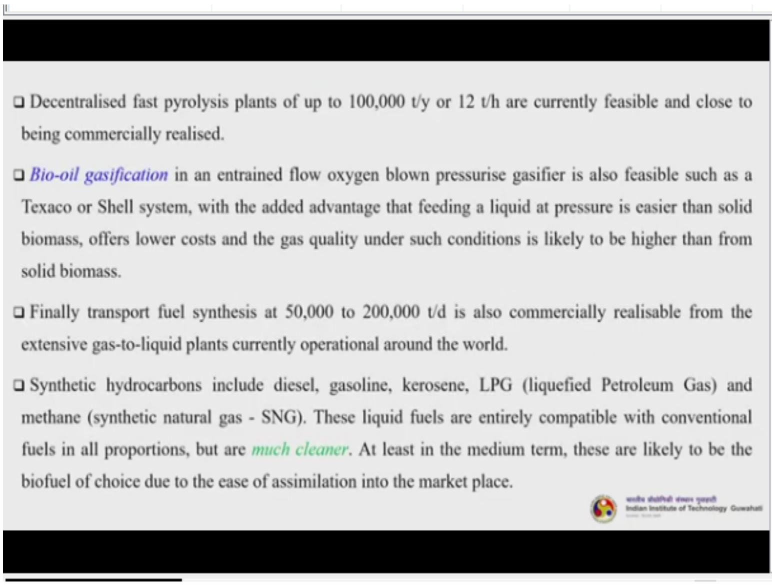

- Decentralised fast pyrolysis plants of up to 100,000 t/y or 12 t/h are currently feasible and close to being commercially realised.
- *Bio-oil gasification* in an entrained flow oxygen blown pressurise gasifier is also feasible such as a Texaco or Shell system, with the added advantage that feeding a liquid at pressure is easier than solid biomass, offers lower costs and the gas quality under such conditions is likely to be higher than from solid biomass.
- Finally transport fuel synthesis at 50,000 to 200,000 t/d is also commercially realisable from the extensive gas-to-liquid plants currently operational around the world.
- Synthetic hydrocarbons include diesel, gasoline, kerosene, LPG (liquefied Petroleum Gas) and methane (synthetic natural gas - SNG). These liquid fuels are entirely compatible with conventional fuels in all proportions, but are *much cleaner*. At least in the medium term, these are likely to be the biofuel of choice due to the ease of assimilation into the market place.

Decentralized fast pyrolysis plants up to 100,000 tons per year or 12 tons per hour are currently feasible and close to being commercially realized. Biooil gasification in an entrained flow oxygen blown pressurized gasifier is also feasible such as a Texaco or Shell system with the added advantage that feeding a liquid at pressure is easier than solid biomass, offers lower cost and the gas quality under such condition is likely to be higher than from the solid biomass.

Finally, transport fuel synthesis at 50,000 to 200,000 tons per day is also commercially realizable from the extensive gas to liquid plants currently operational around the world. Synthetic hydrocarbons include diesel, gasoline, kerosene, LPG and methane. These liquid fuels are entirely compatible with conventional fuels in all proportions but are much cleaner. At least in the medium term, these are likely to be the biofuel of choice due to the ease of assimilation into the market place.

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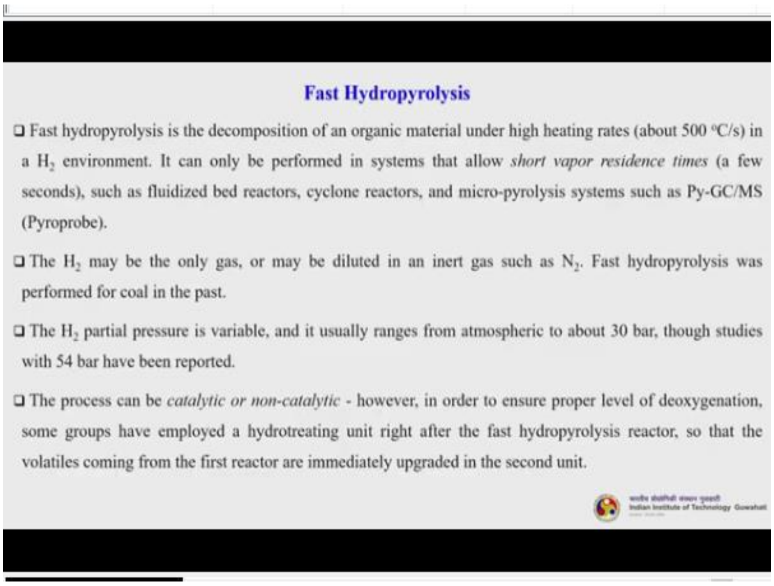

