Waste to energy conversion
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Lecture – 34
Energy production from waste through transesterification – I

Good morning, now will start discussion on a new module Energy Production from Waste through Transesterification. So far we have discussed on different thermal and bio chemical routes for the production of energy from the waste and biomass. And now will concentrate on a chemical route, and the transesterification is an important chemical route for the waste energy conversion method. And in this process some waste which is having triglycerides or oil that is bio-oil can be converted to esters, that is fatty acids alkyl esters. And these fatty acid alkyl esters are the component of bio diesel. So, after this process, the product which we get that will be having some fuel value and can be used by blending with diesel or directly in the Indian.

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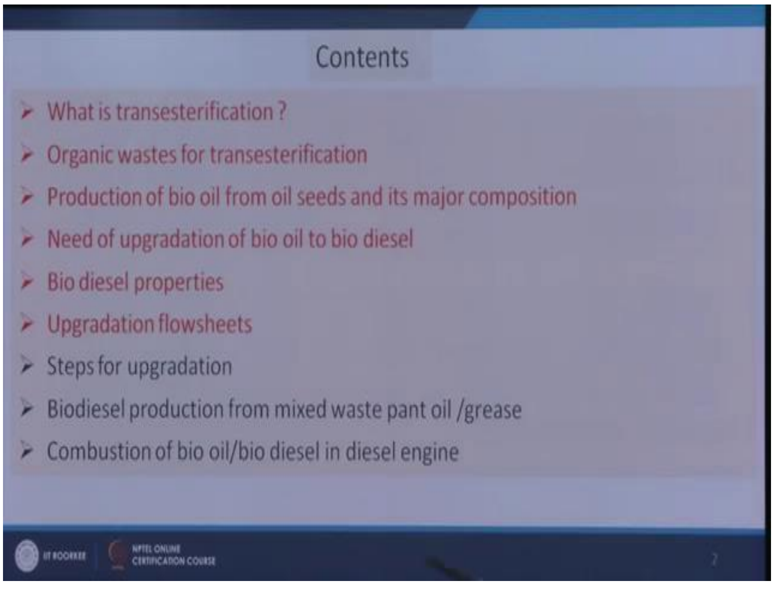

Contents

- What is transesterification ?
- Organic wastes for transesterification
- Production of bio oil from oil seeds and its major composition
- Need of upgradation of bio oil to bio diesel
- Bio diesel properties
- Upgradation flowsheets
- Steps for upgradation
- Biodiesel production from mixed waste pant oil /grease
- Combustion of bio oil/bio diesel in diesel engine

So, in this module, we will discuss what is the transesterification organic waste for transesterification, production of bio-oil from the oil seeds and it major composition need of up gradation of bio-oil, to biodiesel and then bio diesel properties upgradation flow sheets there is bio-oil to bio diesel conversion, flow sheets and steps for upgradation biodiesel production from mixed waste plant oil or grease and combustion of bio-oil or bio diesel in diesel engine.

So, let us start, let us see what is the transesterification. So, as the name says it is esterification process, but it is transesterification.

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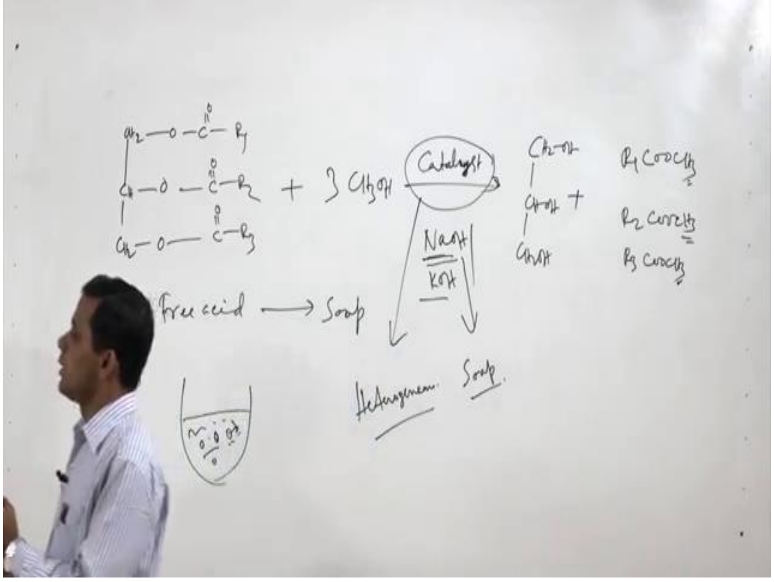

So, in this method as I have already discussed that is triglyceride; so esters of glycerol that is; CH CH CH 2 CH 2 O O O R 1 C O R 2 and say C O R 3. So this is a triglyceride. So, this triglyceride is converted to glycerol some alcohol reacts with it, basically methanol or higher alcohol may be also used. So, let us take some example of methanol; so CH 3 OH. So, some catalyst is used. So, this catalyst it will convert this glyceraldehyde to glycerol and will give the fatty acid alkyl esters. So, R 1 COOCH 3 R 2 COCH 3 and R 3 COOCH 3 when CH 3 OH is used if we use higher alcohol this alkyl group will be higher.

Now, this is the basic chemistry or the basic reaction of the transesterification process. and in this process some catalyst is used. without catalyst the reaction will not take place and sodium hydroxide, potassium hydroxide is mostly used, but in some cases particularly when say in your waste not only the triglyceride is present some free acids is also present. So, if some free acid is present here. So, that will react with sodium hydroxide and potassium hydroxide and produce soap. that is why acid catalyzed transesterification process is also used in some cases particularly when free acid is present in the feed stock.

As I have just discussed if free acid is present or if free acid is not present here some free acid first form say during if we see the mechanism of the transesterification process the free acid is produced in between. So, in which can form react with that and always there is a chance of soap formation for this transesterification process when NaOH is used as catalyst that why efforts are on. And people are trying to develop new catalyst that is heterogeneous catalyst heterogeneous catalyst to remove this difficulty.

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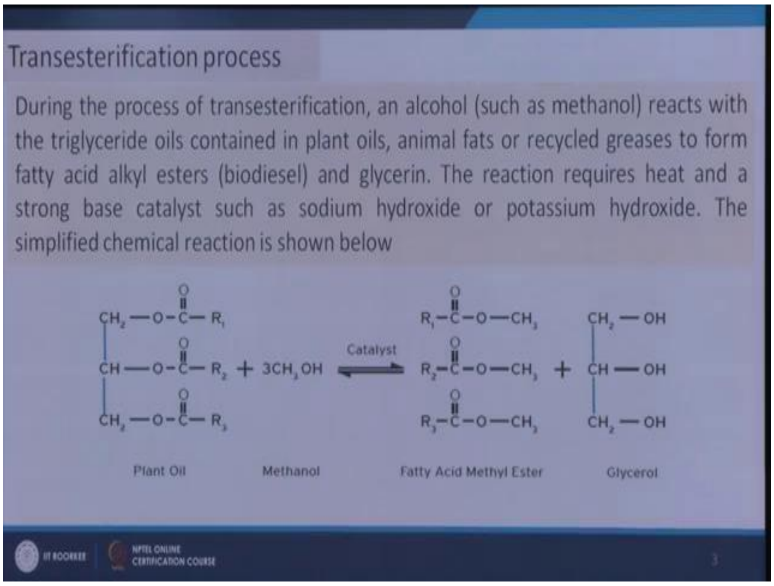

Transesterification process

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

So, this is a basis of the transesterification process. So, by this process what we get we get the fatty acid methyl esters when methanol is used. So, these compounds are the components of bio diesel, but this glycerol is not desirable for fuel applications, but it has immense utility. it can be purified and can be applied in many other applications. So, the triglyceride which is present in the waste material that can be converted to value added product by this process transesterification process and some of this products will be having energy values; so now will be concentrating on this. Before that will see how where from these things are coming that triglyceride from what type of waste we can get.

