## Course on Industrial Biotechnology Professor Debabrata Das Department of Biotechnology Indian Institute of Technology Kharagpur Lecture 52 Module 11 Biodiesel Production

Welcome back to my course on industrial biotechnology. Now in the last class I tried to discuss the cheese making process. Now I am going to switch over to the other type of products the one to you know that nowadays we have been facing lot of energy crises problem because because most of the energy where that we we use for our requirement usually comes from the fossil soil fossil fuels and if you look at this fossil fuel they have the restricted storage after sometimes this storage will be exhausted.

So naturally that that it is a major concern of the of the scientist that how we can generate the the alternative energy sources and it has been observed that renewable energy sources plays very important role and as per renewable energy sources that we have different type of renewable energy source first the things comes that is the solar energy, then we have this wind energy, then may be your (())(1:39) energy.

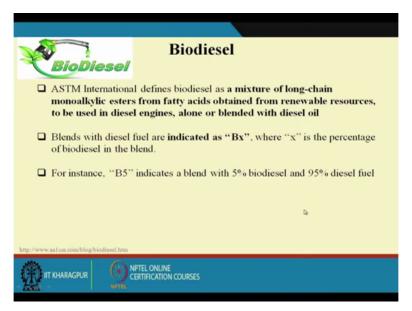
So different type of energy sources we have and renewable energy but one important thing is that biomass, biomass can be also used for different purpose because it can be also converted to some different energy source and what we consider is a bioenergy. Now now coming to lecture I shall concentrate on some two two type of chemical which largely used where as considered as a promising biofuels for the future one is biodiesel, another is (())(2:17) use as a good substitute for fuel.

Now in this lecture I try to concentrate on biodiesel and as per as per the biodiesel is concerned that it can be produced from different sources, it can be produced from vegetables from the seed we can it can be produced and and most and also it can be produced from the algae because the algae is you know we know that algae is considered as a third generation renewable energy sources because because major advantage with the algae that it required various small amount of land for the for the home growth of algae and we can produce quantity of lipid out of that and this lipid out of that and this lipid can be converted because lipid or fat that present in the algae or the or the oil seed that in presence of methyl alcohol

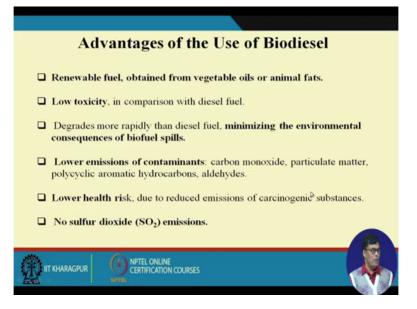
and catalyst it undergo kind transesterification process and it produce the biodiesel and glycerol this is the major product that we have of.

So this this lecture I try to concentrate on that and we will see that how this process is in operation as per India is concerned that we know that India government they are also because I told you that whatever (())(3:57) petroleum reserve we have in India it is for for limited period hardly for 30 years. So so government of India they encourage that for other type of energy sources and the biodiesel is one if the promising area and we know that jatropha and other oil source that largely explored to find out this biodiesel potentiality in India.

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So if you look at this biodiesel the ASTM International define biodiesel as a mixture of longchain monoalkylic ester of the fatty acid obtained from renewable resources to be used as at diesel engine, alone or blended with diesel oil. So you know that it can be used in combination or it can use separately. So blend with diesel indicates the Bx Bx x means percentage of biodiesel in the blend that means for instance if we say B5 indicate that a blend of 5 percent biodiesel and 90 percent 95 percent of diesel fuel when you then we call it B5. (Refer Slide Time: 5:25)

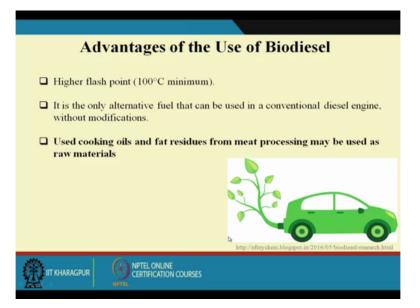


Now advantage of using biodiesel is the renewable fuel because it cannot be renewable means it cannot be exhausted because it will be available with respect to time it is available it not be exhausted that is why we call it renewable. So this will be with us throughout our existence and what we call sustainable this is quite sustainable for a longer period of time.

