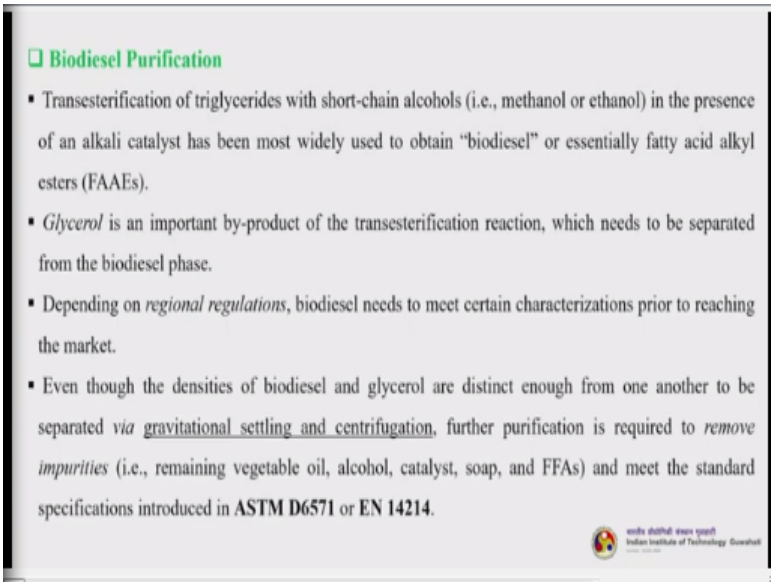
Biomass Conversion and Biorefinery
Prof. Kaustubha Mohanty
Department of Chemical Engineering
Indian Institute of Technology-Guwahati

Module-07
Lecture-21
Biodiesel Purification Fuel Properties

Good morning students. Today is lecture 3 under module 7 and as you know that we are discussing biodiesel under module 7. Today we will be discussing about the biodiesel purification and fuel property. So, let us begin.

(Refer Slide Time: 00:39)

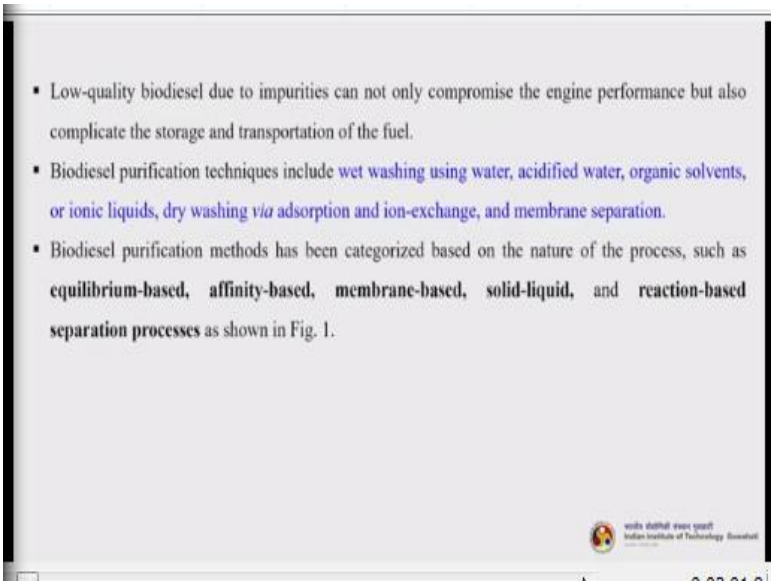


Transesterification of triglycerides with short chain alcohols, that is either methanol or ethanol in the presence of an alkali catalyst has been most widely used to obtain biodiesel or essentially we can say that fatty acid alkyl esters. So, glycerol is an important byproduct of the transesterification reaction which needs to be separated from the biodiesel phase.

So, if you recall in our last class, we have discussed extensively how transesterification reactions happen, what are the different types of reactions, acid catalyzed, base catalyze and everything. So, depending upon the regional regulation biodiesel needs to meet certain characterization prior to reaching the market. Regional regulations essentially means every country has their own regulations and fuel standards, so that you have to meet.

So, even though the densities are biodiesel and glycerol are distinct enough from one another to be separated via gravitational settling and centrifugation, further purification is required to remove impurities? So what are those impurities? Now the remaining vegetable oil, alcohol, catalyst, a little bit quantity of the soap and the free fatty acids which are not purified and meet the standard specification introduced in the ASTM D6571 or EN 14214. So, ASTM is the American Society for testing and materials, and EN is the European standards, any one of these.

(Refer Slide Time: 02:01)



Low quality biodiesel due to impurities cannot only compromise the engine performance, but also complicate the storage and transportation of the fuel. Biodiesel purification techniques include wet washing using water, you can use acidified water also, some organic solvents or ionic liquids, the ionic liquids are a bit costly. Or else you can use dry washing via adsorption or ion exchange and membrane separation.

Now biodiesel purification method has been characterized based on the nature of the process such as either equilibrium based, affinity based, membrane based, solid-liquid or reaction separation based.

(Refer Slide Time: 02:39)

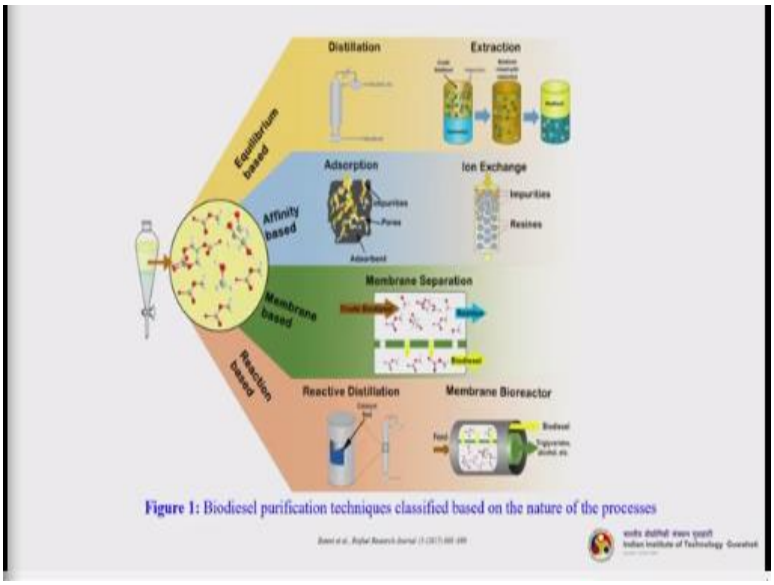


Figure 1: Biodiesel purification techniques classified based on the nature of the processes

So, as shown in the figure. So, this figure I will explain you. You can see this, this is the classical representation of how the biodiesel can be purified, so as to get high purity biodiesel**.** So, 4 things have been shown here, 4 different types or distinct separation processes equilibrium based, so it is distillation. You can see that crude biodiesel, impurities are present, so the biodiesel mixed with solvent, then it will be purified.

Then affinity based is basically adsorption, so AD. So, here you will use different types of adsorbents to remove the impurities. So, all the impurities will be adsorbed either in the surface of the adsorbent or it may get inside the pores also. So, then you or you can have ion exchange also. So, either you can have cation exchange bed, you can have anion exchange bed, so it is a packed bed system, where the impurities will be attached to the ion exchange resins and biodiesel will be purified.

Then membrane based: Membrane has often taken a very important role in most of the process industries using chemicals, pharmaceuticals, then food and beverage industries. Now in this case also biodiesel also can be purified using different types of membrane system maybe ultrafiltration, nanofiltration and others where the beauty of the membrane separation is that you can tailor make membrane to target a specific separation.

So, either you can retain them on the top, all the impurities, or you can pass them to the permeate side depending upon the pore size. Then the last one is reaction based which is called reactive distillation. So, reactive distillation is a distillation process where reaction and distillation both are happening in the same chamber or the same unit, we will discuss this in detail later on or we can have membrane bioreactor.

So, here feed is being processed, feed is being fed to the membrane bioreactor where the biodiesel is getting produced as well as getting purified in a single system**.** So, we will discuss one by one.

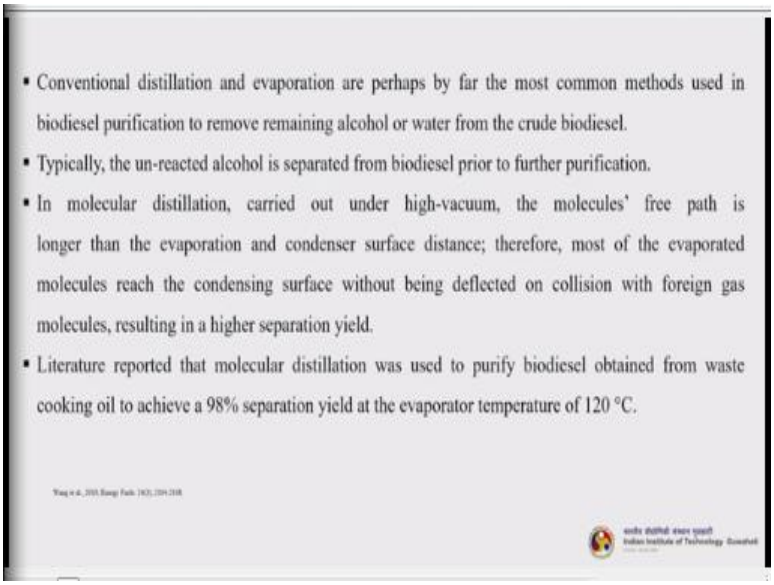
(Refer Slide Time: 04:48)

So, let us discuss the first one which is equilibrium based separation process. So, absorption and distillation as well as supercritical fluid extraction and liquid-liquid extraction are some of the most common equilibrium based separation processes. Absorption is commonly utilized for separating particles and impurities from a gaseous mixture, therefore it does not have a major application in the biodiesel separation which is a liquid phase process.

Let us talk about distillation. So, distillation is the most common method for separation of more volatile compounds from heavier substances in a liquid mixture. There are different distillation techniques including conventional distillation, which are ordinary, vacuum or steam distillation

or azeotropic distillation - if at all the feed streams have formed azeotropes (close boiling point mixtures basically) or you can go for extractive distillation or molecular distillation.

(Refer Slide Time: 05:37)



Now conventional distillation and evaporation are perhaps by far the most common methods used in biodiesel purification to remove the remaining alcohol or water from the crude biodiesel. Typically, the unreacted alcohol is separated from biodiesel prior to further purification. In molecular distillation carried out under high vacuum the molecules' free path is longer than the evaporation and condenser surface distance; therefore, most of the evaporated molecules reach the condensing surface without being deflected on collision with foreign gas molecules resulting in a higher separation yield. Literature reported that molecular distillation was used to purify biodiesel obtained from waste cooking oil to achieve a 98% separation yield at the evaporator temperature of 120 degree. So, if you look at the literature, you will find there are plenty of works when biodiesel has been purified.

Basically the glycerol has been removed. Glycerol is already removed, when you are talking about purification stuff we are just removing the unconverted vegetable oils, some free fatty acids, then alcohol - very important. So, all these things are being very successfully removed by distillation process. Now in certain cases, it has been also observed that distillation followed by another unit operation where it can be treated as a last polishing step to further sometimes you

may have to dehydrate it and some other polishing steps are necessary, so as to get a purified biodiesel.

(Refer Slide Time: 07:04)

So, then is LLE which is called liquid-liquid extraction. So, it is also known as the solvent extraction - is a well-established separation technique to extract desirable components from a liquid feed to a specific solvent. So, this process is the most common method used for biodiesel purification that encompasses all the techniques developed for wet washing. The use of deionized water to remove soap, catalyst, alcohol and other contaminants of biodiesel is one of the most common biodiesel purification methods.

So, water temperature and volume are the key factors in improving purification of the biodiesel phase. So, I will show you one table where we will see the negative effects of contaminants on biodiesel and engines and why we are talking about purifying it?

(Refer Slide Time: 07:43)

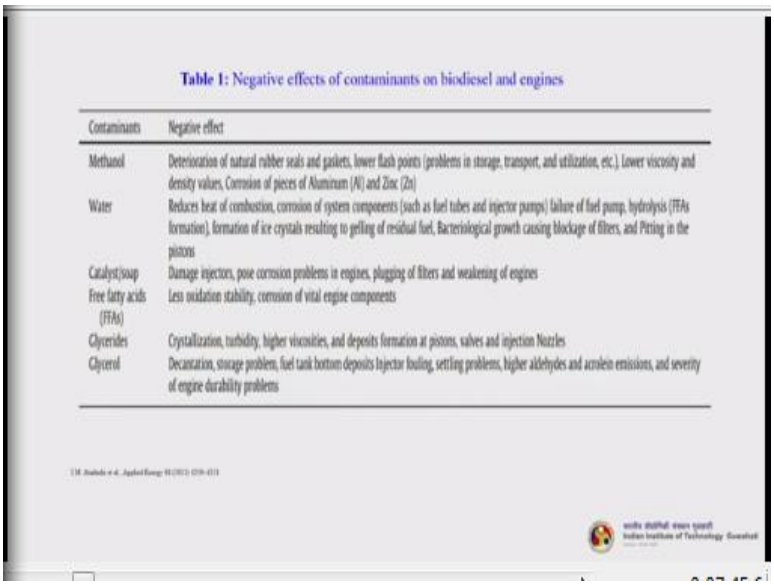


Table 1: Negative effects of contaminants on biodiesel and engines

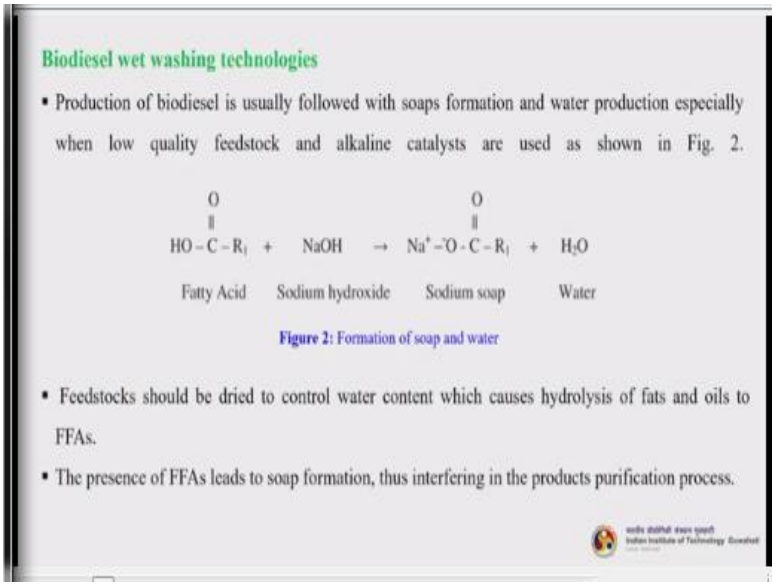
Contaminants	Negative effect
Methanol	Deterioration of natural rubber seals and gaskets, lower flash points (problems in storage, transport, and utilization, etc.), Lower viscosity and density values, Corrosion of pieces of Aluminum (Al) and Zinc (Zn)
Water	Reduces heat of combustion, corrosion of system components (such as fuel tubes and injector pumps) failure of fuel pump, hydrolysis (FFAs formation), formation of ice crystals resulting to gelling of residual fuel, Bacteriological growth causing blockage of filters, and Pitting in the pistons
Catalyst/soap	Damage injectors, pose corrosion problems in engines, plugging of filters and weakening of engines
Free fatty acids (FFAs)	Less oxidation stability, corrosion of vital engine components
Glycerides	Crystallization, turbidity, higher viscosities, and deposits formation at pistons, valves and injection Nozzles
Glycerol	Decantation, storage problem, fuel tank bottom deposits Injector fouling, settling problems, higher aldehydes and acrolein emissions, and severity of engine durability problems

So, you can see that the methanol remains in a quantity which is more than that is desirable. Of course, it is desirable that you remove all methanol, water, any catalyst, free fatty acids everything. So, if methanol is present, then the deterioration of the natural rubber seals and gaskets, lower flash points, problem in storage basically corrosion of pieces of alumina and zinc, all these things will happen.

