Waste to energy conversion

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Lecture – 39
Energy Production from Algal Biomass – 1

Good morning. Now, we will start discussion on a new module energy production from algal biomass. In the previous module we have discussed on the production and cultivation of the algal biomass and its harvesting from the waste water or the liquid media. In this module we will concentrate on the production of energy from the harvested algal biomass.

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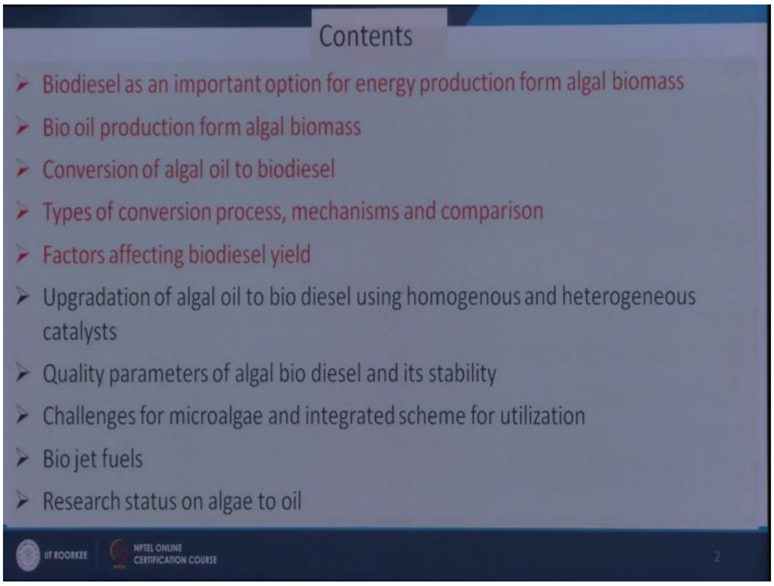

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- Types of conversion process, mechanisms and comparison
- Factors affecting biodiesel yield
- Upgradation of algal oil to bio diesel using homogenous and heterogeneous catalysts
- Quality parameters of algal bio diesel and its stability
- Challenges for microalgae and integrated scheme for utilization
- Bio jet fuels
- Research status on algae to oil

And we will discuss on this topic that is biodiesel as an important option for energy production from algal biomass, then bio oil production from algal biomass, conversion of algal oil to biodiesel, then types of conversion process mechanism and comparison, factors affecting biodiesel yield, upgradation of algal oil to biodiesel using homogenous and heterogeneous catalysts, quality parameters of algal biodiesel and its stability, challenges for microalgae and integrated scheme for utilization, bio jet fuels and finally, research status on algae to oil production.

So, at first we will see biodiesel as an important option for energy production. So, once we are able to get the algal biomass after harvesting we have to use it and there are number of ways we can follow to produce energy as given in this slide, we may process the algal biomass through pyrolysis, we may process it through biogas production that is energy digestion. We can process this through syngas that is gasification that is syngas production and we can go for biodiesel production and bio jet fuel production.

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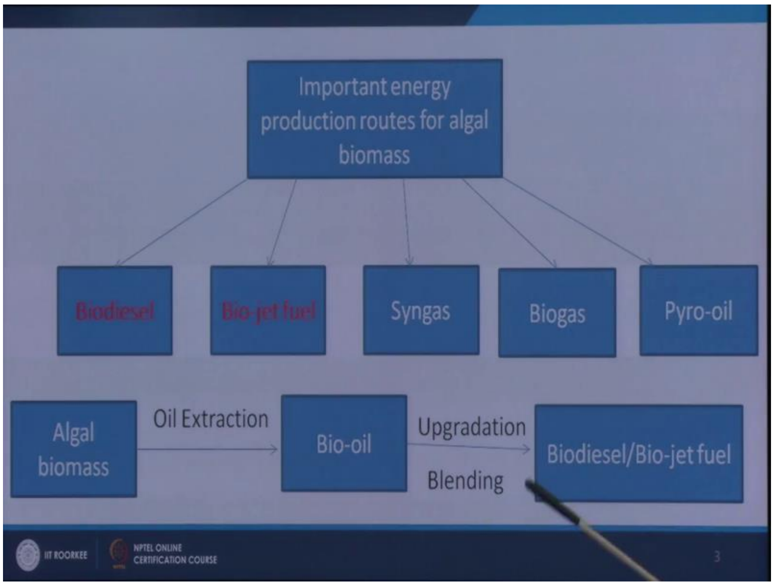

Important energy production routes for algal biomass

Biodiesel

Bio-jet fuel

Syngas

Biogas

Pyro-oil

Algal biomass

Oil Extraction

Bio-oil

Upgradation

Blending

Biodiesel/Bio-jet fuel

So, these are the major important routes through which the algal biomass can be processed for the production of energy. We have discussed all those parts that pyrolysis, gasification, anomic digestion and transesterification for biodiesel production. But here we will concentrate on basically how to produce biodiesel and bio jet fuel from the algal biomass.

So, for this purpose our first step is to produce bio oil from the algal biomass through oil extraction we have already discussed the oil extraction from oil seeds. So, similar methods will be used here, but there will be some difference we will be describing those things later on and this bio oil which will be derived from the algal biomass that is algal bio oil that will be upgraded to biodiesel and bio jet fuel. So, bio jet fuel is a new one we have not ever discussed in this course now will be discussing for the bio jet fuel production using microalgae.

Now, this is the flow sheet which is followed basically for the production of bio oil from the algal biomass.

