Waste to energy conversion
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Lecture – 40
Energy Production form Algal Biomass – 2

Hi friends. Now we will start discussion on the second part of this module Energy Production from Algal Biomass.

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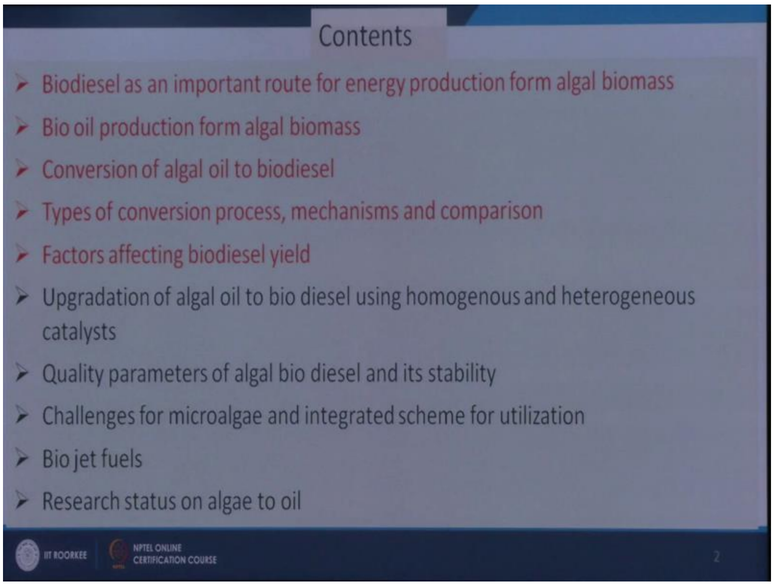

In the first part we have discussed on biodiesel and bio oil production from algal biomass, different types of catalyst which can be used for the biodiesel production and their mechanism and in this part we will discuss on the upgradation of algal oil to biodiesel using homogenous and heterogeneous catalyst, we will giving some examples where this has been used. Then we will go for quality parameters of algal biodiesel and its stability issues. And then we will give some challenges for microalgae and then bio jet fuels and research status on the algae to oil.

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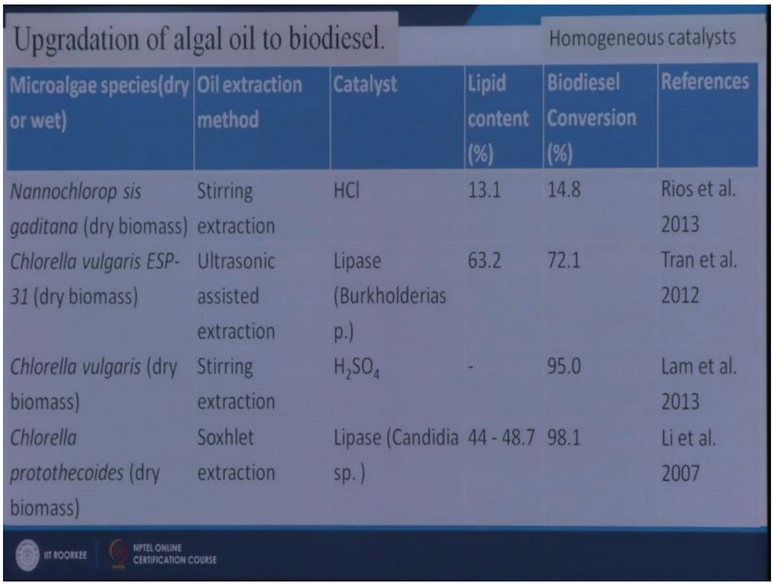

Upgradation of algal oil to biodiesel.

Homogeneous catalysts

Microalgae species(dry or wet)	Oil extraction method	Catalyst	Lipid content (%)	Biodiesel Conversion (%)	References
Nannochlorop sis gaditana (dry biomass)	Stirring extraction	HCl	13.1	14.8	Rios et al. 2013
Chlorella vulgaris ESP-31 (dry biomass)	Ultrasonic assisted extraction	Lipase (Burkholderias p.)	63.2	72.1	Tran et al. 2012
Chlorella vulgaris (dry biomass)	Stirring extraction	H_2SO_4	-	95.0	Lam et al. 2013
Chlorella protothecoides (dry biomass)	Soxhlet extraction	Lipase (Candidia sp.)	44 - 48.7	98.1	Li et al. 2007

Now, see here some homogenous catalyst have been used for the production of biodiesel from the bio oil produced from the microalgae different types of micro algal strains have been used as mentioned here, different types of catalyst has been used, different lipid content of the algal biomass was reported and different biodiesel conversion was achieved. So, from this stability all these information are published in very recent years that is 2012-13, 2017, etcetera.

So, here we see the biodiesel conversion is possible up to 98 percent here as you put it by Li et al with another other cases it is 14.8 percent. So, there is a wide variation of biodiesel productions depending upon the name of the microalgae, depending upon the catalyst used and depending upon they are lipid content etcetera and the oil extraction methods also different.

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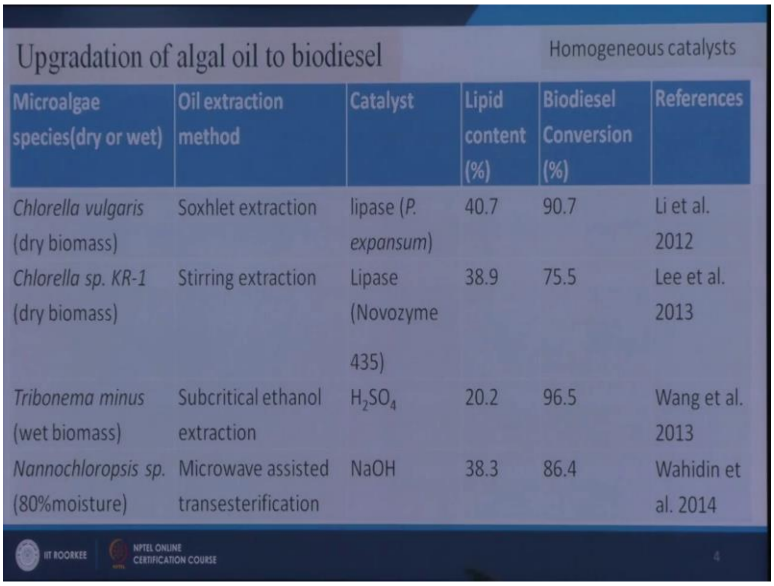