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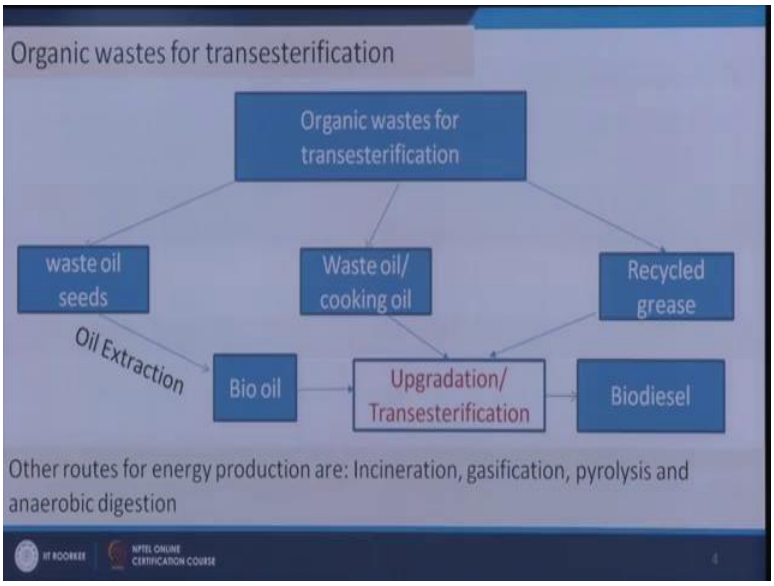

Organic wastes for transesterification

Organic wastes for transesterification

waste oil seeds

Waste oil/ cooking oil

Recycled grease

Oil Extraction

Bio oil

Upgradation/ Transesterification

Biodiesel

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

So, if we consider different types of organic waste for transesterification, we will see that all organic waste are not suitable for the transesterification process, part of the waste or the will be suitable those are having some triglyceride. And those are basically waste oil and cooking oil recycled grease and waste oil seeds; oil seed which are having some bio-oil inside it or liquid inside it that can be used for the production of bio-oil first and then for it is upgradation. So, you see different feed stocks, which are available in waste those will not be processed in the same process. The process steps are different for if it is the waste is waste oil seeds then will go for oil extraction then bio-oil will be produced. bio-oil will be upgraded and then bio diesel will get.

And this upgradation is basically transesterification process if we have waste oil or cooking oil will go for upgradation. we do not need for any bio-oil production if we have recycled grease we will go for upgradation no need of bio-oil again you see here 2 different waste oil or cooking oil and recycle grease 2 different feed stocks are having different properties. Basically recycled grease are having high amount of free fatty acids in it along with triglycerides. So, acid catalyzed transesterification must be there for the processing of this recycled grease, whereas, waste oil and cooking oil these are having very less free fatty acids and the acid catalyzed state may be escaped. So, these are the different feed stocks or type of waste which can be processed through the transesterification process.

Now, at first we will consider the oil, bio-oil production from oil seeds waste oil seeds and will see that.

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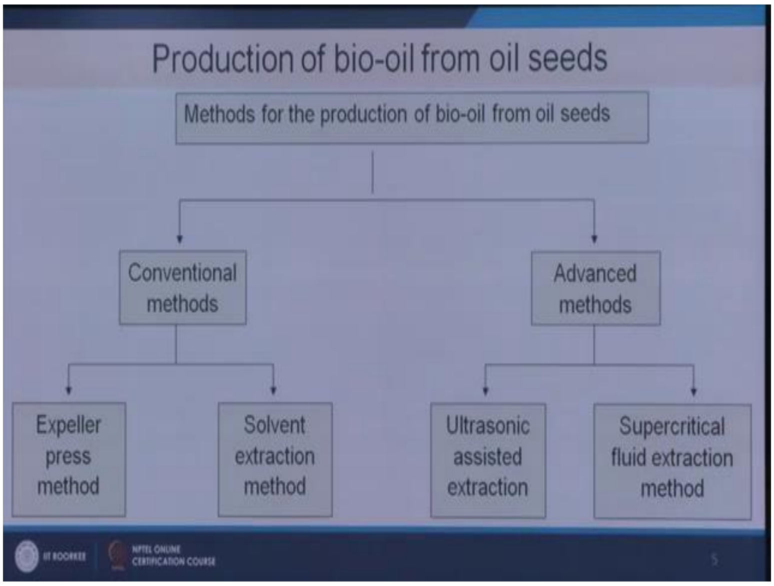

Production of bio-oil from oil seeds

Methods for the production of bio-oil from oil seeds

Conventional methods

Advanced methods

Expeller press method

Solvent extraction method

Ultrasonic assisted extraction

Supercritical fluid extraction method

There are basically 2 types of operation which are used for the extracting of oil from the oil seeds. One is your conventional method and advance method conventional method means there is some physical method, and chemical method physically that are using expeller the oil is taken out extracted from the oil seeds. So, if we have some oil seeds if we place it will be broken the cells will be broken wall will be broken and the oils will be coming out. So, oils will be coming out see this is the mechanism of the expeller place method, but if we use some solvent extraction.

So, if we use some solvent say here we are added some solvent, liquid solvent and some solid particle are broken solid particles the broken parts of these oil seeds or the or the full part or complete part of oil seed then, what will be happening the oil which is inside this that will diffuse and it will come into the solvent if we break this wall. So, we will get more extraction. So, that is solvent extractions is the process through which the oil is first extracted from the bio mass or bio or waste or oil seeds.

And then advanced methods these are basically extraction method somewhere we use the ultrasonic assisted extraction and somewhere we use super critical fluid extraction method. So, these are the different methods which have been used for the extraction of the bio-oil. So, these 2 ultrasonic assisted extractions and supercritical fluid extraction both are under solvent extractions or we can write the same table in different fashion like this.

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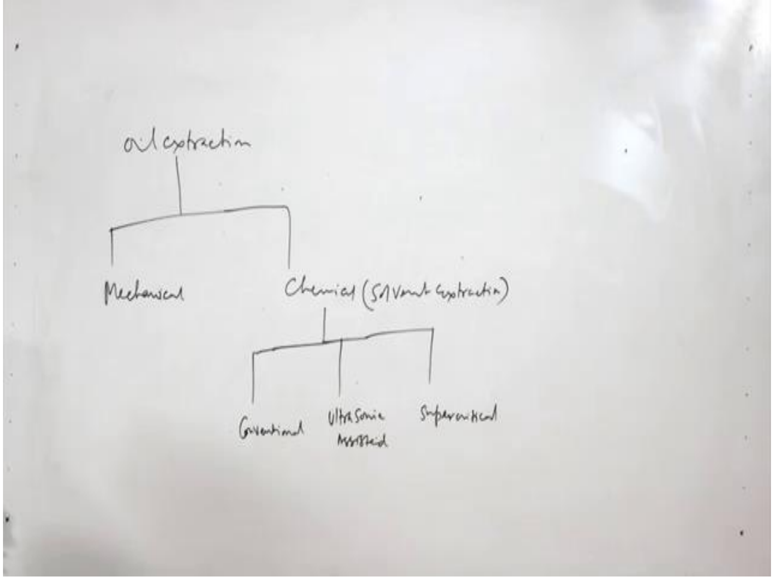

So, we can write say oil extraction, it is having mechanical and it is chemical, that is solvent extraction that may be of conventional or may be of ultrasonic assisted or may be supercritical. So, that way also we can represent this method. Now will see these are 2 pictures the oil press and this is solvent extraction. Normally for the solvent extraction soxhlet apparatus is used. So, as show in the figure this is a soxhlet apparatus the working of this apparatus is like this.