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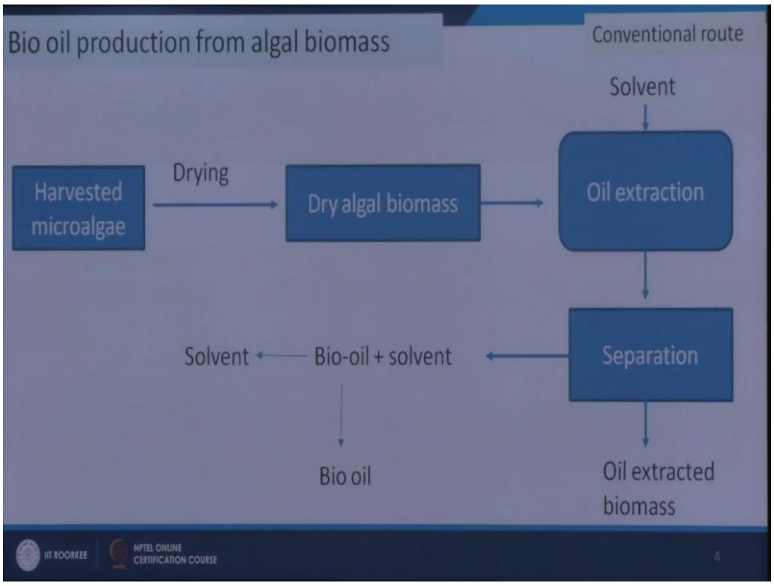

Bio oil production from algal biomass

Conventional route

So, after harvesting the biomass is dried conventionally the high moisture content is removed. So, drying then dried biomass dry algal biomass that is added with some solvent to extract the lipid. So, solvent extraction is the main route for the oil extraction from the algal biomass, but here in the previous case while we are discussing oil or lipid extraction from the vegetable oil seeds in that case solvent was different here solvent will be different because algae will be continuing both polar and non polar lipids. So, solvents will be a polar and non polar nature with some ratio and then we will be able to separate the lipids and that lipid will be further separated, lipid plus biomass on converted biomass or rest of the biomass. So, those biomass will be separated that is oil extracted biomass and oil are lipid part will come here and that lipid will come will the solvent which we are using, so solvent has to be removed from the lipid or bio oil.

So, thereafter we will after separation we will get bio oil and finally, we will be getting insolvent that can be used further for this oil extraction method. So, this is very conventional method, but in this method the drying steps requires very high amount of energy that why this process this process is not so economic. So, people are trying to develop new methodology or new techniques to reduce the drying step or the extent of drying or in place of drying the people are trying to use the weight biomass in (Refer

Time: 05:04) phase directly with some solvent and to get the extraction of the oil, we will be discussing this part later on.

Now, for solvent extraction we have seen that in oil seeds to bio oil production then expeller or mechanical price was used and solvent extraction was also used. So, solvent extraction and here the solvent extraction similar type of mechanism, but only difference only the both polar and non polar solvents are used in this case. So, what happens in this case? What is the mechanism? If we use the algal biomass, so this is the algal biomass this is your cell wall and inside is our cell membrane.

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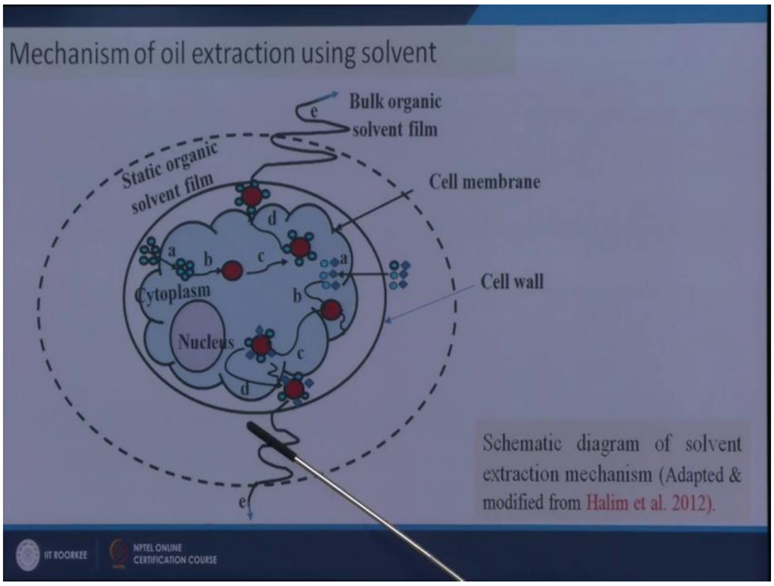

Mechanism of oil extraction using solvent

Schematic diagram of solvent extraction mechanism (Adapted & modified from Halim et al. 2012).

So, we are using solvent. So, solvent are polar and non polar solvent. So, polar non polar solvent will pass through this the cell wall and it will go through the cell membrane and will attach with the proteins which are non polar in nature. So, non polar protein will be attached in non polar solvent. So, it will be getting out from the cell membrane then cell wall and then there will be some layer of the solvent. So, in the solvent layer it is coming ultimately it is going to the bulk of the solvent.

So, this is the mechanism of the extractions of the non polar lipid by this no polar solvent, but if it is a polar solvent then polar solvent will also enter into the cell in the similar way and it will capture the polar lipids. You see as the polar lipid it is taken by this polar solvent and again it is coming back from the cell through cell membrane and cell wall and it is reaching to this the layer of the solvent and ultimately to the bulk of the solvent. So, this is the mechanism for the extractions of bio oil from the algal biomass using conventional solvent. So, I will show you some examples of solvents.

So, here the extraction method is soxhlet extractions and batch extraction was used and these are the micro algal species which was used for the oil extraction.