Microalgae species(dry or wet)	Oil extraction method	Catalyst	Lipid content (%)	Biodiesel Conversion (%)	References
Chlorella vulgaris (dry biomass)	Soxhlet extraction	lipase (*P. expansum*)	40.7	90.7	Li et al. 2012
Chlorella sp. KR-1 (dry biomass)	Stirring extraction	Lipase (Novozyme 435)	38.9	75.5	Lee et al. 2013
Tribonema minus (wet biomass)	Subcritical ethanol extraction	H_2SO_4	20.2	96.5	Wang et al. 2013
Nannochloropsis sp. (80%moisture)	Microwave assisted transesterification	NaOH	38.3	86.4	Wahidin et al. 2014

Some other homogenous catalyst are reported are present in this slide here also we get different types of micro algal strains different types of oil extraction method like Soxhlet operators, stirring exaction, subcritical ethanol extractions and microwave assisted transesterification this is another. So, here biodiesel conversion is also different. So, in this case 75 to say 96.5 percent are reported by different researchers. So, this is say homogeneous catalyst. So, here the conversion is considerable very good that is 80 percent, 90 percent, 75 percent, etcetera, but the difficulties that we have discussed using homogeneous catalyst that soap formation etcetera. So, to reduce this difficulty the people have developed some heterogeneous catalyst also.

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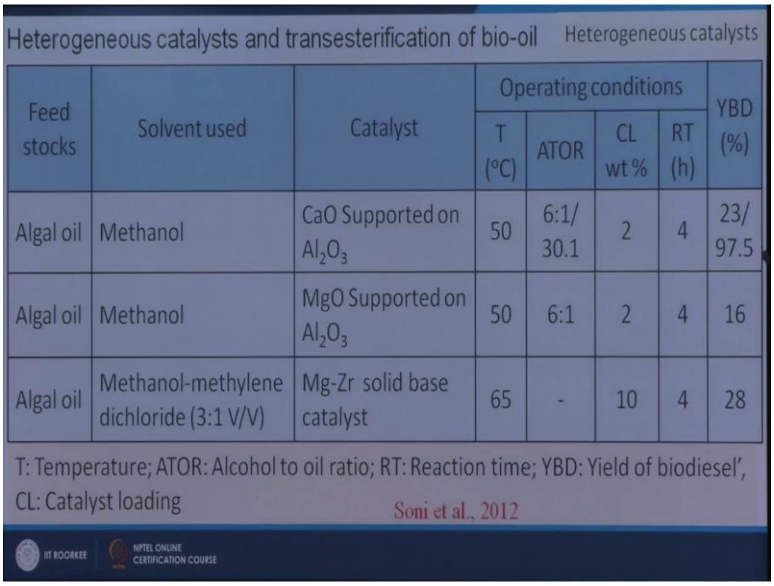

Heterogeneous catalysts and transesterification of bio-oil

Heterogeneous catalysts

Feed stocks	Solvent used	Catalyst	Operating conditions				YBD (%)
			T (°C)	ATOR	CL wt %	RT (h)	
Algal oil	Methanol	CaO Supported on Al_2O_3	50	6:1/ 30.1	2	4	23/ 97.5
Algal oil	Methanol	MgO Supported on Al_2O_3	50	6:1	2	4	16
Algal oil	Methanol-methylene dichloride (3:1 V/V)	Mg-Zr solid base catalyst	65	-	10	4	28

T: Temperature; ATOR: Alcohol to oil ratio; RT: Reaction time; YBD: Yield of biodiesel', CL: Catalyst loading

Soni et al., 2012

So, those heterogeneous catalysts have been used as reported here some of those are calcium oxide supported on Al 2 O 3 and magnesium oxide supported on Al 2 O 3 and magnesium zirconium solid base catalyst. So, these 3 catalysts we have reported in the slide. So, here we see different operating conditions are used temperature is almost 50 to 65 degree centigrade and here alcohol to oil ratio 6 to 30 and catalyst load 2 percent to ten percent and here reaction time is 4 hour.

So, what important information we get here that the bio oil yield biodiesel yield is not very high in this case say 16 percent 28 percent and 23 percent except these case 97.5 percent which was achieved by using 80 percent CaO on Al 2 O 3. So, in general the efficiency or the conversion of biodiesel through this heterogeneous catalyst is lower with respect to the homogenous catalyst with respect to the basically the base catalyze reactions.

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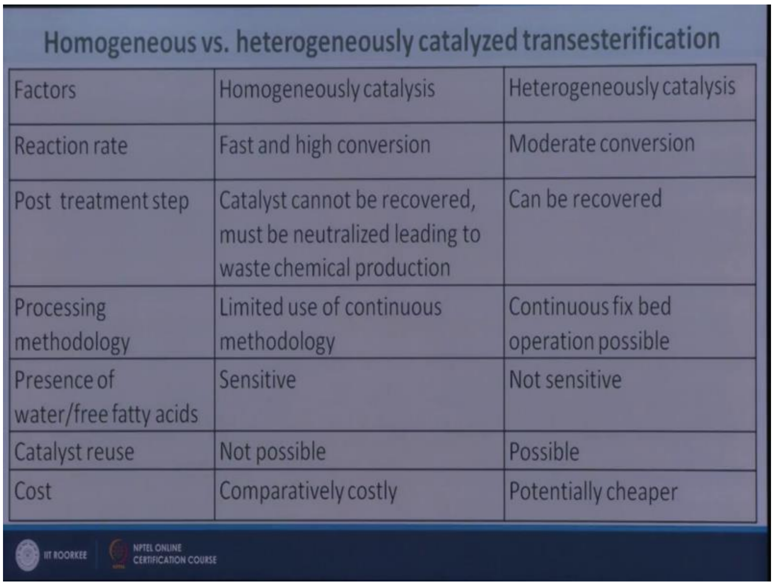