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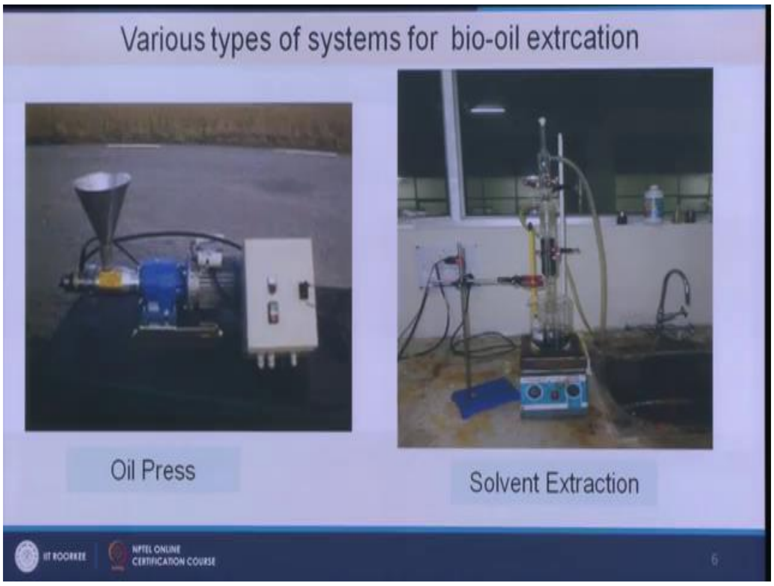

Various types of systems for bio-oil extrcation

Oil Press

Solvent Extraction

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Say as we see here, here is the solvent. We heat it the vapor the vaporized solvent will go up come here is condensed. So, liquid will form. So, liquid solvent will drop here solids will be kept here and finally, liquid will come here the liquid mixing between the liquid and solids and solid liquid will be going to this beaker through syphon action. So, this not very clear I am drawing here.

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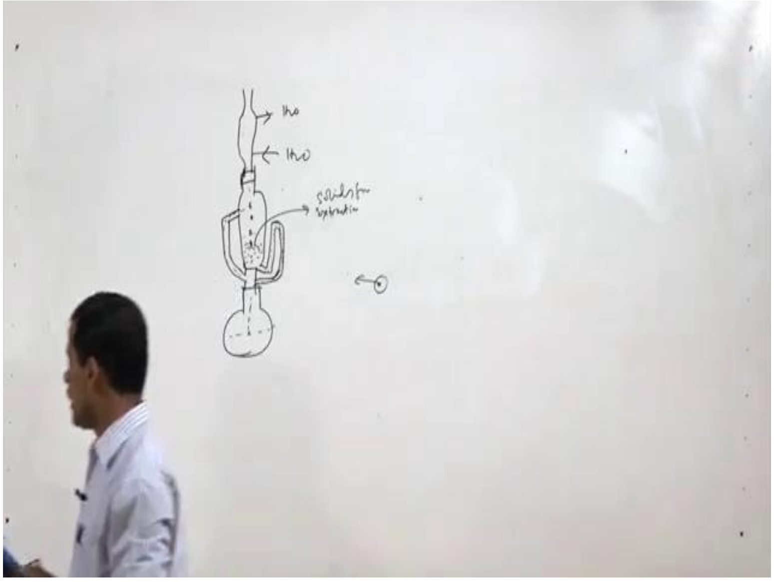

So, we have one beaker here say. So, we will be putting one. So, say this is our soxhlet apparatus at the top will be having some condenser, see I will be sending water cooling water and there will be cooling water out. So, when we are putting the solvent here we are putting the material solid material here that is from where we are interested to extract that is solids for extraction here. So, solvent it is heated. So, heated solvent will go here, and the vapors will go up condense this will drop. And then there will be good mixing of this solid and liquid solvent.

Once the liquid is filled here due to syphon action the liquid solvent will come down here and again come back. And this will be continuing for time hours. So, 2 hours 3 hours 4 hours as we like. So, tau we with time the same process will be continuing solvent will be there. And there will be good mixing between the solid and the liquid and from this solid part the oil molecules will come out and mix with the solvent. So, this is the mechanism of soxhlet apparatus using solvent extraction.

Now, if we use ultrasonic assisted extraction. So, in this case the bio the solids or the seeds from where the oil is getting out the ultrasonic wave helps to break the area the surface or the wall of the seed. So, more oil comes easily as a whole the rate of the process in kgs extraction process in kgs.

Now, the factors which effects the oil extraction I mentioned here, that is type of solvent hexane and n pentane.

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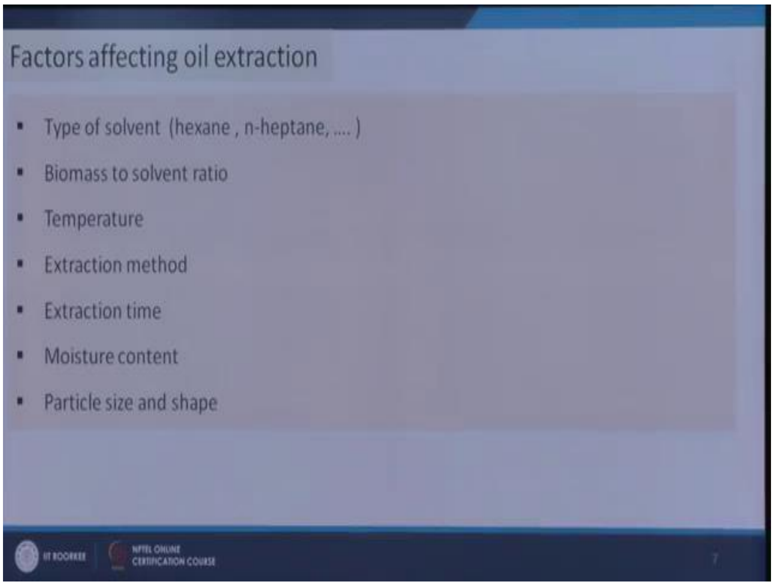

Factors affecting oil extraction

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

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So, oil is present in the oil seeds. So, most of the oils are nonpolar. So, if we use nonpolar solvent we will get more extraction if we use polar solvent we may not get that much of extraction; so biomass to solvent ratio. So, if we use more solvent will be getting more extraction of oil because driving; driving force will be high in that case, but we have to optimize.

Then temperature higher, the temperature higher will be the extraction, but the temperature cannot be. So, high that it is above the boiling point of that solvent. So, temperature has to be decided on the basis of the solvent which you are using. the extraction method what type of extractions are ultrasonification assisted or scalar method any expeller. So, it will be depend upon the extraction, method or supercritical extraction may be extraction time also the time of extractions will give more yield and then moisture content particle size and shape already we have discussed, less of the particle size more surface area and more contact.

So, will be more and moisture content actually moisture content is desirable for this solvent extraction phase in conventional way, but gradually particularly for some feeds stocks particularly for micro algae the moisture content moisture, separation requires very high amount of energy. So, people are trying to develop some process with high moisture that is in liquid media for the extractions of oil.

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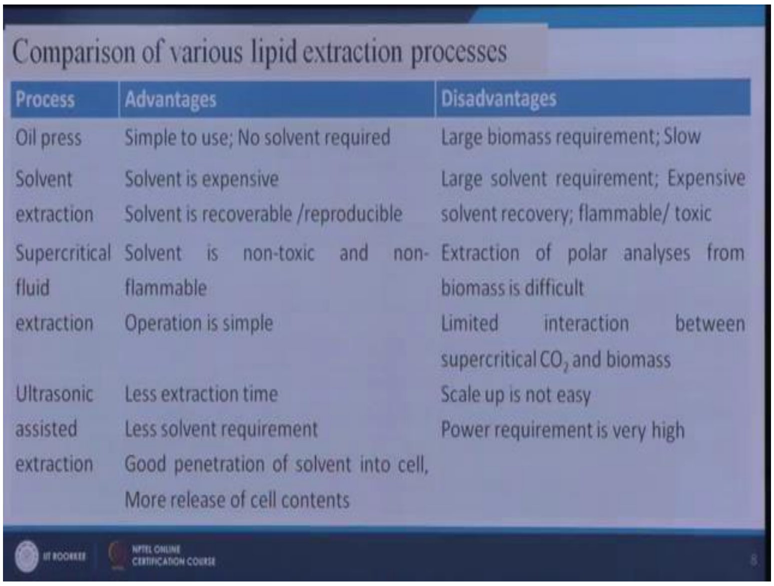

Comparison of various lipid extraction processes

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

Now, here is the comparison of various liquid extraction processes. So, we have explained here expeller process and then we have supercritical liquid extraction ultrasonic and solvent extraction 4 processes are there, out of these solvent extraction is mostly used, but there are some disadvantage of using solvent extraction process is that the solvents are toxic in nature in general, generally and it requires large solvent and then expensive solvent recovery and flammable and toxics.