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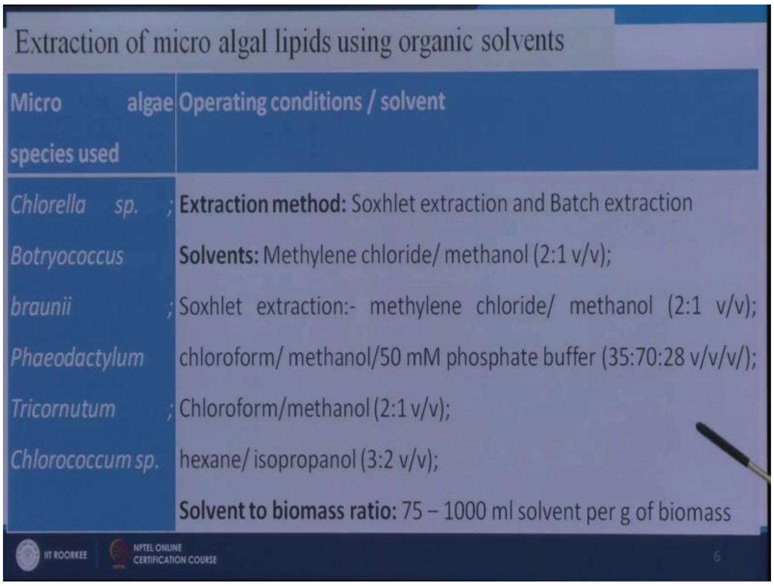

Extraction of micro algal lipids using organic solvents

Micro algae species used	Operating conditions / solvent
Chlorella sp. ; *Botryococcus braunii* ; *Phaeodactylum Tricornutum* ; *Chlorococcum sp.*	**Extraction method:** Soxhlet extraction and Batch extraction **Solvents:** Methylene chloride/ methanol (2:1 v/v); Soxhlet extraction:- methylene chloride/ methanol (2:1 v/v); chloroform/ methanol/50 mM phosphate buffer (35:70:28 v/v/v/); Chloroform/methanol (2:1 v/v); hexane/ isopropanol (3:2 v/v); **Solvent to biomass ratio:** 75 – 1000 ml solvent per g of biomass

So, soxhlet extractions the solvent was used methylene chloride or methanol at the ratio of 2 is to 1, and somewhere chloroform methanol and 50 millimole phosphate buffer in this ratio 35 is to 70 is to 28, somewhere chloroform methanol with 2 is to 1 and somewhere hexane isopropanol 3 is to 2 different solvent ratio, different types of solvent in different ratio was used in this cases and in the process total solvent to biomass ratio was 75 to 1000 ml solvent per gram of biomass. So, these are some example of solvent extraction method.

Now, we will be discussing some advance type of method solvent extraction that is super critical solvent extraction method. So, in this case say this is our algal biomass we are sending the super critical carbon dioxide for example, so super critical carbon dioxide is coming through this and then the algal biomass will be having some layer. So, static super critical carbon dioxide film will form with the biomass and then it will be the bulk of the super critical carbon dioxide flow.

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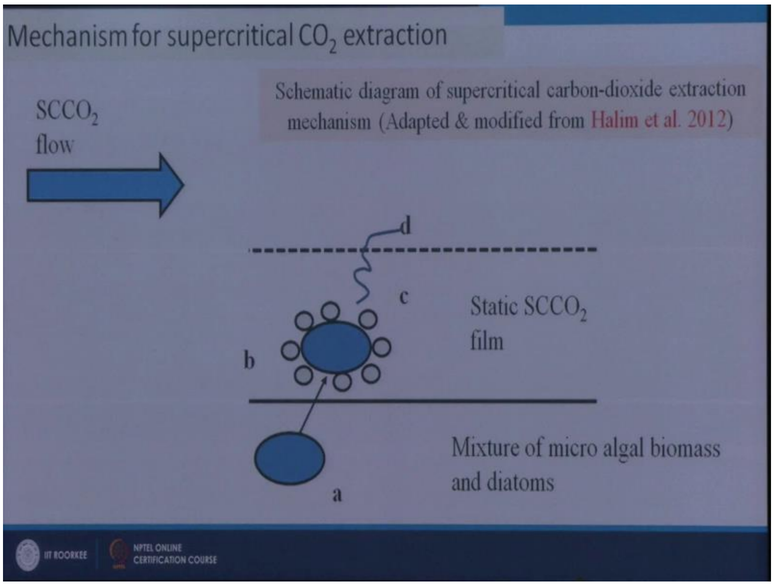

Mechanism for supercritical CO_2 extraction

Schematic diagram of supercritical carbon-dioxide extraction mechanism (Adapted & modified from Halim et al. 2012)

So, here the transfer will take place, the carbon dioxide is not a polar. So, this is a non polar, so non polar proteins will go out from this mass algal biomass but polar protein will be difficult to separate through this method.

So, in some case some polar solvent is added with it we will give some example here. So, extraction pressure this is one example there where extraction pressure was used 400 500 and 700 bar and temperature was 40 and 55 degree centigrade.

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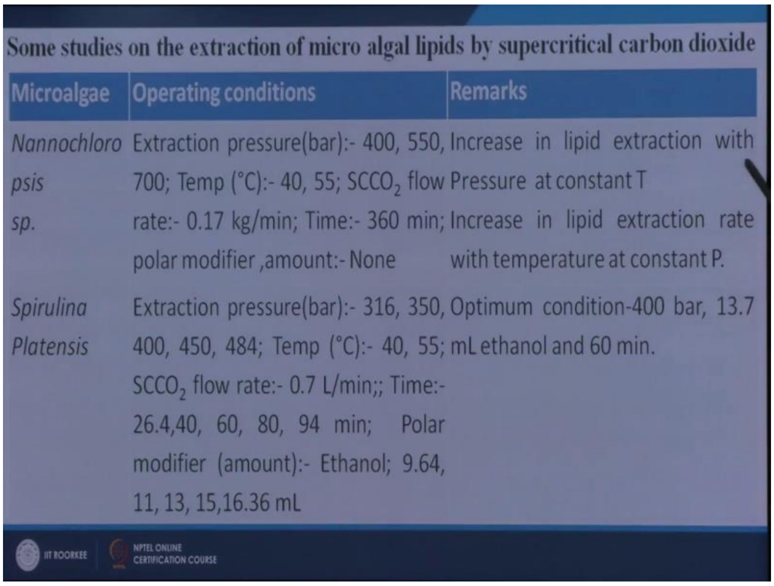