Homogeneous vs. heterogeneously catalyzed transesterification

Factors	Homogeneously catalysis	Heterogeneously catalysis
Reaction rate	Fast and high conversion	Moderate conversion
Post treatment step	Catalyst cannot be recovered, must be neutralized leading to waste chemical production	Can be recovered
Processing methodology	Limited use of continuous methodology	Continuous fix bed operation possible
Presence of water/free fatty acids	Sensitive	Not sensitive
Catalyst reuse	Not possible	Possible
Cost	Comparatively costly	Potentially cheaper

Now, we will make some comparison between homogenous versus heterogeneous catalyst for the transesterification reactions. So, we have identified some factors that is reaction rate post treatment step and then processing methodology presence of water fatty acids and catalyst use and cost. So, on the basis of these parameters we see the homogenously catalyzed and heterogeneously catalyzed are having advantage and disadvantage in some cases. So, reaction rate; obviously, in this case fast and high conversions the homogenous catalyst is very fast reactions, but this is moderate conversion that is why we got laser conversions in this heterogeneous catalyst in the previous slide just we have discussed. And then what we will do with the catalyst in case of homogenous reactions homogenous phase reactions it is difficult to separate the catalyst from the media and it also create some waste chemical. But in case of heterogeneous we can remove the catalyst we can regenerate it and use it, so, limited use of continuous methodology.

So, continuous methods this is not very suitable, but this heterogeneous catalyst process catalytic process is very very suitable for continuous operations using a fixed weight or (Refer Time: 05:57) weight or any other weight reactors. So, this method is sensitive the homogenous method is sensitive to water and free fatty acids, but this our heterogeneously catalyzed reactions is not sensitive to free fatty acids and water present in the oil sample. So, if we can get some more efficient catalyst heterogeneous catalyst that may be the better option because this is not dependent on the free fatty acids and water and the at present the cost is this is comparatively costly and this is potentially cheaper one the heterogeneous. So, heterogeneous catalyst has good potential, but it requires further development in this area and extensive research is going on in this area for it their development.

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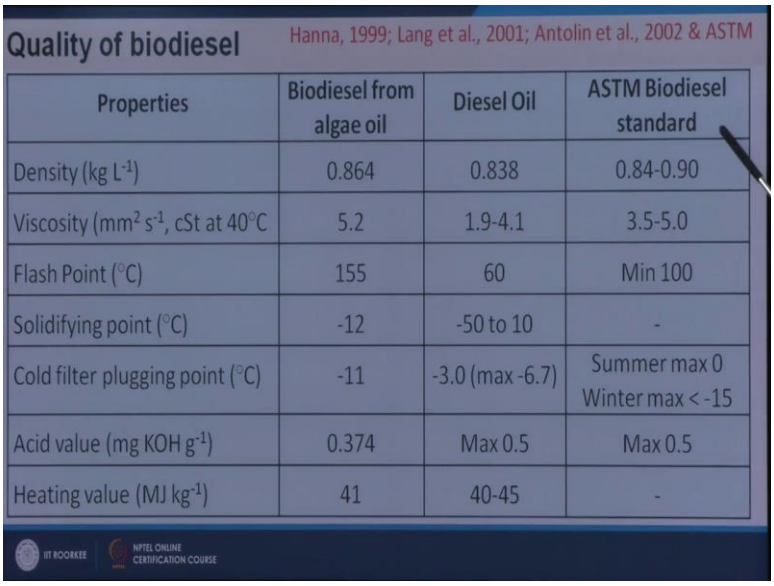

Quality of biodiesel — Hanna, 1999; Lang et al., 2001; Antolin et al., 2002 & ASTM

Properties	Biodiesel from algae oil	Diesel Oil	ASTM Biodiesel standard
Density (kg L^{-1})	0.864	0.838	0.84-0.90
Viscosity ($mm^2 s^{-1}$, cSt at 40°C	5.2	1.9-4.1	3.5-5.0
Flash Point (°C)	155	60	Min 100
Solidifying point (°C)	-12	-50 to 10	-
Cold filter plugging point (°C)	-11	-3.0 (max -6.7)	Summer max 0 Winter max < -15
Acid value (mg KOH g^{-1})	0.374	Max 0.5	Max 0.5
Heating value (MJ kg^{-1})	41	40-45	-

Now, we will see the quality of biodiesel algal diesel and diesel oil and biodiesel ASTM standard if we compare, we see the biodiesel obtained from algal biomass matching the ASTM biodiesel standards.

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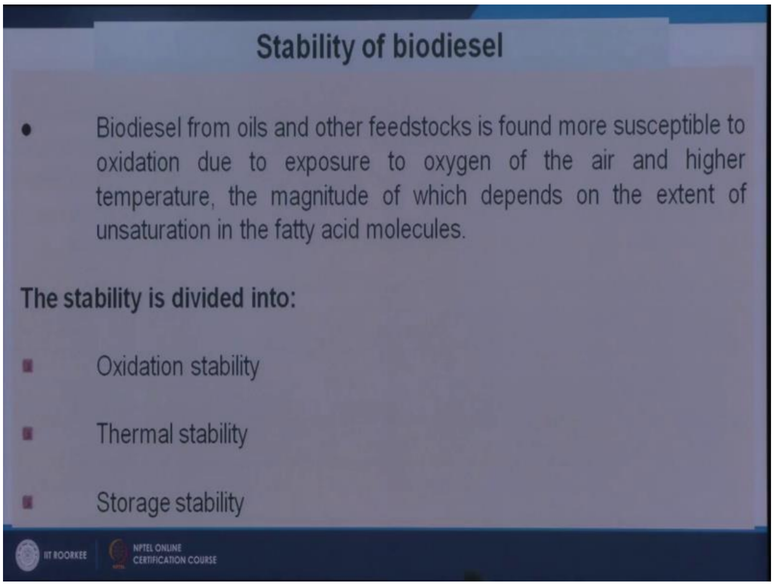

Now, we will start to discuss on the stability of the algal biodiesel. So, stability biodiesel if we keep for a longer time it loses its properties because of the presence of double bond in the fatty acids or double bond in the esters the oxidation takes place. So, this oxidation can be of primary oxidation and secondary oxidation. So, that is oxidation stability the stability loss, loss of properties due to the presence of oxygen that is related to oxidation stability thermal stability is loss of properties due to thermal load and storage conditions also affect some stability of the biodiesel that is called storage stability. So, this 3 type of stability are important for the biodiesel.