So, these are the main disadvantage of this solvent extraction process supercritical fluid extraction the solvent is nontoxic and nonflammable and operation is simple, but it has some disadvantages is that extraction of the polar analyze, if some polar molecules are present in it would be difficult for the separation and limited interaction between supercritical O O 2 and bio mass ultrasonic assisted extractions is one sort of solvent extractions which helps to increase the rate of the production of the bio-oil.

Now, will say what is the bio-oil and what are the fatty acids content means a triglyceride which is present in the bio-oil what types of acids are present there. So, basically major 7 acids are there that is your lauric acid myristic acid as as shown here that is lauric acid O 12 H 24 O 2 myristic acid O 14 H 20 8 O 2 and then palmitic acid O 16 H 32 O 2 and steric acid O 18 H 36 O 2.

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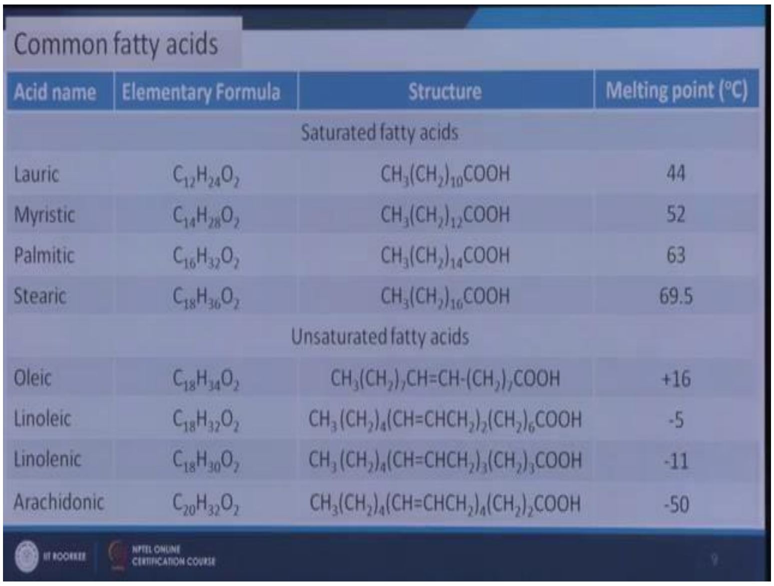

Common fatty acids

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

These are the saturated fatty acids and some unsaturated fatty acids are also there oleic acid say O 18 34 O 2 and linoleic acid is O 18 H 32 O 2 and linolenic acid O 18 H 30 O

2 and asidonic acid O 20 H 32 O 2. And these are the structures and some melting points are given here also. So, here we can get some important information that with the increase of this unsaturation we are getting lesser melting point. So, high melting point and this is lesser melting point. So, these are sometimes helpful for it use as a fuel.

Now, the bio-oil which is produced it requires upgradation, but why the upgradation is required because the bio-oil viscosity is very high. that is why it is difficult to use directly in engine because it is difficult to pump the oil bio-oil to the engine for it automization and then it ignition, as well as if we can use some high pump high capacity pump and the droplet us will be bigger and combustion will not be complete.

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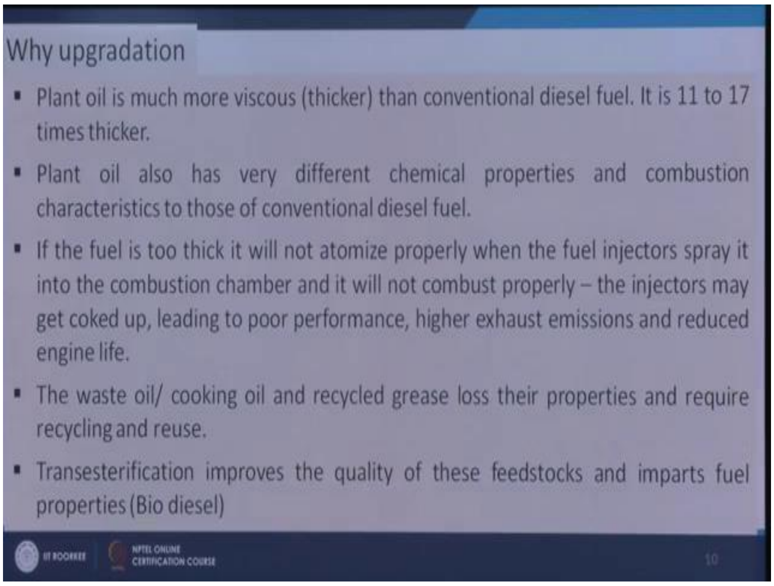

Why upgradation

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

So, these are the major difficulty with the bio-oil. So, bio-oil which is produced from oil seeds or some other waste oil seeds. So, those cannot be directly used, that has to be converted or upgraded through the transesterification that is what the importance of transesterification there is for bio-oil which is produced from the waste oil seeds.

Other 2 sources we have discussed recycled grease and the waste cooking oil and waste plant oil. So, these also are waste materials and lose their fuel properties. So, upgradation improves the quality of it is wastes, and hence upgradation is required and transesterification improves the quality of this feed stocks and impart fuel properties. So, that is why we are doing the upgradation. And ultimately the objective of upgradation is to get the bio diesel the components of the bio diesel that is fatty acid alkyl esters and bio diesel is a mixture of fatty acid alkyl esters.

And it is nonhazardous if we see the composition of the bio diesels as you discussed in the previous slides, there are esters here. So, we have sufficient oxygen in this compound. So, during combustion it will be completely combusted unlike petrol diesel. So, this is relatively pure and nontoxic and biodegradable and it reduces air pollutants such as particulates carbon monoxide and hydrocarbons and air toxins.

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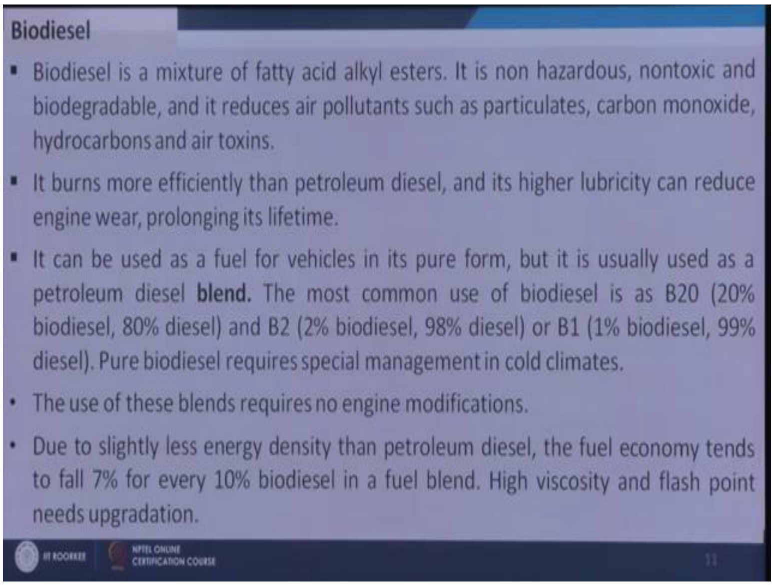

Biodiesel

- Biodiesel is a mixture of fatty acid alkyl esters. It is non hazardous, nontoxic and biodegradable, and it reduces air pollutants such as particulates, carbon monoxide, hydrocarbons and air toxins.
- It burns more efficiently than petroleum diesel, and its higher lubricity can reduce engine wear, prolonging its lifetime.
- It can be used as a fuel for vehicles in its pure form, but it is usually used as a petroleum diesel **blend.** The most common use of biodiesel is as B20 (20% biodiesel, 80% diesel) and B2 (2% biodiesel, 98% diesel) or B1 (1% biodiesel, 99% diesel). Pure biodiesel requires special management in cold climates.
- The use of these blends requires no engine modifications.
- Due to slightly less energy density than petroleum diesel, the fuel economy tends to fall 7% for every 10% biodiesel in a fuel blend. High viscosity and flash point needs upgradation.