Fast Hydropyrolysis

- ❑ Fast hydropyrolysis is the decomposition of an organic material under high heating rates (about 500 °C/s) in a H_2 environment. It can only be performed in systems that allow *short vapor residence times* (a few seconds), such as fluidized bed reactors, cyclone reactors, and micro-pyrolysis systems such as Py-GC/MS (Pyroprobe).
- ❑ The H_2 may be the only gas, or may be diluted in an inert gas such as N_2. Fast hydropyrolysis was performed for coal in the past.
- ❑ The H_2 partial pressure is variable, and it usually ranges from atmospheric to about 30 bar, though studies with 54 bar have been reported.
- ❑ The process can be *catalytic or non-catalytic* - however, in order to ensure proper level of deoxygenation, some groups have employed a hydrotreating unit right after the fast hydropyrolysis reactor, so that the volatiles coming from the first reactor are immediately upgraded in the second unit.

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We will now discuss about fast hydropyrolysis. Fast hydropyrolysis is the decomposition of an organic material under high heating rates almost about 500 degree centigrade per second in a hydrogen environment. It can only be performed in systems that allow short vapour residence time, few seconds only, such as fluidized bed reactors, cyclone reactors, micro pyrolysis systems such as the Py-GC/MS (Pyroprobe).

The hydrogen may be the only gas or may be diluted in an inert gas such as nitrogen. Fast hydropyrolysis was performed for coal in the past. The hydrogen partial pressure is variable and it usually ranges from atmospheric to about 30 bar, though studies with 54 bar have been also reported. The process can be catalytic or non catalytic however in order to ensure proper level of deoxygenation, some groups have employed a hydrotreating unit right after the fast hydropyrolysis reactor, so that the volatiles coming from the first reactor are immediately upgraded in the second unit.

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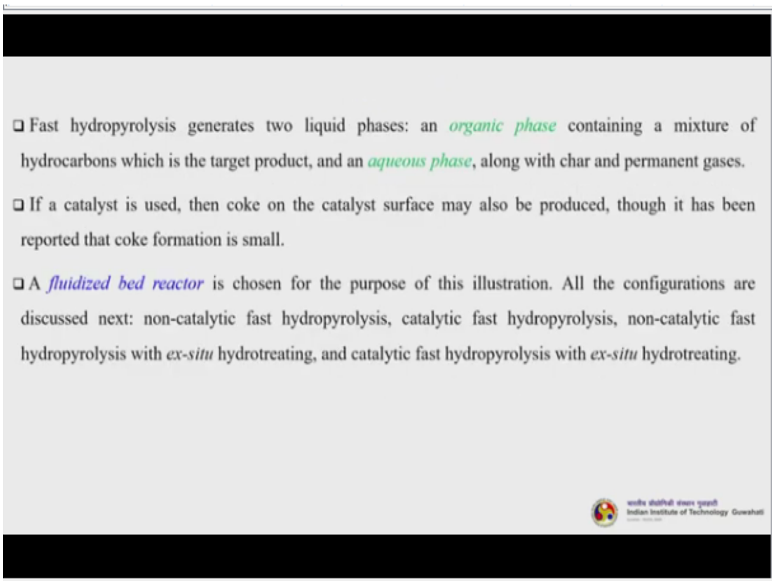

- ❑ Fast hydropyrolysis generates two liquid phases: an *organic phase* containing a mixture of hydrocarbons which is the target product, and an *aqueous phase*, along with char and permanent gases.
- ❑ If a catalyst is used, then coke on the catalyst surface may also be produced, though it has been reported that coke formation is small.
- ❑ A *fluidized bed reactor* is chosen for the purpose of this illustration. All the configurations are discussed next: non-catalytic fast hydropyrolysis, catalytic fast hydropyrolysis, non-catalytic fast hydropyrolysis with *ex-situ* hydrotreating, and catalytic fast hydropyrolysis with *ex-situ* hydrotreating.