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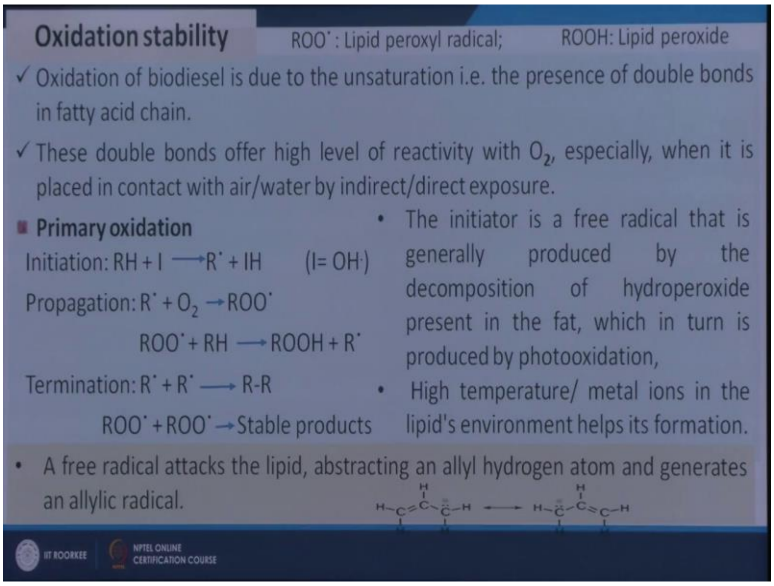

First we discuss the oxidation stability. So, oxidation stability as we have discussed that it can be of primary or it can be of secondary. So, for the primary oxidation how it happens for the primary oxidations there are 3 steps that is initiation propagations and termination and initiation of the oxidation takes place as per this reactions RH plus I is equal to R dash plus IH. So, what is I initiator. So, where from the initiator comes initiator is free radical which is produced by the decomposition of hydro peroxide present in the fat and this hydro peroxide is basically produced due to the photo oxidation in the fat. So, once the initiator that initiator means OH radical.

So, OH radical is produced. So, OH radical will react with RH. So, RH will give us R DOT plus IH. So, what is R dot? R DOT is your allyl radical and H dot which is produced or IH we are getting that is your allyl hydrogen atom. So, these are the reactions. So, when we are getting R dot. So, R DOT r radical is reacting with oxygen and it is giving as ROO dot. So, what is ROO dot this is equal to lipid peroxyl radical. So, lipid peroxyl radical is formed and lipid peroxyl radical is again reacting with RH and giving us R O OH that is equal to lipid peroxide. So, R DOT its radical is again available this R DOT which is not stable R DOT and R DOT that react and gives us R; R product or ROO dot ROO dot reacts and give some stable products.

So, these are these type of reactions takes place when the oxygen is present basically the moisture and oxygen is present and the biodiesel is exposed to moisture and water and oxygen etcetera and this radical formation is favored at high temperature and if metal contamination is there. So, this formation of radicals is favored.

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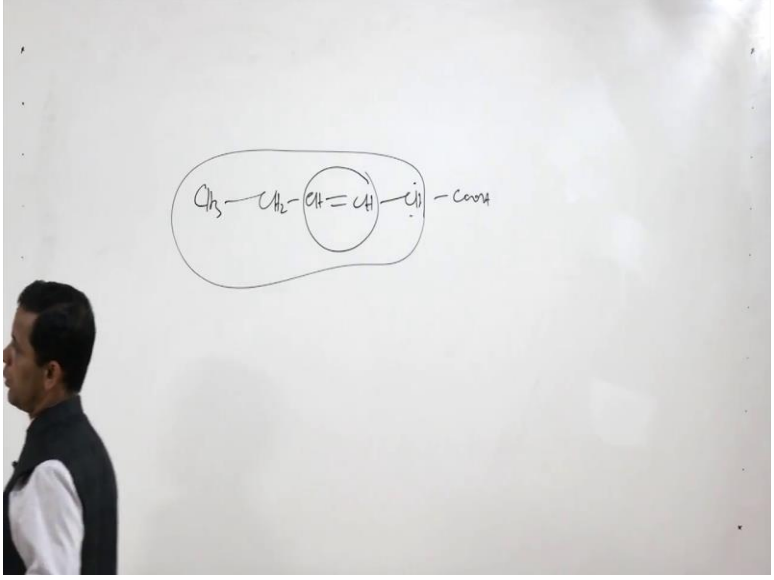

Now we see what is this allyl group? So, allyl group is CH double bond CH CH2, if we have one CH3 CH2 CH CH CH2 COH like this. So, here this group is there. So, this is this hydrogen will be removed here. So, one hydrogen will be removed here and this radical will get this radical will get. So, this is the radical this is the radical which is given here r dash. So, this is the mechanism for the primary oxidation of the biodiesel.

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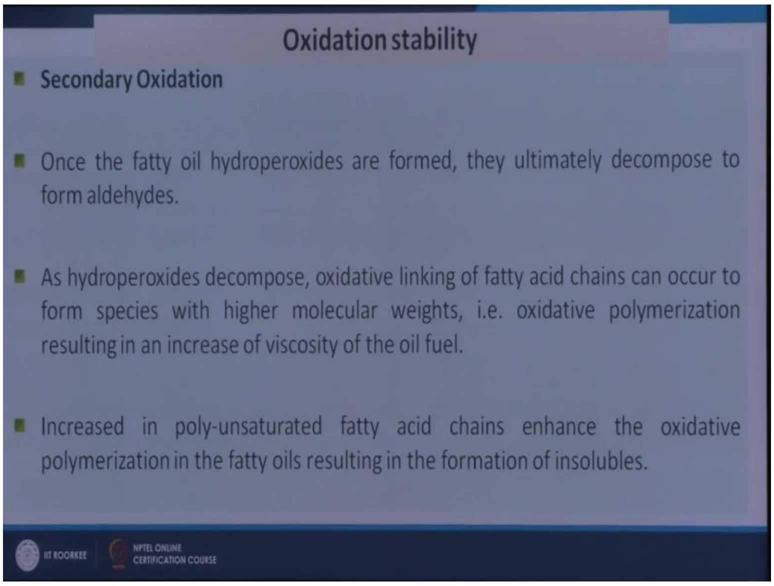

Then we will see the secondary oxidation. So, we have got the hydro peroxides. So, hydro peroxides that are these things which we are getting here those will be further converted and decomposed to aldehyde and as the hydro peroxides decompose oxidative linkages in the fatty acids in the fatty acid chains can occur to form species with higher molecular weight. So, higher molecular weight; that means, there are some oxidative polymerizations in the chain, so oxidative poly polymerization resulting in an increase of viscosity of the oil. So, with time the biodiesel loses its properties and its viscosity increases and increase in poly unsaturated fatty acids chains enhance the oxidative polymerization in fatty oils resulting in formation of insoluble. So, these are the oxidation methods which take place in biodiesel and decrease its property.