So, that is why bio diesel are getting interest in one way, it is having good better quality as well as it will be also meeting some oil requirements from the waste and biomass it burns more efficience more efficiently than petrol and diesel and it is higher lubricity can reduce the engine wear and prolong it is lifetime. So, this is the advantage of biodiesel, but bio diesel can be used as such in the engine, but normally it is used with blend with the diesel; and some commercially available are B 20 B 9 B 2 B 1. So, B 20 means a blend that is 20 percent biodiesel and 80 percent diesel. So, B 2 means 2 percent biodiesel ninety 8 percent diesel. So, B 1 means one percent biodiesel ninety percent diesel. So, all these blended fuels are used in the diesel engine without it is modification, but if if we want to use this completely pure biodiesel, we have to take some action we may need to improve the engine or some other modifications in the systems we will discuss later on.

So, due to slightly less energy density the biodiesels is having certainly less energy density that is why when we make the blend the fuel economy tend to fall 7 percent for every 10 percent biodiesel and it will blend. So, high viscosity and plus point needs up gradations, we will say important properties of biodiesel are first one is ash percentage. So, ash percentage can be determined by approximate analysis we have discussed in earlier modules, and density that is weight per unit volume that picknometer specific gravity can be measured. So, we have discussed these things.

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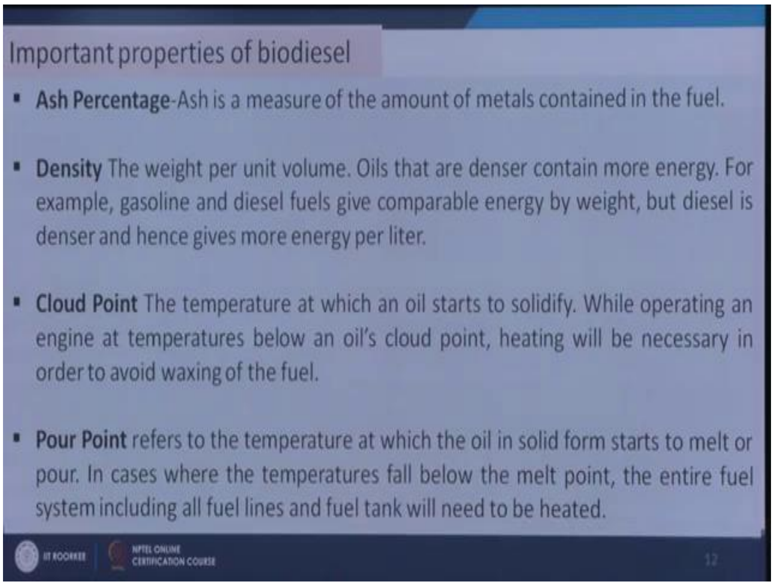

Important properties of biodiesel

- **Ash Percentage**-Ash is a measure of the amount of metals contained in the fuel.
- **Density** The weight per unit volume. Oils that are denser contain more energy. For example, gasoline and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per liter.
- **Cloud Point** The temperature at which an oil starts to solidify. While operating an engine at temperatures below an oil's cloud point, heating will be necessary in order to avoid waxing of the fuel.
- **Pour Point** refers to the temperature at which the oil in solid form starts to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system including all fuel lines and fuel tank will need to be heated.

Here the density is slightly higher than the petrol diesel the density of the biodiesel is slightly higher than that of the petrol diesel. And cloud point and pour point there are 2 important properties of the diesel. So, what are those cloud point is the temperature at which oil appears cloudy that means.

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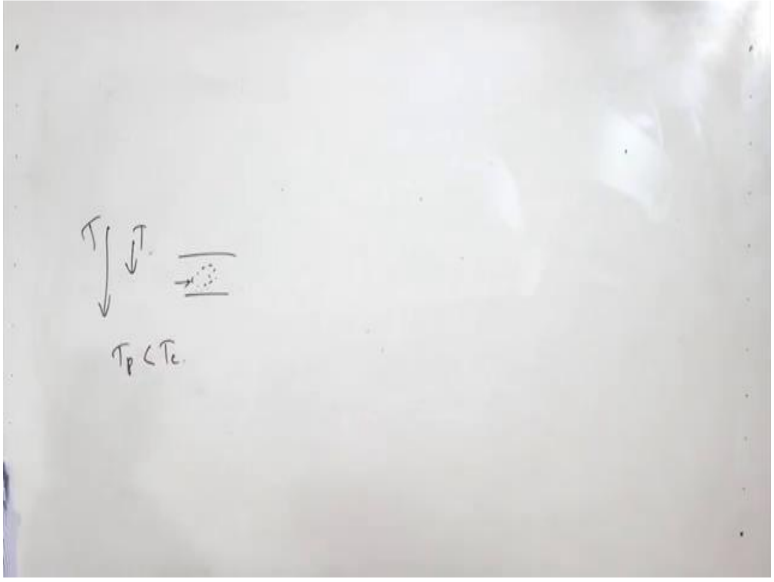

So, biodiesel are diesel having some diesel have some works and bio works in the bio diesel those tends to keep some appearance heginish and it gives to some cloudly. So, the works starts to solidify, and then cloudy appearance comes to the temperature is cloud point we when we reduce the temperature this type of situation comes first if we further reduce the temperature then these will be. So, dense the flow of the fluid will seize. So, that is the pour point, pour point is refers to the temperature at which the oil in solid form and starts to melt or pour. That means, the flow seizes at this temperature so; obviously, the pour point will be lower than pour point is lower than that of cloud point the pour point will be lower than that of the cloud point.

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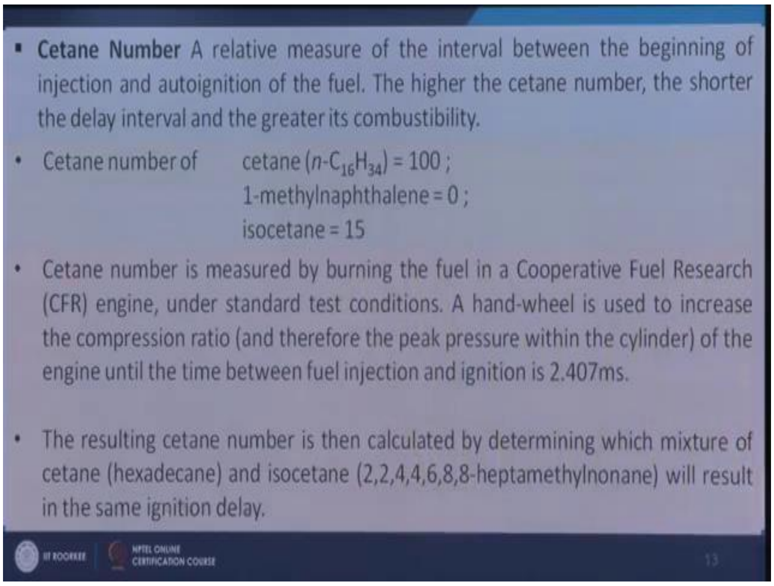

- **Cetane Number** A relative measure of the interval between the beginning of injection and autoignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater its combustibility.
- Cetane number of cetane (n-$C_{16}H_{34}$) = 100 ;
  1-methylnaphthalene = 0 ;
  isocetane = 15
- Cetane number is measured by burning the fuel in a Cooperative Fuel Research (CFR) engine, under standard test conditions. A hand-wheel is used to increase the compression ratio (and therefore the peak pressure within the cylinder) of the engine until the time between fuel injection and ignition is 2.407ms.
- The resulting cetane number is then calculated by determining which mixture of cetane (hexadecane) and isocetane (2,2,4,4,6,8,8-heptamethylnonane) will result in the same ignition delay.