Some studies on the extraction of micro algal lipids by supercritical carbon dioxide

Microalgae	Operating conditions	Remarks
Nannochloropsis sp.	Extraction pressure(bar):- 400, 550, 700; Temp (°C):- 40, 55; $SCCO_2$ flow rate:- 0.17 kg/min; Time:- 360 min; polar modifier ,amount:- None	Increase in lipid extraction with Pressure at constant T Increase in lipid extraction rate with temperature at constant P.
Spirulina Platensis	Extraction pressure(bar):- 316, 350, 400, 450, 484; Temp (°C):- 40, 55; $SCCO_2$ flow rate:- 0.7 L/min;; Time:- 26.4,40, 60, 80, 94 min; Polar modifier (amount):- Ethanol; 9.64, 11, 13, 15,16.36 mL	Optimum condition-400 bar, 13.7 mL ethanol and 60 min.

As you know the critical point of CO 2 is a 31 degree centigrade and 74 pressure bar pressure, but in this case the high pressure was used and temperature is 40 to 55 degree centigrade and the flow rate was 0.17 kg per minute and then time 360. Polar modifier was not added in this case, but in the second case polar modifier was added that is ethanol. So, different amount of ethanol was added and the efficiency was tested to get the optimum amount of ethanol which has to be added with the super critical carbon dioxide solvent.

So, here some observations are obtained and important that is increasingly in lipid extractions with pressure at constant temperature, this temperature remain constant and pressure increases then lipid extractions increases and increase in lipid extraction rate with temperature at constant pressure and it is in this case it has been found that optimum condition is 400 bar with 13.7 ml ethanol and 60 minute of extraction process. Some other examples are given here different types of algal species and different conditions that is 200 bar to 350 bar and extraction temperature 40 to 55 and flow rate is different and time is also different from the others. And in this case another condition is provided that is 100 250 350 bar and temperature 50 60 and modified, modifier was added. The polar modifier that is 10 percent ethanol is added here and here some interesting information is there the lipid increased with pressure at constant temperature, but it decreased with temperature constant lower pressure, but increased with temperature at constant higher pressure.

So, that is one particular type of observation was they have reported here. So, similar effect of temperature and pressure and total lipid yield like chlorella vulgaris was also observed by this micro algal strength or biomass. Now we will see the single step extraction of oil that is no drying is required that is very expensive process.

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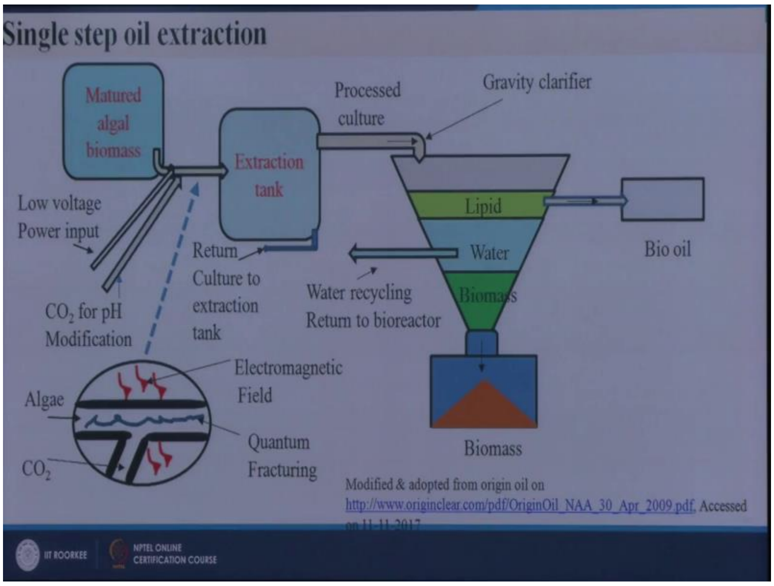

Single step oil extraction

Modified & adopted from origin oil on http://www.originclear.com/pdf/OriginOil_NAA_30_Apr_2009.pdf, Accessed on 11-11-2017

So, this is basically patented technology by the origin oil and in this technology the matured algal biomass in a first phase it is sent to extraction tank through a pipe and when it is passing through this pipe then some carbon dioxide is passed through it to modify the pH of the solution and low voltage power input is provided. So, low voltage power input as proposed by the origin oil, the due to quantum fracturing the algal biomass the lipids from the algal biomass comes out from the cell. So, no drying is required. So, when in the extraction tank, extraction tank we get lipid water as well as biomass. So, when we separate it we can get three layer – lipid, water and biomass, that is lipid in this biomass lipid is less. So, the water is recycled and this lipid is used as bio oil.

Now, we will go to the next part that is we have a got extracted oil now we have to convert it into biodiesel through the transesterification process. So, in the previous module we have already discussed transesterification process and basic reactions involved in it here will be discussing on the mechanistic path what are the chemical reactions going on and what are the mechanisms for different types of catalysts and we will see that.