How to remove or how to stop this oxidation methods; obviously, we can add some antioxidants. So, antioxidants are added to stop the process when we are producing here. So, ROH and R DOT is again remaining. So, if we use some chemicals that can produce a stable radical or stable might be as mentioned here. So, ROO which is produced there ROO dot which is produced here lipid peroxide radical.

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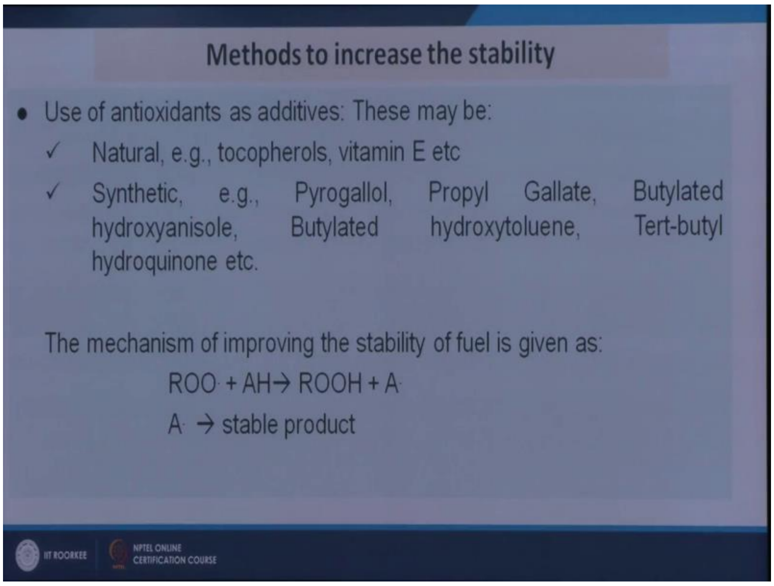

So, that lipid peroxide radical can react with AH some chemicals or antioxidants that will form ROOH plus A dot. So, A dot is stable product if a dot is stable product then the further reactions will not proceed. So, the biodiesel degradation will not take place the stability will retain. So, different types of antioxidants as additives have been added both naturally as well as synthetic products. So, natural antioxidants are tocopherols, vitamin e and synthetics are some examples have pyrogallol, propyl, gallate, butylated hydroxyanisole and butylated hydroxytoluene and tetra butyl hydroquinone. So, these are some examples of the antioxidants used or the maintaining stability of the biodiesel.

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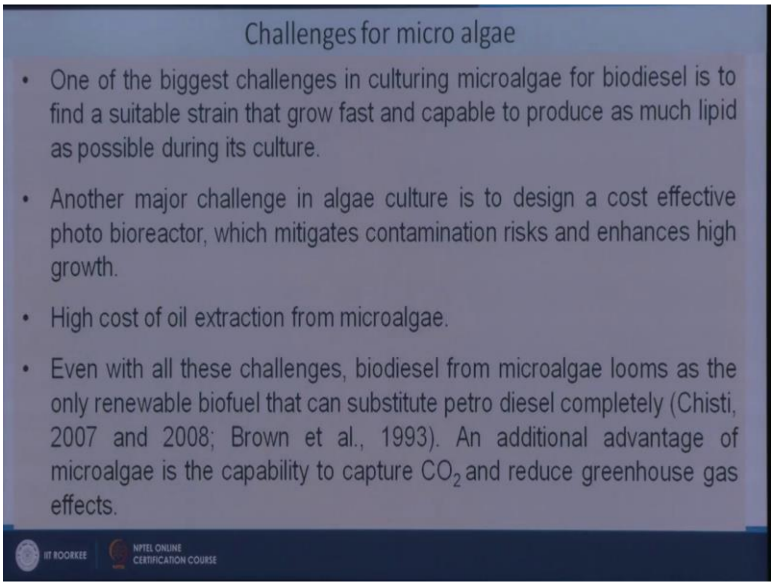

Now, we will see some challenges for micro algal species or microalgae to biodiesel production there are number of challenge in the previous module we have discussed all microalgae is not having equal amount of or higher amount of lipid only few species are having higher amount of lipids. So, we have to identify and we have to monitor we have to develop some technology. So, that the microalgae can improve or produce more amount of lipid in their cell that is one challenge. So, genetic modifications or other stressed etcetera. So, we have to do some development on this another major challenge is in algae culture is to design a cost effective photo bioreactor. So, photo bioreactors are not cost effective it is costly affairs.

So, we have to design some photo bioreactor which is economically feasible and extraction of microalgae that is harvesting and it is again for oil productions it requires drying. So, these steps are very expensive and not economic. So, these are the challenge we have to develop alternate routes to reduce the expenditure in this step and although these are the major disadvantage or the challenges for the algae to oil conversion, but it has some positive sides also and biodiesel from microalgae looms as the only renewable biofilm that can substitute petrol diesel completely as per this references.