Fast hydropyrolysis generates 2 liquid phases; one is that organic phase containing the mixture of hydrocarbons which is the target product or the biooil part and then the aqueous phase along with the char and permanent gases. If a catalyst is used, then coke on the catalyst surface may also be produced though it has been reported that the amount of coke formation is small.

A fluidized bed reactor is basically chosen for this illustration. All the configurations are discussed: non-catalytic fast hydropyrolysis, catalytic fast hydropyrolysis, non-catalytic fast hydropyrolysis with ex-situ hydrotreating and catalytic hydropyrolysis with ex-situ hydrotreating.

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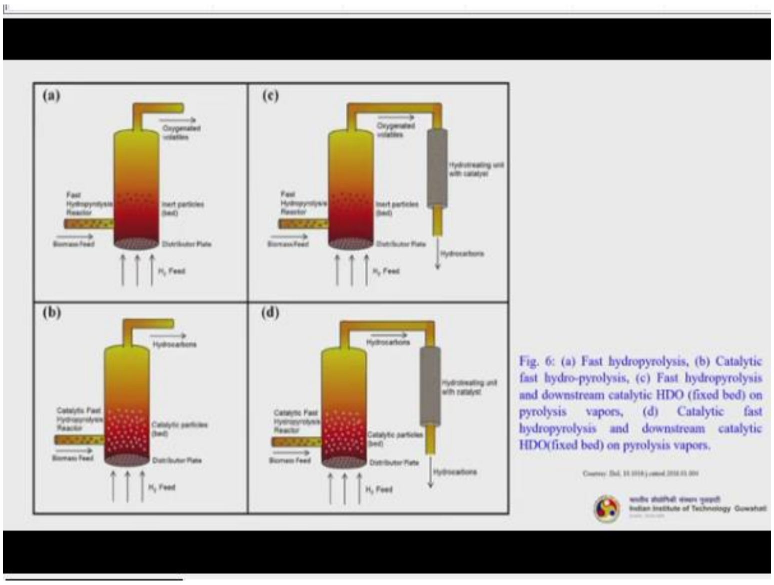

Fig. 6: (a) Fast hydropyrolysis, (b) Catalytic fast hydro-pyrolysis, (c) Fast hydropyrolysis and downstream catalytic HDO (fixed bed) on pyrolysis vapors, (d) Catalytic fast hydropyrolysis and downstream catalytic HDO(fixed bed) on pyrolysis vapors.

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I will show you the schematic representation of these 4 systems what we have just mentioned. The first one. So, this is fast hydropyrolysis, here whatever you are seeing that is a pyrolyzer or pyrolysis reactor; the biomass is being fed and you use some sort of inner particles bed basically to carry out the fluidization, they are not catalyst. So, hydrogen is being fed and you get the oxygenated volatiles.

Now in the second case - b, it is catalytic fast hydropyrolysis; so instead of having the inert particles here we have fluidized catalytic bed particles here. So, and hydrogen is being fed and you carry out this. Now in the third case there is a separate hydrotreating unit without catalyst. So, you do not have a catalyst here, again it is the inert particles to carry out the fluidization process. And you have a secondary unit which is hydrotreating unit, but that hydrotreating unit is having catalyst. Now in the last one you have a catalytic pyrolyzer as well as you have a catalytic hydrotreating unit. So, both the units contain catalyst. So, 4 distinct cases have been studied and the reference is also given below.

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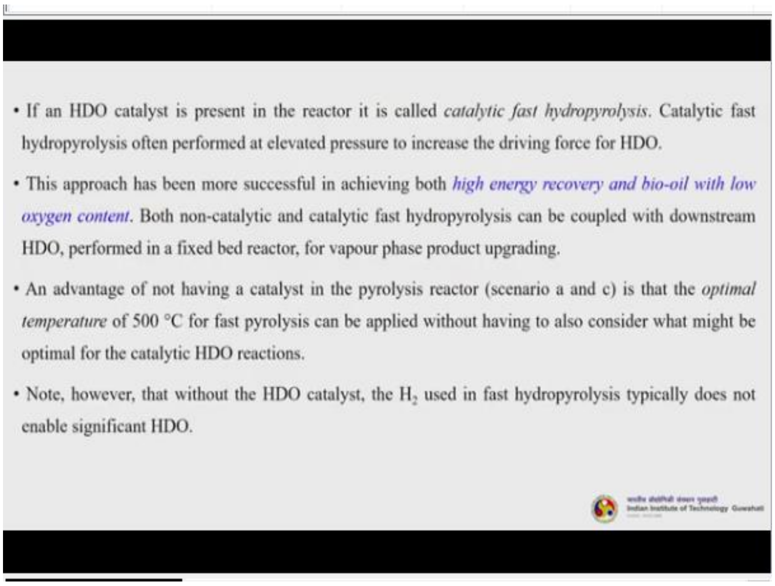