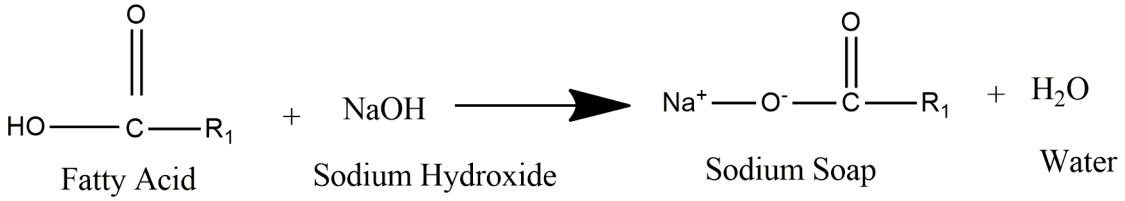
If water will remain in more quantity, then it will reduce the heat of combustion, corrosion of system components, formation of ice crystals, bacteriological growth will also happen if water is present. Then if the catalyst or soap remains then it will damage the injectors, it will pose corrosion problems in engines, plugging up filters and weakening of the engines. If free fatty acids are present then it will reduce the oxidation stability, it will also create corrosion problem in the vital engine components.

Similarly, glycerides and glycerols, so all these things will lead to crystallization, decantation, storage problems and has to be removed.

(Refer Slide Time: 08:48)

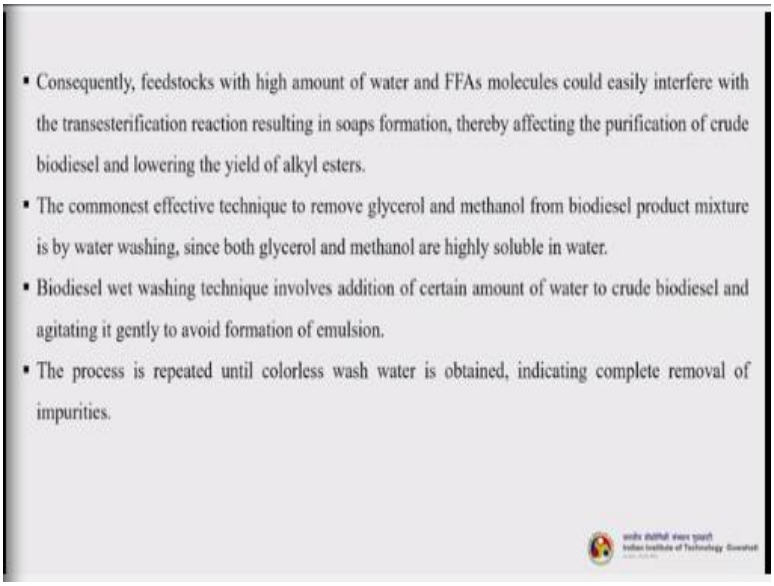


So, let us now understand the wet washing technologies. So, production of biodiesel is usually followed with soaps formation and water production especially when low quality feedstock and alkaline catalysts are used as shown in the figure**.** So, this is a fatty acid, so you are using sodium hydroxide as the catalyst, you get the sodium soap and then water.



So, feedstocks would be dried to control water content, which causes hydrolysis of fats and oils to free fatty acids. The presence of free fatty acids leads to soap formation, thus interfering in the products purification process.

(Refer Slide Time: 09:24)

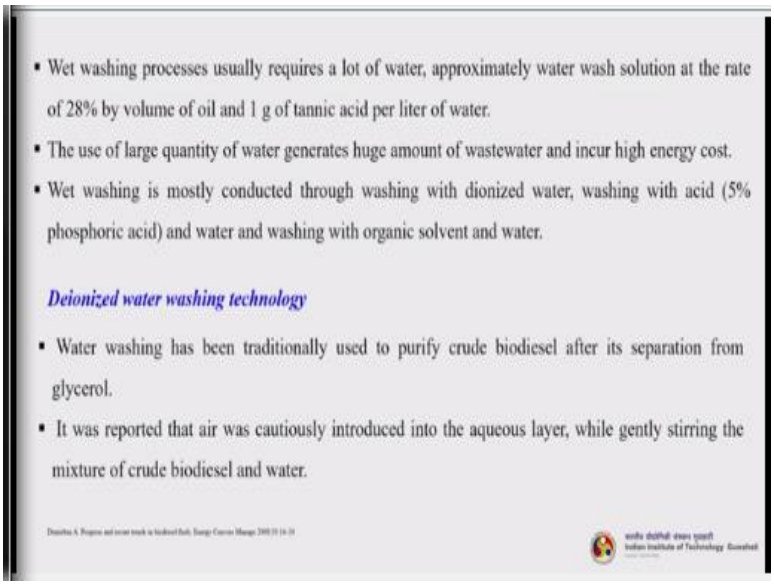


Consequently, feedstocks with high amount of water and free fatty acids molecules could easily interfere with the transesterification reaction, resulting in soaps formation thereby affecting the purification of crude biodiesel and lowering the yield of the alkyl esters. The commonest effective technique to remove glycerol and methanol from biodiesel production mixture is by water washing, since both glycerol and methanol are highly soluble in water.

Biodiesel wet washing technique involves addition of certain amount of water to crude biodiesel and then agitating it gently to avoid formation of emulsion, you have to be very careful beyond certain rpm or rotations per minute. If you do that, then there will be a emulsion formation because it is oil and water will mix with each other and it will form an emulsion. You can observe in the naked eye also, some whitish or milky color formation will start, so that is not actually required.

So, you have to be very careful about the agitation speed. So, the process is repeated until colorless wash water is obtained, indicating complete removal of the impurities.

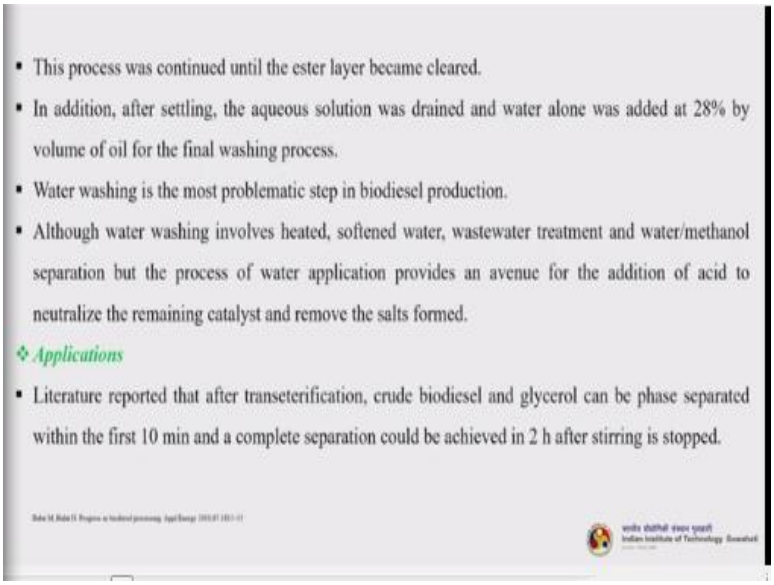
(Refer Slide Time: 10:26)



So, wet washing process usually requires a lot of water approximately water wash solution at the rate of 28% by volume of oil, and 1 gram of tannic acid per litre of water. The use of large quantity of water generates huge amount of wastewater and incur high energy cost, because again you need to process this wastewater. So, wet washing is mostly conducted through washing with deionized water, washing with acid (5% usually phosphoric acid) and water and washing with organic solvent and water**.**

Anyone you can do, either with pure deionized water or with the 5% phosphoric acid mixed water or organic solvent and water mixture. So, let us talk about that deionized water washing technology. Water washing has been traditionally used to purify crude biodiesel after its separation from glycerol. It was reported that air was continuously introduced into the aqueous layer, while gently stirring the mixture of crude biodiesel and water. In one of the significant work for which the reference has been given here.

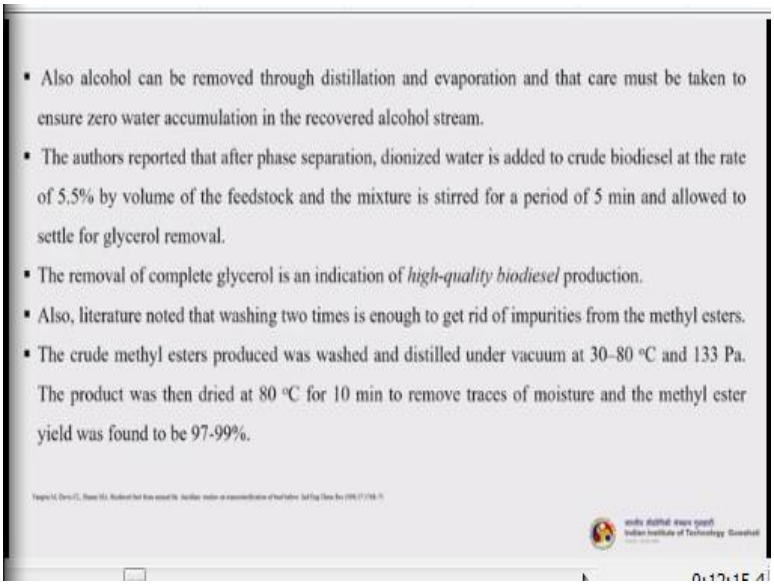
(Refer Slide Time: 11:24)



So, this process was continued until the ester layer becomes clear. In addition, after settling the aqueous solution was drained and water alone was added at 28% by volume of oil for the final washing process. Water washing is the most problematic step in biodiesel production, although water washing involves heated, softened water, wastewater treatment and water methanol separation, but the process of water application provides an avenue for the addition of acid to neutralize the remaining catalyst and remove the salts formed.

Though it has certain drawbacks as we have mentioned, but it is still preferred because of the low cost and it is efficiency, it is a benign process, it is easy to carry out. So, if you talk about applications, literature reported that after transesterification crude biodiesel and glycerol can be phase separated within the first 10 minute, and a complete separation could be achieved in 2 hours after stirring is stopped.

(Refer Slide Time: 12:14)

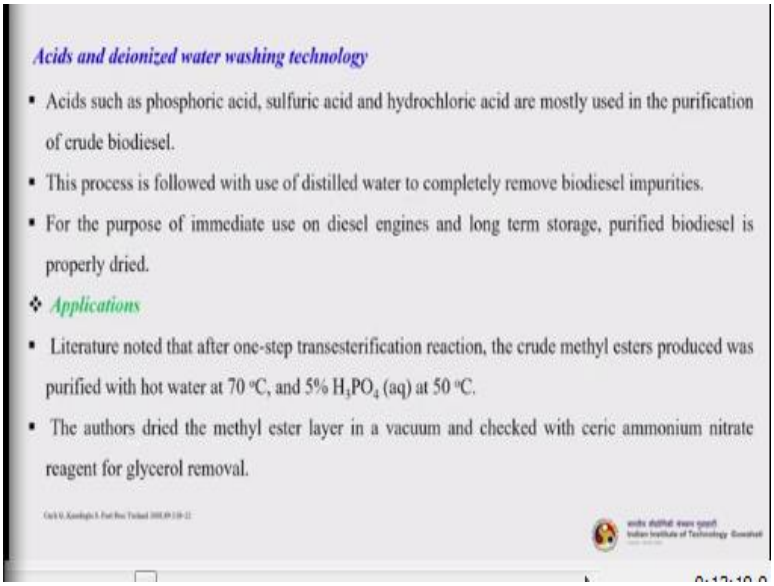


Also alcohol can be removed through distillation and evaporation and that care must be taken to ensure zero water accumulation in the recovered alcohol stream. Authors reported that after phase separation deionized water is added to crude biodiesel at the rate of 5.5% by volume of the feedstock and the mixture is stirred for a period of 5 minutes and allow to settle for glycerol removal.

This is the procedure which is reported in this particular reference which is given here**.** The removal of complete glycerol is an indication of high quality biodiesel production. Also literature noted that washing two times is enough to get rid of impurities from the methyl esters. The crude methyl ester produced was washed and distilled under vacuum at 30 to 80 degrees centigrade and 133 Pascal.

The product was then dried at 80 degrees centigrade for 10 minute to remove traces of moisture and the methyl ester yield was found to be 97 to 99% which is an excellent yield. So, you can please refer to this particular reference, which is reported in the industrial engineering chemistry research journal in 1998, long back but it is a classic study.

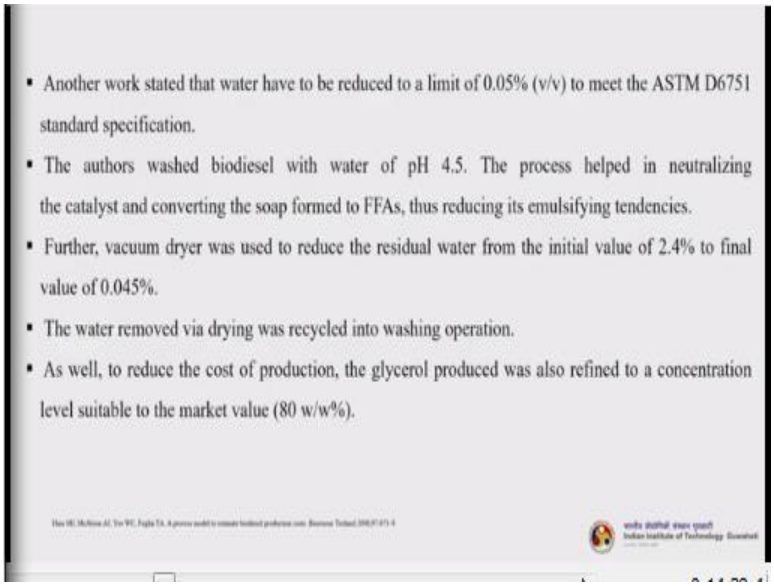
(Refer Slide Time: 13:19)



So, then acids and deionized water washing technology. Acids such as phosphoric acid, sulfuric acid and hydrochloric acid are mostly used in the purification of crude biodiesel. This process is followed with the use of distilled water to completely remove biodiesel impurities. For the purpose of immediate use on diesel engines and long term storage purified biodiesel is properly dried.