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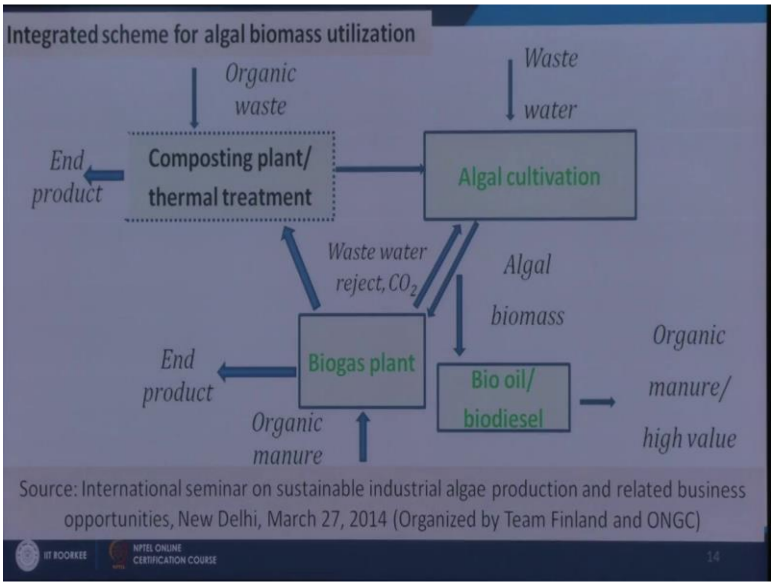

So, considering the challenges the people are trying to integrate different activities and to develop integrated approach say we are not only interested to get the lipid from the microalgae once we are getting the lipid we will be producing the biodiesel from it then the rest part of the biomass which is which is not having lipid will be having carbohydrate or protein etcetera those can be used for other applications for biogas productions or say lipid extractions people are trying to get the protein first then they are going to extract lipid and then the carbohydrate and one example of the integration is shown here that when algal cultivation is going on.

So, algal cultivation can be used for bio oil or bio diesel production this can be used for biogas plant that is a anaerobic digestion bio gas production and after oil or extraction the oil extracted biomass can be sent to biogas plant also after biogas production again we will having some sludge. So, that sludge can be used for composting plant for thermal treatment etcetera. So, through thermal treatment also you can get from energy from this material which is remaining after biogas applications of this material. So, that way the whole process can be integrated and this approach if we can use then this may improve the economy of the process.

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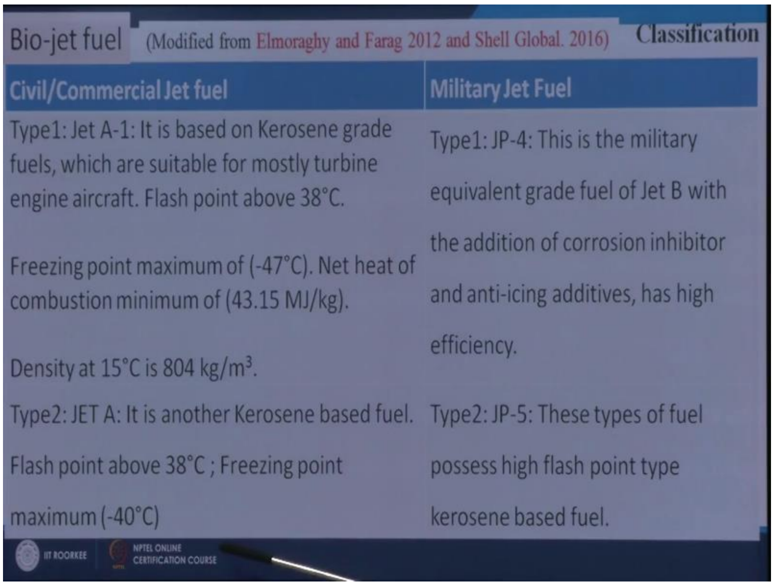

Now, we will discuss the bio jet fuel productions. So, what is bio jet fuel? So, jet fuel which is used in jet engines. So, that can be of commercial jet fuel or it can be of military jet fuel. So, there is slight difference between commercial jet fuel and military jet fuel basically military jet fuel contains more corrosion inhibitor and anti icing additives.

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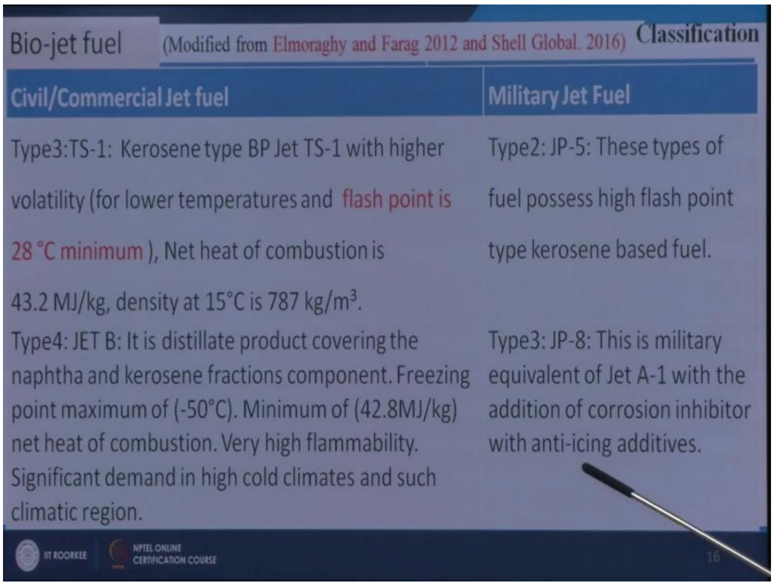

So, commercial jet fuels are basically 4 types as given here; type 1, type 2, type 3 and type 4. Type 1 jet fuel; its flash point is around 38 degree centigrade and freezing point is minus 40-47 degree centigrade. So, these are 2 major parameters which differentiate different types of jet fuels. So, for type 2 this flash point is 30 degree centigrade, but freezing point is minus 40 degree centigrade, type 3 TS 1; the flash point is lower that is 28 degree centigrade minimum that is type 4 and jet b this is having minus 50 degree centigrade of freezing point. So, the freezing point and plus point are varying with the different type of this jet fuel used in commercial skill or in civil aviation, but all those are of kerosene type of fuel and for military jet fuel we are having basically type 1, type 2 and type 3.