- If an HDO catalyst is present in the reactor it is called *catalytic fast hydropyrolysis*. Catalytic fast hydropyrolysis often performed at elevated pressure to increase the driving force for HDO.
- This approach has been more successful in achieving both *high energy recovery and bio-oil with low oxygen content*. Both non-catalytic and catalytic fast hydropyrolysis can be coupled with downstream HDO, performed in a fixed bed reactor, for vapour phase product upgrading.
- An advantage of not having a catalyst in the pyrolysis reactor (scenario a and c) is that the *optimal temperature* of 500 °C for fast pyrolysis can be applied without having to also consider what might be optimal for the catalytic HDO reactions.
- Note, however, that without the HDO catalyst, the H_2 used in fast hydropyrolysis typically does not enable significant HDO.

So, if an HDO catalyst is present in the reactor it is called catalytic fast hydropyrolysis. Catalytic hydropyrolysis often performed at elevated pressure to increase the driving force for the HDO. Now this approach has been more successful in achieving the high energy recovery and biooil with low oxygen content. Both non-catalytic and catalytic fast hydropyrolysis can be coupled with downstream HDO, performed in a fixed bed reactor for vapour phase product upgrading.

An advantage of not having a catalyst in the pyrolysis reactor - scenario a and c here, these 2 are non catalytic, the optimal temperature of 500 degrees centigrade for fast pyrolysis can be applied without having to also consider what might be optimal for the catalytic HDO reactions. Note, however that without HDO catalyst the hydrogen used in the fast hydropyrolysis typically does not enable significant HDO. So, this is one of the disadvantage. So, it is always better to have a catalytic HDO.

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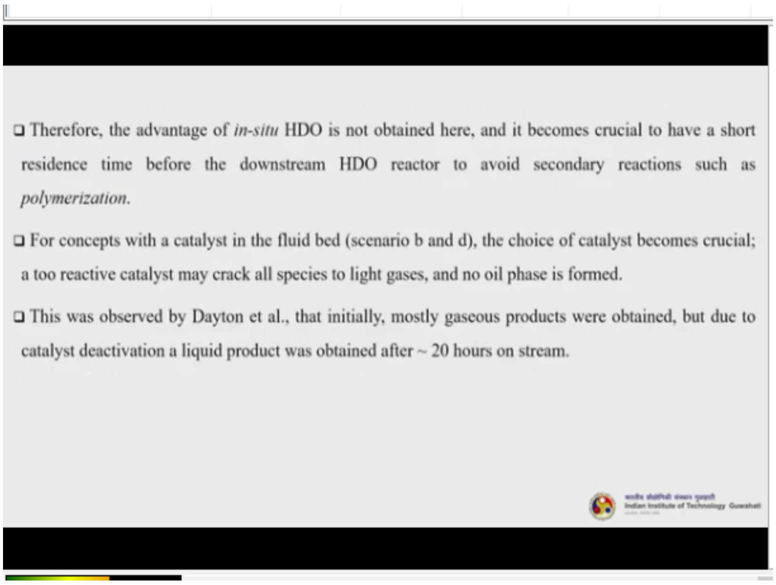

- Therefore, the advantage of *in-situ* HDO is not obtained here, and it becomes crucial to have a short residence time before the downstream HDO reactor to avoid secondary reactions such as *polymerization*.
- For concepts with a catalyst in the fluid bed (scenario b and d), the choice of catalyst becomes crucial; a too reactive catalyst may crack all species to light gases, and no oil phase is formed.
- This was observed by Dayton et al., that initially, mostly gaseous products were obtained, but due to catalyst deactivation a liquid product was obtained after ~ 20 hours on stream.

Therefore, the advantage of in-situ HDO is not obtained here and it becomes crucial to have a short residence time before the downstream HDO reactor to avoid secondary reactions such as polymerization. For concepts with a catalyst in the fluid bed - scenario b and d - where catalyst is used both in the pyrolysis reactor as well as in the hydrotreating units the choice of catalyst becomes very crucial.

