Biomass Conversion and Biorefinery

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Module-07
Lecture-19
Diesel from Vegetable Oils, Microalgae and Syngas

Good morning students, today is lecture 1 of module 7. And this particular module is dedicated to biodiesel. So, in today's class we will understand diesel from different vegetable oils, microalgae as well as syngas. So let us begin.

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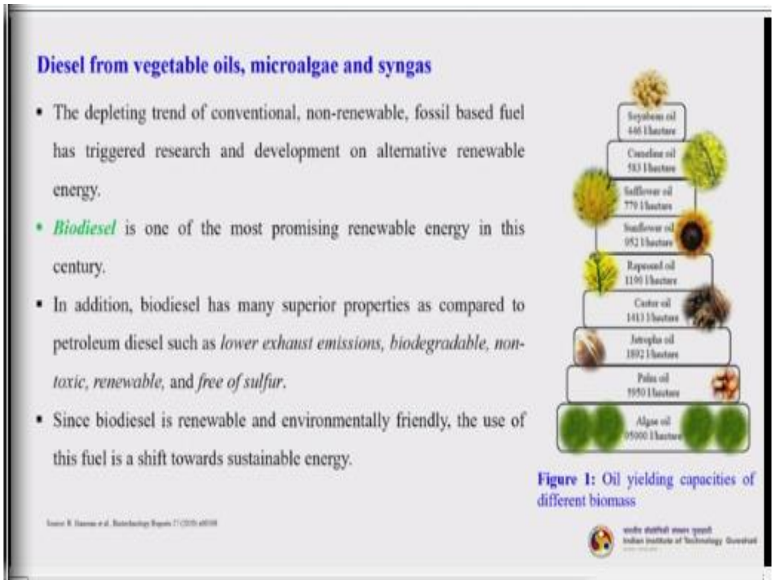

Diesel from vegetable oils, microalgae and syngas

- The depleting trend of conventional, non-renewable, fossil based fuel has triggered research and development on alternative renewable energy.
- *Biodiesel* is one of the most promising renewable energy in this century.
- In addition, biodiesel has many superior properties as compared to petroleum diesel such as *lower exhaust emissions, biodegradable, non-toxic, renewable,* and *free of sulfur*.
- Since biodiesel is renewable and environmentally friendly, the use of this fuel is a shift towards sustainable energy.

Figure 1: Oil yielding capacities of different biomass

The depleting trend of conventional, non-renewable, fossil based fuel has triggered research and development of an alternative energy. So, biodiesel is one of the most promising renewable energy in this century. In addition, biodiesel has many superior properties as compared to petroleum diesel such as lower exhaust emissions, it is biodegradable, non-toxic, renewable, and it is almost free of sulfur.

Since biodiesel is renewable and environmentally friendly, the use of this fuel is a shift towards the sustainable energy. So, in the figure 1 here, you can see the different types of oils and their yield per hectare. So, you can see soybean oil, then cameline oil, safflower, sunflower, rapeseed, castor oil, jatropha, palm oil and algae oil. So, you can see that among all, algae, per hectare yield is very high. So, anyway we will be discussing about most of these oil sources and what are the major composition of all these oils.

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❑ Diesel from vegetable oils

- The history of biodiesel is as long as that of diesel engine itself.
- The use of vegetable oils was investigated as early as the era when diesel engine was developed.
- *Rudolf Diesel* (1858–1913), the inventor of diesel engine, tested *peanut oil as fuel* for his engine.
- Many vegetable oils were investigated during "historic times" which includes *palm oil, soybean oil, cottonseed oil, castor oil*, etc.
- The feedstock for biodiesel production can be categorized as *lipid feedstock* and *alcohol feedstock*.
- The lipid feedstock includes *vegetable oils, animal fats*, and, more recently, other plant-like organisms such as *microalgae and cyanobacteria*.
- The vegetable oils used as lipid feedstock for biodiesel production those are highly dependent on regional climate are *rapeseed oil* in European countries and Canada, *soybean oil* in United States, and *palm oil* in tropical countries such as Indonesia and Malaysia.

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So, let us again, go to that. So, the history of biodiesel is as long as that of diesel engine itself. The use of vegetable oils was investigated as early as the era when diesel engine was developed by Rudolf Diesel - who has actually invented the diesel engine. So, when he invented and tested the diesel engine; he used peanut oil as a fuel for his engine. So, many vegetable oils were investigated during the historic times, which include palm oil, soybean oil, cottonseed oil and castor oil etc.

The feedstock for biodiesel production can be categorized as *lipid feedstock* and *alcohol feedstock.* Now lipid feedstock includes vegetable oils, animal fats, and more recently other plant like organisms such as the cyanobacteria and algae. The vegetable oils used as lipid feedstock for biodiesel production are highly dependent on regional climate. So, some of them are rapeseed oil in European countries and Canada, Soybean oil predominantly in the United States, and palm oil predominantly in the tropical countries such as Malaysia and Indonesia.

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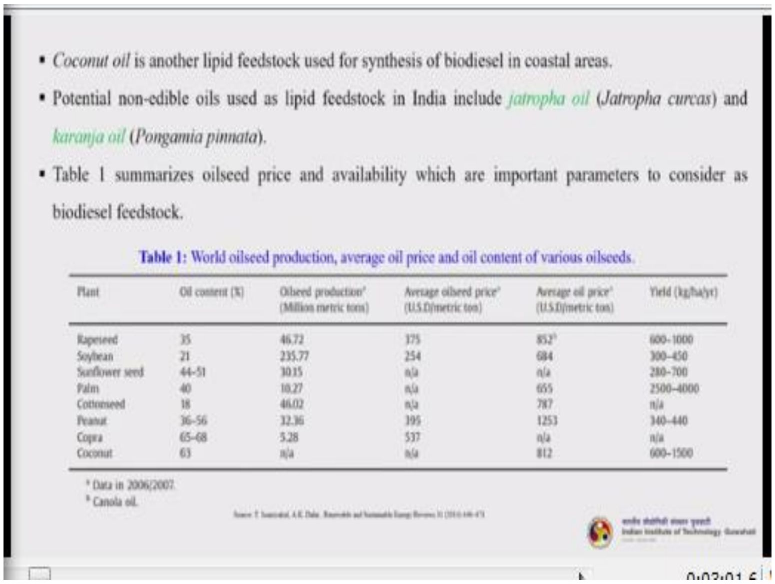

- *Coconut oil* is another lipid feedstock used for synthesis of biodiesel in coastal areas.
- Potential non-edible oils used as lipid feedstock in India include jatropha oil (*Jatropha curcas*) and karanja oil (*Pongamia pinnata*).
- Table 1 summarizes oilseed price and availability which are important parameters to consider as biodiesel feedstock.

Table 1: World oilseed production, average oil price and oil content of various oilseeds.

Plant	Oil content (%)	Oilseed production[a] (Million metric tons)	Average oilseed price[a] (U.S.D/metric ton)	Average oil price[a] (U.S.D/metric ton)	Yield (kg/ha/yr)
Rapeseed	35	46.72	375	852[b]	600–1000
Soybean	21	235.77	254	684	300–450
Sunflower seed	44–51	30.15	n/a	n/a	280–700
Palm	40	10.27	n/a	655	2500–4000
Cottonseed	18	46.02	n/a	787	n/a
Peanut	36–56	32.36	395	1253	340–440
Copra	65–68	5.28	537	n/a	n/a
Coconut	63	n/a	n/a	812	600–1500

[a] Data in 2006/2007.
[b] Canola oil.

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Coconut oil is another lipid feedstock used for synthesis of biodiesel in coastal areas. Potential non edible oils used as lipid feedstock in India include Jatropha oil and karanja oil. Now this table will give you an understanding about the different oil seed plants, their oil content, their oil seed production and average oil seed price and average oil price - given in US dollars and the yield per kg per hectare per year.

So, you can see that rapeseeds, soybean, sunflower seed, palm, cottonseed, peanut, copra and coconut all are listed. So, this gives us an understanding about that we have plenty options of oil seeds available in the world. And most of these here listed are almost the vegetable oils which can be used for the cooking purposes, but not all. Now that is why if you recall our discussion during biorefinery, I have been telling you many times that in India and other developing countries we cannot use such vegetable oils, or say anything, any feedstock that comes under food. So, that is why in India our focus is initially when this biodiesel has started, our focus was completely shifted to the Jatropha, *Jatropha curcas*. And in one of our class I have told you that why Jatropha is not become sustainable, it could not fit to the sustainable; then moreover economy is also a problem with such Jatropha based biodiesel.

So then, we have shifted our attention to other non food based seed oils, we can call them as non edible oil seeds and in our lecture perhaps 5, we have discussed about various types of non edible oil seeds, whether it is mahuya, karanja, neem and there are many**.**

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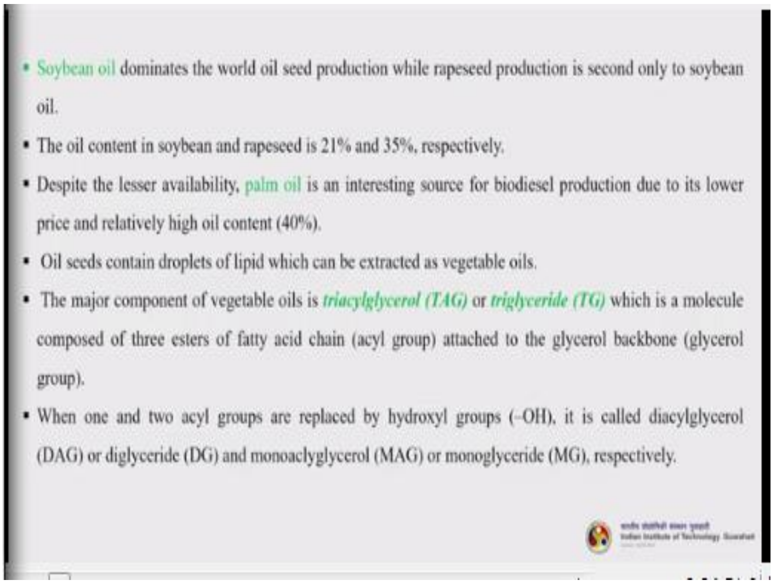

- Soybean oil dominates the world oil seed production while rapeseed production is second only to soybean oil.
- The oil content in soybean and rapeseed is 21% and 35%, respectively.
- Despite the lesser availability, palm oil is an interesting source for biodiesel production due to its lower price and relatively high oil content (40%).
- Oil seeds contain droplets of lipid which can be extracted as vegetable oils.
- The major component of vegetable oils is *triacylglycerol (TAG)* or *triglyceride (TG)* which is a molecule composed of three esters of fatty acid chain (acyl group) attached to the glycerol backbone (glycerol group).
- When one and two acyl groups are replaced by hydroxyl groups (–OH), it is called diacylglycerol (DAG) or diglyceride (DG) and monoaclyglycerol (MAG) or monoglyceride (MG), respectively.

Soybean oil dominates the world oil seed production while rapeseed production is second only to soybean oil. The oil content in soybean and rapeseed is 21% and 35% respectively. Despite the lesser availability, palm oil is an interesting source for biodiesel production due to it is lower price and relatively high oil content, it is almost 40%. So, oil seeds contain droplets of lipid which can be extracted as vegetable oils.

But extraction, many times, is an energy intensive as well as a cost intensive process. So, the major component of vegetable oil is triacylglycerol - which is called as TAG, or triglyceride, which is called as TG - which is a molecule composed of three esters of fatty acid chain attached to the glycerol backbone, so basically the glycerol group. So, when 1 and 2 acyl groups are replaced by hydroxyl groups, it is called diacylglycerol – DAG, or diglycerides – DG; or monoacylglycerol – MAG, or monoglyceride - MG respectively.

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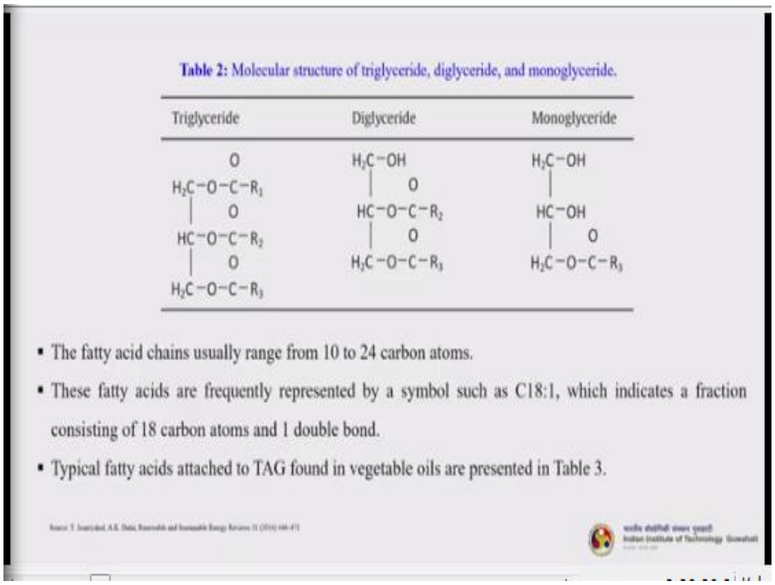

Table 2: Molecular structure of triglyceride, diglyceride, and monoglyceride.

Triglyceride	Diglyceride	Monoglyceride
O $H_2C-O-C-R_1$ | O $HC-O-C-R_2$ | O $H_2C-O-C-R_3$	H_2C-OH | O $HC-O-C-R_2$ | O $H_2C-O-C-R_3$	H_2C-OH | $HC-OH$ | O $H_2C-O-C-R_3$

- The fatty acid chains usually range from 10 to 24 carbon atoms.
- These fatty acids are frequently represented by a symbol such as C18:1, which indicates a fraction consisting of 18 carbon atoms and 1 double bond.
- Typical fatty acids attached to TAG found in vegetable oils are presented in Table 3.

Now this table will give you the understanding about the molecular structure of the triglyceride, diglycerides and monoglyceride. So, the fatty acid chains usually range from 10 to 24 carbon atoms. These fatty acids are frequently represented by a symbol such as C18:1, which indicates that a fraction consists of 18 carbon atoms and 1 double bond. So, typical fatty acids attached to TAG found in vegetable oils are presented in the table 3.

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Table 3: Structures of common fatty acids found in vegetable oils

System name	Common name	Symbol	Formular	Double bond position[a]
Saturated				
Decanoic	Capric	C10:0	$C_{10}H_{20}O_2$	-
Dodecanoic	Lauric	C12:0	$C_{12}H_{24}O_2$	-
Tetradecanoic	Myristic	C14:0	$C_{14}H_{28}O_2$	-
Hexadecanoic	Palmitic	C16:0	$C_{16}H_{32}O_2$	-
Octadecanoic	Stearic	C18:0	$C_{18}H_{36}O_2$	-
Eicosanoic	Arachidic	C20:0	$C_{20}H_{40}O_2$	-
Docosanoic	Behenic	C22:0	$C_{22}H_{44}O_2$	-
Tetracosanoic	Lignoceric	C24:0	$C_{24}H_{48}O_2$	-
Monounsaturated				
Hexadecenoic	Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Octadecenoic	Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c
Octadecenoic	Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Octadecenoic	Elaidic	C18:1	$C_{18}H_{34}O_2$	9t
Octadecenoic	Vaccenic	C18:1	$C_{18}H_{34}O_2$	11c
Eicosenoic		C20:1	$C_{20}H_{38}O_2$	5c
Eicosenoic	Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Eicosenoic	Gondoic	C20:1	$C_{20}H_{38}O_2$	11c
Docosenoic	Erucic	C22:1	$C_{22}H_{42}O_2$	13c
Polyunsaturated				
Hexadecadienoic		C16:2	$C_{16}H_{28}O_2$	
Octadecadienoic	Linoleic	C18:2	$C_{18}H_{32}O_2$	9c12c
Octadecatrienoic	Linolenic-α	C18:3	$C_{18}H_{30}O_2$	9c12c15c
Octadecatrienoic	Linolenic-γ	C18:3	$C_{18}H_{30}O_2$	6c9c12c
Octadecatrienoic	Eleostearic	C18:3	$C_{18}H_{30}O_2$	9c11t13t
Octadecatrienoic	Calendic	C18:3	$C_{18}H_{30}O_2$	8t10t12c

[a] c = cis formation; t = trans formation.

- Naturally occurring fatty acids in vegetable oils have cis-formation whereas the unnatural trans isomers occur due to partial hydrogenation process.
- In cis-isomer, hydrogen atoms are attached on the same side causing "V" shape of the fatty acid chain.
- When two hydrogen atoms are attached on the other side of each other, trans-isomer is formed and the molecular structure is linear.

That means this table; so you can have a glance through this. So, it tells us about the structures of common fatty acids found in vegetable oils. So, three different groups are presented here. The first one is saturated, second is mono-unsaturated and third one is polyunsaturated. So, this is their common name and then this is the symbol and then the formula and double bond position - where the double bond is located, which carbon atom basically**.**

So, naturally occurring fatty acids in vegetable oils have a cis-formation whereas, unnatural trans-isomers occur due to partial hydrogenation process. And in cis-isomer, hydrogen atoms are attached on the same side causing a “V” shape of the fatty acid chain. Now when two hydrogen atoms are attached on the other side of each other, trans-isomer is formed and the molecular structure is linear.