So, type one is nothing, but it is a jet B; jet B for civil or commercial jet fuel which we have jet B, this type that is minus 50 degree centigrade with addition of corrosion inhibitor and anti icing additives similarly type 3 JP 8, this is jet A1. So, that is jet a one type of fuel with some more additives for anti icing and corrosion inhibition. So, these are the type of the jet A1 type of fuel with some more additives for anti icing and corrosion inhibition. So, these are the type object fuels which are used in jet engines now people are trying to get the jet fuel also and US army, US military is actually earning some projects for the production of this bio jet fuel.

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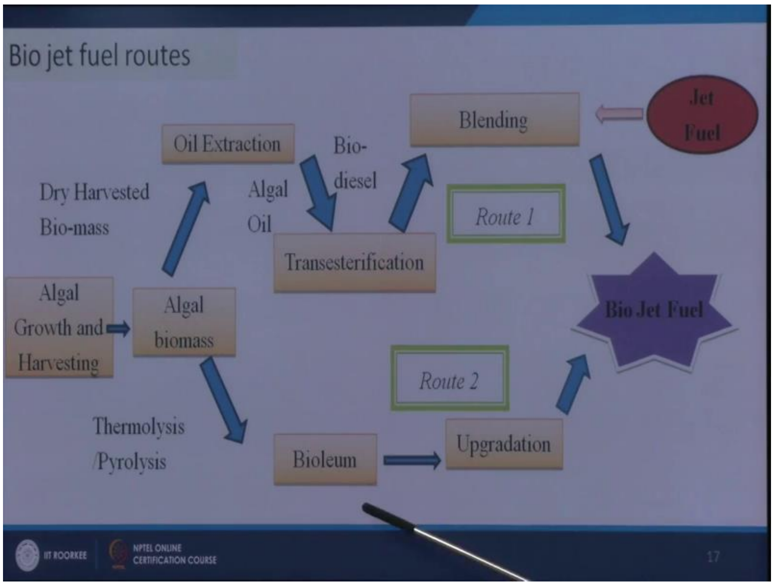

So, bio jet fuel can be produced by basically 2 routes the first route is biodiesel production and make some blend with the jet fuel and then we will get the bio jet fuel. So, already we have discussed all these methods. So, this is one route one another route is there we can get algal biomass after harvesting and then algal biomass can be processed through thermolysis or pyrolysis and then we will get some oleum bioleum. So, that bioleum further we upgraded, but this upgradation is not transesterification it is hydrogenation.

So, hydrogenations or other methods can be used for the upgradation in spite transesterification. And so bio jet fuel can be obtained. So, these are 2 basic routes people are investing for the development of bio jet fuel from the micro algal biomass.

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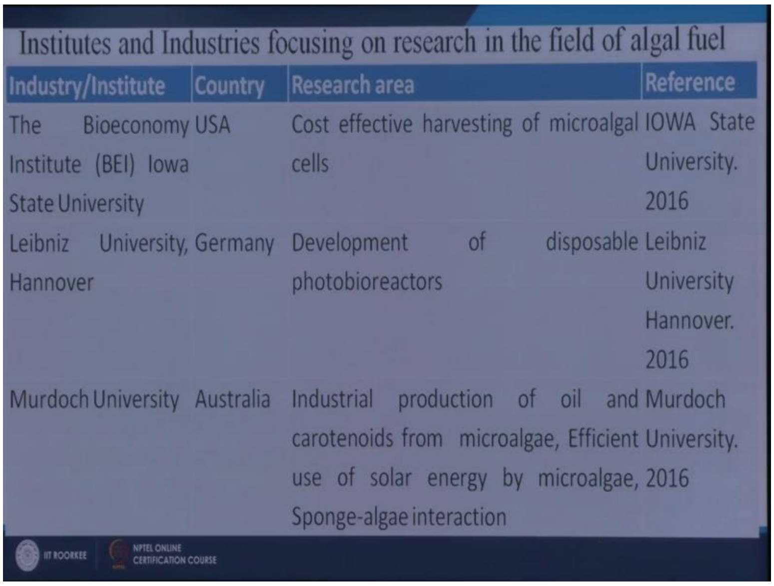

Institutes and Industries focusing on research in the field of algal fuel

Industry/Institute	Country	Research area	Reference
The Bioeconomy Institute (BEI) Iowa State University	USA	Cost effective harvesting of microalgal cells	IOWA State University. 2016
Leibniz University, Hannover	Germany	Development of disposable photobioreactors	Leibniz University Hannover. 2016
Murdoch University	Australia	Industrial production of oil and carotenoids from microalgae, Efficient use of solar energy by microalgae, Sponge-algae interaction	Murdoch University. 2016

Now, we will see some research status. So, different universities and organizations are involved for the development of new techniques in different aspects of different area for the biodiesel or jet fuel or any fuel production from algal biomass some examples are given here. So, IOWA State University in 2016, it is reported that they are involved on cost effective harvesting of micro algal cells, similarly Murdoch University; they are involved in the industrial production of oil and carotenoids from microalgae efficient use of solar energy by micro algae and sponge algae interaction.

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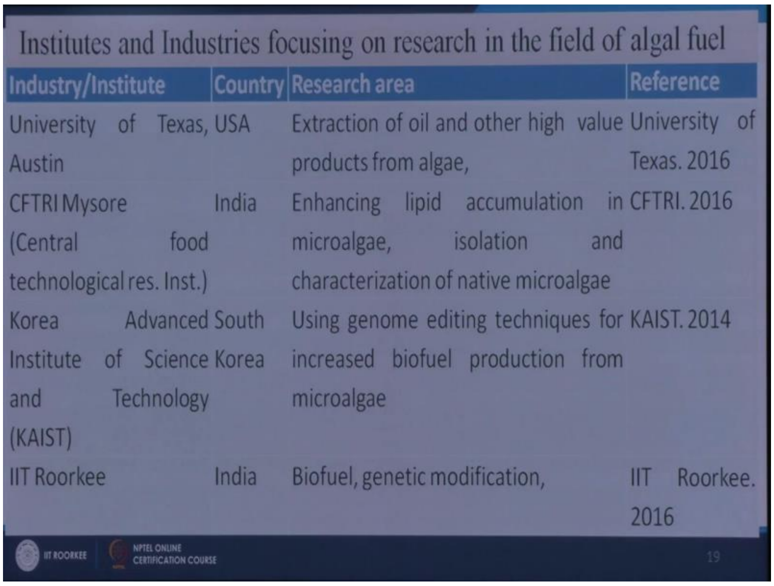