Now, we will discuss on cetane number the one most important properties of bio diesel are diesel is the caeten number. So, what is the cetane number that is the relative measure of the interval between the beginning of the injection and the auto ignition? See injection and auto ignition if there is some delay there will be some spark. So, that is the indication of cetane number higher the ceaten numbers there is the less gap lower the caeten number there will be more interval between these 2. So, higher number is desirable then it is 45 to 55 is value is desirable.

And the cetane number is measured by using a machine that machine is called fuel cooperative fuel research engine CFR engine in CFR engine under standard test condition, a hand wheel is used to increase the compression ratio. So, that maximum pressure can be generated. So, that the delay between these 2 will be minimum the delay between injections and ignition is becoming 2.407 millisecond.

So, we are using one fuel we are increasing the compression ratio and we are getting the gap between injection and ignition is 2.407 millisecond. Then we will be using a mixture of fuels that is cetane and iso cetane. cetane and iso cetane with different ratio a ratio will come that will be having the similar ignition properties in the same engine same conditions. So, that ratio of cetane will be the cetane number of this oil sample investigated. So, cetane number is 100 for cetane and 0 for alpha methylnaphthalene or one methylnaphthalene and 15 for iso cetane. So, initially these was used the alpha methylnaphthalene for this measurement, but later on the iso cetane has been introduced.

Next, we are coming to flash point. So, flash point is also another property of any fuel liquid fuel basically. So, flash point in this case, if we heat the fuel if the raise the temperature of the fuel and put one and keep one fire open fire momentarily on the top of it.

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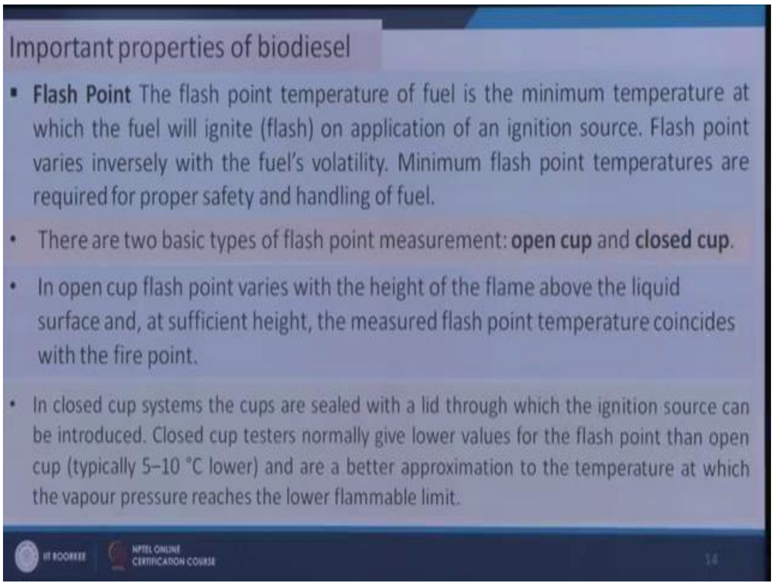

Important properties of biodiesel

- **Flash Point** The flash point temperature of fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of fuel.
- There are two basic types of flash point measurement: **open cup** and **closed cup**.
- In open cup flash point varies with the height of the flame above the liquid surface and, at sufficient height, the measured flash point temperature coincides with the fire point.
- In closed cup systems the cups are sealed with a lid through which the ignition source can be introduced. Closed cup testers normally give lower values for the flash point than open cup (typically 5–10 °C lower) and are a better approximation to the temperature at which the vapour pressure reaches the lower flammable limit.

So, there will be some momentary flash. So, that is called flash point. So, if we raise the temperature then fire will catch. So, that will be the fire point. So, fire point and flashpoint are the important properties of the fuels. So, there are 2 methods for the measurement of flash point one is closed cup and another is open cup method.

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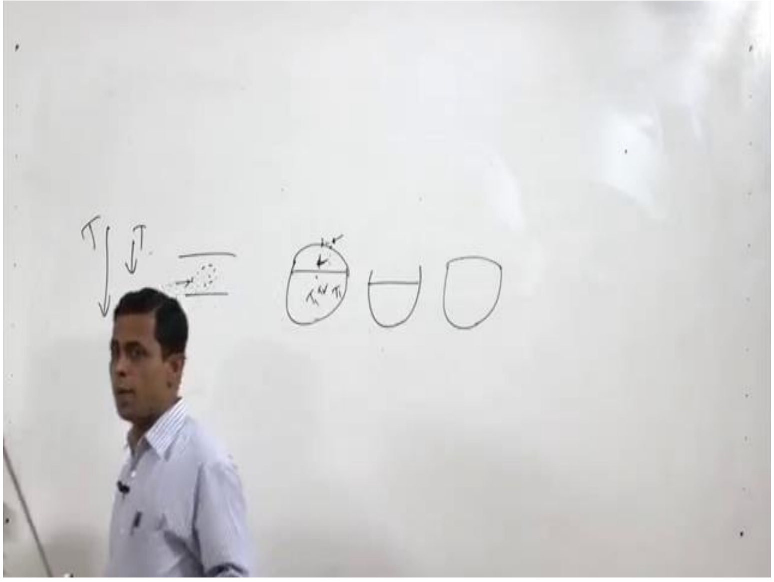

The same sample in open cup and same sample in closed cup if we taste for the flash point, we will be getting some differences that is 5 to 10 degree centigrade lower in case of this that is a closed cup, will be in this lower. So, this is a flash point measurement for this oil.

And new now we will see the heating value and iodine value heating value we have already discussed in our previous module. So, we are not discussing here that is amount of heat released per unit amount of material or the fuel and it depends on the CH and concentration of this which is determined through ultimate analysis. And now iodine value that is also one important property of this bio diesel iodine value gives the indication of unsaturation present in it. So, unsaturation present in it.

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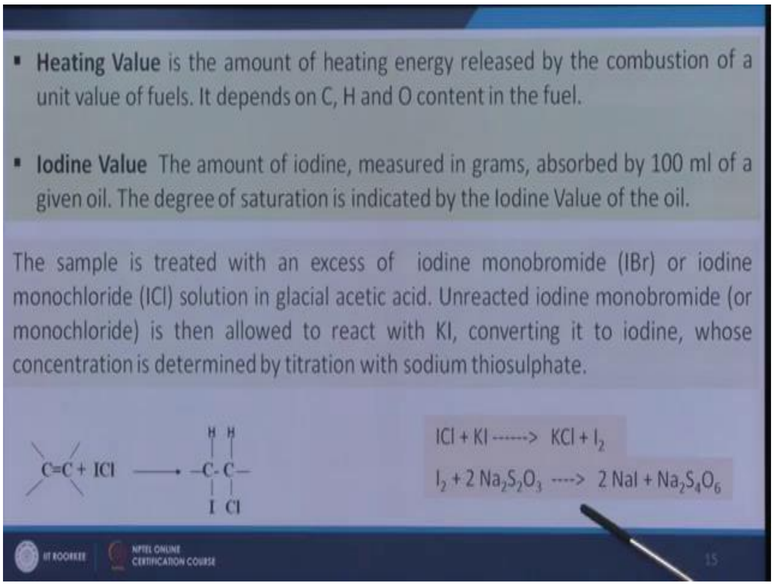

- **Heating Value** is the amount of heating energy released by the combustion of a unit value of fuels. It depends on C, H and O content in the fuel.
- **Iodine Value** The amount of iodine, measured in grams, absorbed by 100 ml of a given oil. The degree of saturation is indicated by the Iodine Value of the oil.