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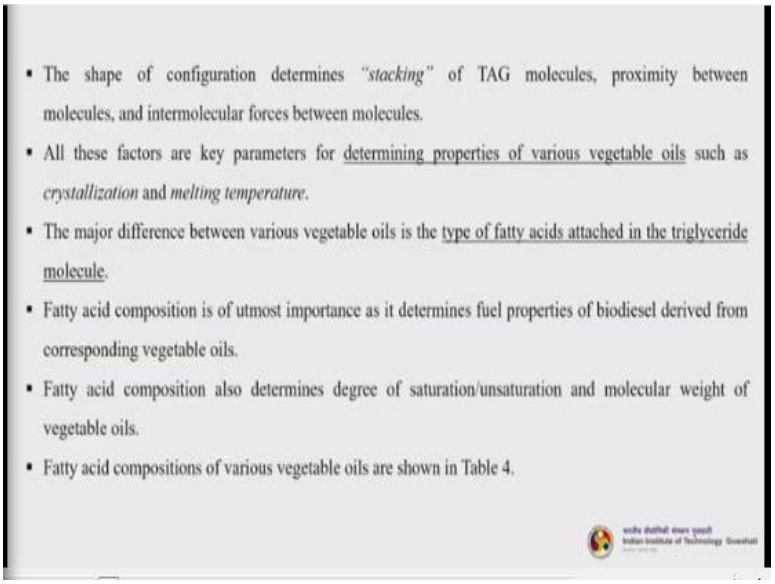

- The shape of configuration determines *“stacking”* of TAG molecules, proximity between molecules, and intermolecular forces between molecules.
- All these factors are key parameters for determining properties of various vegetable oils such as *crystallization* and *melting temperature*.
- The major difference between various vegetable oils is the type of fatty acids attached in the triglyceride molecule.
- Fatty acid composition is of utmost importance as it determines fuel properties of biodiesel derived from corresponding vegetable oils.
- Fatty acid composition also determines degree of saturation/unsaturation and molecular weight of vegetable oils.
- Fatty acid compositions of various vegetable oils are shown in Table 4.

So, the shape of the configuration determines stacking of TAG molecules, proximity between molecules and intermolecular forces between the molecules. Now all these factors are key parameters for determining properties of various vegetable oils, such as crystallization and melting temperature. The major difference between various vegetable oils is the type of fatty acids attached in the triglyceride molecule.

Fatty acid composition is of utmost importance, as it determines fuel properties of biodiesel derived from corresponding vegetable oils. Fatty acid composition also determines degree of saturation, unsaturation and the molecular weight of vegetable oils. Fatty acid compositions of various vegetable oils are shown in table 4. So, in the next table I will show you.

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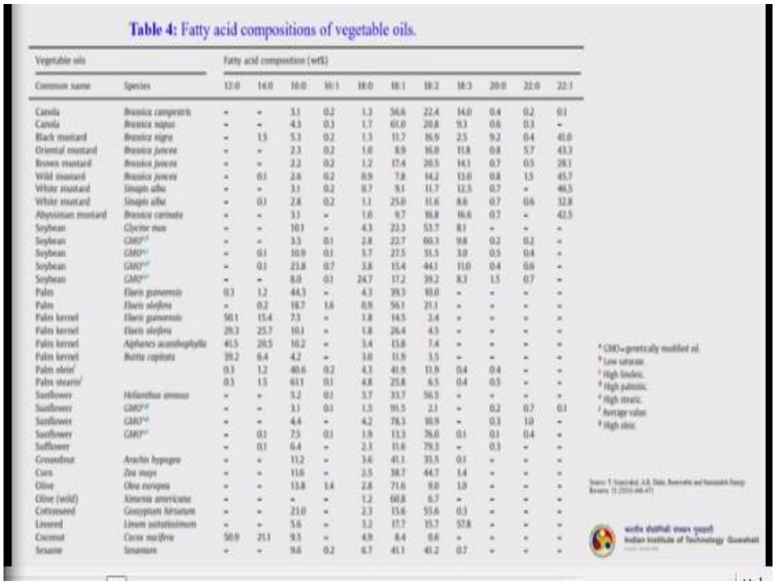

Table 4: Fatty acid compositions of vegetable oils.

Vegetable oils		Fatty acid composition (wt%)										
Common name	Species	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:0	22:1
Canola	*Brassica campestris*	-	-	3.1	0.2	1.3	56.6	22.4	14.0	0.4	0.2	0.1
Canola	*Brassica napus*	-	-	4.3	0.3	1.7	61.0	20.8	9.3	0.6	0.3	-
Black mustard	*Brassica nigra*	-	1.5	5.3	0.2	1.3	11.7	16.9	2.5	9.2	0.4	41.0
Oriental mustard	*Brassica juncea*	-	-	2.3	0.2	1.0	8.9	16.0	11.8	0.8	5.7	43.1
Brown mustard	*Brassica juncea*	-	-	2.2	0.2	1.2	17.4	20.5	14.1	0.7	0.5	38.1
Wild mustard	*Brassica juncea*	-	0.1	2.6	0.2	0.9	7.8	14.2	13.0	0.8	1.5	45.7
White mustard	*Sinapis alba*	-	-	3.1	0.2	0.7	9.1	11.7	12.5	0.7	-	46.5
White mustard	*Sinapis alba*	-	0.1	2.8	0.2	1.1	25.0	11.6	8.6	0.7	0.6	32.8
Abyssinian mustard	*Brassica carinata*	-	-	3.1	-	1.0	9.7	16.8	16.6	0.7	-	42.5
Soybean	*Glycine max*	-	-	10.1	-	4.3	22.3	53.7	8.1	-	-	-
Soybean	GMO[a,b]	-	-	3.3	0.1	2.8	22.7	60.3	9.8	0.2	0.2	-
Soybean	GMO[a,c]	-	0.1	10.9	0.1	5.7	27.5	51.5	3.0	0.5	0.4	-
Soybean	GMO[a,d]	-	0.1	23.8	0.7	3.8	15.4	44.1	11.0	0.4	0.6	-
Soybean	GMO[a,e]	-	-	8.0	0.1	24.7	17.2	39.2	8.3	1.5	0.7	-
Palm	*Elaeis guineensis*	0.3	1.2	44.3	-	4.3	39.3	10.0	-	-	-	-
Palm	*Elaeis oleifera*	-	0.2	18.7	1.6	0.9	56.1	21.1	-	-	-	-
Palm kernel	*Elaeis guineensis*	50.1	15.4	7.3	-	1.8	14.5	2.4	-	-	-	-
Palm kernel	*Elaeis oleifera*	29.3	25.7	10.1	-	1.8	26.4	4.5	-	-	-	-
Palm kernel	*Alphanes acanthophylla*	41.5	20.5	10.2	-	3.4	15.8	7.4	-	-	-	-
Palm kernel	*Buttia capitata*	39.2	6.4	4.2	-	3.0	11.9	3.5	-	-	-	-
Palm olein[f]		0.3	1.2	40.6	0.2	4.3	41.9	11.9	0.4	0.4	-	-
Palm stearin[f]		0.3	1.5	61.1	0.1	4.8	25.8	6.5	0.4	0.5	-	-
Sunflower	*Helianthus annuus*	-	-	5.2	0.1	3.7	33.7	56.5	-	-	-	-
Sunflower	GMO[a,g]	-	-	3.1	0.1	1.5	91.5	2.3	-	0.2	0.7	0.1
Sunflower	GMO[a,g]	-	-	4.4	-	4.2	78.3	10.9	-	0.3	1.0	-
Sunflower	GMO[a,c]	-	0.1	7.5	0.1	1.9	11.3	76.0	0.1	0.1	0.4	-
Safflower		-	0.1	6.4	-	2.3	11.6	79.3	-	0.3	-	-
Groundnut	*Arachis hypogea*	-	-	11.2	-	3.6	41.1	35.5	0.1	-	-	-
Corn	*Zea mays*	-	-	11.6	-	2.5	38.7	44.7	1.4	-	-	-
Olive	*Olea europea*	-	-	13.8	1.4	2.8	71.6	9.0	1.0	-	-	-
Olive (wild)	*Ximenia americana*	-	-	-	-	1.2	60.8	6.7	-	-	-	-
Cottonseed	*Gossypium hirsutum*	-	-	23.0	-	2.3	15.6	55.6	0.3	-	-	-
Linseed	*Linum usitatissimum*	-	-	5.6	-	3.2	17.7	15.7	57.8	-	-	-
Coconut	*Cocos nucifera*	50.9	21.1	9.5	-	4.9	8.4	0.6	-	-	-	-
Sesame	*Sesamum*	-	-	9.6	0.2	6.7	41.1	41.2	0.7	-	-	-

[a] GMO = genetically modified oil.
[b] Low saturate.
[c] High linoleic.
[d] High palmitic.
[e] High stearic.
[f] Average value.
[g] High oleic.

Source: T. Issariyakul, A.K. Dalai, Renewable and Sustainable Energy Reviews 31 (2014) 446-471

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So, this table gives us the fatty acid composition of vegetable oil. So, the vegetable oils common name, species is given, and then fatty acid composition by weight percentage. So, we can see one; let us see the soybean; the usual soybean or *Glycine max*. So, you can see that 10 weight percent is to 0 fatty acid composition, so 16 carbon atoms and no double bond basically.

Then if you proceed again, you will see that 18 carbon atoms no double bond is 4.3 weight percent. Then 18 carbon atoms and 1 double bond is 22.3%. So, similarly so many other vegetable oils and their fatty acid composition has been listed, so you can go through it later.

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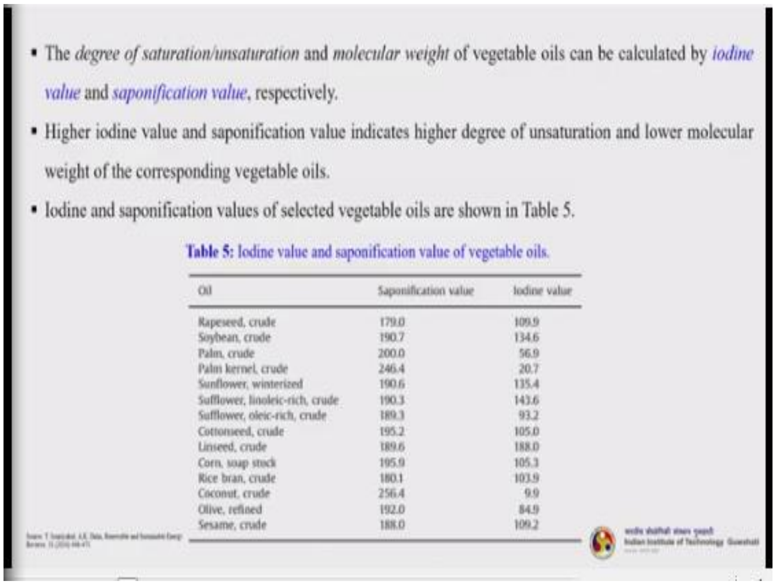

- The *degree of saturation/unsaturation* and *molecular weight* of vegetable oils can be calculated by *iodine value* and *saponification value*, respectively.
- Higher iodine value and saponification value indicates higher degree of unsaturation and lower molecular weight of the corresponding vegetable oils.
- Iodine and saponification values of selected vegetable oils are shown in Table 5.

Table 5: Iodine value and saponification value of vegetable oils.

Oil	Saponification value	Iodine value
Rapeseed, crude	179.0	109.9
Soybean, crude	190.7	134.6
Palm, crude	200.0	56.9
Palm kernel, crude	246.4	20.7
Sunflower, winterized	190.6	135.4
Safflower, linoleic-rich, crude	190.3	143.6
Safflower, oleic-rich, crude	189.3	93.2
Cottonseed, crude	195.2	105.0
Linseed, crude	189.6	188.0
Corn, soap stock	195.9	105.3
Rice bran, crude	180.1	103.9
Coconut, crude	256.4	9.9
Olive, refined	192.0	84.9
Sesame, crude	188.0	109.2

Source: T. Issariyakul, A.K. Dalai, Renewable and Sustainable Energy Reviews 31 (2014) 446-471

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So, we will move ahead. So, the degree of saturation/unsaturation and molecular weight of vegetable oils can be calculated by two things, first is something called an iodine value and second is called saponification value (respectively). Now higher iodine value and saponification value indicates higher degree of unsaturation and lower molecular weight of the corresponding vegetable oils. Iodine and saponification values of selected vegetable oils are shown in the table 5.

So, you can see few oils are being listed, so rapeseed oil, soybean, palm, and sunflower cottonseed, linseed, rice bran and their corresponding saponification value and iodine values have been listed.

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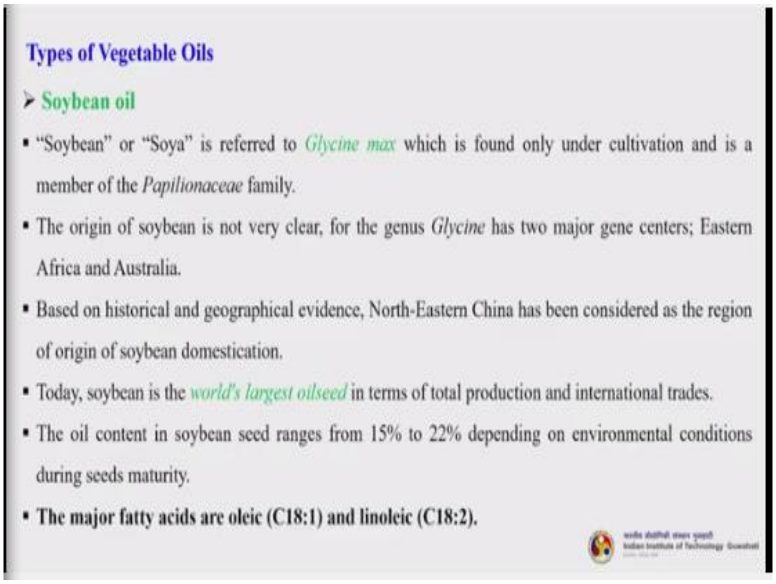

Types of Vegetable Oils

➤ Soybean oil

- "Soybean" or "Soya" is referred to *Glycine max* which is found only under cultivation and is a member of the *Papilionaceae* family.
- The origin of soybean is not very clear, for the genus *Glycine* has two major gene centers; Eastern Africa and Australia.
- Based on historical and geographical evidence, North-Eastern China has been considered as the region of origin of soybean domestication.
- Today, soybean is the *world's largest oilseed* in terms of total production and international trades.
- The oil content in soybean seed ranges from 15% to 22% depending on environmental conditions during seeds maturity.
- **The major fatty acids are oleic (C18:1) and linoleic (C18:2).**

Now we will quickly glance through the different types of vegetable oils that has been used in many places to produce biodiesel. So the first one is soybean oil; soybean or soya is referred to as *Glycine max* which is found only under cultivation and is a member of the *Papilionaceae* family. The origin of soybean is not very clear, for the genus *Glycine* has two major gene centers; Eastern Africa and Australia.

So, many literatures will tell us that this soybean has been originated from Eastern Asia, but there is no proper proof for that. So, based on historical and geographical evidence, north eastern China has been considered as the region of origin of soybean domestication. So, today soybean is world's largest oil seed in terms of total production and in international trades. The oil content in soybean seed ranges from 15 to 22%, depending on environmental conditions during the seeds maturity. The major fatty acids are oleic acid, which is C18:1, we can say that 18 carbon atoms and 1 double bond and linoleic which is having two double bonds.

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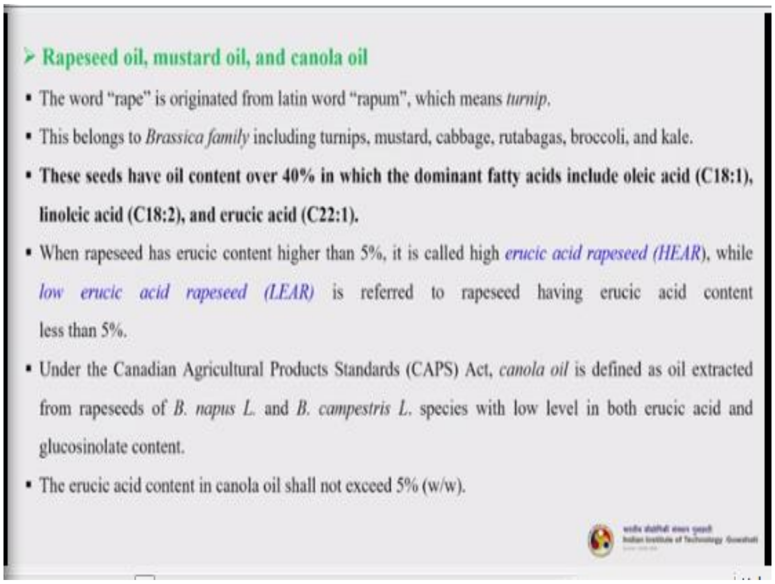

➢ **Rapeseed oil, mustard oil, and canola oil**

- The word "rape" is originated from latin word "rapum", which means *turnip*.
- This belongs to *Brassica family* including turnips, mustard, cabbage, rutabagas, broccoli, and kale.
- **These seeds have oil content over 40% in which the dominant fatty acids include oleic acid (C18:1), linoleic acid (C18:2), and erucic acid (C22:1).**
- When rapeseed has erucic content higher than 5%, it is called high *erucic acid rapeseed (HEAR)*, while *low erucic acid rapeseed (LEAR)* is referred to rapeseed having erucic acid content less than 5%.
- Under the Canadian Agricultural Products Standards (CAPS) Act, *canola oil* is defined as oil extracted from rapeseeds of *B. napus L.* and *B. campestris L.* species with low level in both erucic acid and glucosinolate content.
- The erucic acid content in canola oil shall not exceed 5% (w/w).