A too reactive catalyst also may crack all species to light gases and no oil phases form. So, you do not get oil. So, the catalyst selection is very important, this was observed by Dayton et al, that initially most gaseous products were obtained but due to catalyst deactivation a liquid product was obtained after 20 hours on stream.

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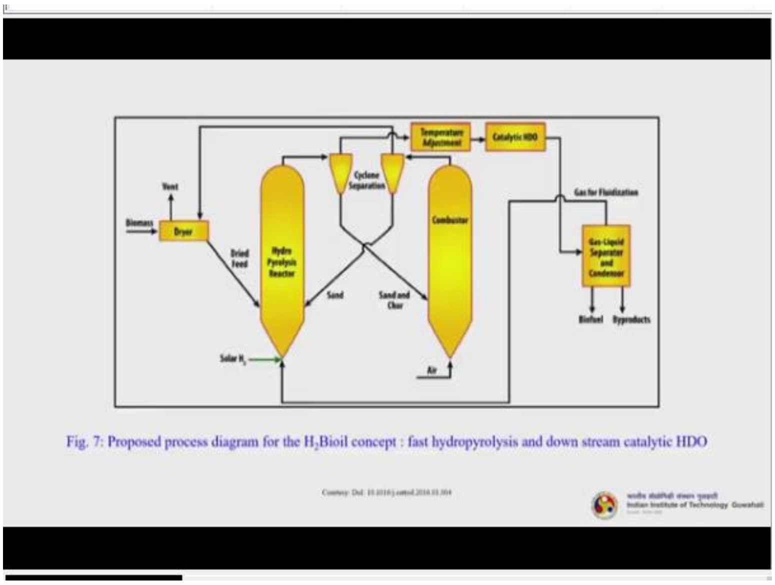

Fig. 7: Proposed process diagram for the H_2Bioil concept : fast hydropyrolysis and down stream catalytic HDO

Courtesy: Doi: 10.1016/j.cattod.2016.01.304

So, this is a proposed process diagram for the H_2 biooil concept. The reference is given here. The fast hydropyrolysis and downstream catalytic HDO. So, what is happening is this, here the hydropyrolysis reactor here the biomass is being dried, then fed directly to the hydropyrolysis reactor. So, hydrogen is being fed here, then whatever you get here so it goes through the series of cyclone separators.

So, in the first one the cyclone will separate the sand and char. Now this sand and char will be fed to a combusting unit and whatever is coming out in this combusting unit is being fed to another cyclone separator where the sand will be re-circulated back to the pyrolyser, sand is a heating medium. Now the gases, the pyrolytic vapours now those from here actually it goes to the temperature adjustment, then catalytic HDO process.

Then it can go to the gas liquid separator and condensor. Now again I am telling you that there can be many small, small unit operations involved in the entire scheme which are not being shown here**.** Let you understand that what are the main units that are responsible for carrying out this H_2 biooil process.

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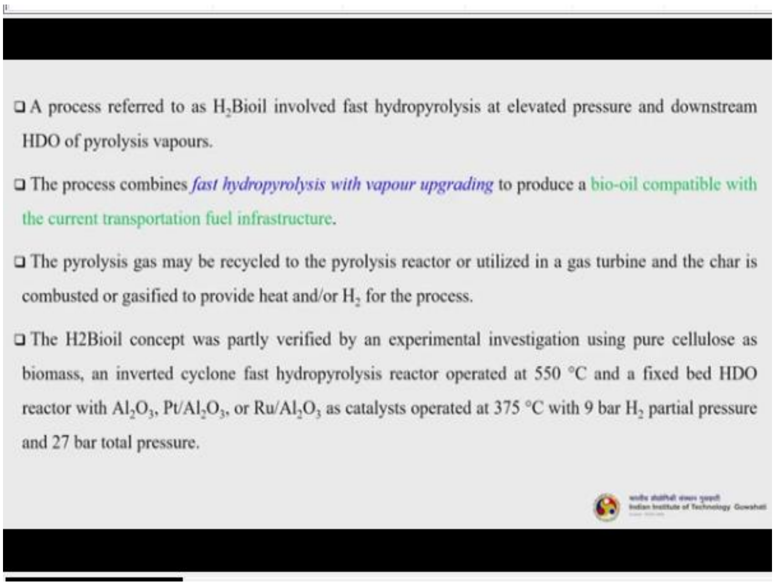

❑ A process referred to as H_2Bioil involved fast hydropyrolysis at elevated pressure and downstream HDO of pyrolysis vapours.