So renewable it is called renewable fuel, obtained from vegetable oil or animal fat, that low toxicity as compared to the diesel fuel and degrade more rapidly than than diesel fuel and and minimizing the environmental consequences that consequences of biofuel spills. That lower emission of contaminants like carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons and aldehydes.

Low health risk due to reduced of emission of carcinogenic substances and no sulphur dioxide emission because sulphur contain because in this because we know that whenever we run any kind of four wheeler or three wheeler we have seen lot of smell sometimes coming out that is mainly due to the presence of the sulphur present in the oil. So that kind of problems we will not get in case of biodiesel because it does any kind of sulphur source.

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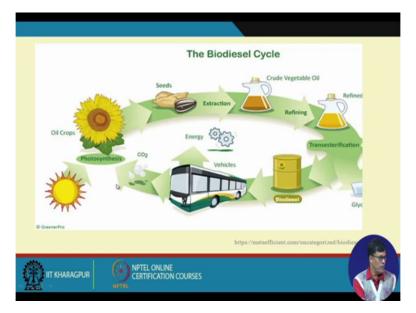


Now other advantages is that that it has the higher flash point 100 degree centigrade and it is only alternative fuel that can be use in a conventional diesel engine without modification that you know that you do not have to do any kind of modification because I told you when we use the ethanol ethanol also considered as a power alcohol but when it has been observed that upto 20 percent if you if you substitute the gasoline then whatever engine configuration is there that cannot be changed because you know with that configuration is good enough for running this gas engine.

But but when you when you go for higher then that then we shall have to we have to change the configuration of the engine. Now I can I have given the example of (())(7:46) does not have any kind of good petroleum. So they surely depend on this cane because they have larger they are the largest cane producer in the world and they produce the alcohol they produce from the cane molasses that that alcohol they largely use a power alcohol. So they changes the configuration of the engine so that largely they can use the ethanol due to a great extent for running this engine.

So here in case of biodiesel you do not have to do any kind of modification of the engine. Use of cooking oil and fat residue from meat processing may be used as a raw materials. Because sometimes we we have seen the we have seen different shops where we have different five material they use lot of cooking oil cooking oil and this cooking oil after sometimes it is not of edible quality. So this is this oil can be used for the generation of biodiesel.

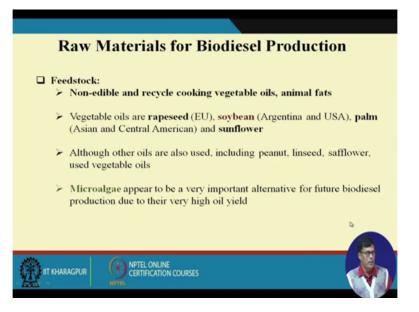
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Now this is the process that we have roughly it can be shows like this that is the seed that we produce from the plant that which containing good amount of oil this is the oil seed which comes from the plant and then we do the extraction of the oil so that we get the good vegetable oil. Then we refined this this oil within through the refining process and then it undergo transesterification I told you if presence of methanol and and kind of catalyst acid or alkalic catalyst, it can be converted to mono alkyl esters that is called this biodiesel and that can be used for the operation of vehicles.

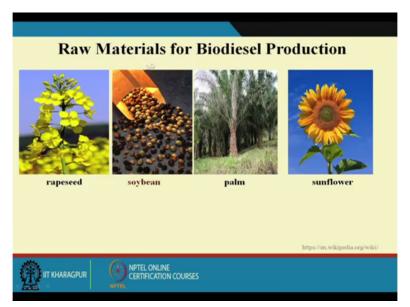
This is how again carbon-di-oxide whatever after after burning whatever carbon-di-oxide is produced that can be again utilized by the plant for this growth and we can get again this is how what you call biodiesel cycle we can have you know in our system.

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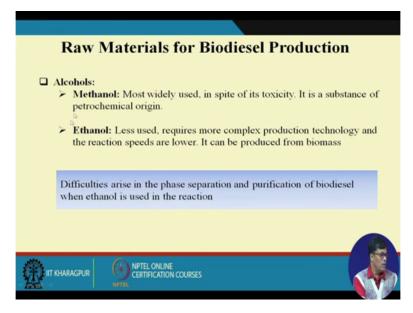
Now that you know the raw materials use for the biodiesel production that is non-edible and recycle cooking vegetable and the animal fat that is largely used. Vegetable oils are rapeseed oils soybean, palm and sunflower that is largely used. Although the other oil are also used including the peanut, linseed and safflower safflower then used for as a vegetable oil. Microalgae appears to be very important alternative for future biodiesel due to the high oil yield because you know that I told you at the beginning that algae algae can be grow in a it is considered as the third generation renewable energy source because it can grow in a very small area and and also the fat content is very high, so we can use for the biodiesel production.