The next is rapeseed oil, mustard, oil and canola oil. So, the word "rape" is originated from the Latin world "rapum" which means turnip. Now this belongs to *Brassica* family including turnips, mustard, cabbage, rutabagas, broccoli and kale. Now these seeds have oil content over 40%, in which the dominant fatty acids include oleic acid, linoleic acid and erucic acid. Now when rapeseed has erucic acid content higher than 5%, it is called HEAR, it is called high erucic acid rapeseed. While a low erucic acid rapeseed which is known as LEAR is referred to as rapseed having erucic acid concentration less than 5%. Now under Canadian Agricultural Product Standards (CAPS) Act, canola oil is defined as oil extracted from rapeseeds of *B. napus* and *B. campestris* species with low level in both erucic acid and glucosinolate content. The erucic acid content in canola oil shall not exceed 5%, that is weight by weight.

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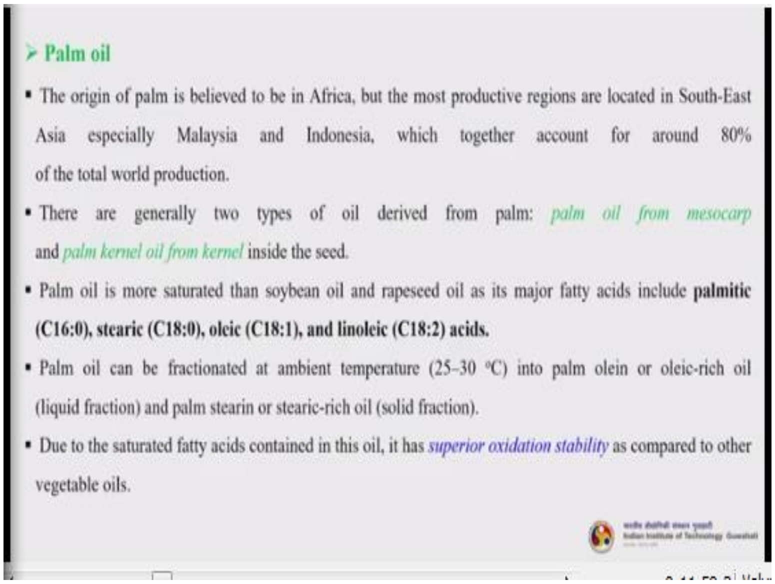

➢ Palm oil

- The origin of palm is believed to be in Africa, but the most productive regions are located in South-East Asia especially Malaysia and Indonesia, which together account for around 80% of the total world production.
- There are generally two types of oil derived from palm: *palm oil from mesocarp* and *palm kernel oil from kernel* inside the seed.
- Palm oil is more saturated than soybean oil and rapeseed oil as its major fatty acids include **palmitic (C16:0), stearic (C18:0), oleic (C18:1), and linoleic (C18:2) acids.**
- Palm oil can be fractionated at ambient temperature (25–30 °C) into palm olein or oleic-rich oil (liquid fraction) and palm stearin or stearic-rich oil (solid fraction).
- Due to the saturated fatty acids contained in this oil, it has *superior oxidation stability* as compared to other vegetable oils.

The next is palm oil. The origin of palm oil is believed to be in Africa, but most productive regions are located in Southeast Asia especially Malaysia and Indonesia, which together account for around 80% of the world production. There are generally two types of oil derived from the palm, so palm oil from the mesocarp and then the palm kernel oil from the kernel inside the seed. Palm oil is more saturated than soybean oil and rapeseed oil, as it is major fatty acids include palmitic, stearic, oleic, and linoleic acids.

Now palm oil can be fractionated at ambient temperatures in Palm olein or oleic-rich oil and palm stearin or stearic-rich oil. So, that is the solid fraction and the earlier one that is the oleic rich oil is the liquid fraction. Now due to the saturated fatty acids contained in this oil, it has superior oxidation stability as compared to other vegetable oils.

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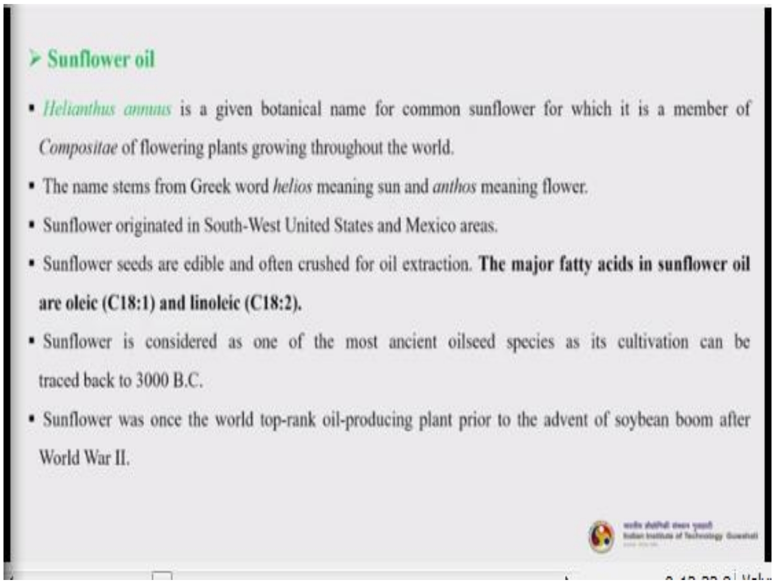

➢ **Sunflower oil**

- *Helianthus annuus* is a given botanical name for common sunflower for which it is a member of *Compositae* of flowering plants growing throughout the world.
- The name stems from Greek word *helios* meaning sun and *anthos* meaning flower.
- Sunflower originated in South-West United States and Mexico areas.
- Sunflower seeds are edible and often crushed for oil extraction. **The major fatty acids in sunflower oil are oleic (C18:1) and linoleic (C18:2).**
- Sunflower is considered as one of the most ancient oilseed species as its cultivation can be traced back to 3000 B.C.
- Sunflower was once the world top-rank oil-producing plant prior to the advent of soybean boom after World War II.

The next is sunflower oil. So, *Helianthus annuus* is the botanical name of the common sunflower species for which it is a member of the *Compositae* of flower plants growing throughout the world. The name stems from Greek word *helios* meaning sun, and *anthos* meaning flower. Sunflower originated in South-West United States and Mexico areas. Sunflower seeds are edible and often crushed for oil extraction. The major fatty acids in sunflower oil are oleic and linoleic.

Sunflower is considered as one of the most ancient oil seed species as it is cultivation can be traced back to 3000 B.C. Sunflower was once the world top rank oil producing plant prior to the advent of soybean boom after World War II.

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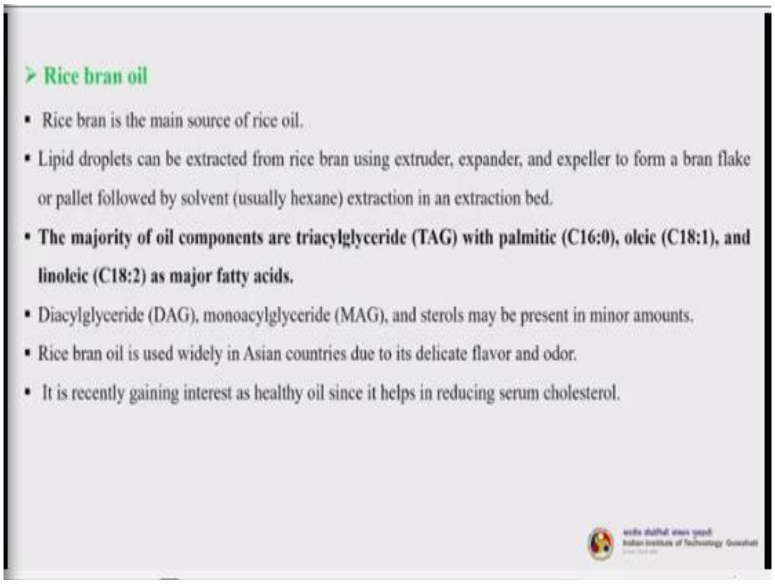

➢ **Rice bran oil**

- Rice bran is the main source of rice oil.
- Lipid droplets can be extracted from rice bran using extruder, expander, and expeller to form a bran flake or pallet followed by solvent (usually hexane) extraction in an extraction bed.
- **The majority of oil components are triacylglyceride (TAG) with palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) as major fatty acids.**
- Diacylglyceride (DAG), monoacylglyceride (MAG), and sterols may be present in minor amounts.
- Rice bran oil is used widely in Asian countries due to its delicate flavor and odor.
- It is recently gaining interest as healthy oil since it helps in reducing serum cholesterol.

The next is rice bran oil. So, rice bran is the main source of the rice oil. Lipid droplets can be extracted from the rice bran using extruder, expander and expeller to form a bran flake or pallet followed by solvent - usually hexane is being used for the extraction process in the extraction bed. The majority of the oil components are triacylglyceride with palmitic, oleic and linoleic as the major fatty acid present in the rice bran oil.

Diacylglyceride, monoacylglyceride and sterols may be present in minor amounts in rice bran oil. Rice bran oil is used widely in Asian countries due to it is delicate flavour and odor. It is recently gaining interest as healthy oil since it helps in reducing serum cholesterol. Recently rice bran has been widely adopted in India and sub continents. And one of our premier research labs in India which is CSIR Indian Institute of Chemical Technology has formulated an excellent rice bran oil and that has been commercially produced now.

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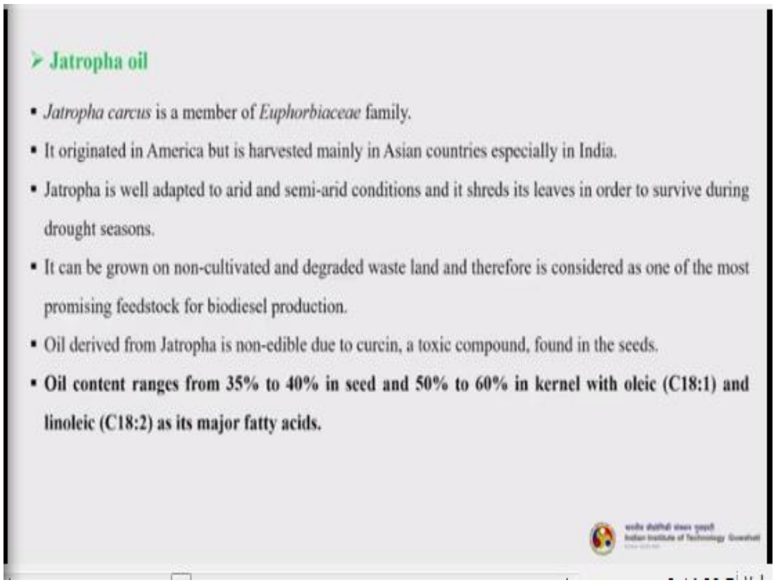

➤ Jatropha oil

- *Jatropha carcus* is a member of *Euphorbiaceae* family.
- It originated in America but is harvested mainly in Asian countries especially in India.
- Jatropha is well adapted to arid and semi-arid conditions and it shreds its leaves in order to survive during drought seasons.
- It can be grown on non-cultivated and degraded waste land and therefore is considered as one of the most promising feedstock for biodiesel production.
- Oil derived from Jatropha is non-edible due to curcin, a toxic compound, found in the seeds.
- **Oil content ranges from 35% to 40% in seed and 50% to 60% in kernel with oleic (C18:1) and linoleic (C18:2) as its major fatty acids.**

The next is Jatropha, now we are coming to the non-edible oils. *Jatropha curcas* is the member of the *Euphorbiaceae* family. It originated in America but is harvested mainly in Asian countries especially in India. Jatropha is well adapted to arid and semi arid conditions and it shreds it is leaves in order to survive during the drought seasons. So, it can be grown on non cultivated and degraded wasteland, and therefore is considered as one of the most promising feedstock for biodiesel production.

Oil derived from Jatropha is non edible due to curcin, a toxic compound that is found in the seeds. The oil content ranges from 35 to 40% in the seed and 50 to 60% in the kernel with oleic and linoleic as it is major fatty acid content. Having said that, you know we have already discussed that why again in India, let us talk about Indian context. Now you do not see Jatropha plantation anywhere in India because of the sustainable problem which we have already discussed when we discussed about the *Jatropha curcas* cycle**.**

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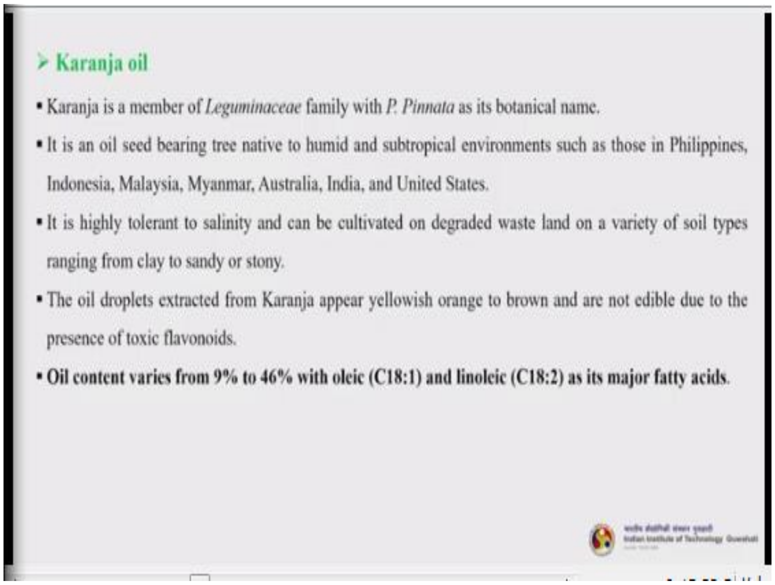

➤ Karanja oil

- Karanja is a member of *Leguminaceae* family with *P. Pinnata* as its botanical name.
- It is an oil seed bearing tree native to humid and subtropical environments such as those in Philippines, Indonesia, Malaysia, Myanmar, Australia, India, and United States.
- It is highly tolerant to salinity and can be cultivated on degraded waste land on a variety of soil types ranging from clay to sandy or stony.
- The oil droplets extracted from Karanja appear yellowish orange to brown and are not edible due to the presence of toxic flavonoids.
- **Oil content varies from 9% to 46% with oleic (C18:1) and linoleic (C18:2) as its major fatty acids.**

The next is karanja oil. So, karanja is a member of the *Leguminaceae* family with *Pongamia pinnata* as it is botanical name. It is an oil seed bearing tree native to humid and subtropical environments, such as those in Philippines, Indonesia, Malaysia, Myanmar, Australia, India and the United States. It is highly tolerant to salinity and can be cultivated on degraded wasteland on a variety of soil types, ranging from clay to sandy or stony.

The oil droplets extracted from Karanja appear yellowish orange to brown and are not edible due to the presence of toxic flavonoids. Oil content varies from 9% to 46% with oleic and linoleic acids major fatty acids.

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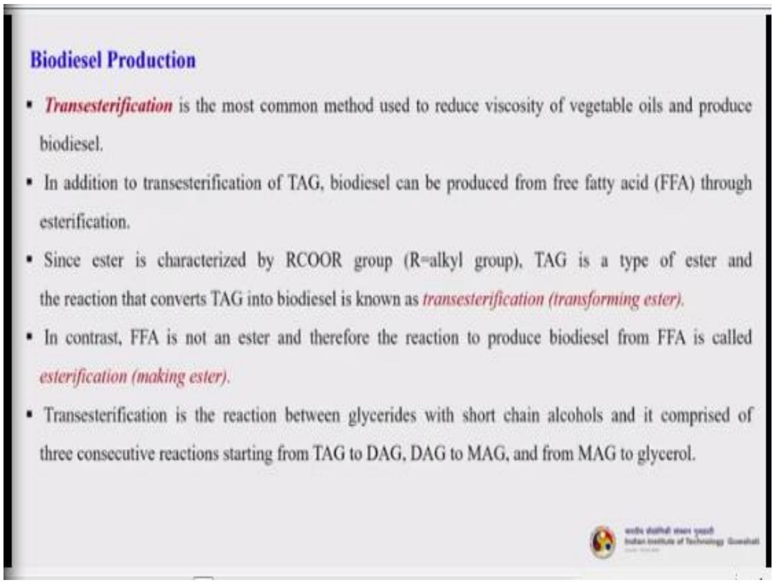

Biodiesel Production

- ***Transesterification*** is the most common method used to reduce viscosity of vegetable oils and produce biodiesel.
- In addition to transesterification of TAG, biodiesel can be produced from free fatty acid (FFA) through esterification.
- Since ester is characterized by RCOOR group (R=alkyl group), TAG is a type of ester and the reaction that converts TAG into biodiesel is known as *transesterification (transforming ester).*
- In contrast, FFA is not an ester and therefore the reaction to produce biodiesel from FFA is called *esterification (making ester).*
- Transesterification is the reaction between glycerides with short chain alcohols and it comprised of three consecutive reactions starting from TAG to DAG, DAG to MAG, and from MAG to glycerol.