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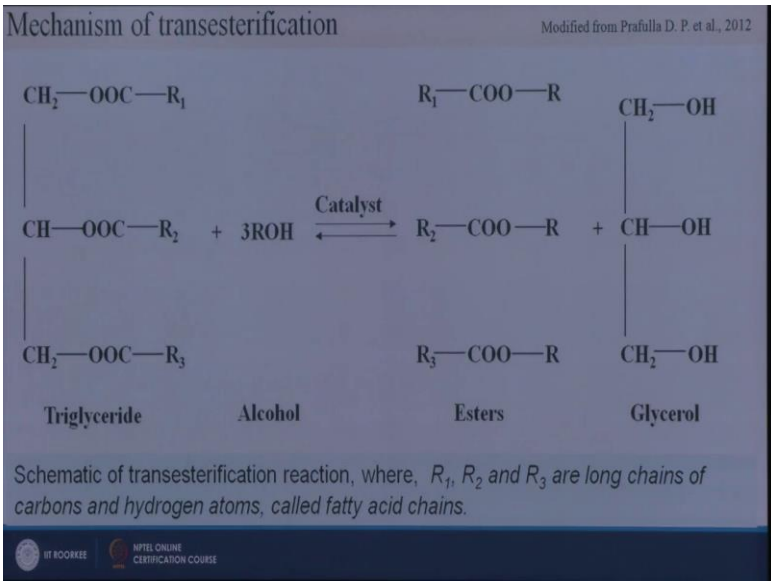

Mechanism of transesterification

Modified from Prafulla D. P. et al., 2012

Schematic of transesterification reaction, where, *R_1, R_2 and R_3 are long chains of carbons and hydrogen atoms, called fatty acid chains.*

This is the basic reactions as you have discussed earlier that is triglyceride reacts with some alcohol the methanol ethanol or any higher alcohol and then in presence of catalyst. So, they gives us esters and this is glycerol. So, this esters are our desired product for the biodiesel and this catalyst may be base catalyst acid catalyst and heterogeneous acid base catalyst. So, if we can classify the type of catalyst we can get different types of catalyst here that is catalyzed transesterification process may be homogenous base catalyst, homogenous acid catalyst, heterogeneous base catalyst, heterogeneous acid catalyst and enzyme catalyzed.

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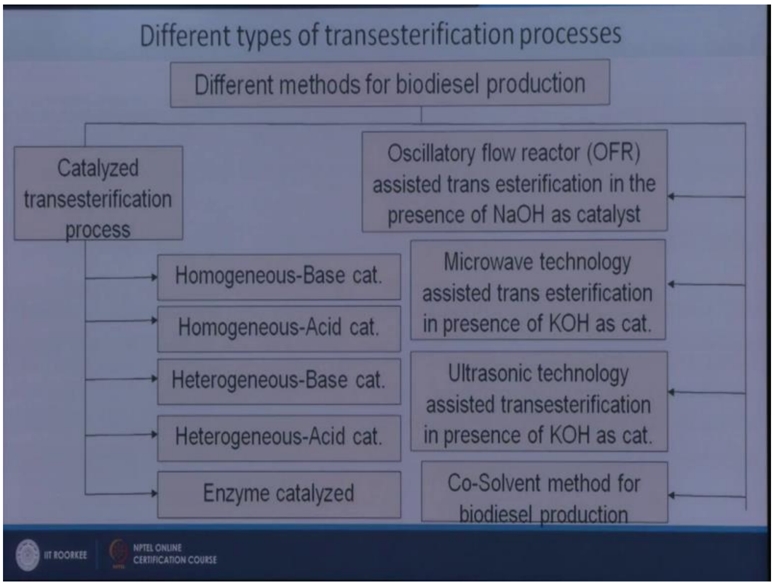

Different types of transesterification processes

Different methods for biodiesel production

Catalyzed transesterification process

- Homogeneous-Base cat.
- Homogeneous-Acid cat.
- Heterogeneous-Base cat.
- Heterogeneous-Acid cat.
- Enzyme catalyzed

Oscillatory flow reactor (OFR) assisted trans esterification in the presence of NaOH as catalyst

Microwave technology assisted trans esterification in presence of KOH as cat.

Ultrasonic technology assisted transesterification in presence of KOH as cat.

Co-Solvent method for biodiesel production

So, these are the basic types of catalytic reactions which have been tested for the production of biodiesel from algal bio oil, apart from this some improved technology or process also been used. Like say oscillatory flow reactor, assisted transesterification in presence of NaOH as catalyst, then microwave assisted transesterification in presence of KOH as catalyst, ultrasonic technology assisted transesterification in presence of KOH as catalyst and co solvent method for biodiesel production. So, these methods have been applied to further improve the efficiency of the process.

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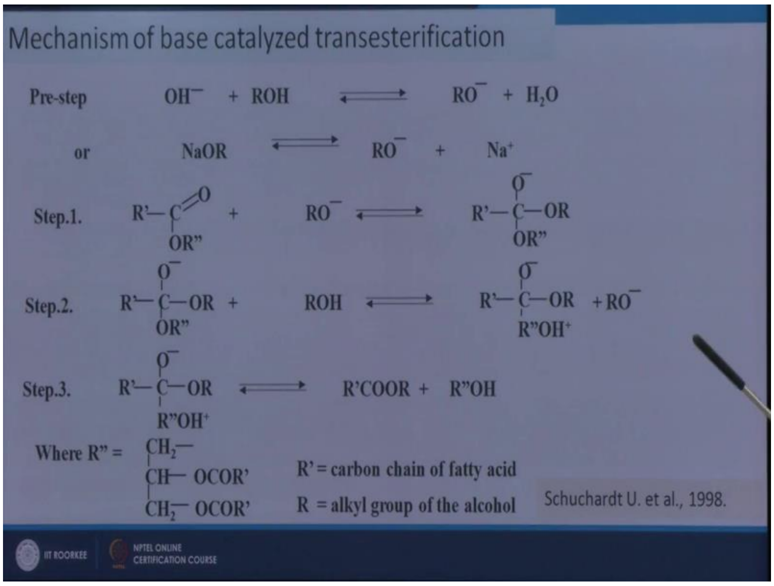

Mechanism of base catalyzed transesterification

Pre-step $OH^- + ROH \rightleftarrows RO^- + H_2O$

or $NaOR \rightleftarrows RO^- + Na^+$

Step.1. $R'-C(=O)(OR'') + RO^- \rightleftarrows R'-C(O^-)(OR)(OR'')$

Step.2. $R'-C(O^-)(OR)(OR'') + ROH \rightleftarrows R'-C(O^-)(OR)(R''OH^+) + RO^-$

Step.3. $R'-C(O^-)(OR)(R''OH^+) \rightleftarrows R'COOR + R''OH$

Where R" = CH_2-, $CH-OCOR'$, CH_2-OCOR'

R' = carbon chain of fatty acid

R = alkyl group of the alcohol

Schuchardt U. et al., 1998.