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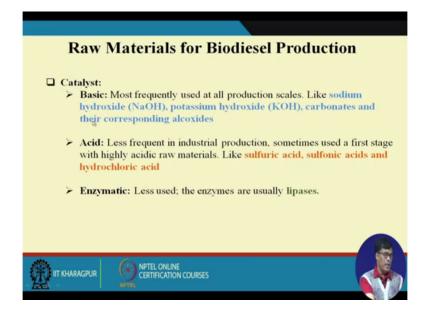
Now this is the raw materials that we have for biodiesel rapeseed how it looks, soybean, this is this is palm palm tree and this is sunflower this is used.

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The alcohol raw materials that is used the methanol the mostly widely used in spite of its toxicity is the substance used for petrochemical petrochemical origins. Ethanol is used very less amount because it required more complex production technology and reaction speeds are low. It can be produced from the biomass. Difficulties arises in the phase separation and purification of biodiesel where the ethanol is used in the reaction. So that is the reason why the methanol is mostly used for the biodiesel production, we do not used ethanol for the biodiesel mostly we use the methanol for this process.

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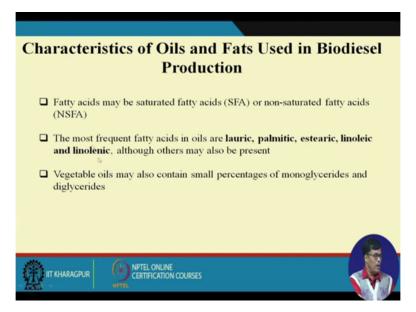
Now catalyst as I mentioned that it is used two types one is called basic, another is the acidic. Basic means most frequently used at all production scales like sodium hydroxide, potassium hydroxide, carbonate and their corresponding alcoxides. The acids that less frequency that is used that is sulphuric acid, sulfonic acid and hydrochloric acid. The enzymes that also used very less what you called lipase that we use to a great extent.

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Characteristics of Oils and Fats Used in Biodiesel Production
Oils and fats, known as lipids, are hydrophobic substances insoluble in water and are of animal or vegetal origin
□ From a chemical viewpoint, lipids are fatty glycerol esters known as Triglycerides $ \begin{array}{c} H_2C - OCOR_1 \\   \\ HC - OCOR_2 \\   \\ H_2C - OCR_3 \end{array} $
R <sub>1</sub> , R <sub>2</sub> and R <sub>3</sub> represent hydrocarbon chains of fatty acids
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Now youre your if you look at the oil that usually form usually remain in in the form of triglycerides, triglyceride is like this so it has different hydrocarbons that we have here. The different organic acid they form the esters here you can see that.

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And and the fatty acids this fatty acids are may be saturated, may be non-saturated. But one thing I want to point out here the usually the non-saturated fatty acid is usually preferable because if the saturated there is every every possibility of formation of solidification of the oil that is undesirable because the oil should remain always in the liquid form so that burning characteristics and other we do not have any problem.

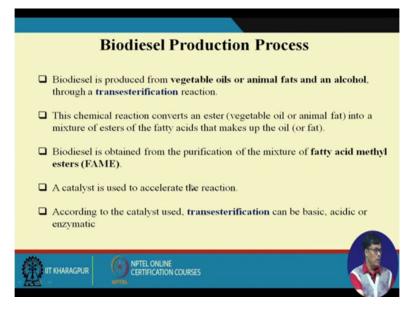
So the most frequent fatty acid in oil is a lauric acid, palmitic acid, estearic, linoleic and linolenic acid, although the others may also present. Vegetable oil may also contain small percentage of monoglycerides and diglycerides. They also contain not only triglycerides, they contain monoglycerides and diglycerides.

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Characteristics of Alcohols Used in Biodiesel Production		
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Alcohols that can be used in biodiesel production are those with s chains, including methanol, ethanol, butanol, and amylic alcohol	hort	
□ The most widely used alcohols are methanol (CH <sub>3</sub> OH) and ethanol (C <sub>2</sub> H <sub>5</sub> OH) because of their low cost and properties	ы	
Methanol: Most widely used, in spite of its toxicity. It is a substar petrochemical origin.	nce of	
Ethanol: Less used, requires more complex production technolog reaction speeds are lower. It can be produced from biomass.	y and the	

Non characteristics of alcohol used biodiesel, I told you that mostly the methanol is used we methanol is find mostly suitable because because it is it is more preferable in case of biodiesel production process.