So, let us talk about biodiesel production. So under this module, in our next class that is a lecture 2 of module 7, we will be discussing in detail how do you produce biodiesel by transesterification process, the reaction mechanism - how the reaction happens, how you conduct it in a lab scale - All these things we will be discussing in our next class. Today in a gist we will just go through and in detail we will discuss in our next class.

So, transesterification is the most common method used to reduce viscosity of vegetable oils and produce biodiesel. In addition to transesterification of TAG biodiesel can be produced from free fatty acids through esterification. Since ester is characterized by RCOOR group (R = alkyl group, R is alkyl group), TAG is a type of ester and reaction that converts TAG into biodiesel is therefore known as transesterification, that means transforming the ester.

In contrast, free fatty acid is not an ester and therefore the reaction to produce biodiesel from free fatty acids is called esterification, that means making ester. Transesterification is the reaction between glycerides with short chain alcohols and is comprised of three consecutive reactions starting from TAG to DAG, DAG to MAG and from MAG to glycerol. We will discuss this in detail in our next class.

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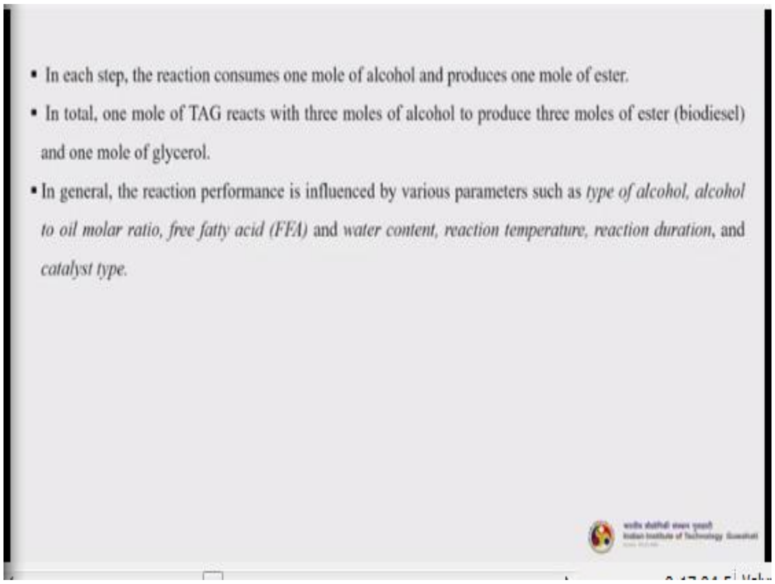

- In each step, the reaction consumes one mole of alcohol and produces one mole of ester.
- In total, one mole of TAG reacts with three moles of alcohol to produce three moles of ester (biodiesel) and one mole of glycerol.
- In general, the reaction performance is influenced by various parameters such as *type of alcohol, alcohol to oil molar ratio, free fatty acid (FFA)* and *water content, reaction temperature, reaction duration*, and *catalyst type*.

In each step, the reaction consumes one mole of alcohol and produces one mole of ester. In total, one mole of TAG reacts with three moles of alcohol to produce three moles of ester that is biodiesel and one mole of glycerol. So, glycerol is one of the most important byproducts having a lot of commercial value and application from the biodiesel industries. So, in general the reaction performance is influenced by various parameters such as type of alcohol, alcohol to oil molar ratio, free fatty acid content, water content, reaction temperature, reaction duration and the type of catalysts that you are using.

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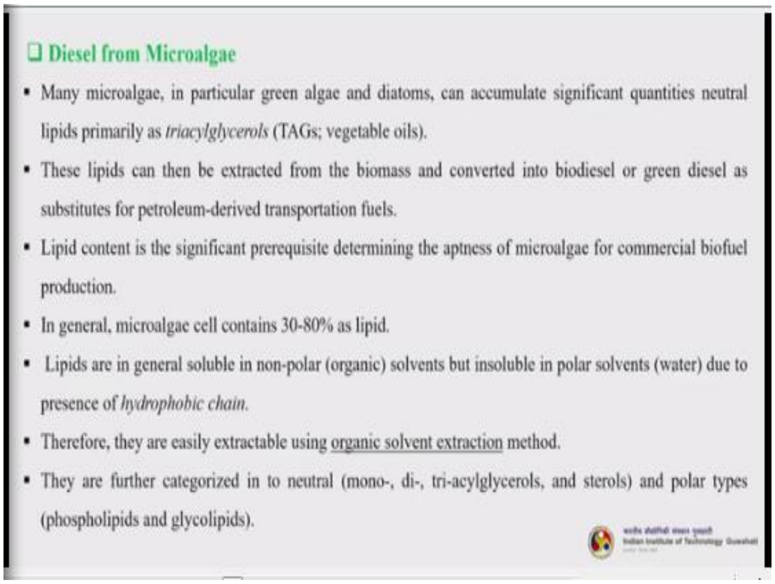

❑ Diesel from Microalgae

- Many microalgae, in particular green algae and diatoms, can accumulate significant quantities neutral lipids primarily as *triacylglycerols* (TAGs; vegetable oils).
- These lipids can then be extracted from the biomass and converted into biodiesel or green diesel as substitutes for petroleum-derived transportation fuels.
- Lipid content is the significant prerequisite determining the aptness of microalgae for commercial biofuel production.
- In general, microalgae cell contains 30-80% as lipid.
- Lipids are in general soluble in non-polar (organic) solvents but insoluble in polar solvents (water) due to presence of *hydrophobic chain*.
- Therefore, they are easily extractable using organic solvent extraction method.
- They are further categorized in to neutral (mono-, di-, tri-acylglycerols, and sterols) and polar types (phospholipids and glycolipids).

Now let us talk about the diesel that is coming out from microalgae. We have discussed about microalgae in one of our previous classes that why microalgae suddenly become a big bloom and of research interest for many of the scientists and academicians across the globe. So, today we will discuss how diesel can be produced from microalgae. So many microalgae, in particular the green algae and diatoms can accumulate significant quantities of neutral lipids primarily as triacylglycerols - TAGs.

Now these lipids can then be extracted from the biomass and converted into biodiesel or green diesel as substitutes for petroleum derived transportation fuels**.** So, having said that, I am telling you that, once you produce biodiesel, it needs some further processing, which we are going to discuss in our subsequent lectures under this module, maybe in the lecture 3 under module 7. So, you need to purify it, it is not that you produce and directly it can be used in the engines, it is not so. We will discuss how this will eventually happen.

So the lipid content is the significant prerequisite determining the aptness of the microalgae for commercial biofuel production. In general, microalgae cell contains 30 to 80% lipid. Lipids are in general soluble in non-polar solvents but insoluble in polar solvents due to the presence of hydrophobic chain. Therefore, they are easily extractable using organic solvent extraction method. They are further categorized into neutral and polar type.

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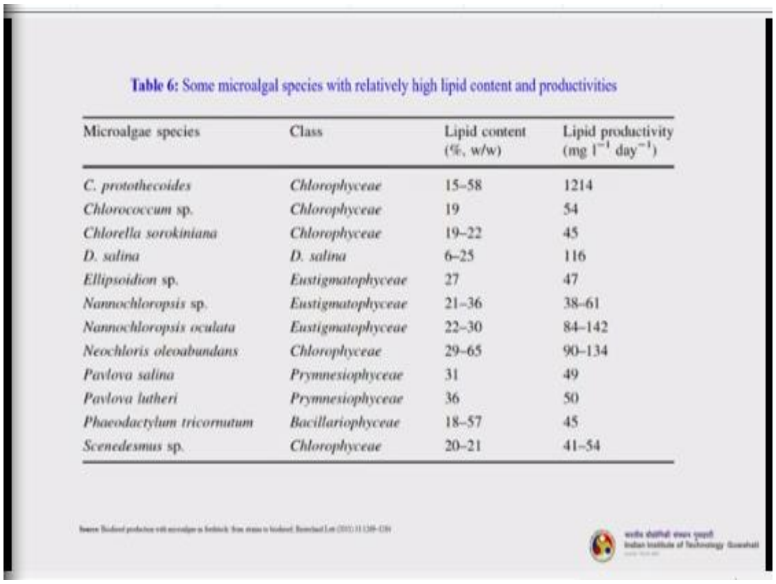

Table 6: Some microalgal species with relatively high lipid content and productivities

Microalgae species	Class	Lipid content (%, w/w)	Lipid productivity (mg l^{-1} day^{-1})
C. protothecoides	*Chlorophyceae*	15–58	1214
Chlorococcum sp.	*Chlorophyceae*	19	54
Chlorella sorokiniana	*Chlorophyceae*	19–22	45
D. salina	*D. salina*	6–25	116
Ellipsoidion sp.	*Eustigmatophyceae*	27	47
Nannochloropsis sp.	*Eustigmatophyceae*	21–36	38–61
Nannochloropsis oculata	*Eustigmatophyceae*	22–30	84–142
Neochloris oleoabundans	*Chlorophyceae*	29–65	90–134
Pavlova salina	*Prymnesiophyceae*	31	49
Pavlova lutheri	*Prymnesiophyceae*	36	50
Phaeodactylum tricornutum	*Bacillariophyceae*	18–57	45
Scenedesmus sp.	*Chlorophyceae*	20–21	41–54

So, this particular table will make you understand or give you some information about some of the typical microalgal species with relatively high lipid content and productivities which can be used or has been used for the biodiesel production. Please understand that we have more than 200,000 species of microalgae and out of that almost 50,000 might have been tested.

Please note that all species do not contain a huge amount of lipid which can be grown and harvested for the biodiesel production, it cannot be. So, these are some of the already well tested microalgal species which are having very high lipid content. So like *C. protothecoides*, then *Chlorococcum*, *Chlorella sorokiniana*, *D. salina* all these things, there are so many different types of species, even the *Scenedesmus* species also.

You can see that the first one, it comes under the *Chlorophyceae* genus; it has a lipid content about 15 to 58% again depending upon the species (w/w). And the lipid productivity, if you talk about the productivity in milligrams per litre per day, so it is the highest almost among those are listed 1214. And one of the most important species is the *Scenedesmus* species; it can be grown easily, it is very widely adapted, climatically adapted species along with even *Chlorella vulgaris* and all other. So, it has also a good lipid content and a very nice lipid productivity.

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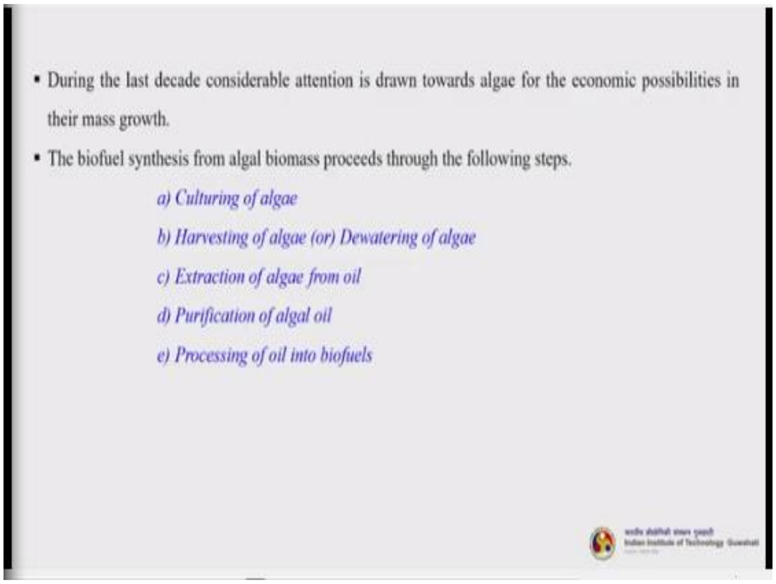

- During the last decade considerable attention is drawn towards algae for the economic possibilities in their mass growth.
- The biofuel synthesis from algal biomass proceeds through the following steps.
    - *a) Culturing of algae*
    - *b) Harvesting of algae (or) Dewatering of algae*
    - *c) Extraction of algae from oil*
    - *d) Purification of algal oil*
    - *e) Processing of oil into biofuels*

So, during the last decade considerable attention is drawn towards algae for the economic possibilities in their mass growth. It is not about only biodiesel, but there are various other applications of the microalgae which I have already told you - what are the different types of components or the value added products that can be extracted from microalgae or further process to make directly commercial products.

So, the biofuel synthesis from algae proceeds through the following 5 steps. First is that you need to culture the algae; second is harvesting the algae or dewatering algae. So, this is right now also this is one of the most important steps, because it consumes energy and it takes time also. So, when you have huge amount of algae that needs to be dewatered and harvested; so, you have to have a proper technology, which should be faster as well as it should be low in cost.

The third is the extraction of algae from oil (oil from algae). So, you can either go for this chemical based extraction or physical extraction, it depends on what type of species it is, what is the oil content. So, there are so many other parameters to be thought of, but again extraction is also a cost intensive process. Then purification of the algal oil, so the downstream purification you need to remove whatever water content, glycerol and any other components which are not the fuel components needs to be removed. And the last one is the processing of oil into biofuels.

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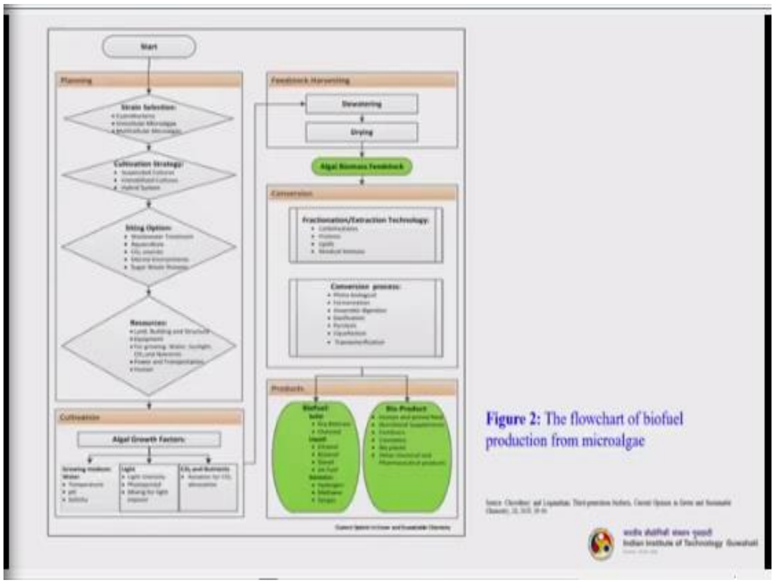

Figure 2: The flowchart of biofuel production from microalgae

So, please have a look at this particular flowchart. This is the flowchart for biofuel production from the microalgae. So, it starts from the strain selection - the first and foremost important thing that which strain you are going to use for the biofuel production. So, now let us say I am in

Guwahati, in Guwahati in my group alone we have strain, we have almost more than 100 different strains which we have screened for different purposes.

It is not only for the biodiesel production; we have used it for different purposes. And we have seen that certain strains are naturally having very high lipid content. So, we can use those strains for the biodiesel production. So the strain selection is very important. So, after that you have to go for cultivation strategy, what type of cultivation strategy was going to add up? Suspended cultures, immobilized cultures, hybrid systems, how we are growing them?

In raceway ponds, photobioreactors, open, closed so many things are coming into picture. Then the sitting options, so wastewater treatment, aquaculture, carbon dioxide sources; it is again some sort of hybrid digestion you can tell that. If you talk about wastewater treatment - in one of the class I have already told you that if we can grow algae in wastewaters, then it is a win-win situation.

Because it will purify the wastewater or let us say it will treat the wastewater, as well as the microalgal growth will be there, so of course, you can harvest it. So, two things are happening in a single thing, and you will be depending less on the amount of freshwater. So, thereby you can recycle the harvested water after maybe some minor treatment back to the raceway pond or bioreactors.

Then resources like of course, this is capital cost that is coming into picture. Then cultivation, different factors will be there growing medium, light, carbon dioxide, nutrients. Then harvesting, then it goes for the conversion process, what type of conversion process you are looking for? Fractionation extraction technology, lipid extraction, extraction of carbohydrate, other things, proteins; then conversion, photobiological, fermentation, anaerobic digestion, gasification, pyrolysis, liquefaction and the last transesterification for the biodiesel production.

Then, once you do that, so you get majorly 2 different types of products - the biofuels, like solid also dry biomass - that de-oiled cake you can say, charcoal. Under liquid we may get ethanol from the carbohydrate platform, then butanol also from the carbohydrate platform, diesel coming from the lipid**.** Then jet fuel and gaseous if you talk about hydrogen, methane, syngas maybe from anaerobic digestion and FTA and other processes. Then other various bio products like cosmetic, fertilizers, bio plastics, antibiotics, vitamins and so many other things.