Institutes and Industries focusing on research in the field of algal fuel

Industry/Institute	Country	Research area	Reference
University of Austin	Texas, USA	Extraction of oil and other high value products from algae,	University of Texas. 2016
CFTRI Mysore (Central food technological res. Inst.)	India	Enhancing lipid accumulation in microalgae, isolation and characterization of native microalgae	CFTRI. 2016
Korea Advanced Institute of Science and Technology (KAIST)	South Korea	Using genome editing techniques for increased biofuel production from microalgae	KAIST. 2014
IIT Roorkee	India	Biofuel, genetic modification,	IIT Roorkee. 2016

Similarly, University of Texas; they are involved on extraction of oil and other high value products from algae. So, CFTRIs, they are involved in enhancing lipid accumulations in microalgae isolations and characterization of native microalgae, KAIST that is Korean Institute of Science and Technology, Korea they are developing they are using genome editing techniques for increased biofuel production from microalgae and IIT, Roorkee developing biofuel and genetic modification of the microalgae.

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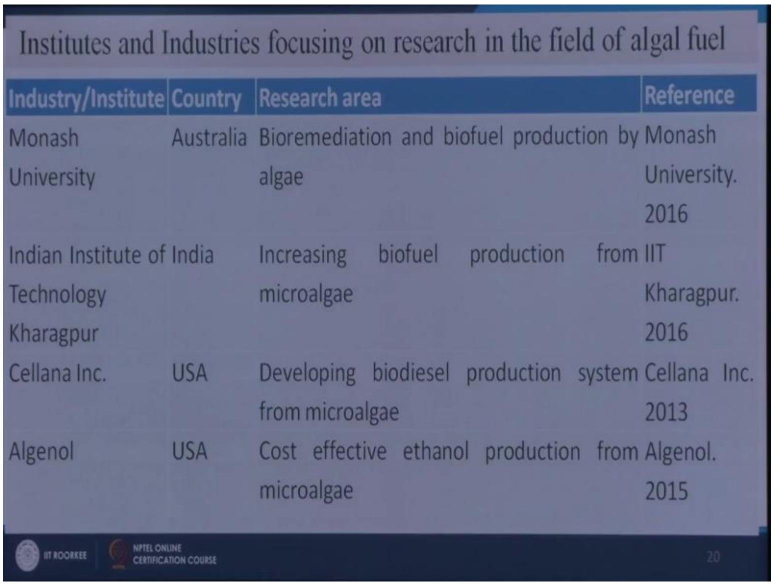

Institutes and Industries focusing on research in the field of algal fuel

Industry/Institute	Country	Research area	Reference
Monash University	Australia	Bioremediation and biofuel production by algae	Monash University. 2016
Indian Institute of Technology Kharagpur	India	Increasing biofuel production from microalgae	IIT Kharagpur. 2016
Cellana Inc.	USA	Developing biodiesel production system from microalgae	Cellana Inc. 2013
Algenol	USA	Cost effective ethanol production from microalgae	Algenol. 2015

Monash University is involved in bioremediations and bio fuel products by algae IIT Kharagpur increasing bio fuel productions from microalgae. And these are two company they are involved Cellana are involved on developing biodiesel production system from microalgae and Alagenol they are they are developing cost effective ethanol production from microalgae.

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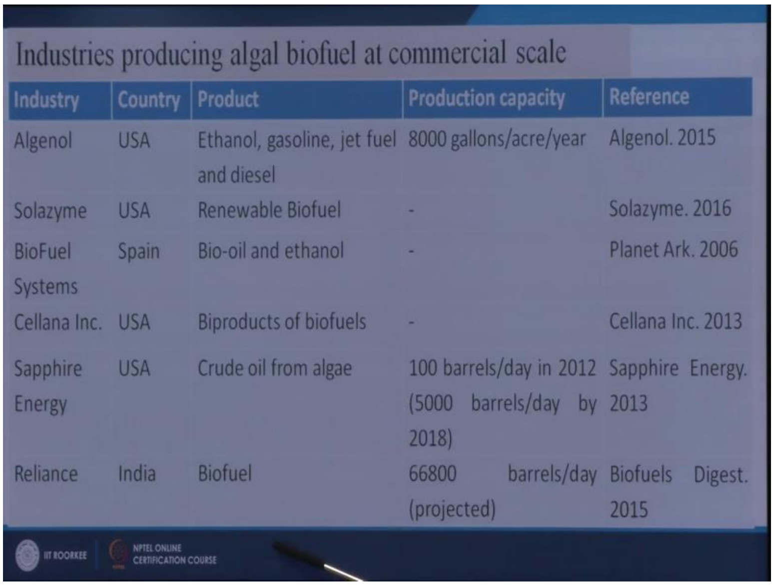

Industries producing algal biofuel at commercial scale

Industry	Country	Product	Production capacity	Reference
Algenol	USA	Ethanol, gasoline, jet fuel and diesel	8000 gallons/acre/year	Algenol. 2015
Solazyme	USA	Renewable Biofuel	-	Solazyme. 2016
BioFuel Systems	Spain	Bio-oil and ethanol	-	Planet Ark. 2006
Cellana Inc.	USA	Biproducts of biofuels	-	Cellana Inc. 2013
Sapphire Energy	USA	Crude oil from algae	100 barrels/day in 2012 (5000 barrels/day by 2018)	Sapphire Energy. 2013
Reliance	India	Biofuel	66800 barrels/day (projected)	Biofuels Digest. 2015

So, other industries which are involved for the developments of technology are provided here will see they are located in different countries USA, Spain, India, etcetera. So, they are products are different, but biodiesel, products of biofuels, crude oil from algae from somewhere bio fuel etcetera. And this is the capacity that is sapphire energy USA that is capacity is 100 barrels per day in 2012, crude oil from algae. And this is 5,000 per day and in India that is Reliance Industry they are proposing to produce 66,800 barrels per day biofuels in as per a report in 2015, but when they will produce this is not clear.

So, up to this, in this module and with this module we have also at the end of the course. And best wishes to all of you who will be opting for the examination for getting certificate.

Thank you very much.