❑ The process combines *fast hydropyrolysis with vapour upgrading* to produce a bio-oil compatible with the current transportation fuel infrastructure.

❑ The pyrolysis gas may be recycled to the pyrolysis reactor or utilized in a gas turbine and the char is combusted or gasified to provide heat and/or H_2 for the process.

❑ The H2Bioil concept was partly verified by an experimental investigation using pure cellulose as biomass, an inverted cyclone fast hydropyrolysis reactor operated at 550 °C and a fixed bed HDO reactor with Al_2O_3, Pt/Al_2O_3, or Ru/Al_2O_3 as catalysts operated at 375 °C with 9 bar H_2 partial pressure and 27 bar total pressure.

So, a process referred to as the H_2 biooil involved fast hydropyrolysis at elevated pressure and downstream HDO of the pyrolysis vapours. The process combines fast hydropyrolysis with vapour upgrading to produce a biooil compatible with the current transportation fuel infrastructure. The pyrolysis gas may be recycled to the pyrolysis reactor or utilized in a gas turbine and the char is combusted or gasified to provide heat and/or hydrogen for the process.

The H2 biooil concept was partly verified by an experimental investigation using pure cellulose as biomass and inverted cyclone fast hydropyrolysis reactor operated at 550 degree centigrade and a fixed bed HDO reactor with alumina, platinum alumina or ruthenium alumina as catalyst operated at 375 degree centigrade with 9 bar hydrogen partial pressure and 27 bar total pressure. So, this is a very good study and this has been commercially adapted, the H2 biooil process.

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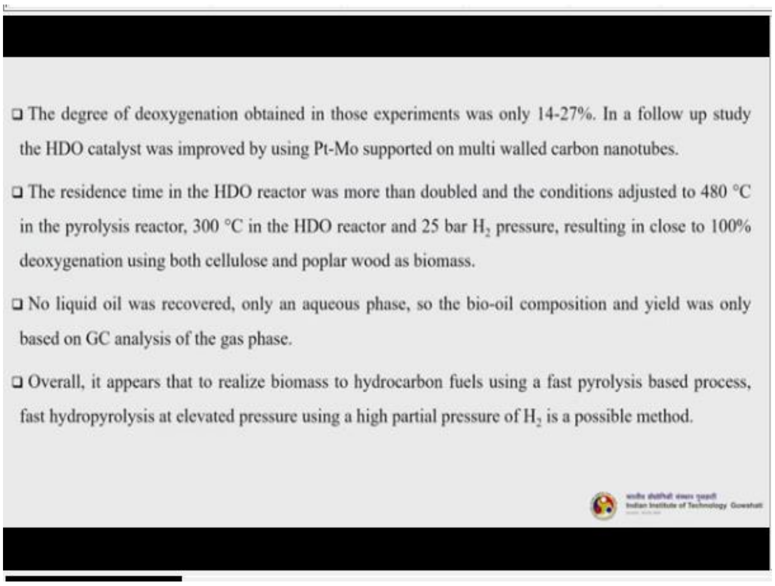

- ❑ The degree of deoxygenation obtained in those experiments was only 14-27%. In a follow up study the HDO catalyst was improved by using Pt-Mo supported on multi walled carbon nanotubes.
- ❑ The residence time in the HDO reactor was more than doubled and the conditions adjusted to 480 °C in the pyrolysis reactor, 300 °C in the HDO reactor and 25 bar H_2 pressure, resulting in close to 100% deoxygenation using both cellulose and poplar wood as biomass.
- ❑ No liquid oil was recovered, only an aqueous phase, so the bio-oil composition and yield was only based on GC analysis of the gas phase.
- ❑ Overall, it appears that to realize biomass to hydrocarbon fuels using a fast pyrolysis based process, fast hydropyrolysis at elevated pressure using a high partial pressure of H_2 is a possible method.

Now the degree of deoxygenation obtained in those experiments were only 14 to 27%. In a follow-up study the HDO catalyst was improved by using platinum molybdenum support on multi walled carbon nanotubes. Now you understand that the significance of the catalyst - the selection of catalyst is very important. The residence time in the HDO reactor was more than double and the conditions adjusted to 480 degree centigrade in the pyrolysis reactor, 300 degree centigrade is the HDO reactor and 25 bar hydrogen pressure resulting in close to 100% deoxygenation using both cellulose and popular wood as biomass.