The sample is treated with an excess of iodine monobromide (IBr) or iodine monochloride (ICl) solution in glacial acetic acid. Unreacted iodine monobromide (or monochloride) is then allowed to react with KI, converting it to iodine, whose concentration is determined by titration with sodium thiosulphate.

$$C{=}C + ICl \longrightarrow -\overset{H}{\underset{I}{C}}-\overset{H}{\underset{Cl}{C}}-$$

$ICl + KI \dashrightarrow KCl + I_2$

$I_2 + 2\,Na_2S_2O_3 \dashrightarrow 2\,NaI + Na_2S_4O_6$

So, if unsaturation is present in it what is happen in this case for the measurement of iodine value ICl or IBr that is iodine mono chloride or iodine mono bromide solution is added in the fuel and then this ICl reacts with this cc double bond and this forms this type of structure and if we add ICl in excess. So, the remaining ICl will be available in the solution we will be adding some amount of potassium iodide excess potassium iodide. So, that potassium iodide converts ICl to iodine; so this excess this iodine which is now generated in the solution can be titrated by using sodium thiosulphate. So, sodium thiosulphate will be converted into tetra nitrate and sodium iodide will form. So, by using some indicator by this titration we can determine what amount of iodine is present in the solution which was not used, and ICl if you know the initial concentration of ICl, and if you know the now know the iodine unused.

So, what is the use of iodine we can calculate and one molar iodide attaching with one unsaturation carbon bond. So, that is why gram of iodine absorbed by hundred ml of given oil is a iodine value. So, potassium percentage and sulphur percentage another 2 important properties of the bio diesel. So, when bio diesel is produced as we have discussed that potassium hydroxide which can be used as a catalyst. So, that can be available in the biodiesel and that percentage has to be measured as it is coming from the biomass feed stocks. So, it can have some sulphur and sulphur can be measured. So, there are number of methods for measurement of sulphur one is very primitive one that is you colorimetric method, if we use barium chloride in the solution then it will be having some barium sulphate white precipitate through white color and some weak bond combustion method and X-ray fluorescence and icp ms is there.

So, these are the different methods through which we can measure the sulphur content in bio diesel.

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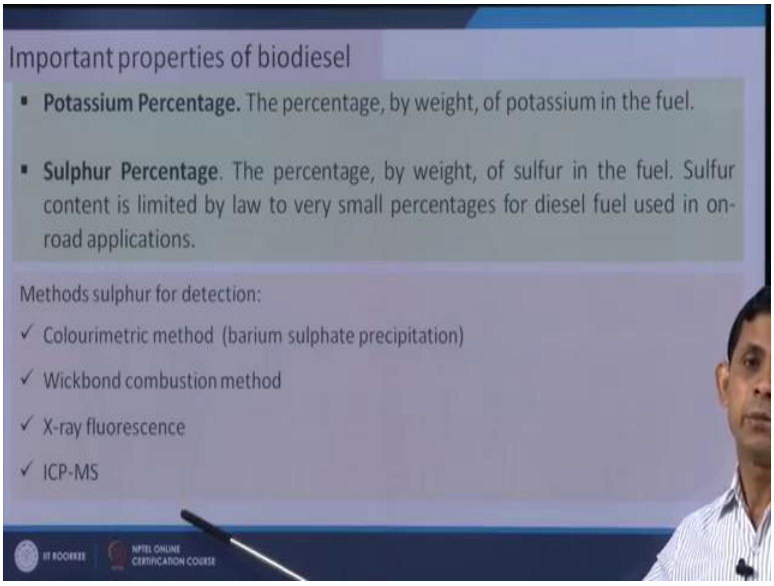

Important properties of biodiesel

- **Potassium Percentage.** The percentage, by weight, of potassium in the fuel.
- **Sulphur Percentage**. The percentage, by weight, of sulfur in the fuel. Sulfur content is limited by law to very small percentages for diesel fuel used in on-road applications.

Methods sulphur for detection:

- ✓ Colourimetric method (barium sulphate precipitation)
- ✓ Wickbond combustion method
- ✓ X-ray fluorescence
- ✓ ICP-MS

Now, viscosity is another property of the biodiesel which is related to the thickness of this and this is measured through different viscometers. And as per the Poisson equation if a liquid flows through a tube the liquid will be having the minimum velocity of the wall and maximum velocity at the center.

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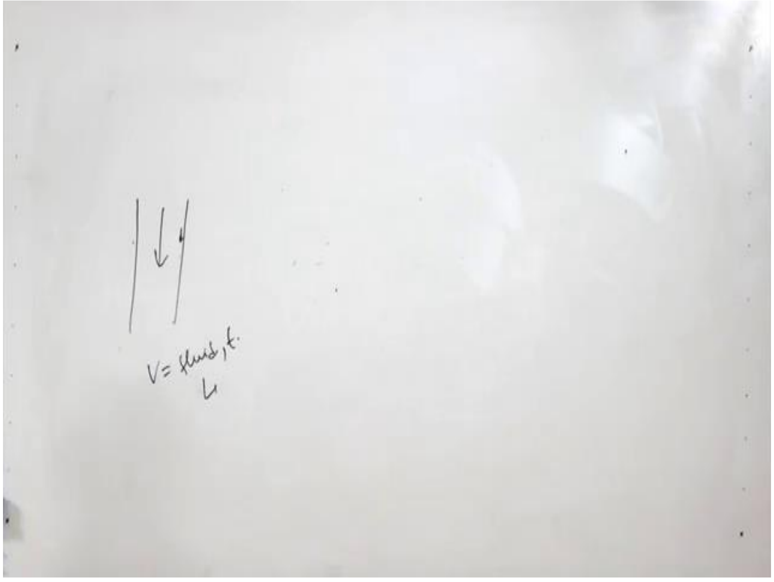

So, minimum velocity at the wall and maximum velocity at the center; so due to the friction here pressure drops will be developed, now this type of flow when a fluid is passed through a tube or a nozzles or at that time the flow is defined in that in this formula that is a viscosity coefficient is equal to pi into R to the power of 4 p into t divided by 8 into V into L where t is the time B is the time of flow and V is the volume of liquid volume of flow.

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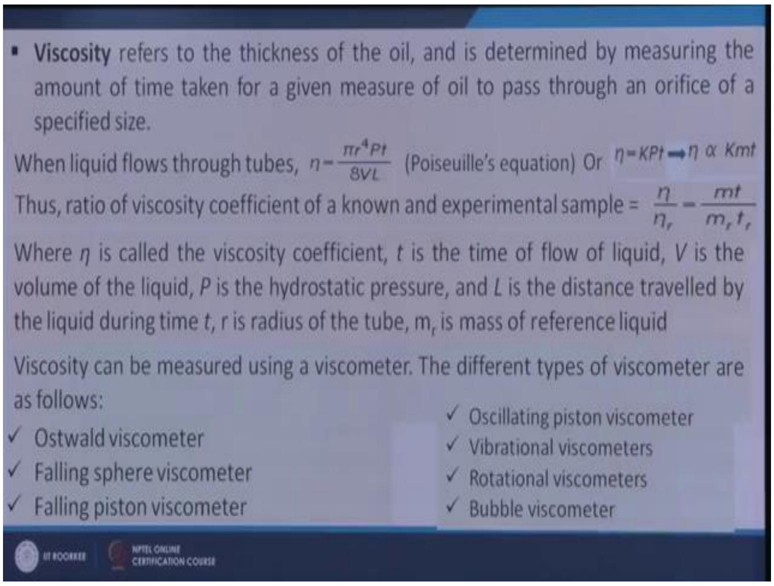

- **Viscosity** refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size.