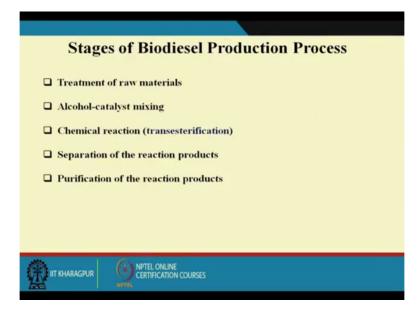
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The biodiesel is produced from the vegetable and animal fat or alcohol through the transesterification process. This reaction converts the esters into the mixture of esters of fatty acids that makes the oil. The biodiesel is obtained from the purification of the mixture of fatty acid methyl ester fatty acid methyl esters we call it FAME. A catalyst is used to accelerate the reaction. According to the catalyst used, transesterification can be basic, acidic or enzymatic.

So we have different type of this transesterification process because we we we convert that alcohol to one form to the ester form one form to other form that you know that is this takes place in place of acidic catalyst in presence of alcoholic catalyst or in presence of this what you call enzymatic like a lipase in presence of lipase also it can be produced.

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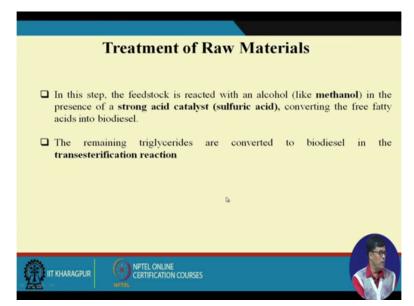
Stages involved for biodiesel production treatment of raw materials, alcohol catalyst mixing, chemical reaction what you call (transesterification), separation of the reaction product and purification of the reaction product. So these are the different steps involved for the biodiesel production.

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And first is the treatment of raw materials some feedstock must be pretreated before they go through the transesterification process, feedstock with less than 4 percent free fatty acid which include in the vegetable oil or some food-grade animal fat not required the pretreatment. But if required it has more than 4 percent fatty acid this required some kind of pretreatment before this process.

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Now treatment of raw materials in this step the feedstock is reacted with alcohol what you call methanol in the presence of strong acid catalyst like sulphuric acid which convert the free acid to biodiesel. So your the your organic acid is in presence of methanol it forms the ester methyl ester of that particular organic acid and that is we call is biodiesel. The remaining triglycerides is converted to biodiesel in the transesterification process.

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Chemical reaction (transesterification)	
A generic <b>transesterification reaction</b> is presented as follows	
<b>RCOOR'</b> + <b>R''OH</b> $\stackrel{Catalyst}{\leftrightarrow}$ <b>R'OH</b> + <b>RCOOR''</b>	
When methanol is the alcohol used in the transesterification process, the product of the reaction is a mixture of methyl esters	
$\Box$ If ethanol were used, the reaction product would be a mixture of ethyl esters	
□ In both cases, glycerin will be the co-product of the reaction	
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I shall show you the reaction of the process, it is like this that you can you can see that this is the ester that we have in the in the in the oil and in presence of suppose this is methanol, this is CH3OH, in presence of acid catalyst it produce the this this this suppose here you have monoglyceride we have some kind of alcohol is produced and from here we get some kind of esters of the methyl alcohol and this is called biodiesel this is called biodiesel and this is called transesterification process.

So here we have this ester and it changes to this ester. So trans one form of ester is changing to the other form of ester, so that is why we call it transesterification process. When the methanol is the alcohol used in the transesterification process the product of the reaction is a mixture of methyl esters. And and if you look at the catalyst the alcohol alcohol used for biodiesel production must be mixed with the catalyst before adding the oil.

So the alcohol must be water-free it should be anhydrous, the alcohol-to-oil volume ratio, R, is the another key variable in the transesterification process and it has been observed this should be 1 is to 4. The necessary amount of catalyst is determined taking into account of acidity of the oil by titration.