If you talk about applications, then literature noted that after one-step transesterification reaction, the crude methyl esters produced was purified with hot water at 70 degrees centigrade and 5% phosphoric acid at 50 degrees centigrade. The authors dried the methyl ester layer in a vacuum and checked with ceric ammonium nitrate reagent for glycerol removal and the reference has been given here. It is also a very interesting work reported in the fuel processing technology journal in 2008.

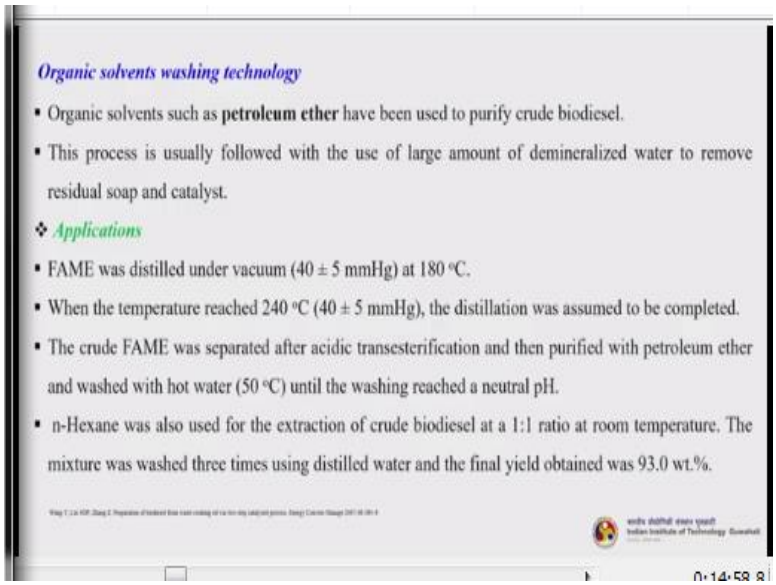
(Refer Slide Time: 14:08)



Another work stated that water have to be reduced to a limit of 0.05% volume by volume to meet the ASTM D6751 standard specification. The authors washed biodiesel with water at a pH 4.5, the process helped in neutralizing the catalyst and converting the soap formed to free fatty acids, thus reducing it is emulsifying tendencies. So, one of the major aim of this work is to reduce the emulsification.

So, further vacuum dryer wash used to reduce the residual water from initial value of 2.4% to a final value of 0.045%. The water removed via drying was recycled into washing operation. As well, to reduce the cost of production, the glycerol produced was also refined to a concentration level suitable to the market value, that is approximately 80 weight by weight percent.

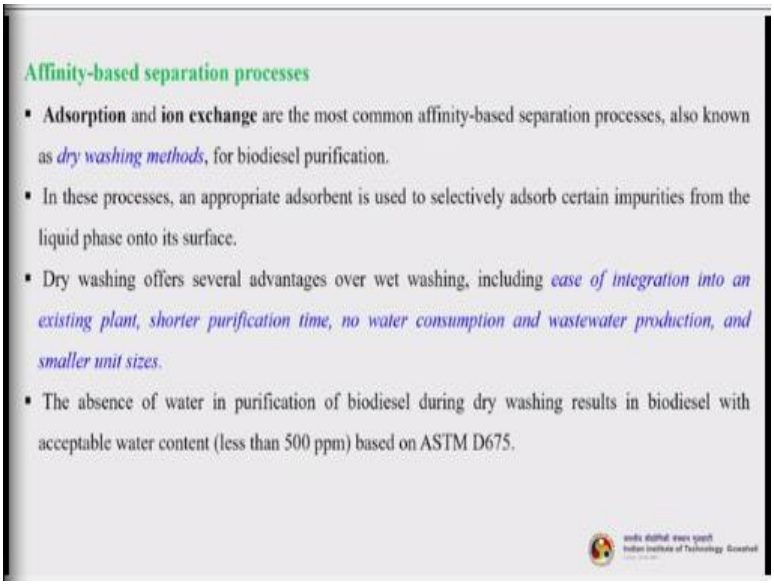
(Refer Slide Time: 14:56)



So, the next is organic solvent washing technology. Organic solvents such as petroleum ether has been used to purify crude biodiesel. Now this process is usually followed with the use of the large amount of demineralized water to remove residual soap and catalyst. So, let us talk about some applications. The fatty acid methyl esters was distilled under vacuum at 180 degrees centigrade, when the temperature reached 240 degrees centigrade, that distillation was assumed to be completed.

The crude FAME was separated after acidic transesterification and then purified with petroleum ether and washed with hot water until the washing reached a neutral pH. n-Hexane was also used for the extraction of crude biodiesel at 1 : 1 ratio at room temperature, the mixture was washed three times using distilled water and the final yield obtained was 93 weight percent. So, the references also been given, it is also an excellent work published in energy conversion management journal in 2007.

(Refer Slide Time: 15:50)



So, let us go ahead and talk about other separation processes. We will talk about affinity based separation process. So, adsorption and ion exchange are the most common affinity based separation processes, also known as that dry washing methods for biodiesel purification. In these processes an appropriate adsorbent is used to selectively adsorb certain impurities from the liquid phase onto it is surface.

As you know that adsorption is a very selective process and you can also make certain adsorbents, so as to target a specific impurity. Dry washing offers several advantages over wet washing which includes the ease of integration into an existing plant, shorter purification time, no water consumption and wastewater production and smaller unit sizes. The absence of water in purification of biodiesel during dry washing results in biodiesel with acceptable water content, which is less than 500 ppm that is based on the ASTM D675 standard.

(Refer Slide Time: 16:46)

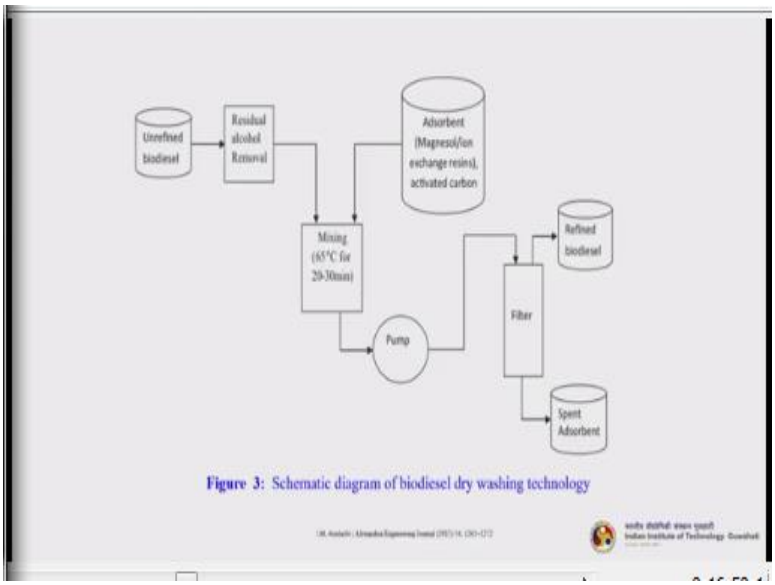


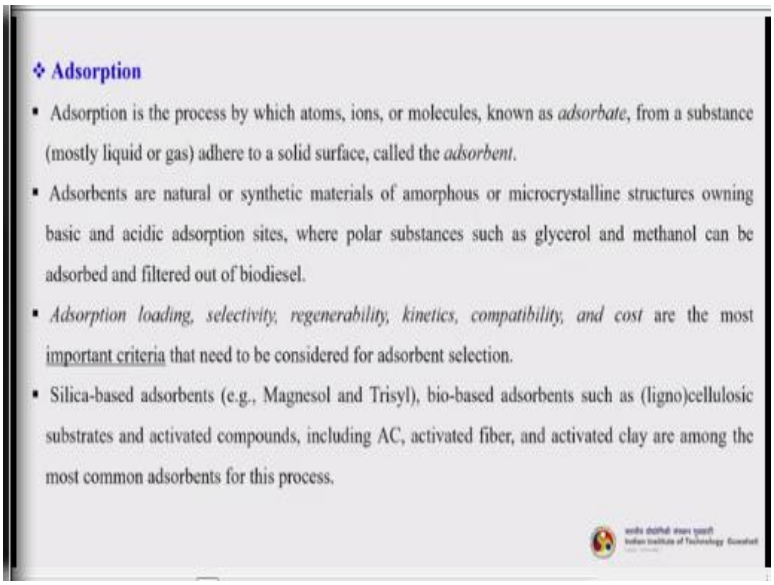
Figure 3: Schematic diagram of biodiesel dry washing technology

This is a simple schematic diagram of the biodiesel by dry washing technology. So, you can see this unrefined biodiesel which is produced. So, then it goes to the residual alcohol, removal. Initially you will remove alcohol, most probably this will be a distillation unit. Then you mix it and goes for a mixing unit, so at 65 degrees centigrade for 20 to 30 minutes with a certain agitation speed which should also take care that emulsification should not happen, so the speed should be less than that.

Then you can add the adsorbent here, basically it can be magnesol ion exchange resins, activated carbon. It can be in a suspended mode, in the liquid phase or you can go for a packed bed. Usually many commercial scale applications are all packed bed units**.** Then whatever it is coming out from the stream that goes to a filter section where you get the refined biodiesel, and here spent adsorbent can be recovered and regenerated and can be reused back.

So, it is the simplfied system again, as I told you many times that whenever I am showing any sketches, so there in between so many small, small unit operations and steps, which are not usually shown in that schematic diagram because it is easy to understand in nutshell if the schematic representation is concentrated only the major unit operations.

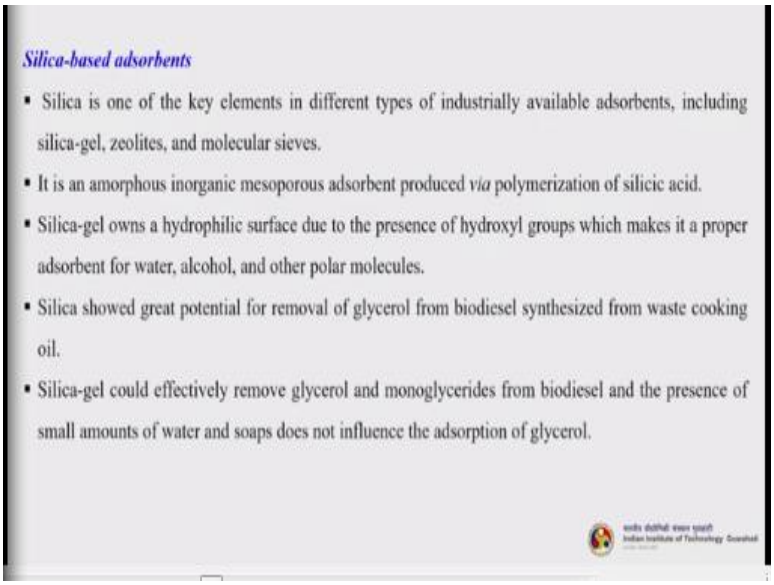
(Refer Slide Time: 18:14)



So, let us talk about adsorption. Adsorption is the process by which atoms, ions or molecules known as adsorbate, from a substance mostly liquid or gas adhere to a solid surface called as adsorbent. Adsorbents are natural or synthetic materials of amorphous or micro crystalline structures, owning basic and acidic adsorption sites, where polar substances such as glycerol and methanol can be adsorbed and filtered out of the biodiesel.

Adsorption loading, selectivity, regenerability, kinetics, compatibility and cost are the most important criteria that need to be considered for adsorbent selection. Silica based adsorbents such as Magnesol and Trisyl, bio-based adsorbents such as lignocellulosic substrates and activated compounds, including the famous activated carbon, then you have activated fiber and activated clay are among the most common adsorbents for this process.

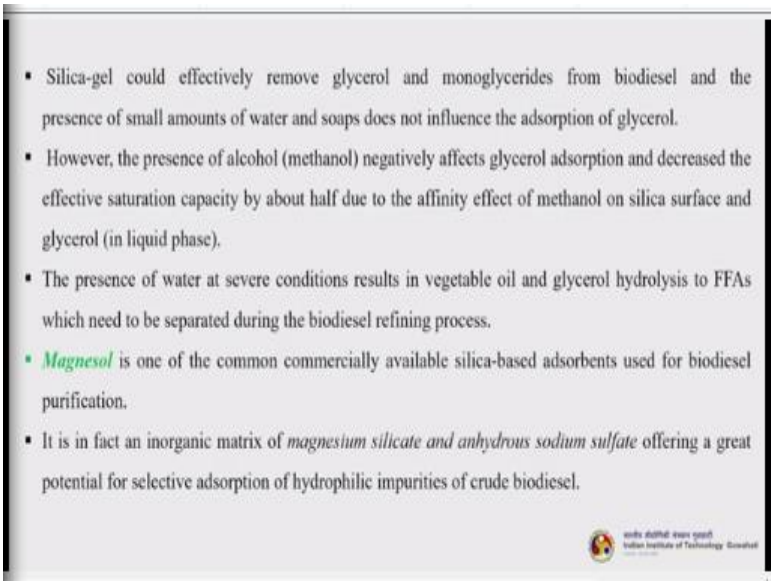
(Refer Slide Time: 19:05)



So, silica based adsorbents. So, silica is one of the key elements in different types of industrially available adsorbents including silica gel, zeolites and molecular sieves. It is an amorphous inorganic mesoporous adsorbent produced via polymerization of the silicic acid. Silica gel owns a hydrophilic surface due to the presence of hydroxyl group, which makes it a proper adsorbent for water, alcohol and other polar molecules.

Silica showed a great potential for removal of glycerol from biodiesel synthesized from waste cooking oil. Silica gel could effectively remove glycerol and monoglycerides from biodiesel, and the presence of small amounts of water and soaps does not influence that adsorption of glycerol.

(Refer Slide Time: 19:45)



Silica gel could effectively remove glycerol and monoglycerides from biodiesel and the presence of small amounts of water and soap does not influence the adsorption of glycerol. However, the presence of alcohol usually methanol negatively affects glycerol adsorption and decrease the effective saturation capacity by about half due to the affinity effect of the methanol on silica surface and glycerol in liquid phase.