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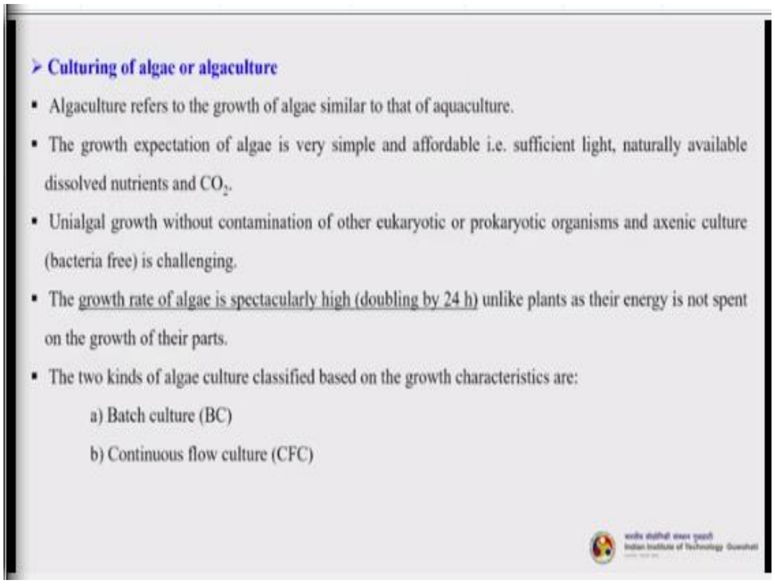

➢ Culturing of algae or algaculture

- Algaculture refers to the growth of algae similar to that of aquaculture.
- The growth expectation of algae is very simple and affordable i.e. sufficient light, naturally available dissolved nutrients and CO_2.
- Unialgal growth without contamination of other eukaryotic or prokaryotic organisms and axenic culture (bacteria free) is challenging.
- The growth rate of algae is spectacularly high (doubling by 24 h) unlike plants as their energy is not spent on the growth of their parts.
- The two kinds of algae culture classified based on the growth characteristics are:
  a) Batch culture (BC)
  b) Continuous flow culture (CFC)

So, culturing up algae or algaculture. So, algal culture refers to the growth of algae similar to that of aquaculture. The growth expectation of algae is very simple and affordable, that is, sufficient light, naturally available dissolved nutrients and carbon dioxide is what the algae needs to grow. Unialgal growth without contamination of other eukaryotic or prokaryotic organisms and axenic culture (that means bacteria free) is challenging, especially when you are growing it openly.

So, the growth rate of algae is spectacularly high, it is almost doubling in 24 hours, unlike plants as their energy is not spent on the growth of their parts. There are two kinds of algae culture classified based on the growth characteristics are either batch culture or continuous flow culture, BC and CFC.

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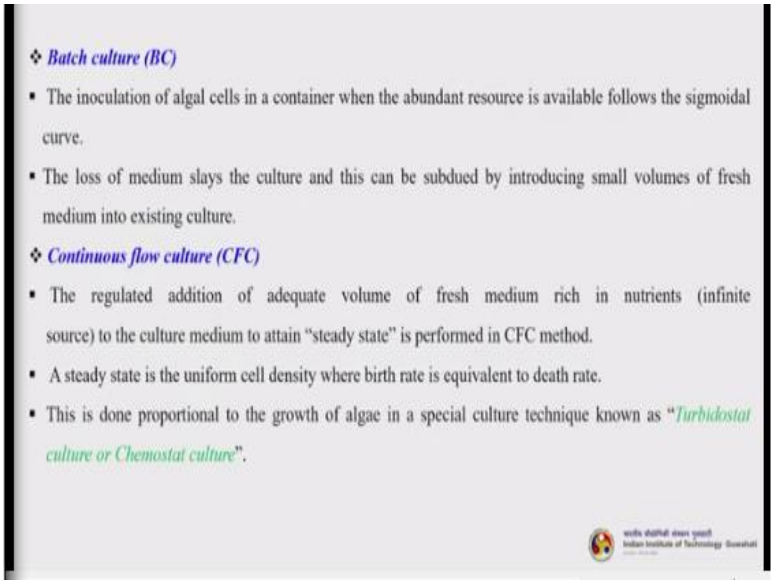

❖ ***Batch culture (BC)***

- The inoculation of algal cells in a container when the abundant resource is available follows the sigmoidal curve.
- The loss of medium slays the culture and this can be subdued by introducing small volumes of fresh medium into existing culture.

❖ ***Continuous flow culture (CFC)***

- The regulated addition of adequate volume of fresh medium rich in nutrients (infinite source) to the culture medium to attain "steady state" is performed in CFC method.
- A steady state is the uniform cell density where birth rate is equivalent to death rate.
- This is done proportional to the growth of algae in a special culture technique known as "*Turbidostat culture or Chemostat culture*".

Now let us see the BC. The inoculation of algal cell in a container when the abundant resource is available, follows the sigmoidal curve in the batch culture. The loss of medium slays the culture and this could be subdued by introducing small volumes of fresh medium into the existing culture. Then comes the continuous flow culture, CFC. The regulated addition of adequate volume of fresh medium rich in nutrients to the culture medium to attain steady state is performed in the CFC method.

A steady state is the uniform cell density where the birth rate is equal to the death rate. This is the definition of steady state with respect to the CFC. Now this is done proportional to the growth of algae in special culture technique known as Turbidostat culture or Chemostat culture.

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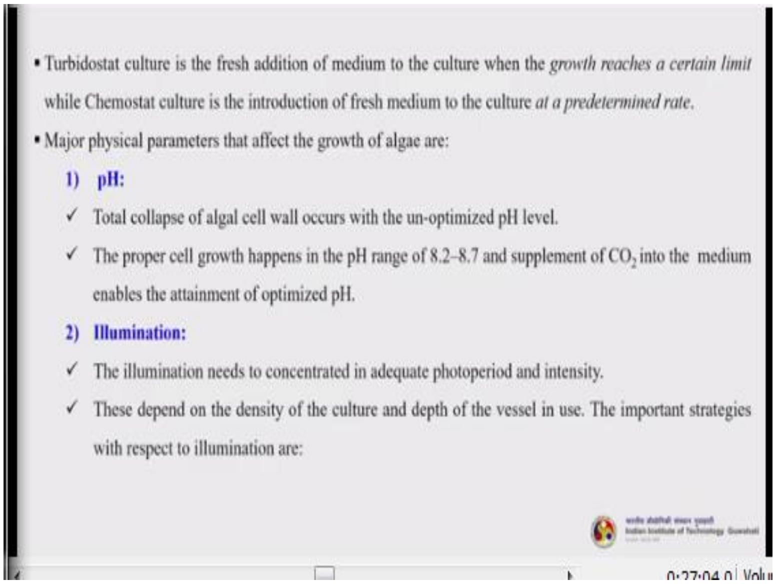

- Turbidostat culture is the fresh addition of medium to the culture when the *growth reaches a certain limit* while Chemostat culture is the introduction of fresh medium to the culture *at a predetermined rate*.
- Major physical parameters that affect the growth of algae are:

1) pH:

✓ Total collapse of algal cell wall occurs with the un-optimized pH level.

✓ The proper cell growth happens in the pH range of 8.2–8.7 and supplement of CO_2 into the medium enables the attainment of optimized pH.

2) Illumination:

✓ The illumination needs to concentrated in adequate photoperiod and intensity.

✓ These depend on the density of the culture and depth of the vessel in use. The important strategies with respect to illumination are:

Now Turbidostat culture is the fresh addition of medium to the culture when the growth reaches a certain limit, whereas, chemostat culture is the introduction of fresh medium to the culture at a predetermined rate. So, let us now understand the major physical parameters that affects the growth of the algae. The first and foremost important thing is pH, I have told you many times whenever you deal anything with the aqueous medium pH always plays a big role.

The total collapse of algal cell wall occurs with the un-optimized pH level; so you have to be very careful of the pH. And the proper cell growth happens in the pH range of 8.2 to 8.7 and supplement of carbon dioxide into the medium enables the attainment of the optimized pH. Then illumination, another important factor. Illumination needs to be concentrated in adequate photoperiod and intensity.

These depend on the density of the culture and depth of the vessel in use. The important strategies with respect to illumination are:

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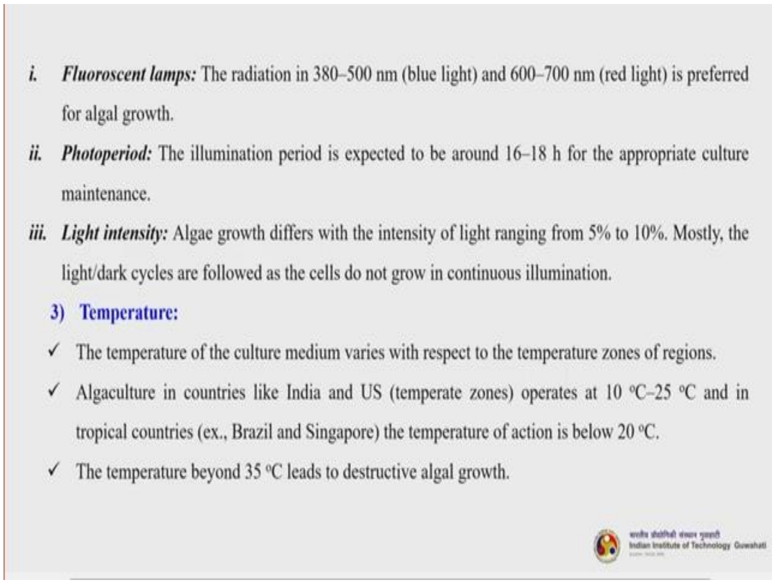

i. ***Fluoroscent lamps:*** The radiation in 380–500 nm (blue light) and 600–700 nm (red light) is preferred for algal growth.

ii. ***Photoperiod:*** The illumination period is expected to be around 16–18 h for the appropriate culture maintenance.

iii. ***Light intensity:*** Algae growth differs with the intensity of light ranging from 5% to 10%. Mostly, the light/dark cycles are followed as the cells do not grow in continuous illumination.

3) Temperature:

- ✓ The temperature of the culture medium varies with respect to the temperature zones of regions.
- ✓ Algaculture in countries like India and US (temperate zones) operates at 10 °C–25 °C and in tropical countries (ex., Brazil and Singapore) the temperature of action is below 20 °C.
- ✓ The temperature beyond 35 °C leads to destructive algal growth.

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Fluorescent lamps, photoperiod and light intensity. So, in fluorescent lamps the radiation in 380 to 500 nanometer usually the blue light and 600 to 700 nanometer usually the red light is preferred for the algal growth. Photoperiod, the illumination period is expected to be around 16 to 18 hour for the appropriate culture maintenance. Again these so many things which we are discussing all the parameters that also depends on a particular species.

Light intensity; algae growth differs with the intensity of light ranging from 5% to 10%. Mostly the light and dark cycles are followed as the cells do not grow in continuous illumination. The next is temperature, temperature of the culture medium varies with respect to the temperature zone of the regions. Algaculture in countries like India and United States (basically temperate zones) operates at 10 degree centigrade to 25 degrees centigrade.

And in tropical countries, especially Brazil and Singapore the temperature of action is below 20 degrees centigrade. The temperature beyond 35 degree centigrade leads to destructive algal growth.

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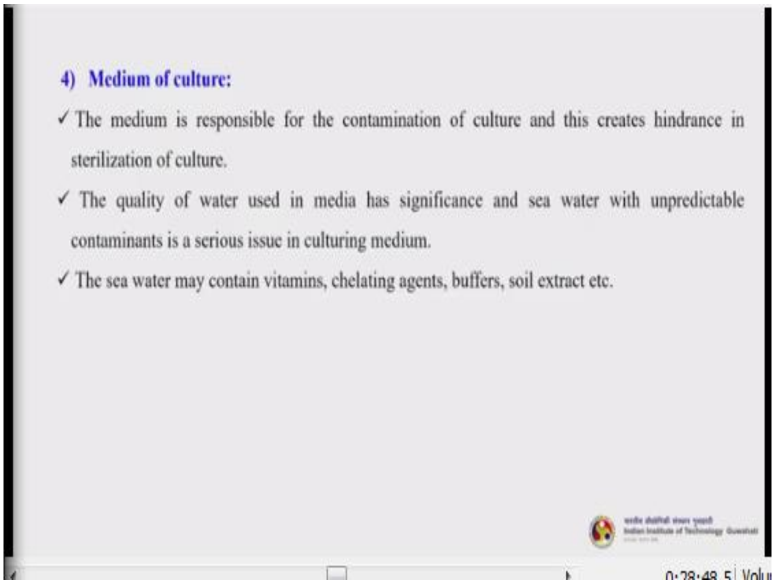

4) **Medium of culture:**

- ✓ The medium is responsible for the contamination of culture and this creates hindrance in sterilization of culture.
- ✓ The quality of water used in media has significance and sea water with unpredictable contaminants is a serious issue in culturing medium.
- ✓ The sea water may contain vitamins, chelating agents, buffers, soil extract etc.

Then the medium of culture; the medium is responsible for the contamination of culture and it creates a hindrance in the sterilization also. The quality of water used in media has significance and sea water with unpredictable contaminant is a serious issue in culturing medium. So, seawater may contain vitamins, chelating agents, buffers, soil extract etc. and sometimes it needs to be purified.

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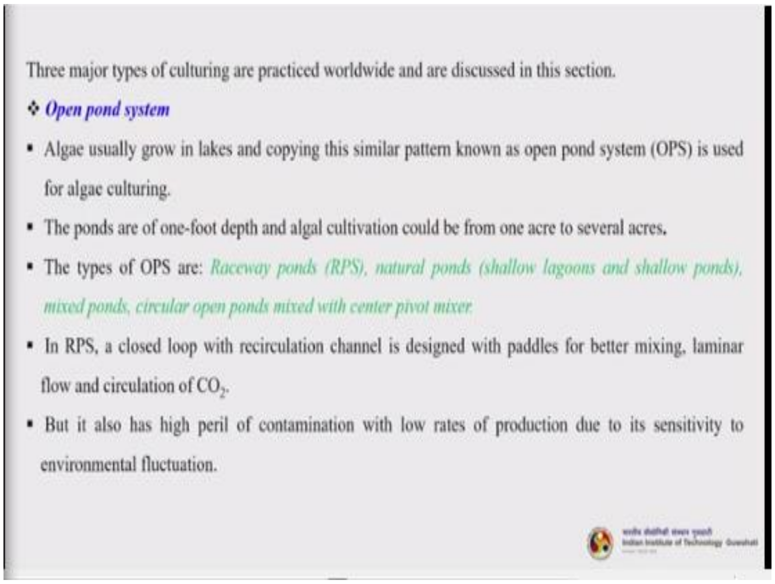

Three major types of culturing are practiced worldwide and are discussed in this section.

❖ ***Open pond system***

- Algae usually grow in lakes and copying this similar pattern known as open pond system (OPS) is used for algae culturing.
- The ponds are of one-foot depth and algal cultivation could be from one acre to several acres.
- The types of OPS are: *Raceway ponds (RPS), natural ponds (shallow lagoons and shallow ponds), mixed ponds, circular open ponds mixed with center pivot mixer.*
- In RPS, a closed loop with recirculation channel is designed with paddles for better mixing, laminar flow and circulation of CO_2.
- But it also has high peril of contamination with low rates of production due to its sensitivity to environmental fluctuation.

So, three major types of culturing are practiced worldwide and are discussed in this section, we will try to understand in a nutshell. So, open pond system: algae usually grow in lakes and copying this similar pattern is known as the open pond system for algal culturing. The ponds are of one-foot depth and alga cultivation could be from one acre to several acres. The types of open pond system are raceway ponds (which are the most common), natural ponds (so they are the shallow lagoons and shallow ponds), mixed ponds, circular open ponds mixed with center pivot mixer. In raceway ponds, a closed loop with recirculation channel is designed with paddles for better mixing, laminar flow and circulation of carbon dioxide. But it also has a high peril of contamination with low rates of production due to it is sensitivity to the environmental fluctuation.

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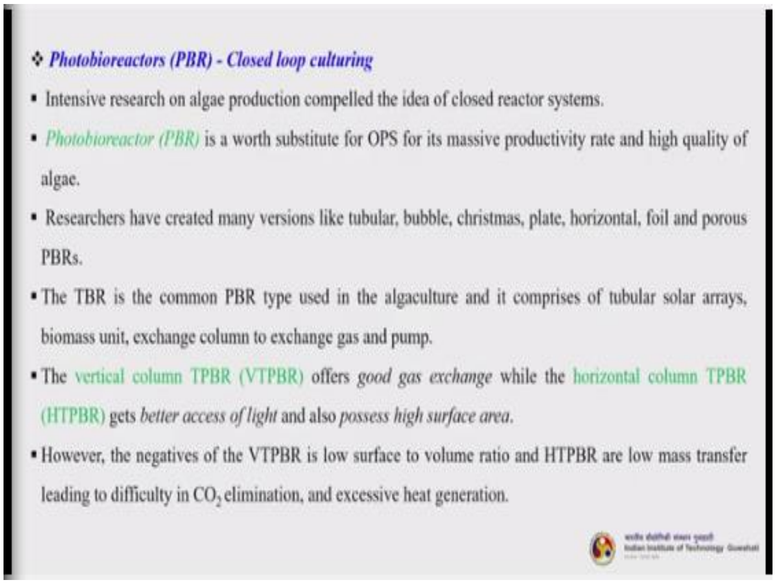

❖ ***Photobioreactors (PBR) - Closed loop culturing***

- Intensive research on algae production compelled the idea of closed reactor systems.
- *Photobioreactor (PBR)* is a worth substitute for OPS for its massive productivity rate and high quality of algae.
- Researchers have created many versions like tubular, bubble, christmas, plate, horizontal, foil and porous PBRs.
- The TBR is the common PBR type used in the algaculture and it comprises of tubular solar arrays, biomass unit, exchange column to exchange gas and pump.
- The vertical column TPBR (VTPBR) offers *good gas exchange* while the horizontal column TPBR (HTPBR) gets *better access of light* and also *possess high surface area.*
- However, the negatives of the VTPBR is low surface to volume ratio and HTPBR are low mass transfer leading to difficulty in CO_2 elimination, and excessive heat generation.