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<b>Chemical reaction (transesterification)</b>
$\begin{array}{ccc} H_2C - OCOR_1 & H_2C - OH & CH_3 - OCOR_1 \\   &   \\ \end{array}$
$HC - OCOR_2 + 3 CH_3OH \leftrightarrow HC - OH + CH_3 - OCOR_2$
$H_2C - OCOR_3$ $H_2C - OH$ $CH_3 - OCOR_3$
$H_{2}C - OCOR_{1}$ $H_{2}C - OH$ $CH_{2}CH_{2} - OCOR_{1}$
$HC - OCOR_2 + 3 CH_3 CH_2 OH \iff HC - OH + CH_3 CH_2 - OCOR_2$
$ $ $ $ $ $ $H_2C-OCOR_1$ $H_2C-OH$ $CH_3CH_2-OCOR_1$
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So this is the reaction that we have chemical reaction so this is the triglyceride you can see and in presence of methyl alcohol and KOH it it form the glycerol and we have this organic acid different organic acid, we have different esters, we have what you call methyl esters with the R1, R2 and R3 we form, this is biodiesel and this is so glycerine is the by-product of the biodiesel production process.

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Chemical reaction (transesterification)		
□ The temperature for <b>transesterification</b> at atmospheric pressure is usually in the range between 50 and 60°C.		
The absence of mono- and diglycerides at the beginning of the chemical reaction, the reaction confirm that the production of esters from the triglycerides takes place in three steps		
	$\mathrm{TG} + \mathrm{MOH} \mathop{\longrightarrow}\limits^{\mathrm{KOH}} \mathrm{DG} + \mathrm{ME}$	
	$\text{DG} + \text{MOH} \xrightarrow{\text{KOH}} \text{MG} + \text{ME}$	
N	$MG + MOH \xrightarrow{KOH} G + ME$	
Where MOH indicates methanol, ME are the methyl esters, TG, DG and MG are tri-, di- and monoglycerides, respectively, and G is the glycerin		
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The temperature of transesterification at atmospheric pressure usually in the range of 50 to 60 degree centigrade. The absence of mono and diglyceride at the beginning and the chemical reaction, the reaction confirm the production of esters from the triglycerides takes place in

three steps. This is the triglyceride, then this is the methyl alcohol this form diglycerides and methyl ester.

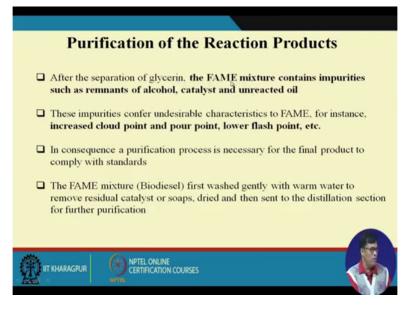
Then diglycerides in the methyl alcohol in presence of KOH it produce monoglycerides and the methyl esters and monoglycerides and methyl alcohol it produce glycerine and the methyl ester, this is how it if formed.

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Separation of the Reaction Products	
The separation of reaction products takes place by decantation: the mixtur fatty acids methyl esters (FAME) separates from glycerin forming two pl (because of different densities)	
FAME floats up at the top while glycerin settles down at the bottom. the phases may be physically separated	two
□ In some cases, a centrifuge is used to separate the two materials faster.	
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The separation of the reaction products the separation of reaction product takes place by decantation the mixture of fatty acid methyl esters separate from the glycerine forming two phases. And FAME floats up at the top of the glycerine settle down at the bottom the two phases may be physically separated. In some cases, centrifugation is is used to separate the two materials faster. So this is how we can separate the glycerol from the biodiesel.

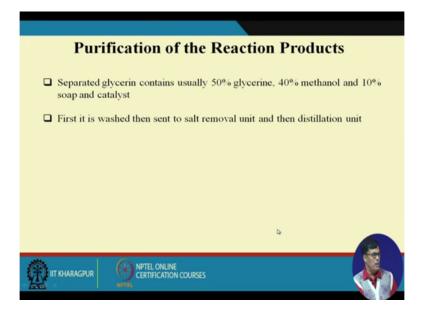
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Now purification of the product is like this after the separation of glycerine, the FAME mixture contains the impurities of some kind of alcohol, catalyst and unreacted oil. So this is to be separated out. These impurities confer the undesirable characteristic of FAME, for instance, increases the cloud point the pour the pour point and flash point that lower the flash point. In consequence a purification process is necessary for the final product complying the standard.