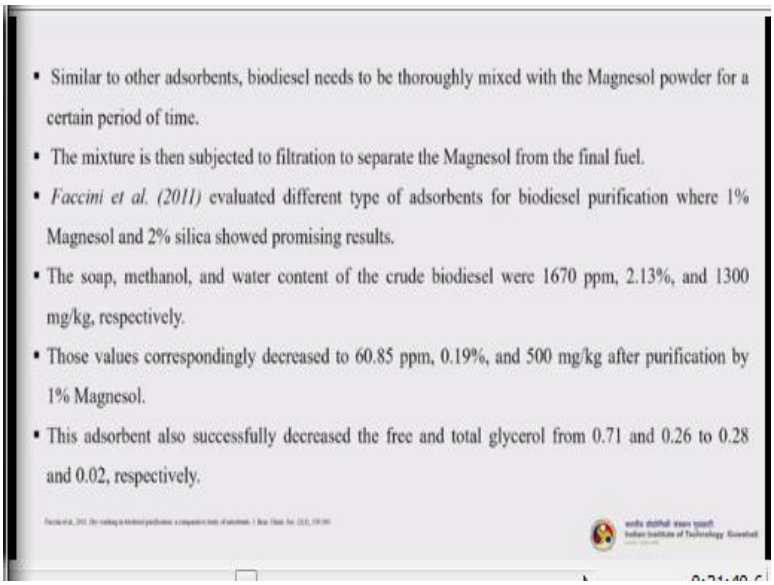
One of the most important thing let me tell you about this entire adsorption phenomena is that whenever we talk about adsorption and a system or a process that we are carrying out where there are more number of impurities to be removed - It is not a single one or two there are many then these impurities will try to adsorb on the surface of the adsorbent which is known as a competitive adsorption, due to their inherent physiochemical properties as well as the physiochemical properties of the adsorbent.

So, in this case, let us say if the methanol is trying to get adsorbed on the surface of the adsorbent more than that of glycerol, so then that creates a problem. So, we have to choose adsorbent selectively in such a way that initially either glycerol will be adsorbed or methanol or some other impurities, then we can have successive columns. So, one will remove that glycerol completely another will remove methanol completely - like that. But please understand that this also adds on cost, as an as more unit operations you are adding that means you are increasing the cost of the final product, so that also has to be taken care of.

So, the presence of water at severe conditions results in vegetable oil and glycerol hydrolysis to free fatty acids which need to be separated during the biodiesel refining process. Magnesol is one of the common commercially available silica based adsorbents used for biodiesel purification.

It is in fact an inorganic matrix of magnesium silicate and anhydrous sodium sulfate offering a great potential for selective adsorption of hydrophilic impurities of the crude biodiesel.

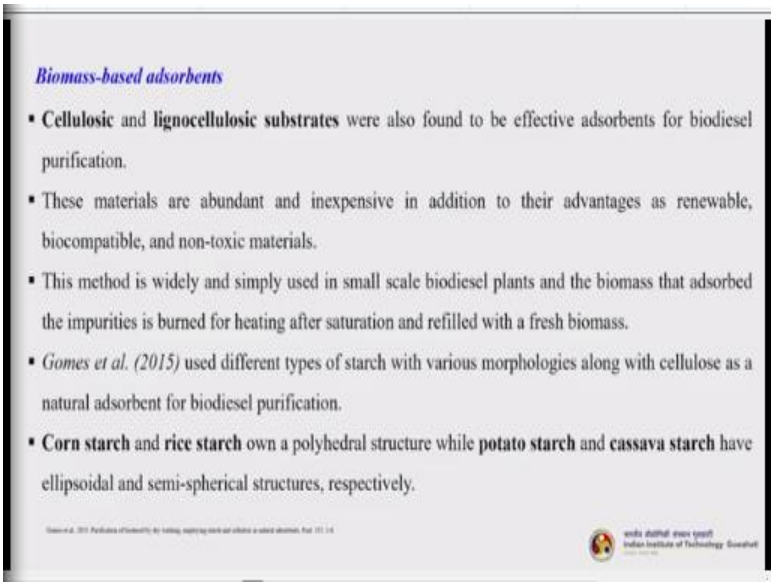
(Refer Slide Time: 21:40)



Similar to other adsorbents, biodiesel needs to be thoroughly mixed with the magnesol powder for a certain period of time. The mixture is then subjected to filtration to separate magnesol from the final Fuel. Faccini et al in one of the very important work, so they have evaluated different types of adsorbents for biodiesel purification, where 1% magnesol and 2% silica salt showed promising results.

The soap, methanol and water content of the crude biodiesel were about 1670 ppm, 2.13% and 1300 milligrams per kg, respectively. Those values correspondingly decreased to 60.85, 0.19% and 500 milligrams per kg after purification by 1% magnesol which is good purification result. So, this adsorbent also successfully decrease the free and total glycerol from 0.71 and 0.26 to 0.28 to 0.02 respectively, the reference has been listed below.

(Refer Slide Time: 22:35)

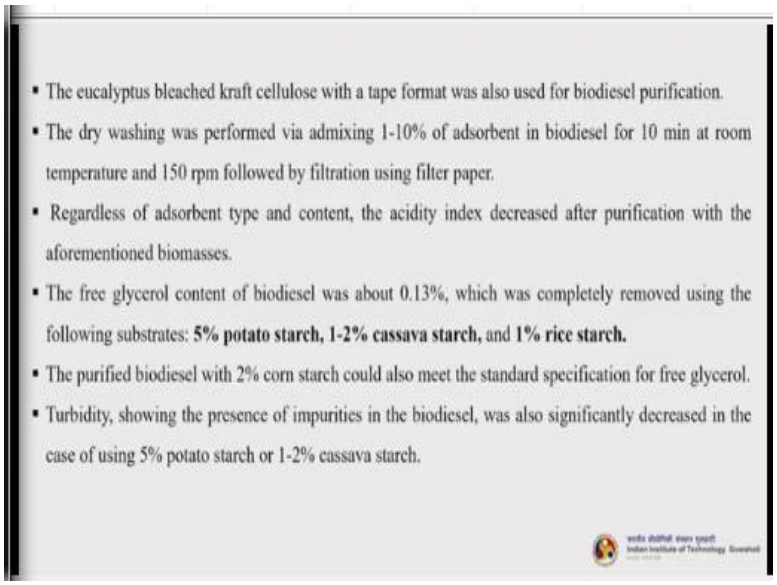


We will talk about biomass based adsorbents; so cellulosic and lignocellulosic substrates were also found to be effective adsorbents for the biodiesel purification due to the enormous cost of most of the synthetic adsorbents focus has been more on developing low cost or readily available, renewable biomass based adsorbent. So, people have concentrated more and more on lignocellulosic substrates.

These materials are abundant and inexpensive in addition to their advantages as renewable, biocompatible and non toxic materials. This method is widely and simply used in small scale biodiesel plants, and the biomass that adsorbs the impurities is burned for heating after saturation and refilled with a fresh biomass. Gomes et al in 2015 use different types of starch with various morphologies along with cellulose as a natural adsorbent for biodiesel purification.

Corn starch and rice starch own a polyhedral structure while potato starch and cassava starch have ellipsoidal and semi spherical structures respectively.

(Refer Slide Time: 23:37)



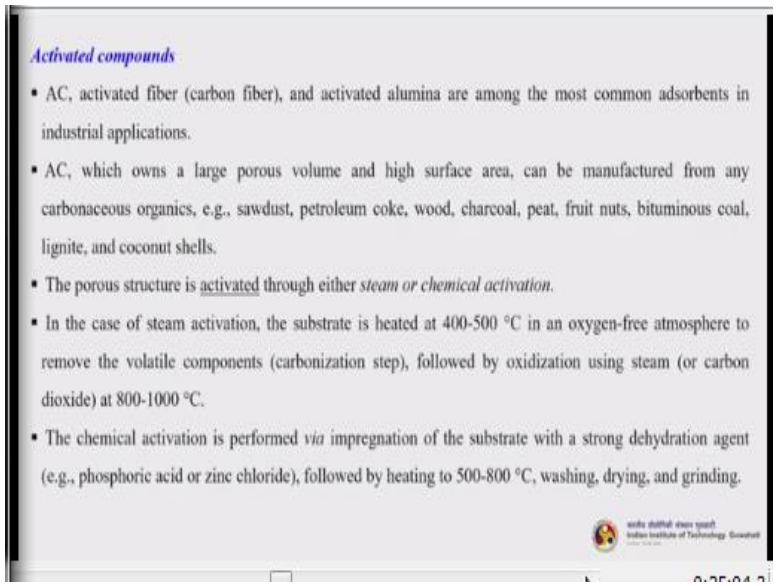
The eucalyptus bleached kraft cellulose with a tape format was also used for biodiesel purification. The dry washing was performed via admixing, 1 to 10% of the adsorbent in biodiesel for 10 minutes at room temperature and 150 rpm followed by filtration using a filter paper. Regardless of the adsorbent type and content the acidity index decreased after purification with the aforementioned biomasses.

The free glycerol content of the biodiesel was about 0.13% which was completely removed using the following substrates - 5% potato starch, 1 to 2% cassava starch and 1% rice starch. The purified biodiesel with 2% corn starch could also meet the standard specification for free glycerol. Turbidity, showing the presence of impurities in the biodiesel was also significantly decreased in the case of using 5% potato starch or 1 to 2% cassava starch.

(Refer Slide Time: 24:29)

Rice husk ash showed promising performance in biodiesel purification up to 5% dose. The adsorption capability of the rice husk ash is attributed to it is high silica content and the presence of meso and macropores in its structure, so it is a very good adsorbent. Although the water content of the purified biodiesel with RHA was still above the acceptable value, it was significantly lower than that of the purified biodiesel using acidified water, 1% phosphoric acid actually and magnesol using 1% magnesol.

(Refer Slide Time: 25:01)



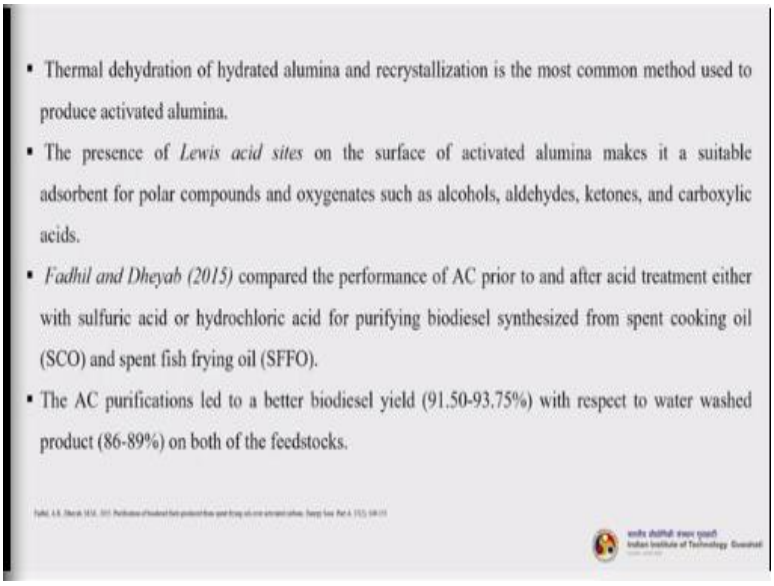
Then activated compounds: So, activated carbon activated fiber which is known as carbon fiber and activated alumina are among the most common adsorbents in industrial applications. Activated carbon which owns a large porous volume and high surface area can be manufactured

from any carbonaceous organics. As for example, sawdust, petroleum coke, wood, charcoal, peat, fruit nuts, bituminous coal, lignite and coconut shells.

The porous structure is activated through either steam or chemical activation. Two types of activation usually done, steam activation is also called as physical activation. And chemical activation use some sort of chemicals, either acids or bases to do the activation. So, in the case of steam activation, the substrate is heated to 400 to 500 degree centigrade in an oxygen free atmosphere to remove the volatile components, that step is called the carbonization step.

That is followed by the oxidization step using the steam or carbon dioxide at 800 to 1000 degree centigrade. So, the chemical activation is performed via impregnation of the substrate with a strong dehydrating agent, usually phosphoric acid or zinc chloride. But many times zinc chloride is being not considered because it is little toxic. So, followed by heating to 500 to 800 degree centigrade, then followed by washing, drying and grinding.

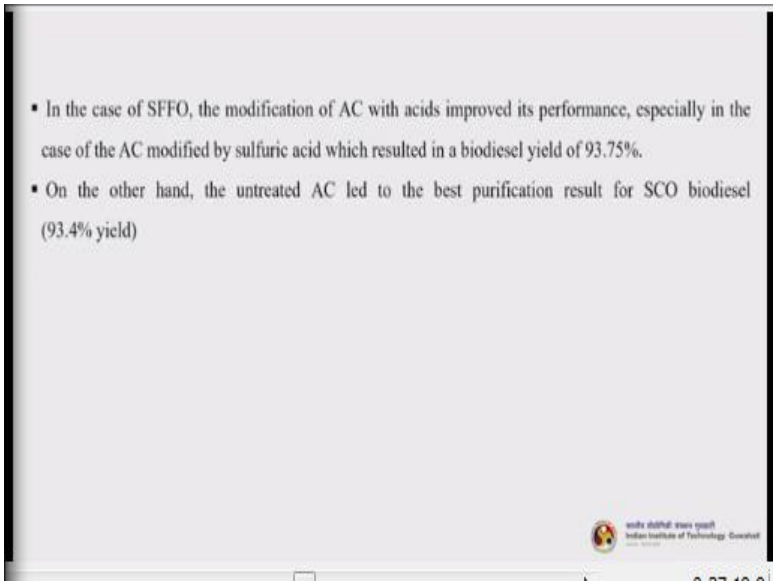
(Refer Slide Time: 26:17)



Thermal dehydration of hydrated alumina and recrystallization is the most common method used to produce activated alumina. The presence of Lewis acids sites on the surface of activated alumina makes it suitable adsorbent for polar compounds and oxygenates such as alcohols, aldehydes, ketones and carboxylic acids. You know Lewis acid are the acids which are ready to give electrons, they are ready to donate electrons, electron pairs you can say**.**

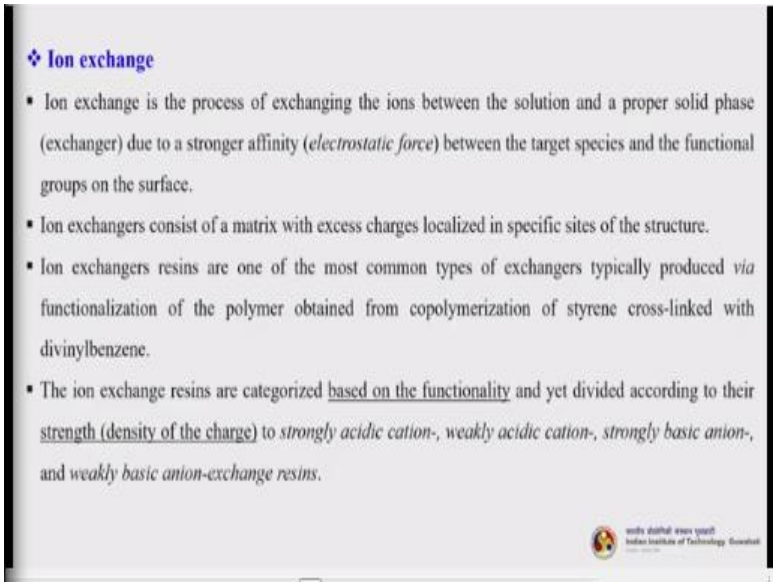
And Fadhil and Dheyab in one of the significant work - the references given here below - compared the performance of activated carbon prior to and after acid treatment either with sulfuric acid or hydrochloric acid for purifying biodiesel synthesized from spent cooking oil and spent fish frying oil. So, the activated carbon purifications led to a better biodiesel yield usually 91.5 to 93.75%. It is a significant yield actually with respect to water washed product which is 86 to 89% on both of the feedstock.