The next are photobioreactors or closed loop culturing. Intensive research on algae production compelled the idea of the closed loop reactor systems. Photobioreactor is a worth substitute for OPS for it is massive productivity rate and high quality of algae. So, everything is good in photobioreactors, that is because it is a closed system, it is very easy to control all the parameters and there is no problem of this contamination also.

Now researchers have created many versions like tubular, bubble, christmas, plate, horizontal, foil and porous photobioreactors. The tubular bioreactor is the common photobioreactor type used in the algal culture and it comprises of tubular solar arrays, biomass unit, exchange column to exchange gas and pump. The tubular solar arrays basically mean the tubular photobioreactors which are placed under the sunlight in open atmosphere.

The vertical column tubular photobioreactor offers good gas exchange while the horizontal column tubular photobioreactor gets better access of light and also possess higher surface area. However, the negatives of the vertical tubular photobioreactor is the low surface to volume ratio, and horizontal column tubular photobioreactor is the low mass transfer leading to difficulty in carbon dioxide elimination and excessive heat generation.

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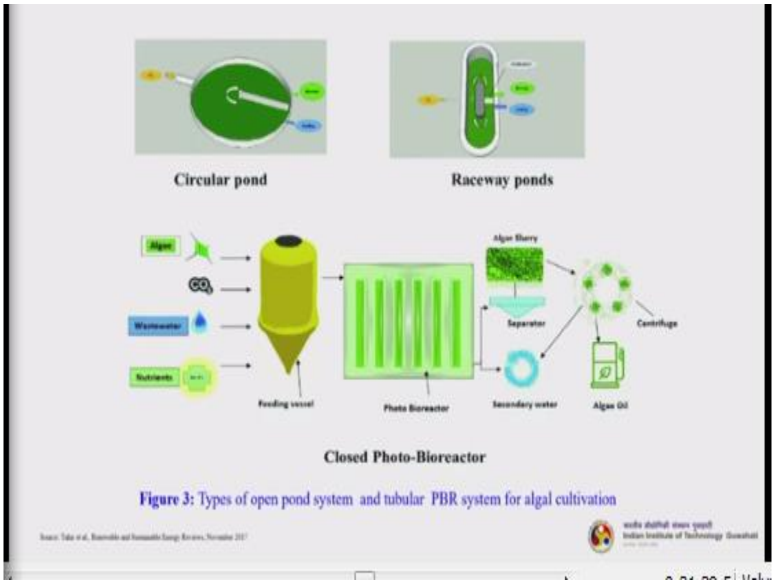

Figure 3: Types of open pond system and tubular PBR system for algal cultivation

So, this is the closed photobioreactor - actually a schematic. So, the algae, carbon dioxide, then water or wastewater whatever**,** the nutrients are all mixed in the feeding vessel, then it goes to the photobioreactor where it is cultured; proper amount of carbon dioxide and light is being given. And a proper light and dark cycle has been maintained, then you see that it goes for the harvesting, the separator where the algal slurry has been separated.

And the secondary water can be used - treated and fed back to the photobioreactor or the raceway pond whatever it is**.** Then the slurry is being centrifuged, so you will get the biomass, the solid biomass which can be further processed, you can extract the lipid, make it biodiesel and other parts also whatever left out in the solid residue can be used for various other platform chemicals or other value added products.

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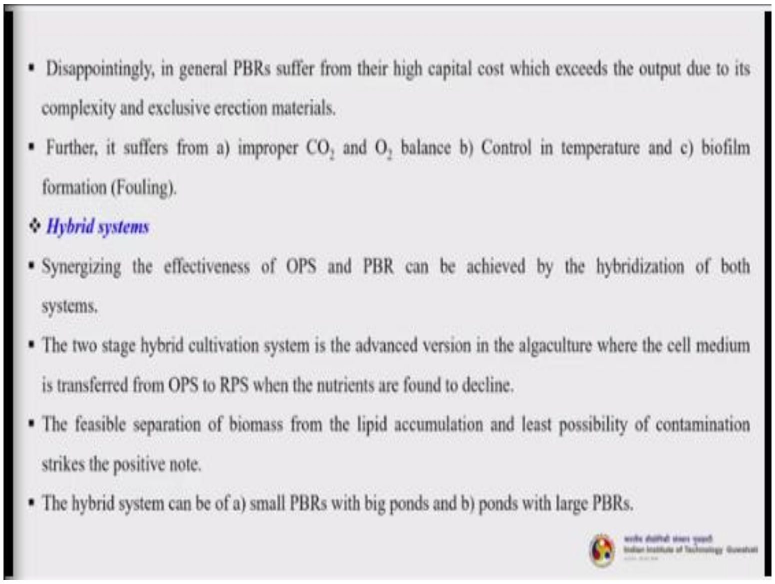

- Disappointingly, in general PBRs suffer from their high capital cost which exceeds the output due to its complexity and exclusive erection materials.
- Further, it suffers from a) improper CO_2 and O_2 balance b) Control in temperature and c) biofilm formation (Fouling).

❖ ***Hybrid systems***

- Synergizing the effectiveness of OPS and PBR can be achieved by the hybridization of both systems.
- The two stage hybrid cultivation system is the advanced version in the algaculture where the cell medium is transferred from OPS to RPS when the nutrients are found to decline.
- The feasible separation of biomass from the lipid accumulation and least possibility of contamination strikes the positive note.
- The hybrid system can be of a) small PBRs with big ponds and b) ponds with large PBRs.

Disappointingly, in general photobioreactors suffer from their high capital cost (this is one of the most important thing actually which hinders its application in large commercial sector) which exceeds the output due to it is complexity and exclusive erection materials. Further, it suffers from improper carbon dioxide and oxygen balance, control in temperature and biofilm formation - fouling.

So, the next is hybrid systems. Synergizing the effectiveness of the open pond system and photobioreactor can be achieved by the hybridization of both the systems. The two stage hybrid cultivation system is the advanced version of the alga culture, where the cell medium is transferred from the open pond system to the raceway pond system when the nutrients are found to decline.

The feasible separation of biomass from the lipid accumulation and least possibility of contamination strike the positive note. The hybrid system can be of small PBRs with big ponds or ponds with large PBRs, anyone of these combinations.

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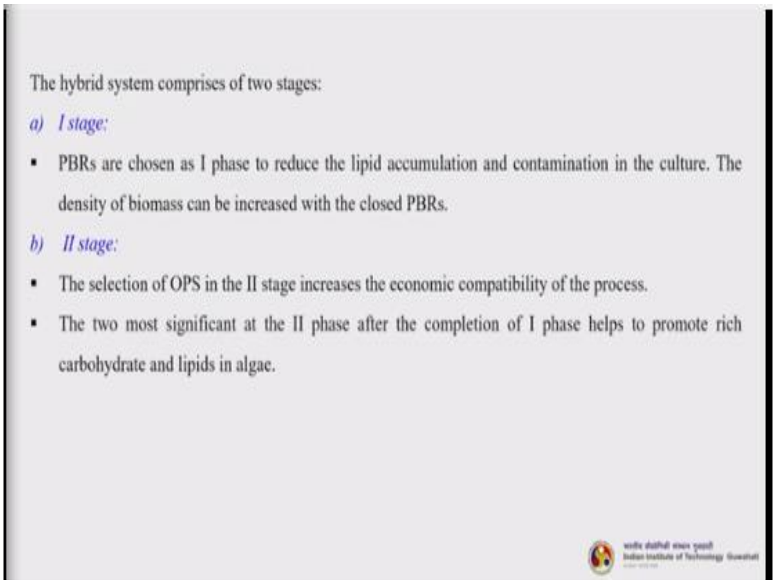

The hybrid system comprises of two stages:

a) I stage:

- PBRs are chosen as I phase to reduce the lipid accumulation and contamination in the culture. The density of biomass can be increased with the closed PBRs.

b) II stage:

- The selection of OPS in the II stage increases the economic compatibility of the process.
- The two most significant at the II phase after the completion of I phase helps to promote rich carbohydrate and lipids in algae.

The hybrid system comprises of two stages. Stage I: PBRs are chosen as phase I to reduce the lipid accumulation and contamination in the culture. The density of biomass can be increased in the closed PBR system; once it is done you transfer it to the raceway ponds. In second, stage II: the selection of OPS in the stage II increase the economic compatibility of the process. The two most significant at the phase II after the completion of I phase helps to promote rich carbohydrates and lipids in the algae**.**

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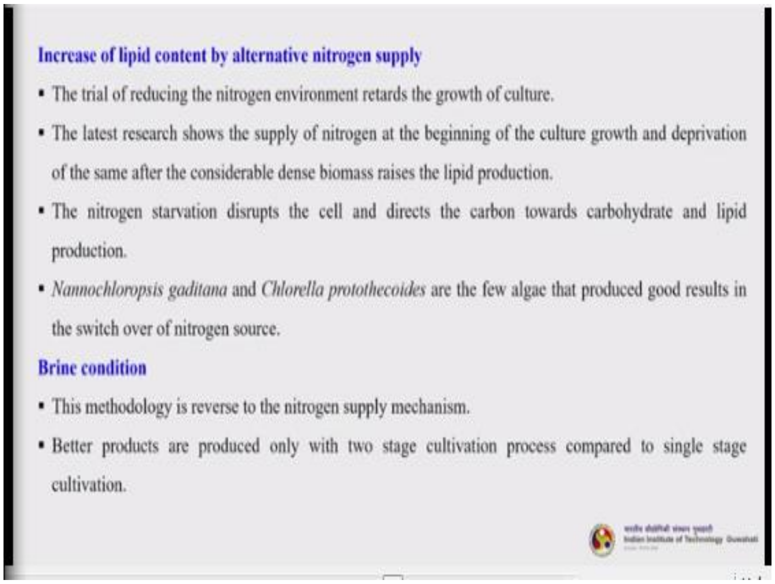

Increase of lipid content by alternative nitrogen supply

- The trial of reducing the nitrogen environment retards the growth of culture.
- The latest research shows the supply of nitrogen at the beginning of the culture growth and deprivation of the same after the considerable dense biomass raises the lipid production.
- The nitrogen starvation disrupts the cell and directs the carbon towards carbohydrate and lipid production.
- *Nannochloropsis gaditana* and *Chlorella protothecoides* are the few algae that produced good results in the switch over of nitrogen source.

Brine condition

- This methodology is reverse to the nitrogen supply mechanism.
- Better products are produced only with two stage cultivation process compared to single stage cultivation.

So, then we will talk about increase of lipid content by alternative nitrogen supply. The trial of reducing the nitrogen environment retards the growth of the culture. The latest research shows the supply of nitrogen at the beginning of the culture growth and then deprive it after the considerable dense biomass raises the lipid production, this is called nitrogen starvation, or nitrogen shock. So, the nitrogen starvation disrupts the cell and directs the carbon towards carbohydrate and lipid production. *Nannochloropsis gaditana* and *Chlorella protothecoides* are the few algal species that produced good results in the switch over of nitrogen sources. So, this is one of the widely studied problem or we can say the aspect of the microalgal culture and growth.

So, then brine condition; now this methodology is reverse to the nitrogen supply mechanism. Better products are produced only with two stage cultivation process compared to single stage cultivation.

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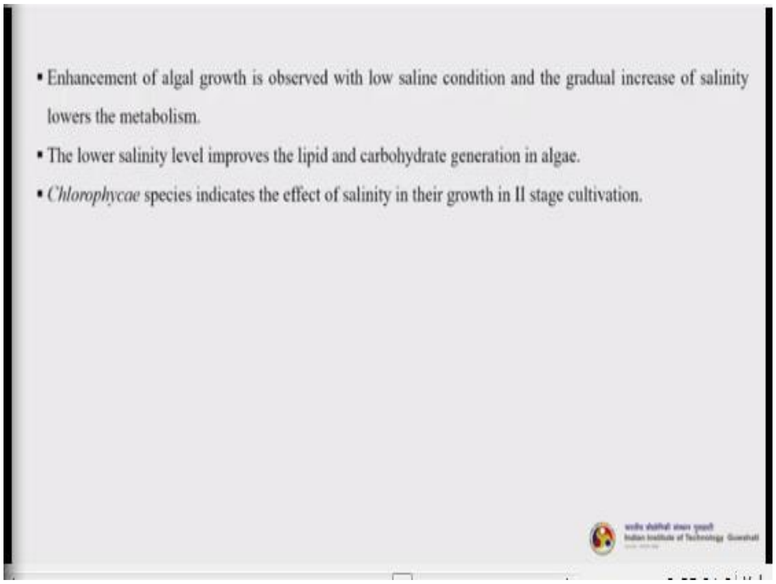

- Enhancement of algal growth is observed with low saline condition and the gradual increase of salinity lowers the metabolism.
- The lower salinity level improves the lipid and carbohydrate generation in algae.
- *Chlorophycae* species indicates the effect of salinity in their growth in II stage cultivation.

Enhancement of algal growth is observed with saline condition and the gradual increase of salinity lowers the metabolism. The lower salinity level improves the lipid and carbohydrate generation in algae. *Chlorophyceae* species indicates the effect of salinity in their growth in stage II cultivation.

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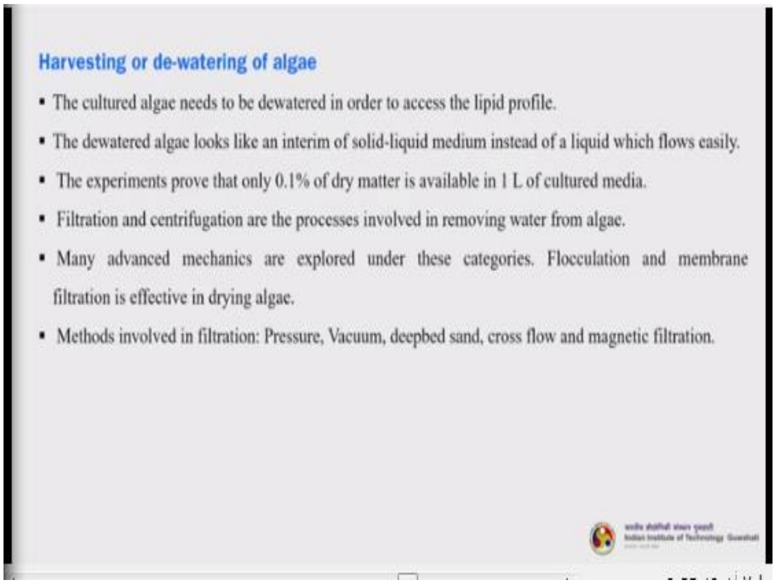

Harvesting or de-watering of algae

- The cultured algae needs to be dewatered in order to access the lipid profile.
- The dewatered algae looks like an interim of solid-liquid medium instead of a liquid which flows easily.
- The experiments prove that only 0.1% of dry matter is available in 1 L of cultured media.
- Filtration and centrifugation are the processes involved in removing water from algae.
- Many advanced mechanics are explored under these categories. Flocculation and membrane filtration is effective in drying algae.
- Methods involved in filtration: Pressure, Vacuum, deepbed sand, cross flow and magnetic filtration.

Then harvesting or dewatering of algae. The cultured algae needs to be dewatered in order to access the lipid profile. The dewatered algae looks like an interim of solid-liquid medium instead of a liquid which flows easily. The experiments prove that only 0.1% of dry matter is available in 1 litre of the culture media. Filtration and centrifugation are the processes involved in removing water from algae.

Many advanced mechanics are explored under these categories. Flocculation and membrane filtration is effective in drying the algae. Methods involved in filtration are pressure, vacuum, deepbed sand, cross flow and magnetic filtration. Huge amount of work is still going on, on this particular harvesting technology.