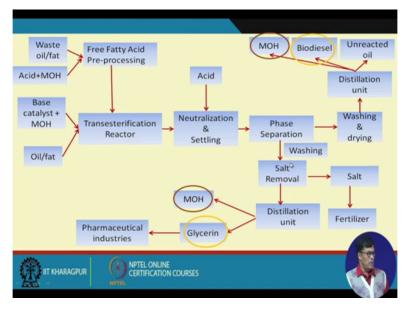
The FAME mixture what you call biodiesel first washed gently with warm water to remove the residual catalyst or soap, dried and then sent to the distillation section of the further purification.

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The purification of this product the glycerine contains about 50 percent glycerine, 40 percent methanol and 10 percent soap and catalyst. So this this even we want to use glycerine we we can separate the glycerine through phase separation process but this remain in the mixture. So this is can be separate methanol can be separated the distillation process and this can the soaps and catalyst can be used by using by washing with water. First it is washed then the salt is removal unit, then the distillation unit.

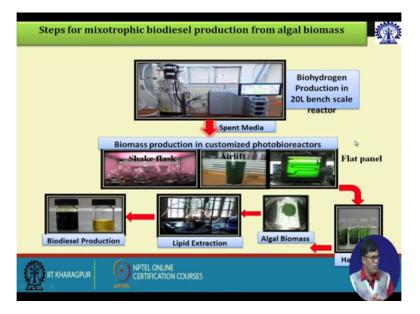
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Now this process schematic that you know if you look at the flow diagram it look block flow diagram is like this we have waste fat and oil, we have that acid and methyl alcohol, the free fatty acid pre-processing, then base catalyst and oil fat all this way you can do that it comes to the transesterification reactor, then we do the acid for neutralization and settling, then we have the phase separation in phase separation we do the the washing and drying and distillation we get the methyl alcohol, we get biodiesel, we get the unreacted oil.

And and this phase separation we can have the salt removal again we have some some distillation unit from which we get the glycerine as a (())(23:05) and methyl alcohol as the distil product and this is this glycerine can be used in the pharmaceutical industries, this is the kind of block flow diagram that we have in the biodiesel production.

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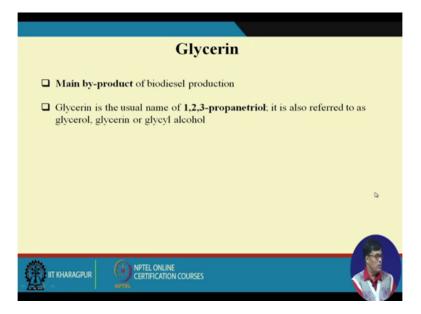


Now I was talking about that you know microalgae also can be produced produced for the biodiesel production, we have been working with this algal fermentation process for more than a decade and we we had the collaboration I mentioned with the Oslo university, also the Uppsala university Sweden and also we have the collaboration with the technical university of Denmark.

Now we try to explore how this microalgae can be used for the biodiesel production, our process is very simple that this is the process one process we we there are three different process through which the algae can be produced I one is called autotrophic, another we call heterotrophic, another is the mycotrophic. Now during the spirulina production I I discussed this process in details, here I showed you the mycotrophic process where the organic material mixed organic material can be used as a raw materials for the growth of algae. So here what is happening this we we have been walking on bio hydrogen production process for more than 2 decades and we produce different organic waste and we convert it into hydrogen and after the fermentation is over whatever the metabolites present in the fermentation broth we take in the this photobioreactor and then here we grow this algae and algae can be growth in different reactors you can see it is the shake flask, then airlift reactor and flat panel reactor we get the biomass.

Then biomass is separated through the harvesting process and through harvesting we get the cell mass and this cell mass we contains good amount of lipid we through we extract the the oil from that and through the distillation process or or from the solvent recovery process and then we use this oil convert this oil to biodiesel through the transesterification process.

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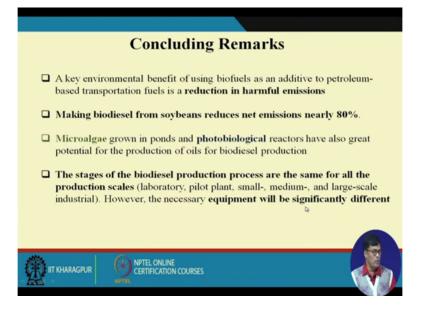
So glycerine is the main by-product of the biodiesel production process.