So, now at first we will see the mechanism of different types of catalytic conversion process. So, if it is a base catalysis process. So, in this case we have to add some base catalyst say NaOH is added. So, NaOH will react with alcohol and NaOR will form. So, NaOR will give us OR minus plus Na plus, so OR minus and Na plus. So, this OR minus plus triglyceride at the C O double dash this will give us this moiety.

Now you see what is this R double dash that is equal to this one CH 2, CH OCOR and CH 2 OCOR dash. So, this is our triglyceride moiety, triglyceride that will react with RO minus we are getting R dash C O minus OR OR double dash. So, this we are getting. So, from this, this moiety is again reacting with ROH another alcohol. So, it is converting to R dashed C O minus OR OH plus; that means, and then this one will further be converted to R dashed C O OR and this will be R OH, R double dashed OH that will be formed.

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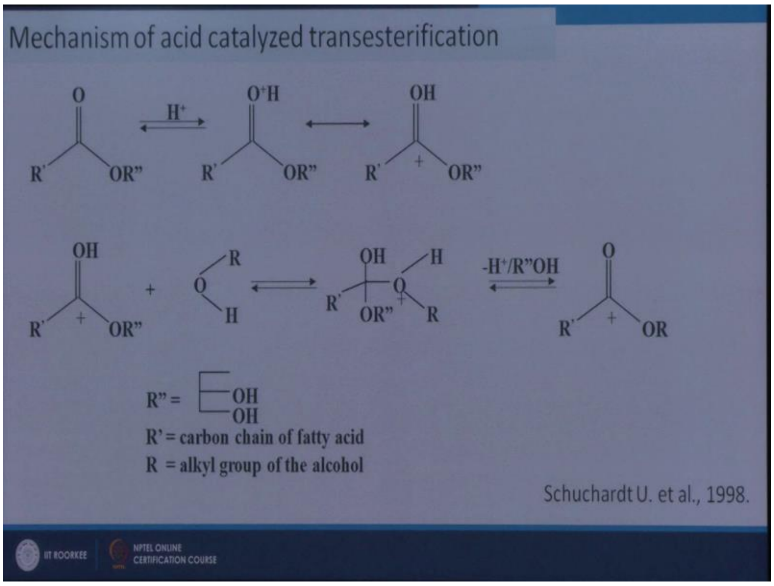

Mechanism of acid catalyzed transesterification

R' = carbon chain of fatty acid

R = alkyl group of the alcohol

Schuchardt U. et al., 1998.

So, this is the based catalyzed reaction mechanism and acid catalyzed reaction mechanism is different from this. So, here this is our triglyceride. So, this triglyceride in presence of H plus this it is converted to this one. So, H plus is first attached with the oxygen, then this moiety is formed. So, from this it is converted to the H plus starts sift. So, it is coming to this one. So, this moiety further reacts with alcohol and produces this intermediate product. So, this intermediate product is further converted to R dash C O OR. So, we had R dash C O OR double dashed now we are getting R dashed C O OR this is our desirable product and this is transesterification. So, here it is interesting that R double dashed is equal to this glycerol group because acid catalyzed reactions are basically used we have discussed in the previous module to esterify the free fatty acids.

So, free fatty acids are shown here or this can also be used with esters. So, OH can also be replaced by R. So, this is the mechanism for the acid catalysis reactions for the transesterification and for the heterogeneous catalysis the reaction mechanism is similar to base catalyzed reactions.

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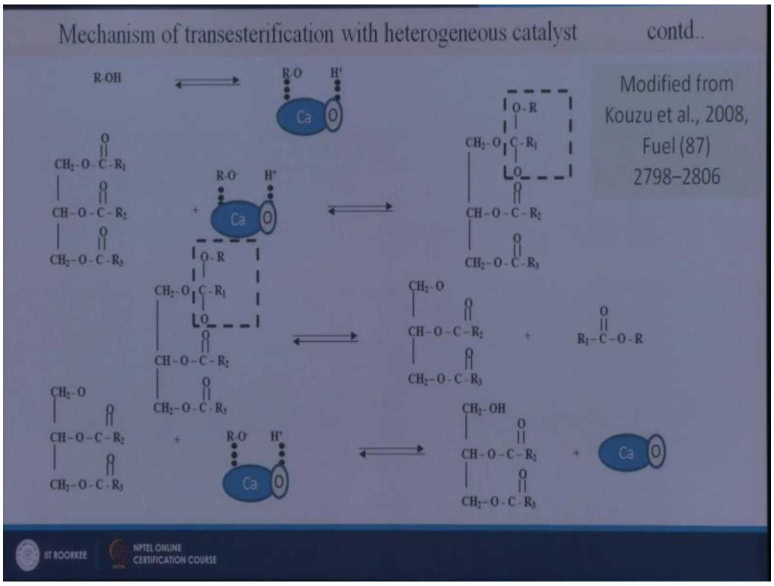

Mechanism of transesterification with heterogeneous catalyst contd..