(Refer Slide Time: 27:19)



In case of the spent fish frying oil, the modification of activated carbon with acids, improved its performance especially in the case of activated carbon modified by sulfuric acid, which resulted in a biodiesel yield of 93.75%. On the other hand, the untreated activated carbon led to the best purification result for the spent cooking oil biodiesel, so almost you get 93.4% yield.

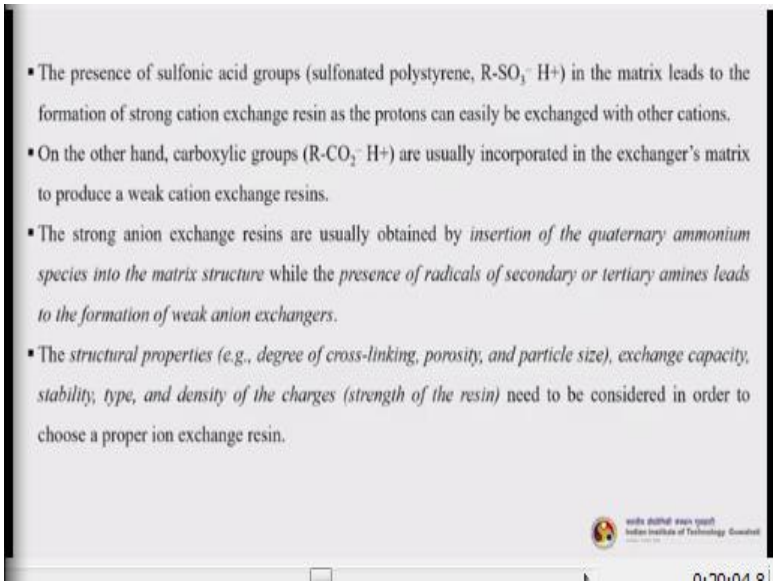
(Refer Slide Time: 27:44)



So, the next category is ion exchange. So, ion exchange is the process of exchanging the ions between the solution and a proper solid phase due to a stronger affinity, basically the electrostatic force between the target species and the functional groups on the surface. Ion exchangers consist of a matrix with excess charges localized in specific sites of the structure. Ion exchangers resins are one of the most common types of exchangers typically produced via fictionalization of the polymer obtained from copolymerization of styrene crosslinked with divinylbenzene.

The ion exchange resins are categorized based on the functionality and yet divided according to their strength (basically density of the charge) to strongly acidic cation, weakly acidic cations, strongly basic anion and weakly basic anion exchange resins. So, basically 4 distinct types of resins.

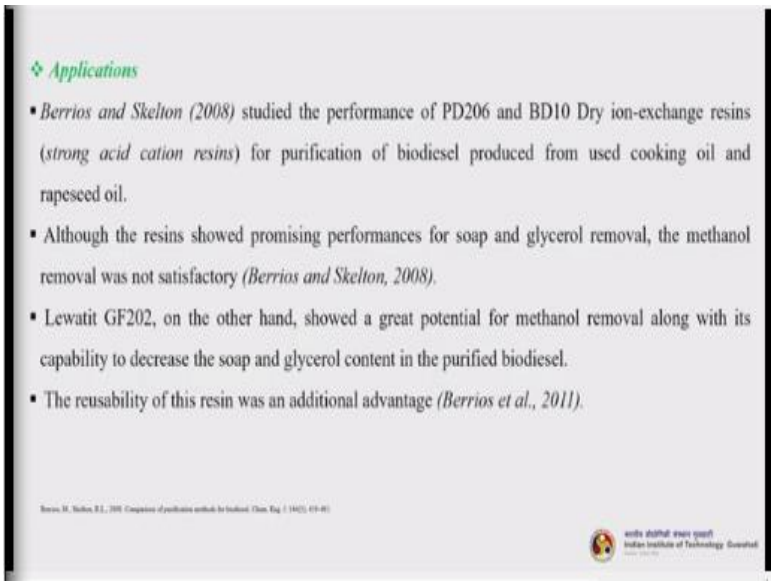
(Refer Slide Time: 28:34)



The presence of sulfonic acid groups (sulfonated polystyrene basically) in the matrix leads to the formation of strong cation exchange resin as the protons can easily be exchanged with other cations. On the other hand, carboxylic groups are usually incorporated in the exchanger's matrix to produce a weak cation exchange resin. The strong anion exchange resins are usually obtained by insertion of the quaternary ammonium species into the matrix structure while the presence of radicals of secondary or tertiary amines leads to the formation of weak anion exchangers.

The structural properties, that is degree of crosslinking, porosity and particle size exchange capacity, stability, type and density of the charges need to be considered in order to choose a proper ion exchange resin.

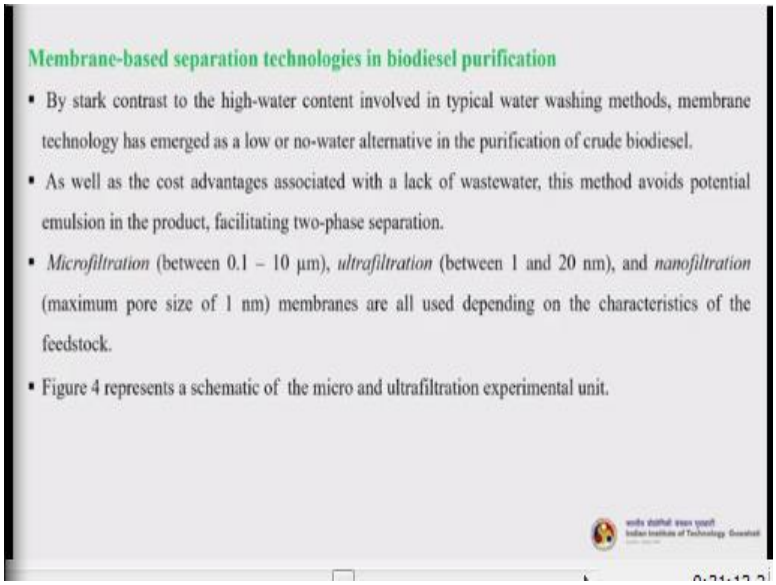
(Refer Slide Time: 29:20)



Let us discuss about applications. So, Boris and Skelton studied the performance of PD206 and BD10 dry ion exchange resins which are strong acid cation resins for purification of biodiesel produced from used cooking oil and rapeseed oil. Although the resins showed promising performance for soap and glycerol removal, the methanol removal was not satisfactory. Lewatit GF202, on the other hand showed a great potential for the methanol removal, along with it is capability to decrease the soap and glycerol content in the purified biodiesel.

The reusability of this resin was an additional advantage. Now again, as I told you just few minutes before, again I am telling you that in case of whether it is adsorption, ion exchange, ion exchange resins or absorbent, no single species will purify the entire amount of different types of impurities that we used to remove - that is not possible. Therefore, there is a need that we develop different systems with higher efficiency to remove one particular component, either glycerol, then followed by methanol, followed by water, soap and free fatty acids like that. So, you need to fine tune and optimize your process in such a way that we will have minimum number of columns to achieve that in a stage wise separation also can be done. So, this is where the design engineers play a vital role in designing a low cost purification step otherwise the final product cost will be too high.

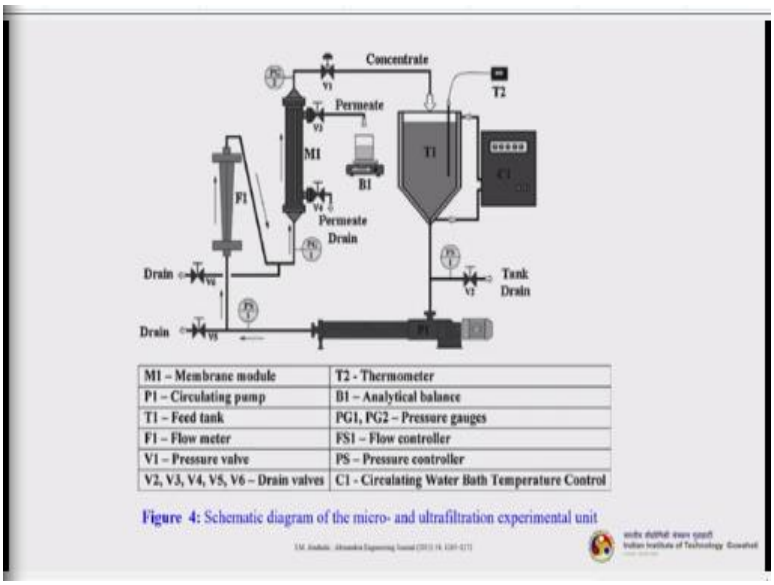
(Refer Slide Time: 31:00)



So, now let us talk about the membrane based separation technologies in biodiesel purification. So, these are the latest developments; some of these are also been commercialized. By stark contrast to the high water content involved in typical water washing methods, membrane technology has emerged as a low or no water alternative in the purification of crude biodiesel. So, as well as the cost advantages associated with the lack of wastewater, this method avoids potential emulsion in the product facilitating two phase separation.

Since we are not using water, so there is no question of any emulsion formation. So, micro filtration which is basically 0.1 to 10 micron in that range, ultrafiltration between 1 to 20 nanometer and nanofiltration maximum pore size is of almost 1 nanometer. So, all these types of membranes are all used depending on the characteristics of the feedstock. So, in the next figure, I will show you a schematic of the micro and ultrafiltration experimental unit which was used by a Atadashi et al and published in 2015 in a very good work.

(Refer Slide Time: 31:57)



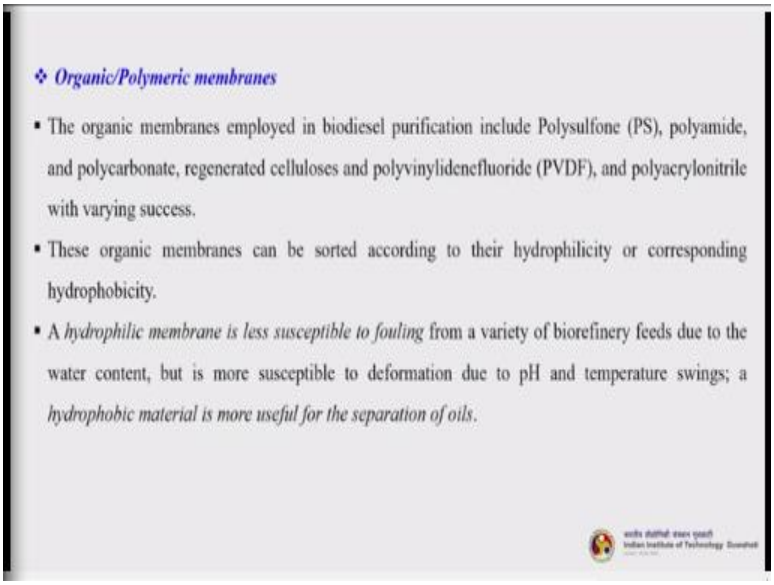
M1 – Membrane module	T2 - Thermometer
P1 – Circulating pump	B1 – Analytical balance
T1 – Feed tank	PG1, PG2 – Pressure gauges
F1 – Flow meter	FS1 – Flow controller
V1 – Pressure valve	PS – Pressure controller
V2, V3, V4, V5, V6 – Drain valves	C1 - Circulating Water Bath Temperature Control

Figure 4: Schematic diagram of the micro- and ultrafiltration experimental unit

So, it's a simplified membrane based biodiesel purification unit. So, this is a feed tank, from here the feed is getting pumped, these are rotameters and all and this is your membrane unit M1. So, M1 is the membrane module, it is a hollow fiber membrane module here. So, it can be ultrafiltration, it can be any other membrane separation, nanofiltration and all. So, whatever you get the concentrate that concentrate goes back to feed tank again.

And the permeate can be recovered and the membrane separation units are very easy to handle. And they are simple to design also, not much unit operations and much other accessories are required. And energy requirement is also very, very low compared to other energy intensive processes. Here whatever the energy is required is just the pumping cost, the membrane itself does not need any energy to do the purification. You can refer particular work in this particular journal which is published in 2015, it is a nice work.

(Refer Slide Time: 33:19)

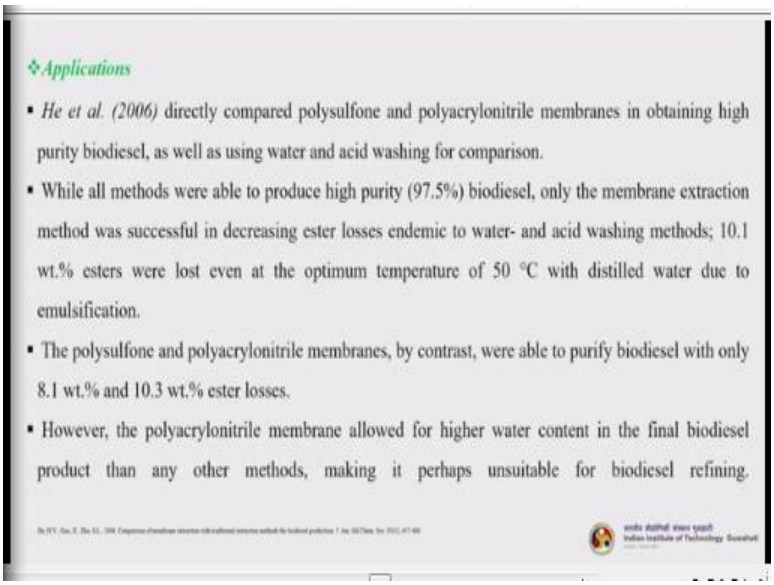


Then we will talk about organic and polymeric membranes. The organic membranes employed in biodiesel purification include Polysulfone, polyamide, and polycarbonate, regenerated celluloses, polyvinylidene fluoride which is known as PVDF and polyacrylonitrile with varying success. These organic membranes can be sorted according to their hydrophilicity and corresponding hydrophobicity.

A hydrophilic membrane is less susceptible to fouling from a variety of biorefinery feeds due to the water content but is more susceptible to deformation due to pH and temperature swings. A hydrophobic material is more useful for the separation of oils. So, based upon the hydrophobicity you can choose actually what is your intention and what you are going to remove? Are you going to remove alcohol, are you going to remove glycerol and where you want to remove?

You want to pass them to the permeate side or you want to retain them on the surface of the membrane? All these things has to be pre decided before you go for designing of a membrane unit.