So, this is a case study, you can use other biomass. No liquid oil was recovered, only an aqueous phase, so the biooil composition and yield was only based on the GC analysis of the gas phase. Overall it appears that to realize biomass to hydrocarbon fuels using a fast pyrolysis based process, fast hydropyrolysis at elevated pressure using a high partial pressure of hydrogen is a possible method.

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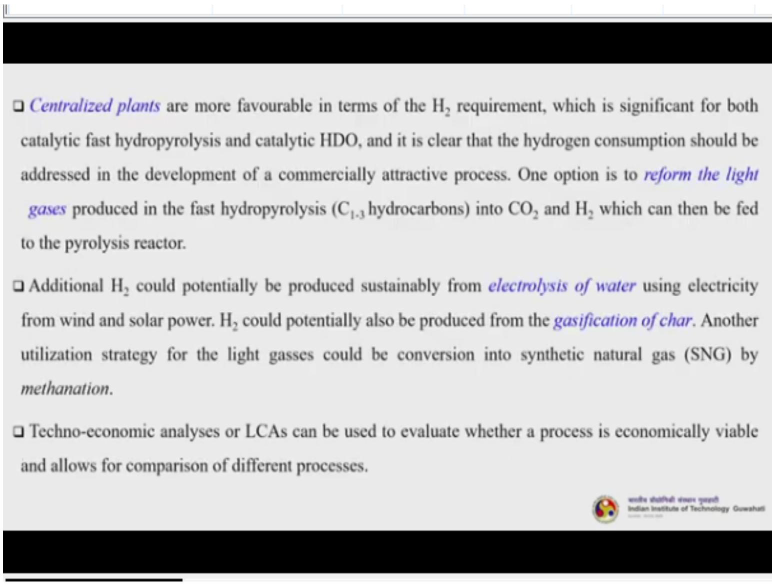

❑ *Centralized plants* are more favourable in terms of the H_2 requirement, which is significant for both catalytic fast hydropyrolysis and catalytic HDO, and it is clear that the hydrogen consumption should be addressed in the development of a commercially attractive process. One option is to *reform the light gases* produced in the fast hydropyrolysis (C_{1-3} hydrocarbons) into CO_2 and H_2 which can then be fed to the pyrolysis reactor.

❑ Additional H_2 could potentially be produced sustainably from *electrolysis of water* using electricity from wind and solar power. H_2 could potentially also be produced from the *gasification of char*. Another utilization strategy for the light gasses could be conversion into synthetic natural gas (SNG) by *methanation*.

❑ Techno-economic analyses or LCAs can be used to evaluate whether a process is economically viable and allows for comparison of different processes.

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So, centralized plants are more favourable in terms of the hydrogen requirement which is significant for both catalytic fast hydropyrolysis and catalytic HDO -hydrodeoxygenation, and it is clear that hydrogen consumption should be addressed in the development of a commercially attractive process. One option is to reform the light gases produced in the fast hydropyrolysis into carbon dioxide and hydrogen which can then be fed to the pyrolysis reactor. And carbon dioxide can be recycled back for other processes.

Additional hydrogen could potentially be produced sustainably from the electrolysis of water using electricity from wind and solar power making entirely the production of hydrogen as sustainable and green. Hydrogen could potentially also be produced from the gasification of char. Another utilization strategy for the light gases could be conversion into synthetic natural gas by using the methanation process. Now techno-economic analysis and life cycle assessments can be used to evaluate whether a process is economically viable and allows for comparison of the different processes**.**