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Uses of Glycerin		
In the pharmaceutical industry, for the manufacture of ointments, creams and lotions		
In the food industry, for the manufacture of sweets, soft drinks, and pet foods and in the conservation of canned fruit		
□ As an additive in the manufacture of soaps, to improve their properties		
□ In the manufacture of nitroglycerin for the production of explosives		
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Now use of glycerine has several in the pharmaceutical industry for the manufacturing of ointment, creams and lotion. In food industry, for the manufacturing of sweet, then soft drinks and pet foods like and in the in the conservation of canned fruits. It is used as a additive for the soap, different type of glycerine soaps is already available in the market. And it is also used for the production of nitro-glycerine for the production of explosives.

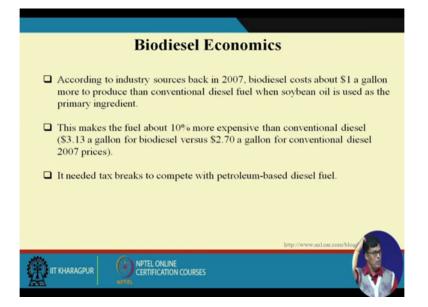
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Now in conclusion I want to tell that a key environmental factor key environmental factor of using biofuel has an additive for the petroleum based transportation fuels is a reduction of harmful emission. And biodiesel is a process through which we can reduce the harmful emission to a great extent particularly particulate matters, carbon-di-oxide and sulphur contains in the sulphur dioxide contain in the the flue gas in the in the the gas coming out (()) (27:07) the burning.

The microalgae grow on grown on in ponds and photobiological reactor have been a great potential for the production of oil for biodiesel production. The stages of biodiesel production process are the same for all production scales laboratory, (())(27:25) small, medium, large scale however the necessary equipment will be necessary for the different purpose.

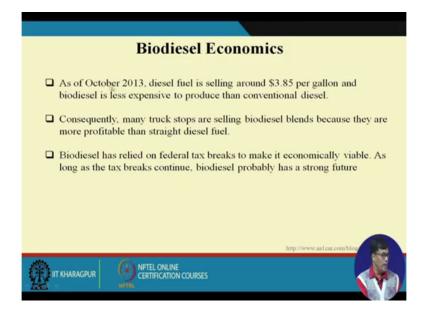
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The biodiesel economy is concern then according to the industry sources back 2007, that biodiesel cost is about 1 ton a gallon more to produce conventional diesel fuel when soybean oil is used as a primary ingredient. This makes the fuel about 10 percent more expensive than the conventional diesel and it need tax breaks to compete with the petroleum based diesel fuel because since the since the diesel has the some kind of advantage for safeguarding the environmental pollution problem.

So if we can get some kind of incentive from the government then price we can this price can be can be matched with the price that that is we have in case of diesel available in the market.

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And in October 2013 the diesel fuel is selling around 3.85 per gallon and biodiesel is less expensive to produce than the conventional diesel. Consequently, many truck truck stops selling this biodiesel blends because they are not profitable than straight diesel fuel. The biodiesel has relied on federal tax break to make it economically viable. As long as tax breaks tax breaks continues, then biodiesel probably has a strong future because this this is this is a environment the great concern nowadays and and and it not only affects our health but also it affects the environment to a great extent because particularly carbon-di-oxide that is coming out that causes some kind of global warming, that is also we have.

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Further reading	
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So this problem is a is a great concern, so I request you you can visit this particular website to get the information more on biodiesel production. So in conclusion what I want to tell that biodiesel is considered as a very effective that fuel for running the vehicles you do not require have to modify the engine because whatever engine is used for diesel that can be replaced by the biodiesel, the only that thing is that we shall have to work out that the suitable sources for the biodiesel production the sources are vegetable oil and the animal oil. The vegetable if we make it cheaper than our biodiesel also will be cheaper.

The oil can be converted to biodiesel very easily with the help of methyl alcohol and the acid catalyst largely used for the it can be used by using alkali and and enzyme but that is not used in the industry because we find acid is more favourable as compare to other two processes. So and this has this has the pollution problem as compare to diesel the biodiesel has some benefit so so we consider that biodiesel has greater future and also we try to explore that how the microalgae can be used for the biodiesel production, the microalgae might be the one of

the important area because we know the microalgae can grow more faster as compare to plant cell or biomass the plant biomass.

So if you can grow this algae in in reactor very fast then we can have more and it contain high lipid and fats then that can be used for biodiesel production. So that is all about the biodiesel in the next class I shall discuss ethanol biomethanol production, thank you.