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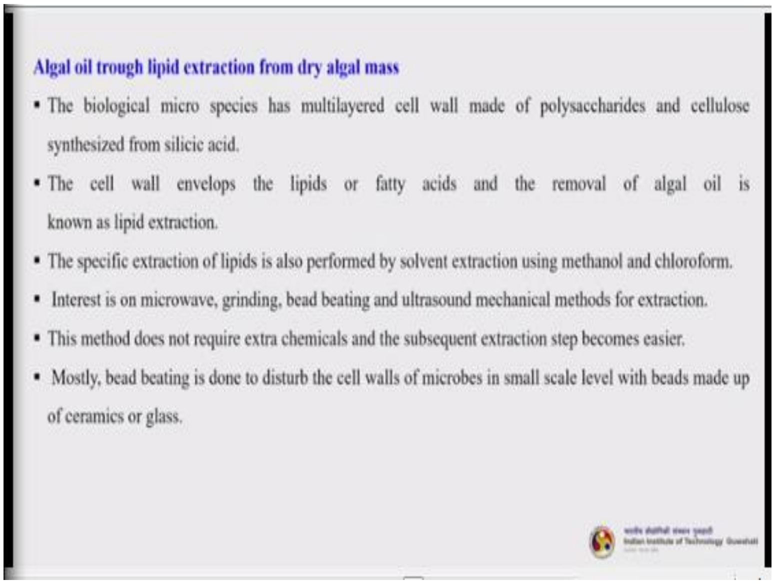

Algal oil trough lipid extraction from dry algal mass

- The biological micro species has multilayered cell wall made of polysaccharides and cellulose synthesized from silicic acid.
- The cell wall envelops the lipids or fatty acids and the removal of algal oil is known as lipid extraction.
- The specific extraction of lipids is also performed by solvent extraction using methanol and chloroform.
- Interest is on microwave, grinding, bead beating and ultrasound mechanical methods for extraction.
- This method does not require extra chemicals and the subsequent extraction step becomes easier.
- Mostly, bead beating is done to disturb the cell walls of microbes in small scale level with beads made up of ceramics or glass.

So, then algal oil through lipid extraction from dry algal mass. The biological micro species has multilayered cell wall made up of polysaccharides and cellulose synthesized from silicic acid. The cell wall envelopes the lipid or fatty acids and the removal of algal oil is known as that lipid extraction. The specific extraction of lipids is also performed by solvent extraction using methanol and chloroform.

Interest is on microwave, grinding, bead beating and ultrasound mechanical methods for extraction. This method does not require extra chemicals and the subsequent extraction step becomes easier. Mostly, bead baiting is done to disturb the cell walls of microbes in small scale level with beads made up of ceramics or glass.

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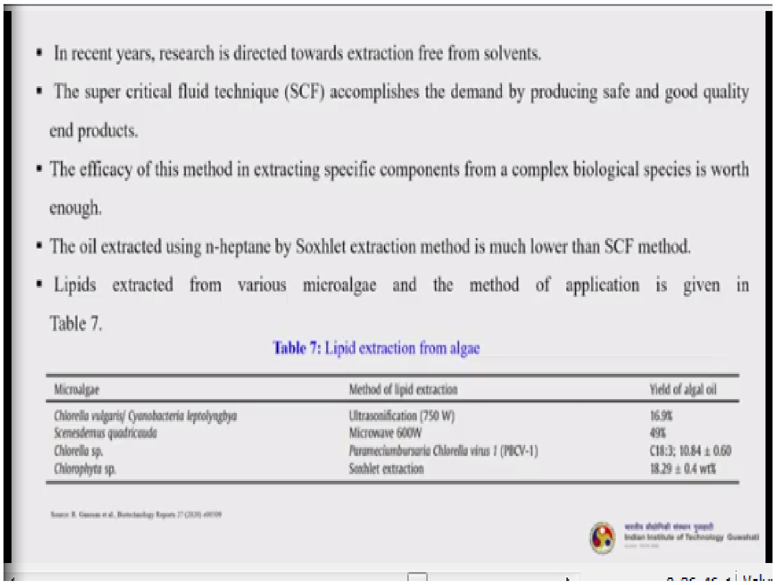

- In recent years, research is directed towards extraction free from solvents.
- The super critical fluid technique (SCF) accomplishes the demand by producing safe and good quality end products.
- The efficacy of this method in extracting specific components from a complex biological species is worth enough.
- The oil extracted using n-heptane by Soxhlet extraction method is much lower than SCF method.
- Lipids extracted from various microalgae and the method of application is given in Table 7.

Table 7: Lipid extraction from algae

Microalgae	Method of lipid extraction	Yield of algal oil
Chlorella vulgaris/ Cyanobacteria leptolyngbya	Ultrasonification (750 W)	16.9%
Scenedesmus quadricauda	Microwave 600W	49%
Chlorella sp.	*Parameciumbursaria Chlorella virus 1* (PBCV-1)	C18:3; 10.84 ± 0.60
Chlorophyta sp.	Soxhlet extraction	18.29 ± 0.4 wt%

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In recent years, research is directed towards extraction free from solvents. The supercritical fluid technique accomplishes the demand by producing safe and good quality end products. The efficacy of this method in extracting specific components from a complex biological species is worth enough. The oil extracted using n-heptane by Soxhlet extraction method is much lower than that of the supercritical fluid extraction.

But please understand that supercritical fluid extraction is a costly process because of the huge capital investment, it requires. So, lipid extracted from various microalgae and the method of application is given in this particular table. You can see the different types of microalgal species here, *Chlorella vulgaris*, *Cyanobacteria*, *Scenesdemus*, again *Chlorella* and *Chlorophyta*. Different types of extraction technologies: Ultrasonification, microwave, using a virus, then Soxhlet extraction. So you can see the type of algal oil it is given there, 16%, somewhere it is 49%, then almost 10 to 11%, and the last one it is 18%**.**

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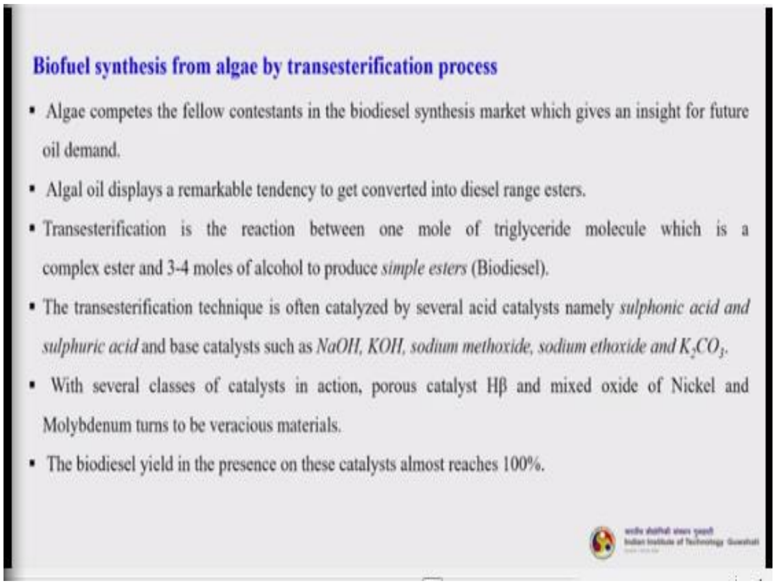

Biofuel synthesis from algae by transesterification process

- Algae competes the fellow contestants in the biodiesel synthesis market which gives an insight for future oil demand.
- Algal oil displays a remarkable tendency to get converted into diesel range esters.
- Transesterification is the reaction between one mole of triglyceride molecule which is a complex ester and 3-4 moles of alcohol to produce *simple esters* (Biodiesel).
- The transesterification technique is often catalyzed by several acid catalysts namely *sulphonic acid and sulphuric acid* and base catalysts such as *NaOH, KOH, sodium methoxide, sodium ethoxide and* K_2CO_3.
- With several classes of catalysts in action, porous catalyst Hβ and mixed oxide of Nickel and Molybdenum turns to be veracious materials.
- The biodiesel yield in the presence on these catalysts almost reaches 100%.

So, now we will discuss biofuel synthesis from algae by transesterification process. So, algae competes the fellow contestants in the biodiesel synthesis market which gives an insight for the future oil demand. Algal oil displays a remarkable tendency to get converted into diesel range esters. Transesterification is the reaction between one mole of triglyceride molecule which is a complex ester and 3 to 4 moles of alcohol to produce simple esters, that is called biodiesel.

The transesterification technique is often catalyzed by several acid catalysts, namely sulphonic acid and sulfuric acid and base catalysts such as sodium hydroxide, potassium hydroxide, sodium methoxide, sodium ethoxide and K_2CO_3. Now with several classes of catalyst in action, porous catalyst Hβ and mixed oxide of nickel and molybdenum turns to be veracious materials. The biodiesel yield in the presence of these catalysts almost reaches 100%.

So, that is excellent yield using this particular catalyst. Lot of research is still going on in developing low cost and high yielding catalyst, which will basically lower the final product cost of the biodiesel.

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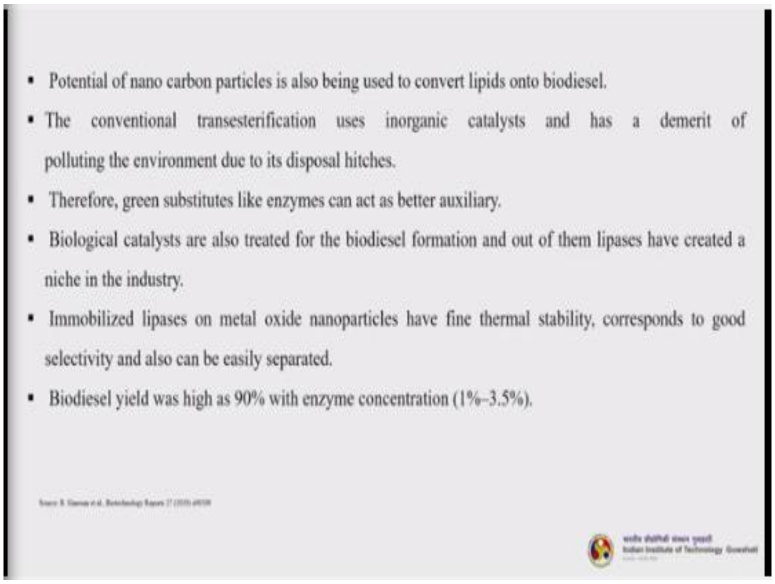

- Potential of nano carbon particles is also being used to convert lipids onto biodiesel.
- The conventional transesterification uses inorganic catalysts and has a demerit of polluting the environment due to its disposal hitches.
- Therefore, green substitutes like enzymes can act as better auxiliary.
- Biological catalysts are also treated for the biodiesel formation and out of them lipases have created a niche in the industry.
- Immobilized lipases on metal oxide nanoparticles have fine thermal stability, corresponds to good selectivity and also can be easily separated.
- Biodiesel yield was high as 90% with enzyme concentration (1%–3.5%).

Potential of nano carbon particles is also being used to convert lipids onto biodiesel. The conventional transesterification uses inorganic catalyst and has the demerit of polluting the environment due to it is disposal hitches. Therefore, green substitutes like enzymes can act as a better auxiliary. Biological catalysts, which are treated for the biodiesel formation and out of them lipases have created a niche in the industry.

Immobilized lipases on metal oxide nanoparticles have fine thermal stability, corresponds to good selectivity and also can be easily separated. Biodiesel yield was as high as 90% with enzyme concentration of only 1 to 3.5%.

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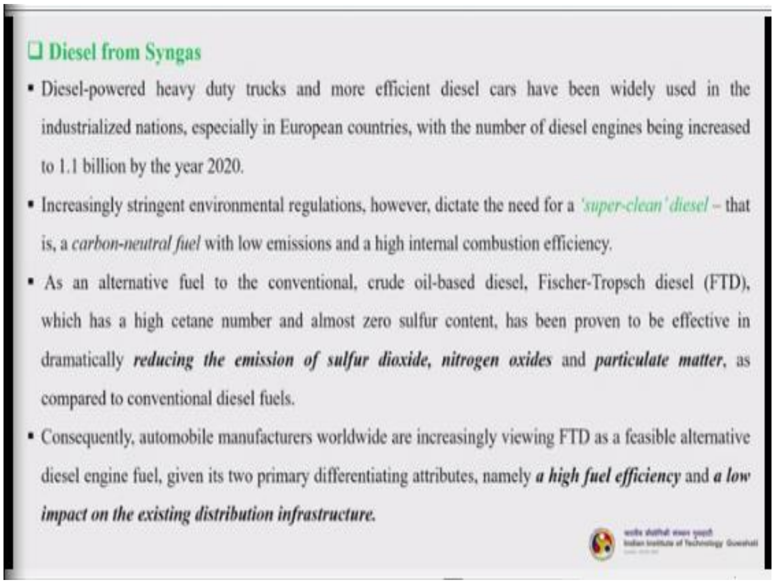

❑ Diesel from Syngas

- Diesel-powered heavy duty trucks and more efficient diesel cars have been widely used in the industrialized nations, especially in European countries, with the number of diesel engines being increased to 1.1 billion by the year 2020.
- Increasingly stringent environmental regulations, however, dictate the need for a *'super-clean' diesel* – that is, a *carbon-neutral fuel* with low emissions and a high internal combustion efficiency.
- As an alternative fuel to the conventional, crude oil-based diesel, Fischer-Tropsch diesel (FTD), which has a high cetane number and almost zero sulfur content, has been proven to be effective in dramatically ***reducing the emission of sulfur dioxide, nitrogen oxides*** and ***particulate matter***, as compared to conventional diesel fuels.
- Consequently, automobile manufacturers worldwide are increasingly viewing FTD as a feasible alternative diesel engine fuel, given its two primary differentiating attributes, namely ***a high fuel efficiency*** and ***a low impact on the existing distribution infrastructure.***

Now we will discuss about diesel from syngas. So, in today's class, as I told you in the beginning we are discussing diesel from three various sources. First is vegetable oil, that we have discussed and understood. Second is from the algae, we have understood in detail how algae can be grown, how it can be cultured, what are the parameters that affect? And the third and last one is the diesel from a syngas.

So, diesel powered heavy duty trucks and more efficient diesel cars have been widely used in industrialized nations, especially in the European countries with the number of diesel engines being increased to 1.1 billion by the year 2020. Increasingly stringent environmental regulations, however dictate the need for a super clean diesel that is a carbon neutral fuel with low emissions and a high internal combustion efficiency.

As an alternative fuel to the conventional crude oil based diesel, the FT diesel which is called the Fischer-Tropsch diesel, has a high cetane number and almost zero sulfur content, has been proven to be effective dramatically reducing the emission of sulfur dioxide, nitrous oxides, nitrogen oxides and particulate matter - all the Sox and NOx all these things - as compared to the conventional fossil fuel diesels.

Now consequently automobile manufacturers worldwide are increasingly viewing Fischer Tropsch diesel as a feasible alternative diesel engine fuel given its two primary differentiating attributes. The first: high fuel efficiency and the second: a low impact on the existing distribution infrastructure. That means you do not have to modify the engines for the biodiesel or the FTD**.**

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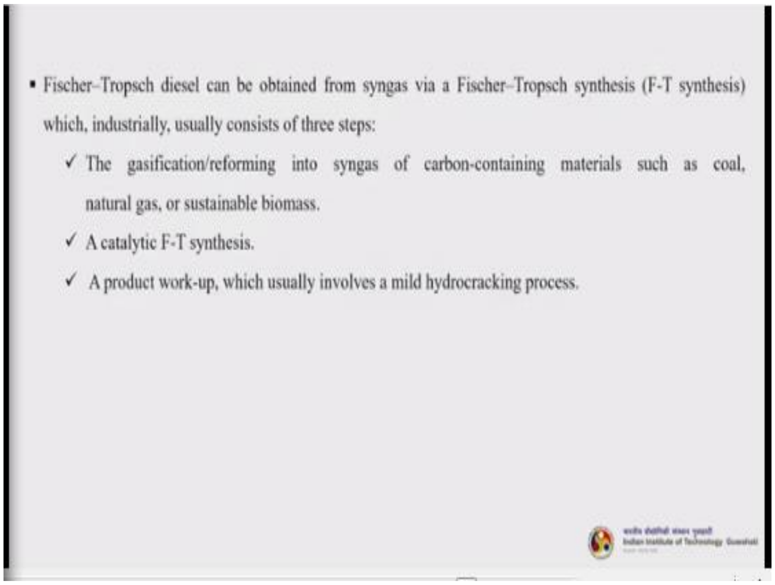

- Fischer–Tropsch diesel can be obtained from syngas via a Fischer–Tropsch synthesis (F-T synthesis) which, industrially, usually consists of three steps:
  - ✓ The gasification/reforming into syngas of carbon-containing materials such as coal, natural gas, or sustainable biomass.
  - ✓ A catalytic F-T synthesis.
  - ✓ A product work-up, which usually involves a mild hydrocracking process.

So, FT diesel can be obtained from syngas via the Fischer Tropsch synthesis process which industrially usually consist of 3 steps. The first is the gasification or reforming into syngas of the carbon containing materials such coal, natural gas or sustainable biomass. Second is the catalytic Fischer Tropsch synthesis. The third: a product work-up, usually involves a mild hydrocracking step.

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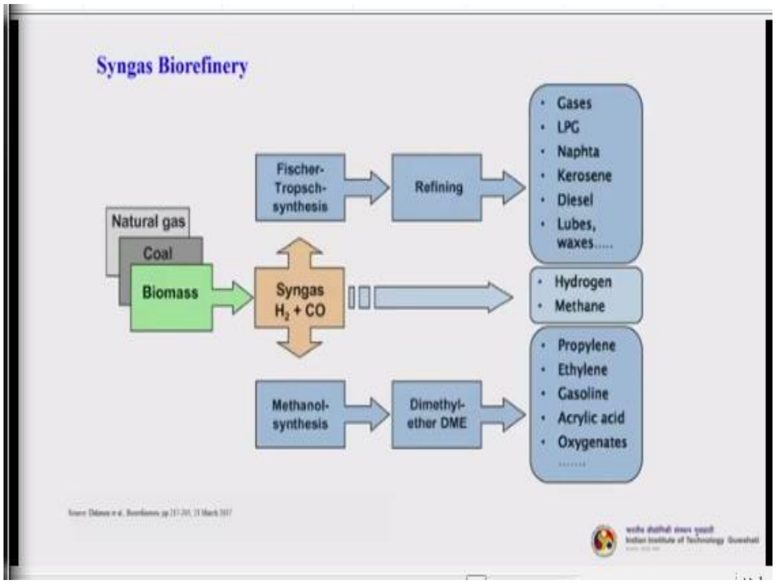

Syngas Biorefinery

Natural gas

Coal

Biomass

Syngas $H_2 + CO$

Fischer-Tropsch-synthesis

Refining

- Gases
- LPG
- Naphta
- Kerosene
- Diesel
- Lubes, waxes.....