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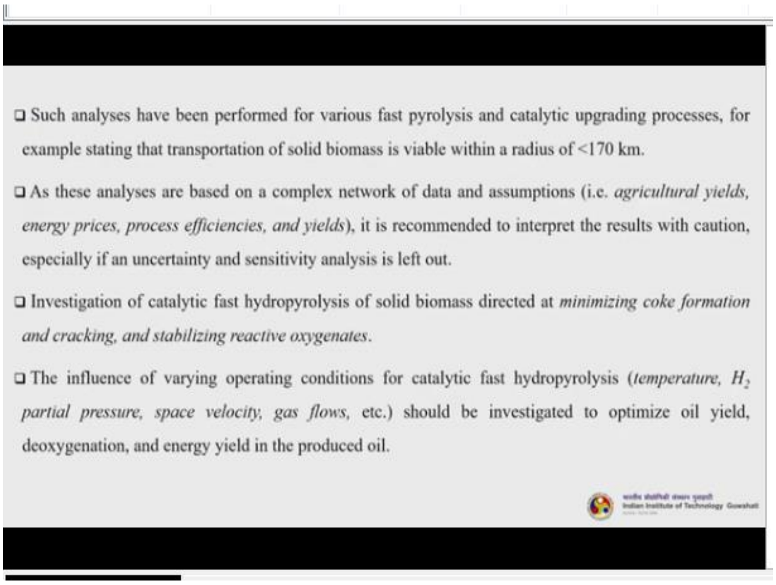

- Such analyses have been performed for various fast pyrolysis and catalytic upgrading processes, for example stating that transportation of solid biomass is viable within a radius of <170 km.
- As these analyses are based on a complex network of data and assumptions (i.e. *agricultural yields, energy prices, process efficiencies, and yields*), it is recommended to interpret the results with caution, especially if an uncertainty and sensitivity analysis is left out.
- Investigation of catalytic fast hydropyrolysis of solid biomass directed at *minimizing coke formation and cracking, and stabilizing reactive oxygenates*.
- The influence of varying operating conditions for catalytic fast hydropyrolysis (*temperature, H_2 partial pressure, space velocity, gas flows,* etc.) should be investigated to optimize oil yield, deoxygenation, and energy yield in the produced oil.

Such analyses have been performed for various fast pyrolysis and catalytic upgrading processes. For example stating the transportation of solid biomass is viable within a radius of less than 170 kilometre. The economics has to be taken into consideration. So, LC and TA studies are very important. As these analyses are based on a complex network of data and assumptions as for example agricultural yields, energy prices, process efficiencies and yields, it is recommended to interpret the results with caution, especially if an uncertainty and sensitivity analysis is left out.

Investigation of catalytic fast hydropyrolysis of solid biomass directed at minimizing coke formation and cracking and stabilizing reactive oxygenates. The influence of various operating conditions for catalytic fast hydropyrolysis, for example temperature, hydrogen partial pressure, space velocity, gas flows, etcetera should also be investigated to optimize the oil yield, deoxygenation and energy yield in the produced oil.

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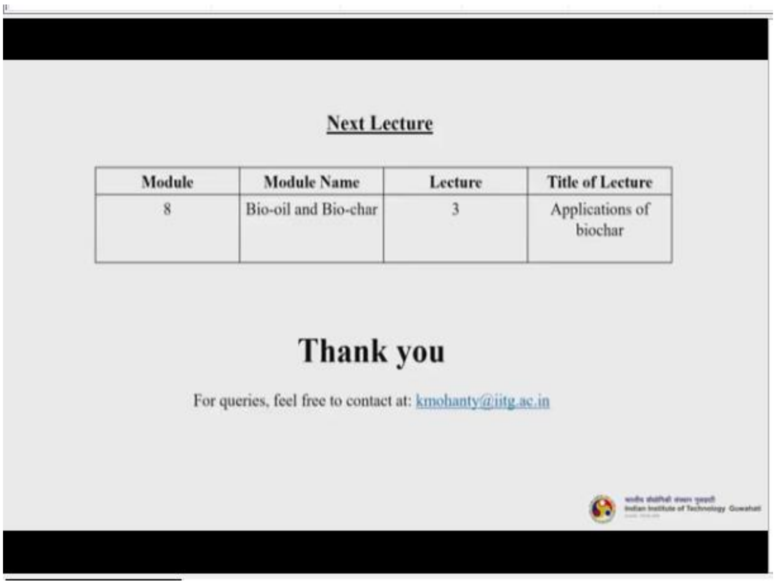

Next Lecture

Module	Module Name	Lecture	Title of Lecture
8	Bio-oil and Bio-char	3	Applications of biochar

Thank you

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

So, with this I conclude today’s lecture. So, in the next lecture that is the last lecture of the module 8 we will be discussing about the applications of biochar and how you do you also characterize the biochar. So, as you know that biochar also is an important value added product or byproduct or side product from the pyrolysis of the biomass. So, if you have any query please register your query in the swayam portal or you can drop a mail to me at kmohanty@iitg.ac.in, thank you.