Modified from Kouzu et al., 2008, Fuel (87) 2798–2806

But in this case the base, in case of base catalyzed reactions, so the NaOH or KOH are used, so both are soluble in the media and Na plus and OH minus is formed, but in this case the catalyst has not soluble it is a solid phase. So, Ca and O's for example, say Ca O catalyst. So, Ca and O will be available in solid form and Ca will help to form the OR minus and O will help to form the H plus when the similar reactions with respect to base catalyst will be taking place, but unlike base catalyst reactions Ca O will not be dissolved in the liquid phase.

So, this the reaction steps R OH will alcohol will react with this and will form this intermediate moiety with catalyst alcohol moiety and that will react with the triglyceride and after this triglyceride reactions this will be the first step or first intermediate product. So, similar type of reactions which we have just discussed here in case of base catalyzed reactions similar type of reactions will take place and then this moiety will further be converted to this one and this one further be converted to this one and our catalyst will be separated. So, this is the mechanism of heterogeneous catalysis for the transesterification.

Now we have already discussed in the previous module also how the process efficiency can be controlled or on which factors the efficiency is dependent. So, those are the factors oil temperature, reaction temperature, ratio of alcohol to oil, catalyst type and concentration, and intensity of mixings purity of reactions.

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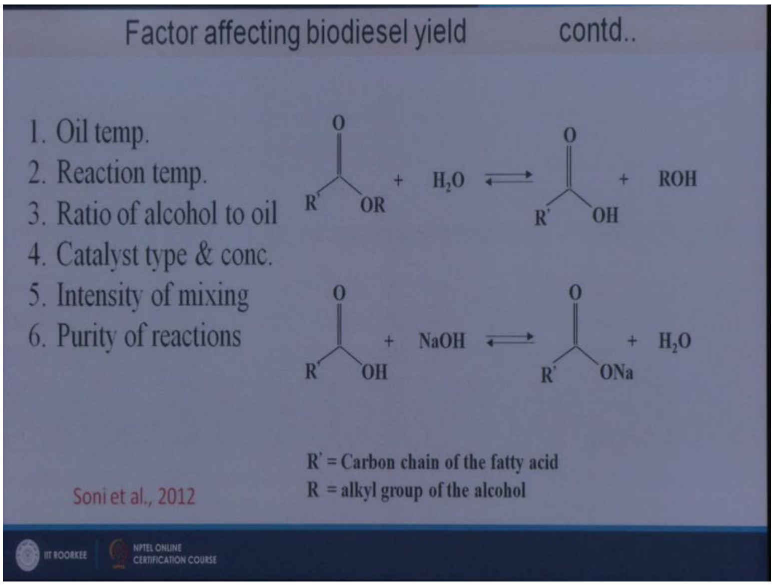

Factor affecting biodiesel yield contd..

1. Oil temp.
2. Reaction temp.
3. Ratio of alcohol to oil
4. Catalyst type & conc.
5. Intensity of mixing
6. Purity of reactions

R' = Carbon chain of the fatty acid
R = alkyl group of the alcohol

Soni et al., 2012

So, the all those things already we have discussed in the previous module also, but one thing we have discussed that in case of base catalyzed reactions acid or free fatty acids or some esters also formed soap. So, that how the soap is formed that reaction is given here. So, this is our R dashed O OR say some free fatty acids or say fatty acid esters if R is H then free fatty acids or in this case it is fatty acid esters. So, this ester will react with H 2 O and this alcohol will form and that will further react with NaOH and that will give us sodium salt of fatty acids. So, that is called soap. So, this is not desirable. So, that is the disadvantage of base catalyzed reaction.

But if we use the heterogeneous catalysis this formation does not take place NaOH cannot C O a H are just given C O example. So, C O cannot join here. So, soap formation cannot take place here will see some comparison of different types of catalyst that is base catalyzed, acid catalyzed and enzyme catalyzed reaction.

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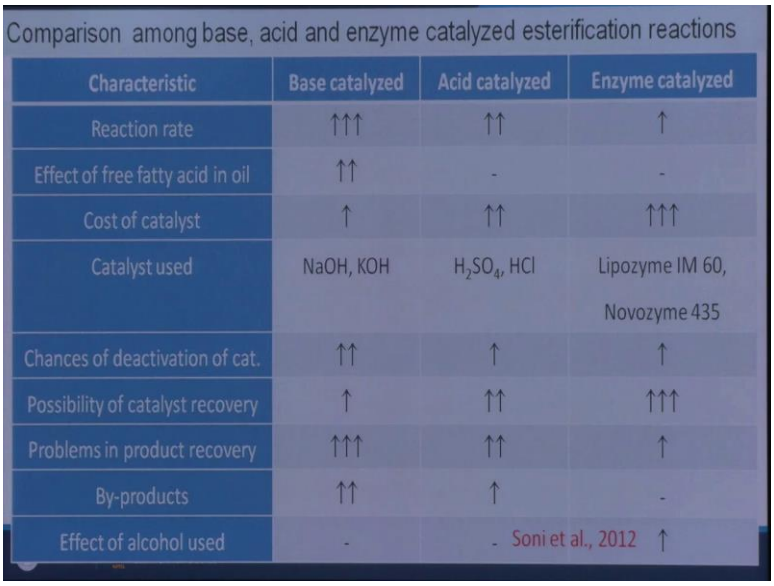

Comparison among base, acid and enzyme catalyzed esterification reactions

Characteristic	Base catalyzed	Acid catalyzed	Enzyme catalyzed
Reaction rate	↑↑↑	↑↑	↑
Effect of free fatty acid in oil	↑↑	-	-
Cost of catalyst	↑	↑↑	↑↑↑
Catalyst used	NaOH, KOH	H_2SO_4, HCl	Lipozyme IM 60, Novozyme 435
Chances of deactivation of cat.	↑↑	↑	↑
Possibility of catalyst recovery	↑	↑↑	↑↑↑
Problems in product recovery	↑↑↑	↑↑	↑
By-products	↑↑	↑	-
Effect of alcohol used	-	-	↑

Soni et al., 2012

So, for the comparison we have to identify some parameters. So, these are the parameters which we have identified that is reaction rate, effect of free fatty acid in oil, cost of catalyst, catalyst used and chances of deactivation of catalyst, possibility of catalyst recovery and the problems in product recovery and by products and what are the effect alcohol used. So, those parameters we have used for the comparison and from this comparison it seems that all the catalyst are having some pros and cons. So, all are having some positive and some negative points and extensive research is going on to develop new catalyst. Out of this three NaOH catalysts have been mostly used and acid catalyst has been less used and in some cases enzyme catalyst has been reported. So, in very few literature.