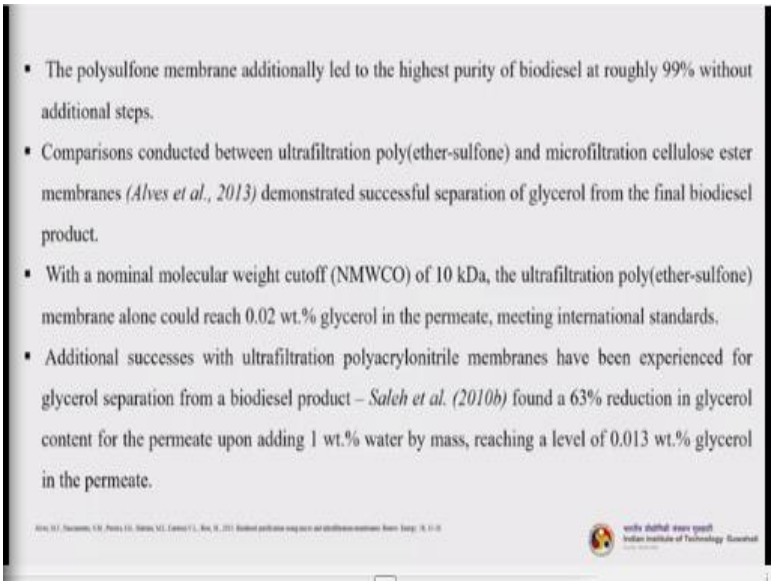
(Refer Slide Time: 34:20)



So, let us talk about applications. He et al directly compared polysulfone and polyacrylonitrile membranes in obtaining high purity biodiesel as well as using water and acid washing for comparison. While all methods were able to produce high purity biodiesel (almost 97.5%), only the membrane extraction method was successful in decreasing ester losses, endemic to water and acid washing methods.

So, 10.1 weight percent esters were lost even at the optimum temperature of 50 degrees centigrade with distilled water due to emulsification. The polysulfone and polyacrylonitrile membranes by contrast, were able to purify biodiesel with only 8.1 weight percent and 10.3 weight percent ester losses. However, the poly acrylonitrile membrane allowed for higher water content in the final biodiesel product than any other methods making it perhaps unsuitable for the biodiesel refining.

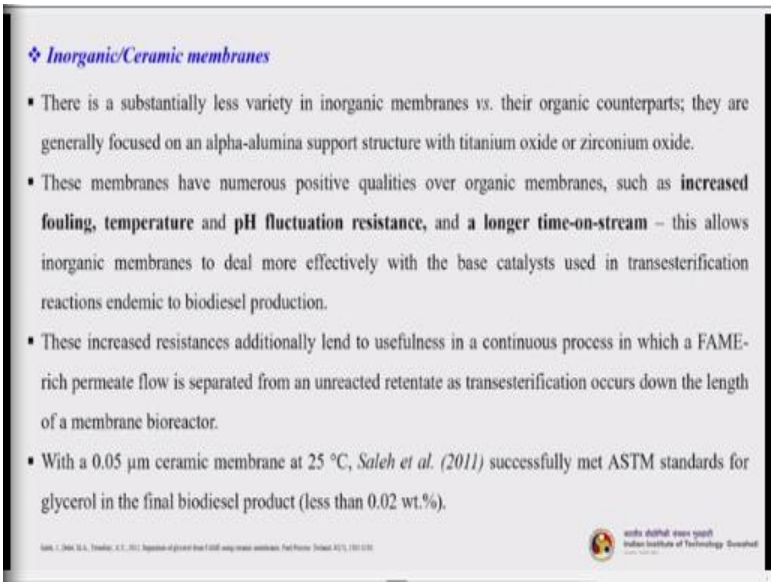
(Refer Slide Time: 35:12)



The polysulfone membrane additionally led to the highest purity of biodiesel at roughly 99% without additional steps. Comparisons conducted between ultrafiltration poly ether-sulfone and microfiltration cellulose ester membrane demonstrated successful separation of glycerol from the final biodiesel product. This particular work reference is also given below it was published in Renewable Energy**.**

And with nominal molecular weight cutoff of 10 kilo Dalton, the ultrafiltration poly ether-sulfone membrane alone could reach 0.02**%** weight percent glycerol in the permeate, meeting international standards. Additional success with ultrafiltration polyacrylonitrile membranes have been experienced for glycerol separation from a biodiesel product. Saleh et al found a 63% reduction in glycerol content in the permeate upon adding 1 weight percent water by mass reaching a level of 0.013 weight percent glycerol in the permeate side.

(Refer Slide Time: 36:04)



So, we will talk about inorganic and ceramic membranes. So, there is a substantially less variety in inorganic membranes versus their organic counterparts. Because they are generally focused on either alpha alumina support structure, usually with titanium oxides or zirconium oxides, we are talking about commercially available ceramic membranes. Now these membranes have numerous positive qualities over organic membranes, such as increased fouling, temperature, pH fluctuation resistance, a longer time on stream.

This allows inorganic membranes to deal more effectively with the base catalyst used in the transesterification reactions endemic to the biodiesel production. Now these increased resistances additionally lend to usefulness in a continuous process in which a FAME rich permeate flow is separated from an unreacted retentate as transesterification occurs down the length of a membrane bioreactor.

With a 0.05 micron ceramic membrane at 25 degrees centigrade, Saleh et al successfully met ASTM standard for glycerol in the final biodiesel product. So, less than 0.02 weight percent - the reference has been given here.

(Refer Slide Time: 37:12)

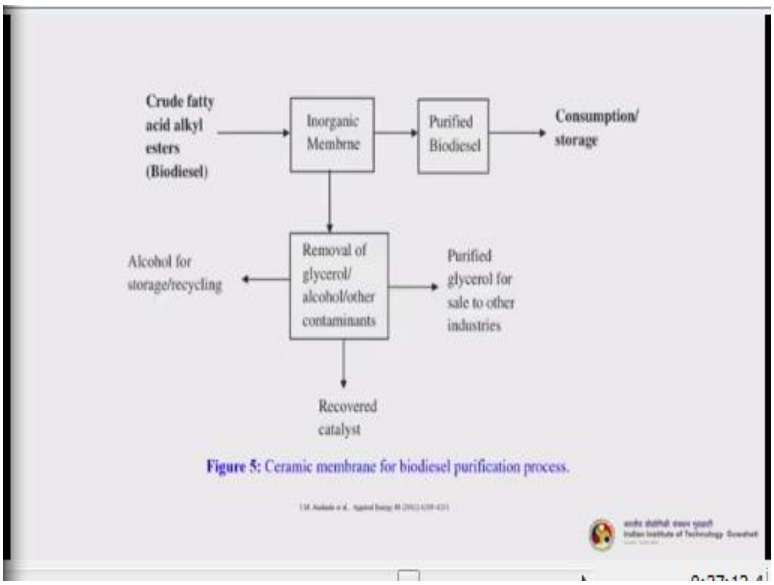


Figure 5: Ceramic membrane for biodiesel purification process.

And this is the schematic representation of the ceramic membrane unit for biodiesel purification process. So you can see that the crude acid alkyl esters - the biodiesel, it goes to the inorganic membrane, then whatever is coming to the permeate side, that is nothing but the removal of the glycerol, alcohol and other contaminants. Alcohol can be stored for further processing, you get the recovered catalyst, you get purified glycerol for sale to other industries.

Please understand, again I am telling this is not a single unit, there are multiple units here but it was shown to simplify the process. And from the inorganic membrane, you get the purified biodiesel mostly in the retentate side and which can go for further drying and further processing some polishing step before it is getting stored.

(Refer Slide Time: 38:01)

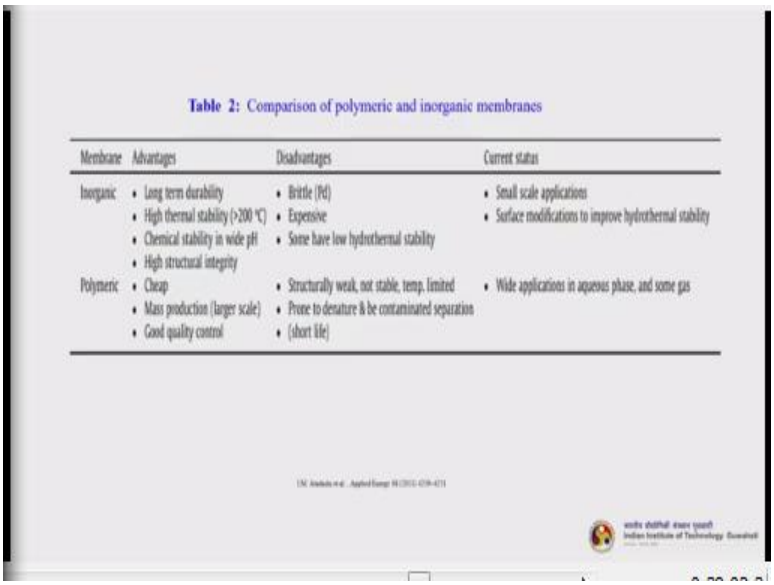


Table 2: Comparison of polymeric and inorganic membranes

Membrane	Advantages	Disadvantages	Current status
Inorganic	• Long term durability • High thermal stability (>200 °C) • Chemical stability in wide pH • High structural integrity	• Brittle (Pd) • Expensive • Some have low hydrothermal stability	• Small scale applications • Surface modifications to improve hydrothermal stability
Polymeric	• Cheap • Mass production (larger scale) • Good quality control	• Structurally weak, not stable, temp. limited • Prone to denature & be contaminated separation • (short life)	• Wide applications in aqueous phase, and some gas

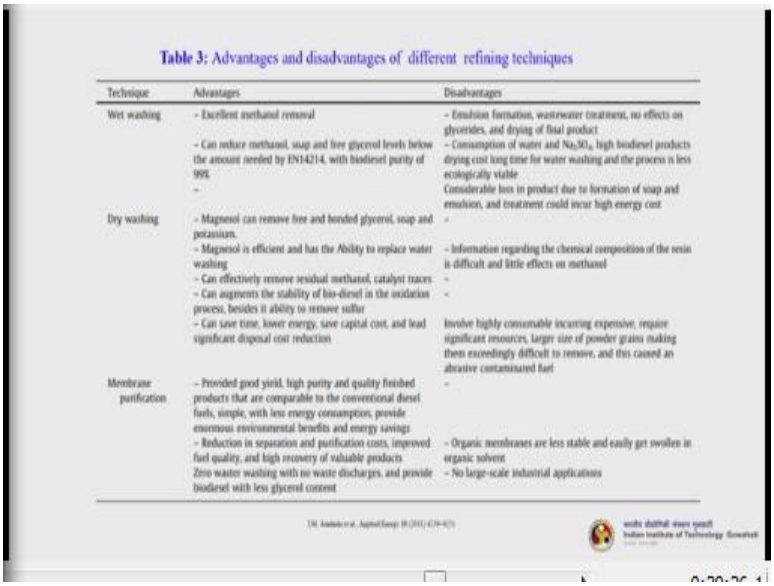
So, this table will give you a comparison of polymeric and different inorganic membranes. So, if you talk about inorganic membranes, the advantages are - they having long term durability, you can use them for many months and years. High thermal stability, they can withstand more than 200 degrees centigrade temperature which the polymeric membrane cannot. Chemical stability in wide pH range they can handle; they can handle high structural integrity also.

Disadvantage is that they are very brittle. So, you have to be very careful otherwise it will break very easily. It is expensive, that is one of the most or you can say the biggest disadvantage right now and as some ceramic membranes have low hydrothermal stability. So, if you talk about current status, so some small scale applications are already going on, and surface modifications to improve hydrothermal stability is also being undertaken.

So, let us talk about polymeric membranes the advantages are that cheap or low cost. You can produce them in mass larger scale productions. So, usually available in large quantities and they have good quality control. However, the disadvantage is that they are structurally weak, not stable, so we are talking about the mechanical stability. And temperature is also they cannot withstand more than 100 - 120 degrees centigrade**.**

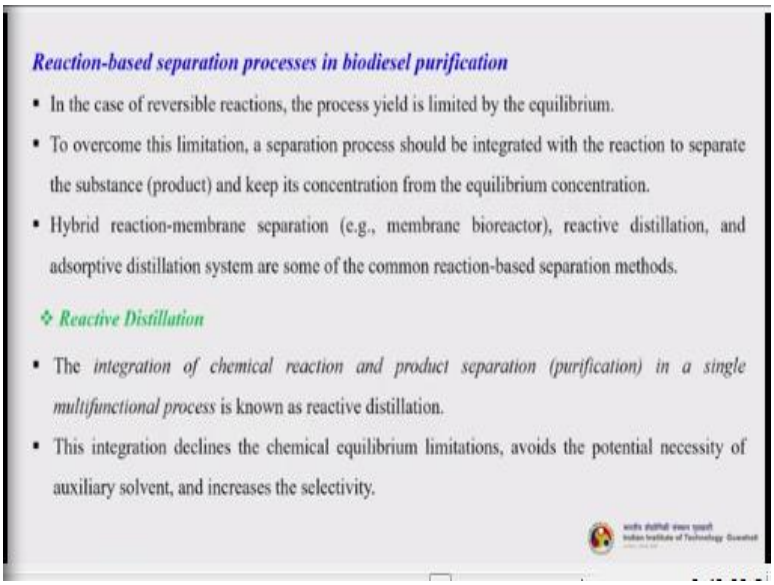
Prone to denature and be contaminated separation and they have a short lifespan; you have to replace them frequently. The current status is that wide applications in aqueous phase and some gaseous phase.

(Refer Slide Time: 39:26)



So, if you look at this particular table, here the advantages and disadvantages of the different refining technologies which we have discussed till now. So, basically the three, one the first one is the wet washing, then the dry washing and the membrane purification. Of course membrane also a part of your dry washing you can say that because you are not using water. So, all the advantages and disadvantages which we have already discussed have been given in a single slide, so you can refer to it later on. So, we will go ahead.

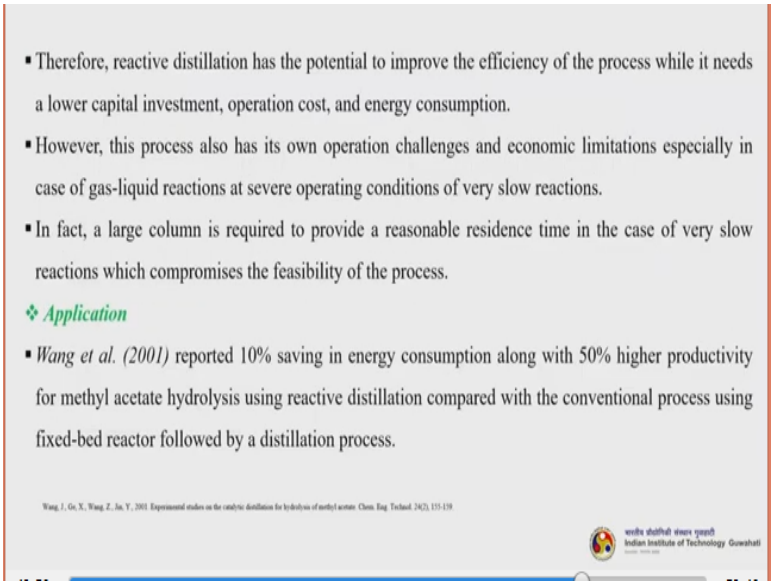
(Refer Slide Time: 39:59)



So, now we will talk about the reaction based separation processes in biodiesel purification. In the case of reversible reactions, the process yield is limited by the equilibrium. To overcome this limitation a separation process that should be integrated with the reaction to separate the substrate, that is basically product and keep it is concentration from the equilibrium concentration. Hybrid reaction, membrane separation as for example, membrane bioreactor, reactive distillation and adsorptive distillation are some of the common reaction based separation methods.