- Hydrogen
- Methane

Methanol-synthesis

Dimethyl-ether DME

- Propylene
- Ethylene
- Gasoline
- Acrylic acid
- Oxygenates

....

So, this is a classical syngas biorefinery schematic presentation, let us understand. So, it can be natural gas, coal, biomass, mostly since we are talking about biodiesel, so it is biomass. However, coal and natural gas also can be co-feeded**.** Then we produce hydrogen and carbon monoxide - the syngas. So, when you talk about the Fischer Tropsch synthesis if you go for the FT synthesis then further refining will give us gases, LPG, naptha, kerosene, diesel all the cuts**.**

Then finally lubes and waxes. And, as it is also we can use hydrogen and methane**.** Then if you go for the methanol synthesis route - we get DME or the dimethyl ether; so it can further be converted to propylene, ethylene, gasoline, acrylic acid and further some oxygenating compounds.

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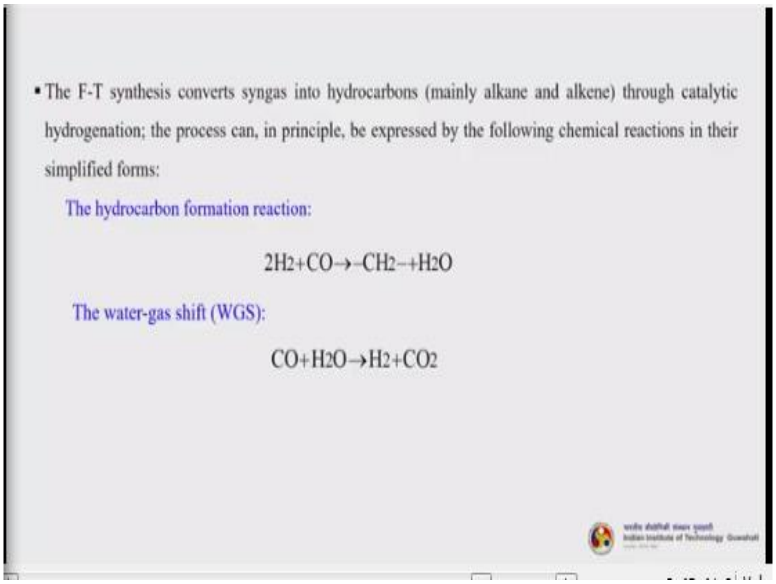

- The F-T synthesis converts syngas into hydrocarbons (mainly alkane and alkene) through catalytic hydrogenation; the process can, in principle, be expressed by the following chemical reactions in their simplified forms:

The hydrocarbon formation reaction:

$$2H_2+CO \rightarrow -CH_2-+H_2O$$

The water-gas shift (WGS):

$$CO+H_2O \rightarrow H_2+CO_2$$

So, the FT synthesis converts syngas into hydrocarbons mainly alkane and alkene through catalytic hydrogenation; the process can in principle be expressed by the following chemical reactions in their simplified forms:

The hydrocarbon formation reaction:

$$2H_2 + CO \rightarrow CH_2 + H_2O$$

The water-gas shift (WGS):

$$CO + H_2O \rightarrow H_2 + CO_2$$

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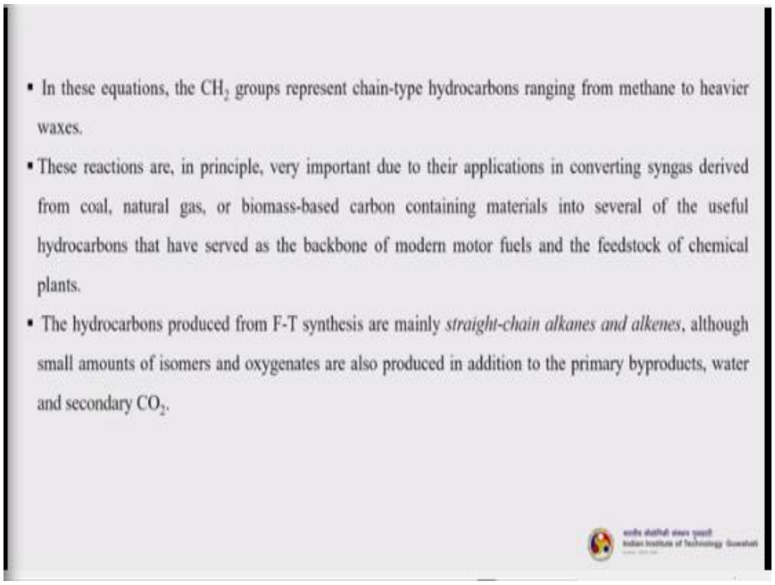

- In these equations, the CH_2 groups represent chain-type hydrocarbons ranging from methane to heavier waxes.
- These reactions are, in principle, very important due to their applications in converting syngas derived from coal, natural gas, or biomass-based carbon containing materials into several of the useful hydrocarbons that have served as the backbone of modern motor fuels and the feedstock of chemical plants.
- The hydrocarbons produced from F-T synthesis are mainly *straight-chain alkanes and alkenes*, although small amounts of isomers and oxygenates are also produced in addition to the primary byproducts, water and secondary CO_2.

Now, in these equations the CH_2 group represent the chain type hydrocarbons ranging from methane to heavier waxes. These reactions are in principle, very important due to their applications in converting syngas derived from coal, natural gas or biomass based carbon containing materials into several of the useful hydrocarbons that has served as the backbone of modern motor fuels and the feedstock of chemical plants.

The hydrocarbons produced from the FT synthesis are mainly straight chain alkanes and alkenes, although small amounts of isomers and oxygenates are also produced in addition to the primary byproducts, water and secondary carbon dioxide.

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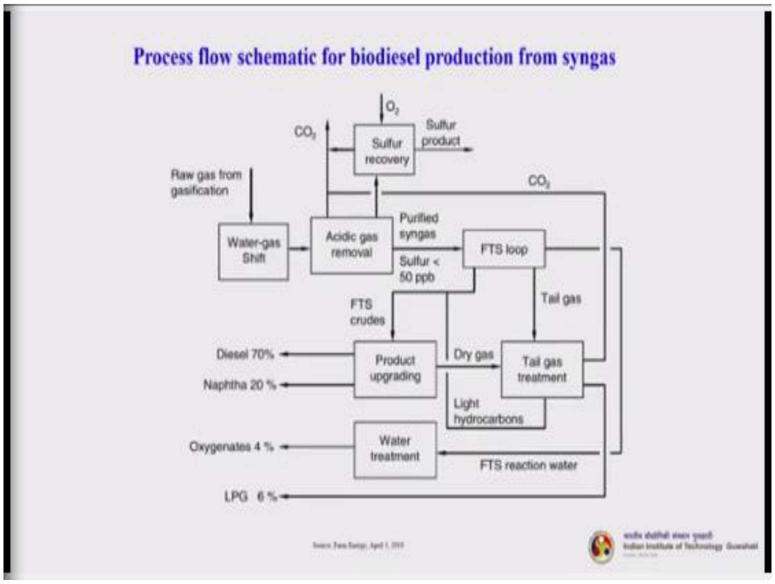

Process flow schematic for biodiesel production from syngas

So, this is an interesting process flow schematic for the biodiesel production from the syngas**.** So, the raw gas from the gasification unit that is coming - it goes to the water gas shift reaction**.** Then it goes to the acidic gas removal where carbon dioxide has been removed and you can have the sulfur recovery coupled with that carbon dioxide removal process**.** And part of the carbon dioxide also can be recycled back to other processes like this tail gas treatment**.**

Then this purified syngas which is having a sulfur content of almost less than 50 PPB goes to the Fischer Tropsch synthesis loop**.** So, where the FTS is being after the process is over, we will get the FTS crude. So, which will further be processed or maybe we can say that upgraded to give us diesel almost 70% and naphtha 20%**.** Then the dry gas part of that FT gas can be sent back to the tail gas treatment unit and again the lighter hydrocarbons can be recycled back.

And whatever is coming out from the tail gas treatment unit is nothing but the LPG - 6% around**.** And from the water treatment plant also which is coming from the FTS loop the water based actually. So, it will get oxygenating compounds almost 4%. So, this is the usual process schematic for the biodiesel production from the syngas**.**

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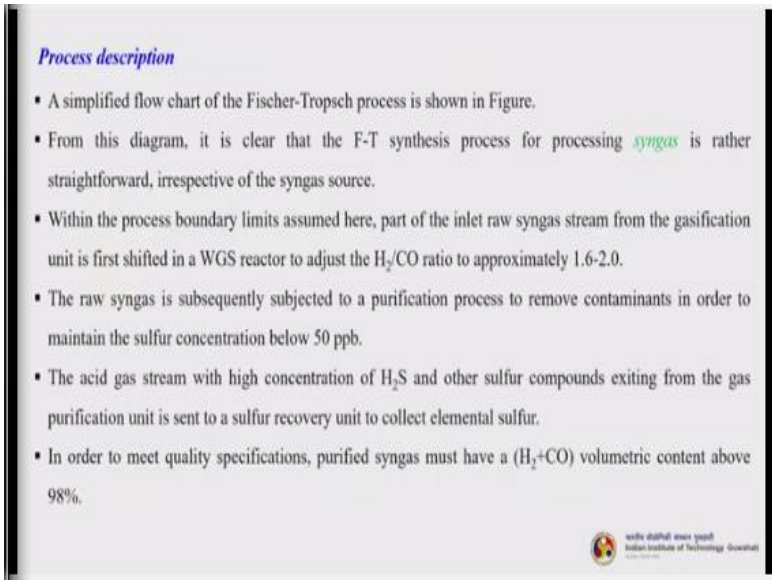

Process description

- A simplified flow chart of the Fischer-Tropsch process is shown in Figure.
- From this diagram, it is clear that the F-T synthesis process for processing *syngas* is rather straightforward, irrespective of the syngas source.
- Within the process boundary limits assumed here, part of the inlet raw syngas stream from the gasification unit is first shifted in a WGS reactor to adjust the H_2/CO ratio to approximately 1.6-2.0.
- The raw syngas is subsequently subjected to a purification process to remove contaminants in order to maintain the sulfur concentration below 50 ppb.
- The acid gas stream with high concentration of H_2S and other sulfur compounds exiting from the gas purification unit is sent to a sulfur recovery unit to collect elemental sulfur.
- In order to meet quality specifications, purified syngas must have a (H_2+CO) volumetric content above 98%.

So, we will try to understand the process in a better way. Let us go through it. So, a simplified flowchart of the Fischer Tropsch process that is what we have already seen it. From this diagram, it is clear that the FT synthesis process for processing syngas is rather very straightforward irrespective of the syngas source. Within the process boundary limits assumed here, part of the inlet raw syngas stream from the gasification unit is first shifted in a water gas shift reactor to adjust the hydrogen carbon monoxide ratio to approximately 1.6 to 2.

It is very important to do that otherwise your reaction will not proceed in the proper direction. The raw syngas is subsequently subjected to a purification process to remove contaminants in order to maintain sulfur concentration below 50 ppb - parts per billion. So, the acid gas stream with high concentrations of hydrogen sulfide and other sulfur compounds exiting from the gas purification unit is sent to a sulfur recovery unit to collect the elemental sulfur.

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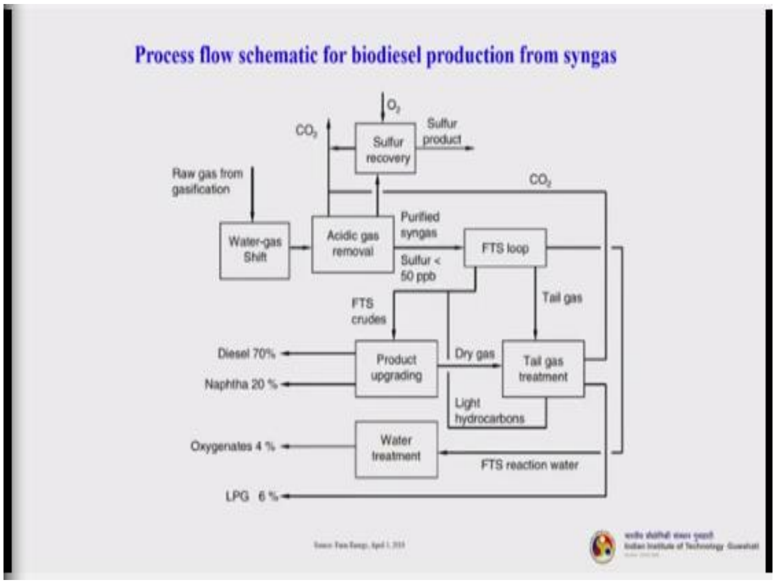

Process flow schematic for biodiesel production from syngas

So, this is the sulfur recovery unit, just I was mentioning about that, it is also very important part. Because you anyway you are recovering the sulfur out of that even if it is a small amount of sulfur that is present in the entire process streams, you can understand that the amount of feedstock the plant is processing per day. So, it is a quite significant amount of sulfur that is needs to be recovered. So, in order to meet the quality specification, purified syngas must have a hydrogen + carbon dioxide volumetric content above 98%.

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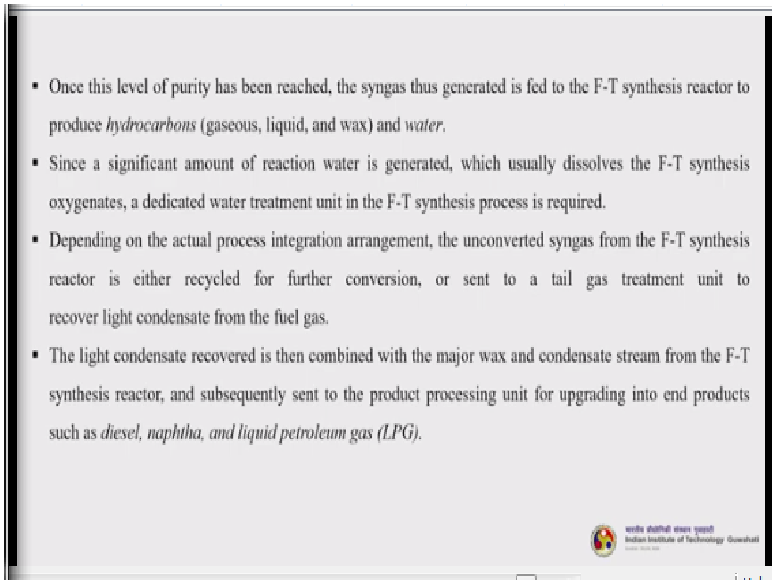

- Once this level of purity has been reached, the syngas thus generated is fed to the F-T synthesis reactor to produce *hydrocarbons* (gaseous, liquid, and wax) and *water*.
- Since a significant amount of reaction water is generated, which usually dissolves the F-T synthesis oxygenates, a dedicated water treatment unit in the F-T synthesis process is required.
- Depending on the actual process integration arrangement, the unconverted syngas from the F-T synthesis reactor is either recycled for further conversion, or sent to a tail gas treatment unit to recover light condensate from the fuel gas.
- The light condensate recovered is then combined with the major wax and condensate stream from the F-T synthesis reactor, and subsequently sent to the product processing unit for upgrading into end products such as *diesel, naphtha, and liquid petroleum gas (LPG)*.

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So, once this level of purity has been reached, the syngas thus generated is fed to the FT synthesis reactor to produce the hydrocarbons, so gaseous, liquid, wax and of course water. Since a significant amount of reaction water is generated which usually dissolves the FT synthesis oxygenates, a dedicated water treatment unit in the FT synthesis process is therefore required. So, this is the water treatment unit which we are right now talking about which is directly coming from the FTS loop the Fischer Tropsch synthesis loop.

The light condensate recovered is then combined with the major wax and condensate stream from the FT synthesis reactor and subsequently sent to the product processing unit for upgrading into end products such as diesel, naphtha and liquid petroleum gas.

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(Overview of next lecture)

Module	Module name	Lecture	Title of lecture
07	Biodiesel	02	Transesterification; FT process, catalysts

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

So, students, with this I windup today’s lecture. So, in the next lecture we will discuss about transesterification, the FT process and catalysts. So, basically we will understand the transesterification reactions including the esterification reaction in detail. And we will also understand what is the importance of catalyst and what are the various types catalyst that are being used for transesterification and FT processes including the homogeneous and heterogeneous catalyst all.

So, thank you, and in case you have any query please register your query in the swayam portal or you can drop me a mail directly at kmohanty@iitg.ac.in.