When liquid flows through tubes, $\eta = \frac{\pi r^4 P t}{8VL}$ (Poiseuille's equation) Or $\eta = KPt \rightarrow \eta \,\alpha\, Kmt$

Thus, ratio of viscosity coefficient of a known and experimental sample = $\frac{\eta}{\eta_r} = \frac{mt}{m_r t_r}$

Where η is called the viscosity coefficient, t is the time of flow of liquid, V is the volume of the liquid, P is the hydrostatic pressure, and L is the distance travelled by the liquid during time t, r is radius of the tube, m_r is mass of reference liquid

Viscosity can be measured using a viscometer. The different types of viscometer are as follows:

- ✓ Ostwald viscometer
- ✓ Falling sphere viscometer
- ✓ Falling piston viscometer
- ✓ Oscillating piston viscometer
- ✓ Vibrational viscometers
- ✓ Rotational viscometers
- ✓ Bubble viscometer

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So, fluid say how much collected t is the time of flow to the tube t is the time, L is the distance travelled by the liquid during time. So, and R is the diameter of the tube. So, then p is the hydrostatic pressure, see if you know then we can get the viscosity coefficient. So, this term is equal to say constant pi R square for a particular system B L and R are constant. So, it is equal to k into p into t and p is hydrostatic pressure, hydrostatic pressure means that is again related to the density, so mass related to mass m by v. So, it is proposal to k into m into t.

If we have one fluid the viscosity is known to that and another one the bio diesel viscosity is not known, see if we use the same setup for the tasting then we get different mass collection at different time. So, viscosity ratio coefficient ratio will be beta by eta R that is equal to mt by mr tr, that is mr is the mass of the reference fluid and this is the mass of biodiesel time or the flow, and ts is tr is the time for the flow of the reference material. So, this is the principles through which the viscosity is measured, and there are number of viscosities the measurement instruments or the viscometers as listed here.

So, this is the comparison of properties of bio diesel from different vegetable oils, if you get from vegetable oil say soya bean oil and babassu oil it is given here.

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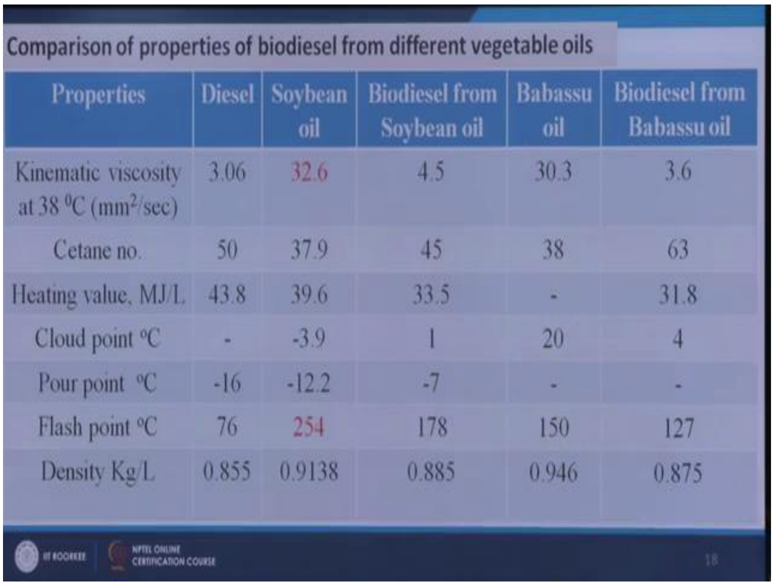

Comparison of properties of biodiesel from different vegetable oils

Properties	Diesel	Soybean oil	Biodiesel from Soybean oil	Babassu oil	Biodiesel from Babassu oil
Kinematic viscosity at 38 ^{0}C (mm^2/sec)	3.06	32.6	4.5	30.3	3.6
Cetane no.	50	37.9	45	38	63
Heating value, MJ/L	43.8	39.6	33.5	-	31.8
Cloud point °C	-	-3.9	1	20	4
Pour point °C	-16	-12.2	-7	-	-
Flash point °C	76	254	178	150	127
Density Kg/L	0.855	0.9138	0.885	0.946	0.875

So, diesel oil properties are given here. So, biodiesel from babassu oil is given and others oil soybean is given. So, here we see the flash point is very high for the bio-oil. So, upgradation is required after upgradations, we have been able to reduce the viscosity

32.6 to 4.5 and this is for bio this is for diesel 3.06 that is millimeter square per second. And flash point is 76, but here we have 254 to the bio-oil that is reduced to 176. So, that way the upgradations or bio-oil to bio diesel conversion helps to improve the properties and here is the comparison.

Now, will see the general flow sheet for bio diesel production from various feed stocks; so if we have say vegetable oils, if we have grease.

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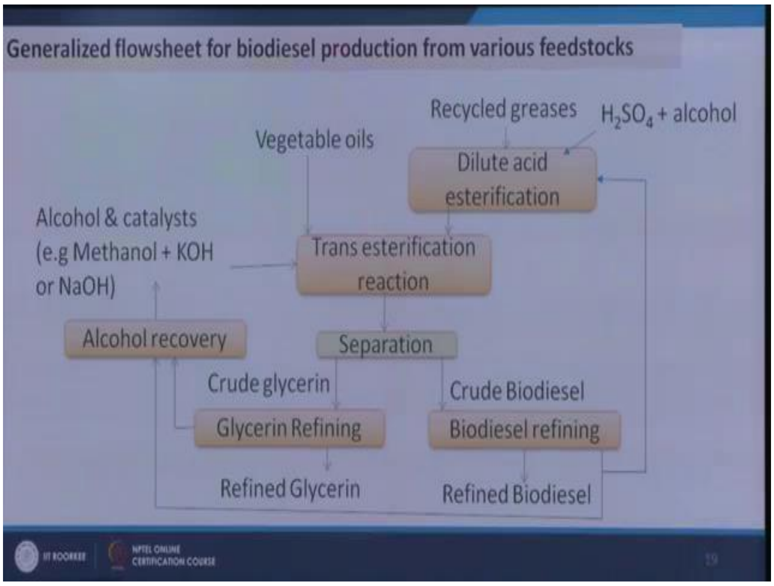

Generalized flowsheet for biodiesel production from various feedstocks

So, grease will be having some dilute acid esterification as I have discussed. So, the feed stocks will be going for transesterification reaction. After transesterification reaction we will be getting various products as we have discussed that the glycerol and alkyl esters the fatty acid esters of alkyls. So, those will be separated. So, one is glycerin and another is crude bio diesel. So, glycerin will be recovered and then glycerin will also be having recovered, and it the crude glycerin will be going to the alcohol recovery and then crude bio diesel will further be refined. And we will get the refined bio diesel will go for alcohol recovery and ultimately this is the flow sheet.

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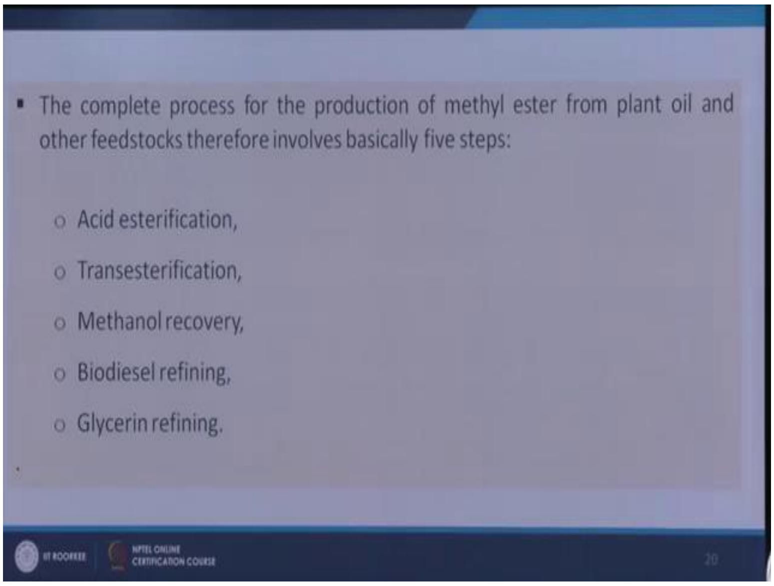

- The complete process for the production of methyl ester from plant oil and other feedstocks therefore involves basically five steps:
  - Acid esterification,
  - Transesterification,
  - Methanol recovery,
  - Biodiesel refining,
  - Glycerin refining.

And we have basically these are the steps, acid esterification transesterification methanol recovery biodiesel refining and glycerin refining. So, up to this in this part and the next part will discuss in next class.

Thank you very much.