So, let us talk about reactive distillation. The integration of chemical reaction and a product separation that is the purification step in a single multifunctional process is known as the reactive distillation. That means, in a single column you are doing the reaction as well as the separation. So, this integration declines the chemical equilibrium limitations, avoids the potential necessity of auxiliary solvent and increases the selectivity.

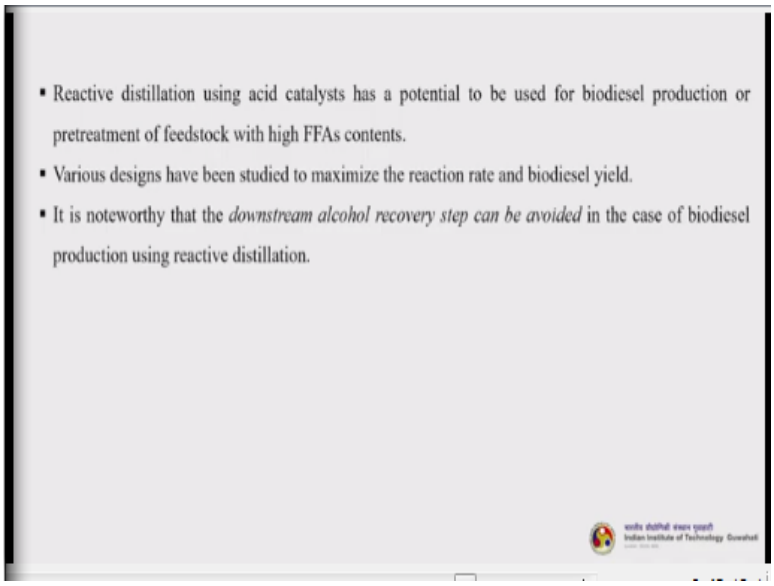
(Refer Slide Time: 40:54)



Therefore, reactive distillation has the potential to improve the efficiency of the process, while it needs a lower capital investment, operation cost and energy consumption. However, this process also has it is own operational challenges and economic limitations, especially in case of the gas liquid reactions at severe operating conditions of very slow reactions. In fact, a large column is required to provide a reasonable residence time in case of very slow reaction which compromises the feasibility of the process. And again, it will increase the operational and fixed cost.

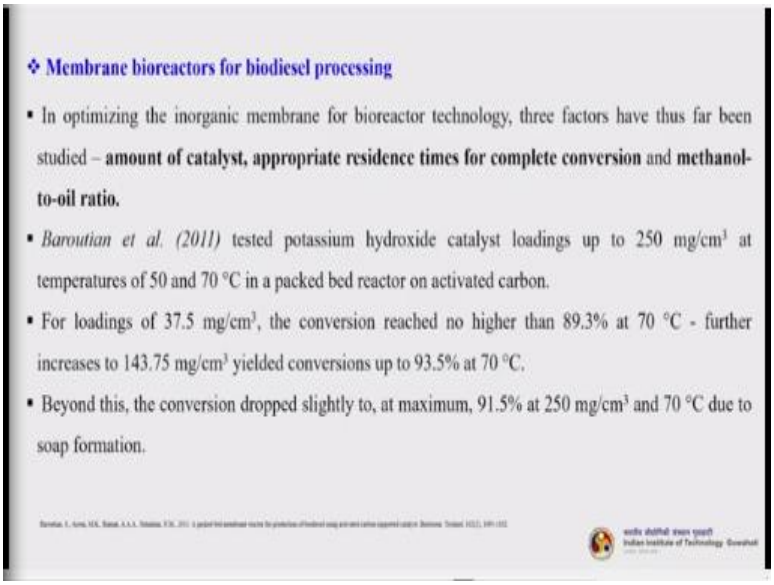
So, if you talk about applications Wang et al in a classical work reported that 10% saving in energy consumption along with 50% higher productivity for methyl acetate hydrolysis using reactive distillation compared with the conventional process using fixed bed reactor followed by a distillation process. So, it is a significant work that reported 10% energy saving as well as 50% higher productivity in a single unit where reaction as well as purification has been carried out.

(Refer Slide Time: 41:56)



Reactive distillation using acid catalyst has a potential to be used for biodiesel production or pretreatment of feedstock with a very high free fatty acid content. Various designs have been studied to maximize the reaction rate and biodiesel yield. It is noteworthy that the downstream alcohol recovery step can be avoided in the case of biodiesel production using reactive distillation.

(Refer Slide Time: 42:19)

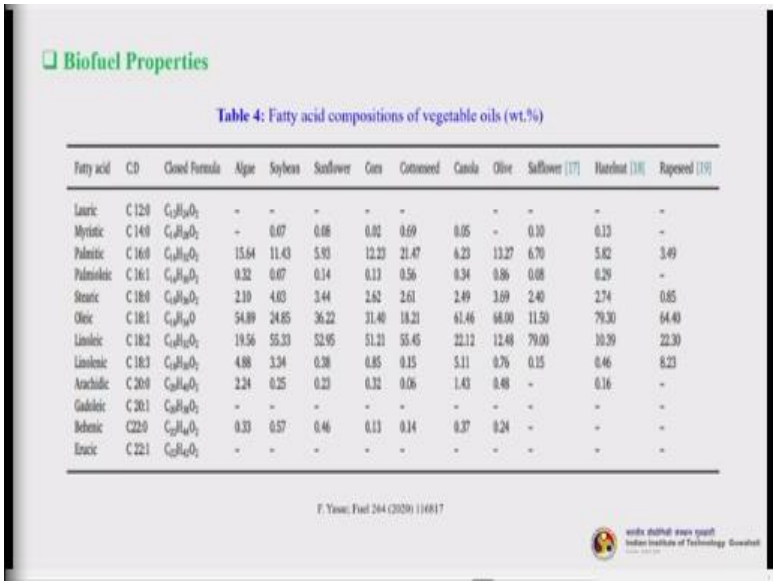


So, let us talk about membrane bioreactors for biodiesel processing. In optimizing the inorganic membrane for bioreactor technology three factors have thus far been studied. First is the amount of catalyst, second is the appropriate residence time for the complete conversion and third is the methanol to oil ratio. Baroutian et al in 2011 tested potassium hydroxide catalyst loadings up to

250 milligram per centimeter cube at temperatures of 50 and 70 degree centigrade in a packed bed reactor system using activated carbon as the adsorbent**.**

So, for loading of 37.5 milligram per centimeter cube the conversion reached no higher than 89.3% at 70 degree centigrade - further increases to 143.75 milligrams per centimeter cube yielded conversions up to 93.5% at same temperature 70 degree centigrade. Now beyond this the conversion dropped slightly to a maximum of 91.5% at 250 milligram per centimeter cube and 70 degree centigrade due to soap formation. The reference has been listed down, it is a very good work published in bioresource technology in 2011.

(Refer Slide Time: 43:26)



So, let us talk about biofuel properties. So, this particular table will give you the free fatty acid composition of vegetable oils**.** I think we have discussed this when we discussed about vegetable oils and all. But I have again added, so that you can understand while we are discussing about the biodiesel purification, so the properties of the fuel, biodiesel as a fuel**.** So, you can see the fatty acids different types of fatty acids are listed here, lauric, mysteric, palmitic, palmioleic, stearic, oleic, linoleic all these things and this is the formula C by D ratio.

And this is the different sources - algae, soybean, sunflower, corn, cotton seed, canola, olive, safflower, hazelnut and rapeseed. So, this is nothing to discuss here, so I leave it to you to refer it

later on when you go through the video**,** so you please see this and the reference has also been given here.

(Refer Slide Time: 44:24)

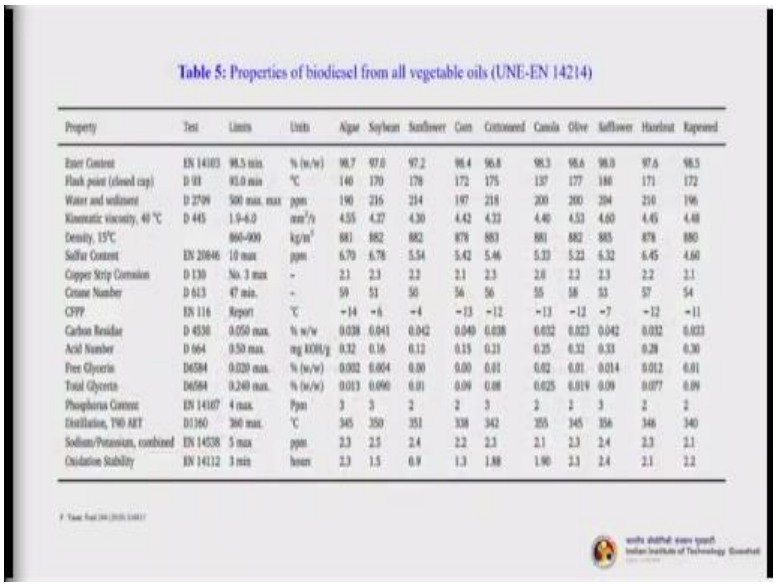
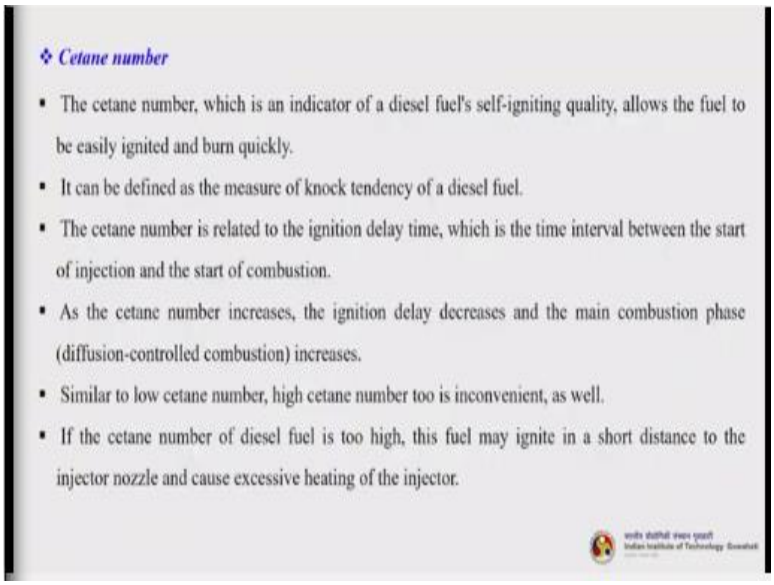


Table 5: Properties of biodiesel from all vegetable oils (UNE-EN 14214)

Property	Test	Limits	Units	Algae	Soybean	Sunflower	Corn	Cottonseed	Canola	Olive	Safflower	Hazelnut	Rapeseed
Ester Content	EN 14103	98.5 min.	% (m/m)	98.7	97.0	97.2	98.4	96.8	98.3	98.6	98.0	97.6	98.5
Flash point (closed cup)	D 93	93.0 min	°C	140	170	178	172	175	137	177	180	171	172
Water and sediment	D 2709	500 max. max	ppm	190	216	214	197	218	200	200	204	210	196
Kinematic viscosity, 40 °C	D 445	1.9-6.0	mm^2/s	4.55	4.27	4.30	4.42	4.33	4.40	4.53	4.60	4.45	4.48
Density, 15°C		860-900	kg/m^3	881	882	882	878	883	881	882	885	878	880
Sulfur Content	EN 20846	10 max	ppm	6.70	6.78	5.54	5.42	5.46	5.33	5.22	6.32	6.45	4.60
Copper Strip Corrosion	D 130	No. 3 max	-	2.1	2.3	2.2	2.1	2.3	2.0	2.2	2.3	2.2	2.1
Cetane Number	D 613	47 min.	-	59	51	50	56	56	55	58	53	57	54
CFPP	EN 116	Report	°C	+14	+6	+4	-13	-12	-13	-12	-7	-12	-11
Carbon Residue	D 4530	0.050 max.	% w/w	0.038	0.041	0.042	0.049	0.038	0.032	0.023	0.042	0.032	0.033
Acid Number	D 664	0.50 max.	mg KOH/g	0.32	0.16	0.12	0.15	0.21	0.25	0.32	0.33	0.28	0.30
Free Glycerin	D6584	0.020 max.	% (m/m)	0.002	0.004	0.00	0.00	0.01	0.02	0.01	0.014	0.012	0.01
Total Glycerin	D6584	0.240 max.	% (m/m)	0.013	0.090	0.01	0.09	0.08	0.025	0.019	0.09	0.077	0.09
Phosphorus Content	EN 14107	4 max.	Ppm	3	3	2	2	3	2	2	3	2	2
Distillation, T90 AET	D1160	360 max.	°C	345	350	351	338	342	355	345	356	346	340
Sodium/Potassium, combined	EN 14538	5 max	ppm	2.3	2.5	2.4	2.2	2.3	2.1	2.3	2.4	2.3	2.1
Oxidation Stability	EN 14112	3 min	hours	2.3	1.5	0.9	1.3	1.88	1.90	2.3	2.4	2.1	2.2

In the next table the properties of the biodiesel from all vegetable oils are listed here. So, the properties like the ester content, flash point, water and sediment, kinematic viscosity, density, cetane number, CFPP, carbon residue, free glycerine, acid number, distillation temperature, everything all the fuel properties. So, please have a close look here all different types of feedstocks are been listed like algae, soybean, safflower, corn, cotton seed, all the vegetable oils**.** So, you can understand that which particular feedstock has is having better fuel properties.

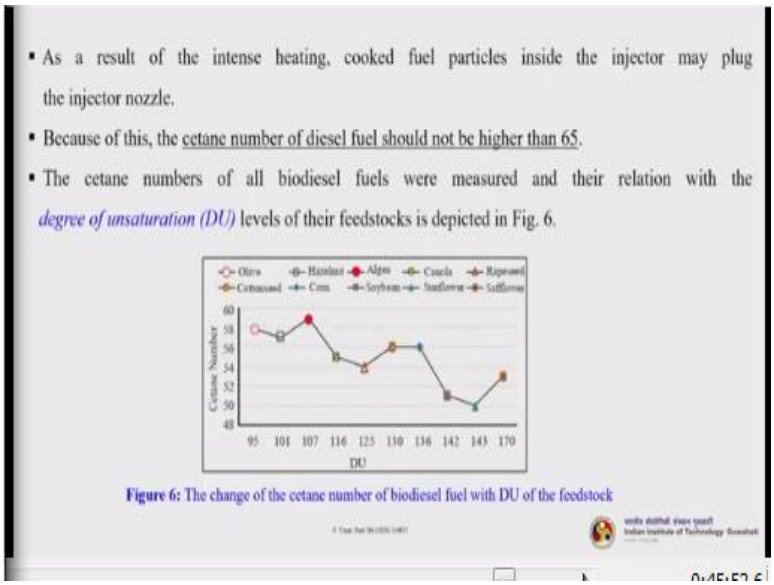
(Refer Slide Time: 45:08)



So, let us talk about the cetane number, it is one of the most important fuel property. The cetane number which is an indicator of a diesel fuel self ignition quality, allows the fuel to be easily ignited and burn quickly. It can be defined as the measure of knock tendency of a diesel fuel. The cetane number is related to the ignition delay time which is the time interval between the start of injection and the start of combustion.