Now, we will see the different methods like say the catalyzed transesterification that is the best process, then we are having catalyzed transesterification using co solvent and another method an oscillatory flow reactor assisted catalyzed transesterification and then microwave technology assisted catalyzed transesterification and then ultrasonic technology assisted catalyzed esterification.

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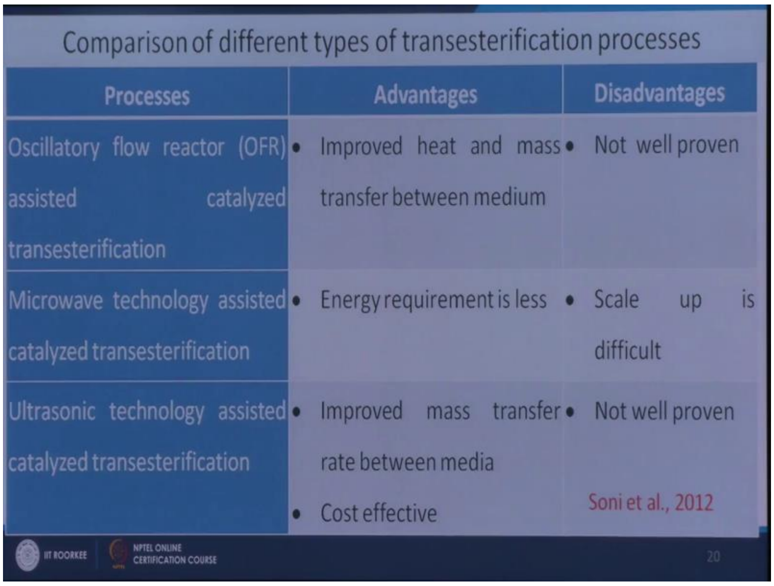

Comparison of different types of transesterification processes

Processes	Advantages	Disadvantages
Oscillatory flow reactor (OFR) assisted catalyzed transesterification	• Improved heat and mass transfer between medium	• Not well proven
Microwave technology assisted catalyzed transesterification	• Energy requirement is less	• Scale up is difficult
Ultrasonic technology assisted catalyzed transesterification	• Improved mass transfer rate between media • Cost effective	• Not well proven

Soni et al., 2012

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So, all those methods are further improvement of the conventional transesterification methods and the advantage and disadvantages are provided in this slide. So, catalyzed in transesterification is very primitive and mostly used process and it is well proven, but its performance can be highly effected with catalyst type.

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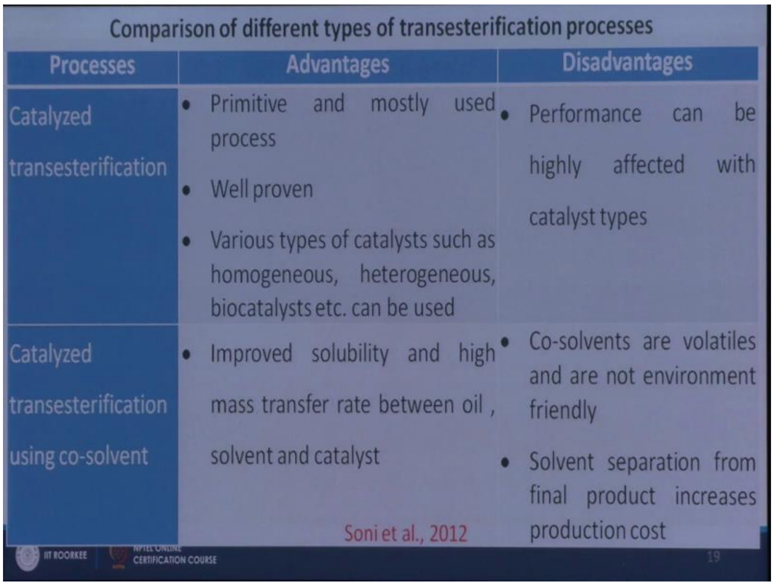

Comparison of different types of transesterification processes

Processes	Advantages	Disadvantages
Catalyzed transesterification	• Primitive and mostly used process • Well proven • Various types of catalysts such as homogeneous, heterogeneous, biocatalysts etc. can be used	• Performance can be highly affected with catalyst types
Catalyzed transesterification using co-solvent	• Improved solubility and high mass transfer rate between oil, solvent and catalyst	• Co-solvents are volatiles and are not environment friendly • Solvent separation from final product increases production cost

Soni et al., 2012

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So, this is catalyst transesterification using co solvent when we are using some co solvent it improves the solubility. So, co solvents are volatiles, the disadvantage is that co solvents are volatile and are not environment friendly.

So, these are the disadvantages and this improves the performance by increasing the solubility of the oil and in the conversion is improved. So, this is the advantage some other things for other process is like say OFR they improve heat and mass transfer between medium, microwave reduces the energy requirements because microwave itself provides some sort of some amount of energy and then ultrasonic improved mass transfer rate between media. So, these are the advantage of this process some disadvantages are provided here these are not so well proven and not well developed technology. So, up to this in this part of this module we will discuss the rest in the next part of this module.

Thank you very much for your patience.