As the cetane number increases the ignition delay decreases and the main combustion phase that is the diffusion control combustion increases. Similar to low cetane number high cetane number too is inconvenience as well. If the cetane number of diesel fuel is too high this fuel may ignite in a short distance to a injector nozzle and causes excessive heating of the injector which is not at all desirable.

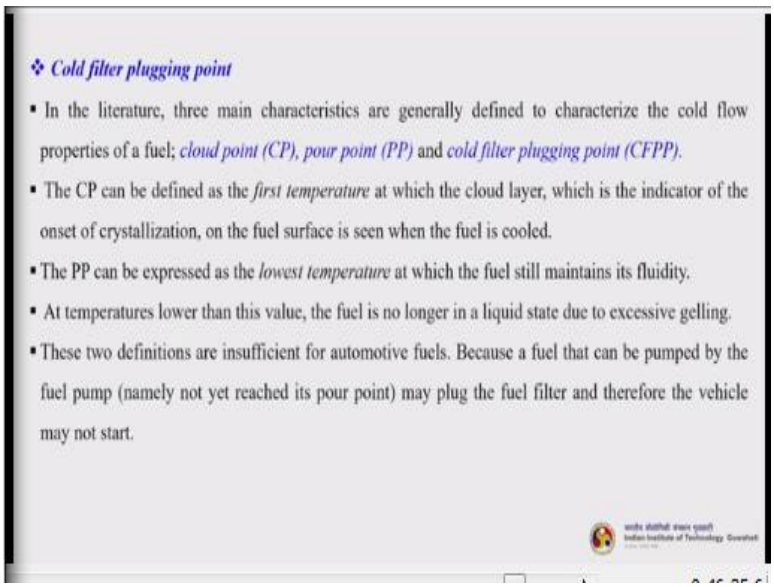
(Refer Slide Time: 45:52)



As a result of the intense heating, cooked fuel properties inside the injector may plug the injector nozzle. Because of this the cetane number of diesel fuel should not be higher than 65. The cetane number of all biodiesel fuels are measured and their relation with the degree of unsaturation levels of their feedstocks is depicted. So, this particular figure you can see how the cetane number is changing with respect to the degree of unsaturation of the particular base oil**.**

Where it is olive oil, hazelnut oil, this red one is algae basically you can see the cetane number is highest for the algal oil because of the very good amount of free fatty acids that is available with the algal oil**.** The quality is actually good compared to other oils**.**

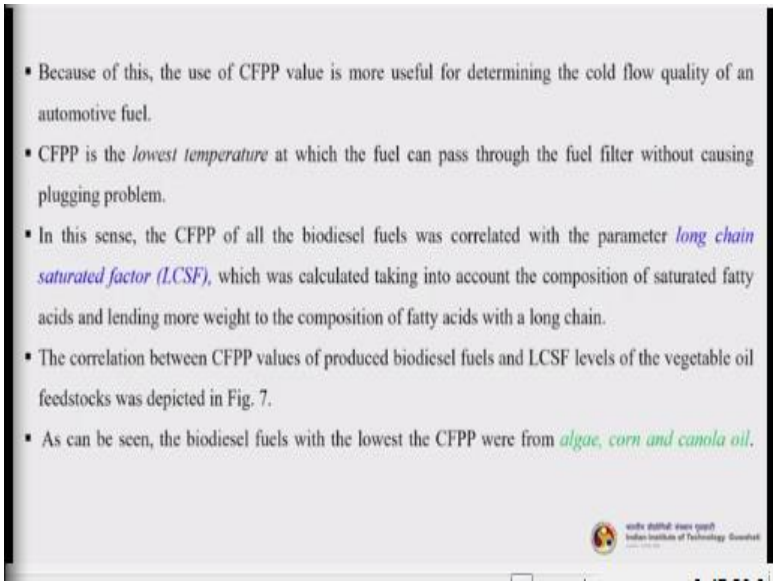
(Refer Slide Time: 46:35)



So, we will talk about cold filter plugging point CFPP. So, in the literature three main characteristics are generally defined to characterize the cold flow properties of the fuel. First is the cloud point, second is the pour point hence third is the cold filter plugging point CFPP. Cloud point can be defined as the first temperature at which the cloud layer which is the indicator of the onset of crystallization on the fuel surface is seen when the fuel is cooled.

The pour point can be expressed as the lowest temperature at which the fuel still maintains it is fluidity. At temperatures lower than this value the fuel is no longer in a liquid state due to excessive gelling. These two definitions are insufficient for automotive fuels, because the fuel that can be pumped by the fuel pump (namely not yet reached to it is pour point) may plug the fuel filter and therefore the vehicle may not start.

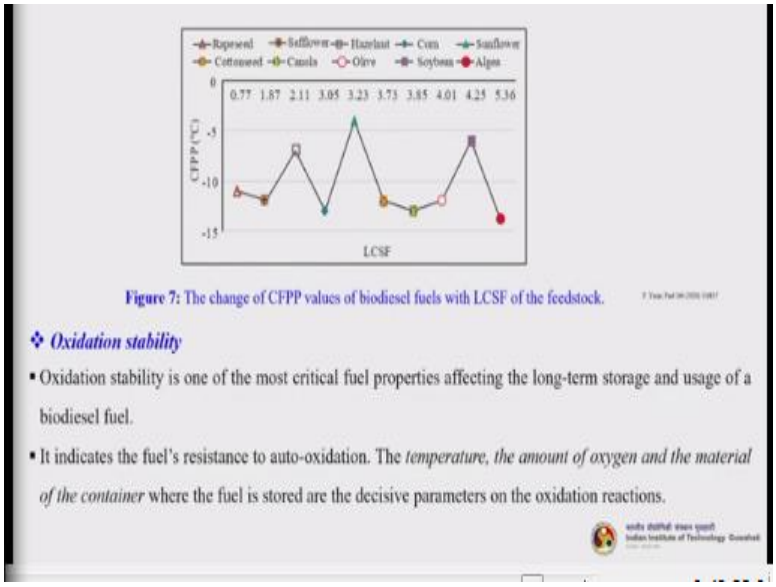
(Refer Slide Time: 47:25)



Because of this, the use of the CFPP value is more useful for determining the cold flow quality of an automotive fuel. CFPP is the lowest temperature at which the fuel can pass through the fuel filter without causing plugging problem. And in this sense, the CFPP of all the biodiesel fuels were correlated with the parameter long chain saturated factor which is known as LCSF, which was calculated taking into account the composition of the saturated fatty acids and lending more weight to the composition of fatty acids with a long chain.

The correlation between CFPP values of produced biodiesel fuels and LCSF levels of the vegetable oil feedstocks was depicted in figure 7, in the next figure I will show you. As can be seen the biodiesel fuels with the lowest CFPP were from algae, corn and canola oil. As I just mentioned you that biodiesel lipid content or the free fatty acid content is very good.

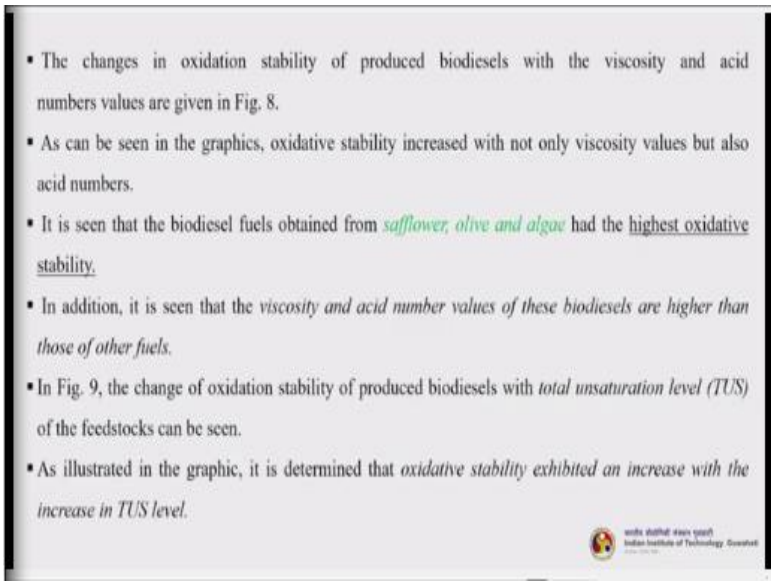
(Refer Slide Time: 48:18)



So, that is why you always get better fuel properties. So, you can see in the figure 7, the change of the CFPP value of the biodiesel along with the LCSF; you can again see that here the CFPP value is better for the sunflower oil and also for some other base oils**.**

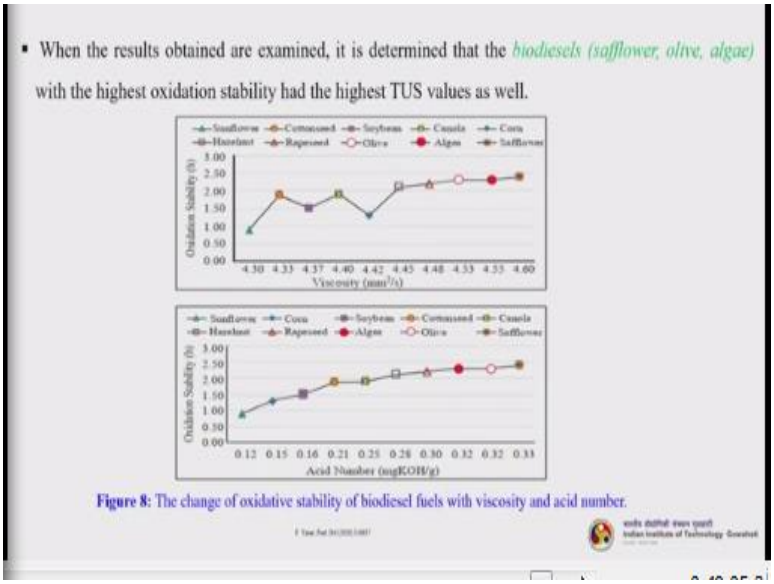
So, the next one oxidation stability; oxidation stability is one of the most critical fuel properties affecting the long term storage and uses of a biodiesel fuel. It indicates the fuel's resistance to auto oxidation. The temperature, the amount of oxygen and the material of the container where the fuel is stored are the decisive parameters on the oxidation reactions.

(Refer Slide Time: 48:58)



The changes in oxidation stability of the produced biodiesel with the viscosity and acid numbers are given in the figure, next figure here.

(Refer Slide Time: 49:05)



So, you can see from these 2 figures how the oxidative stability is changing with respect to the acid number the below figure and the viscosity the top figure for the different oils**.** So, if you go back we can see that, it is seen that the biodiesel fuels obtain from the safflower, olive and algae had the highest oxidative stability. Again algae is supposed to be good in terms of oxidative stability also.

In addition, it is seen that the viscosity and the acid number values of these biodiesels are higher than those of the other fuels. In the figure 9, the change of oxidation stability of the produced biodiesel with total unsaturation level - TUS of the feedstock can be seen. As illustrated in the graphic, it is determined that oxidative stability exhibited an increase with the increase in the TUS level.

(Refer Slide Time: 49:49)

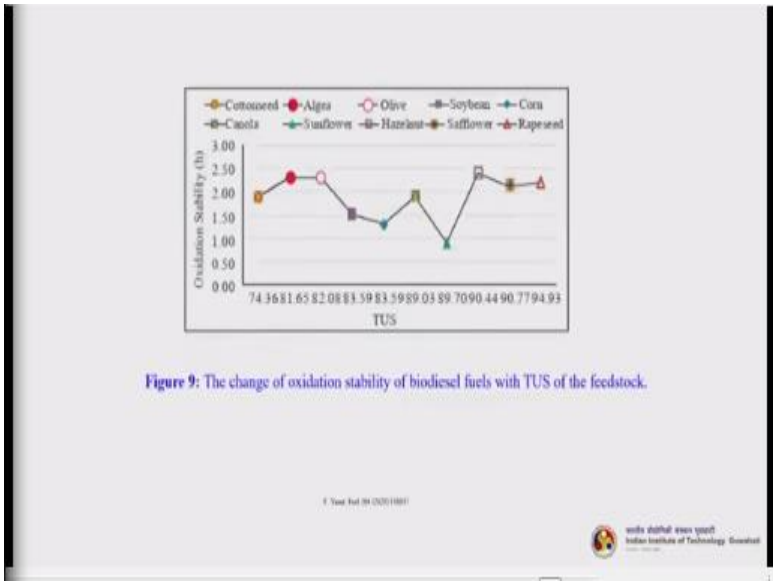
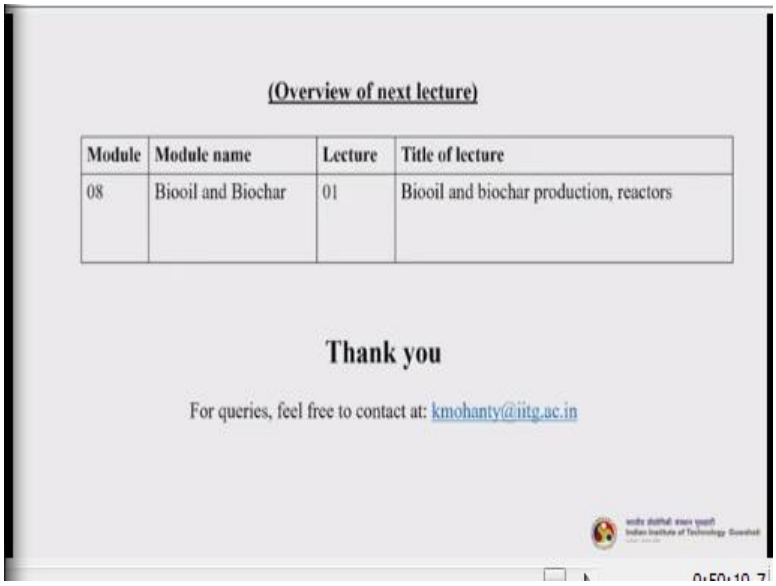


Figure 9: The change of oxidation stability of biodiesel fuels with TUS of the feedstock.

So, this is in this figure you can see here, how the change of the oxidation stability is happening with the TUS number for different types of vegetable oils even the algae. You can see that algae it is good and followed by the hazelnut oil, the stability is better and even for the olive oil also**.**

(Refer Slide Time: 50:11)



So, with this I conclude today's lecture. In case 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 very much.