

Energy Conversion Technologies (Biomass and Coal)

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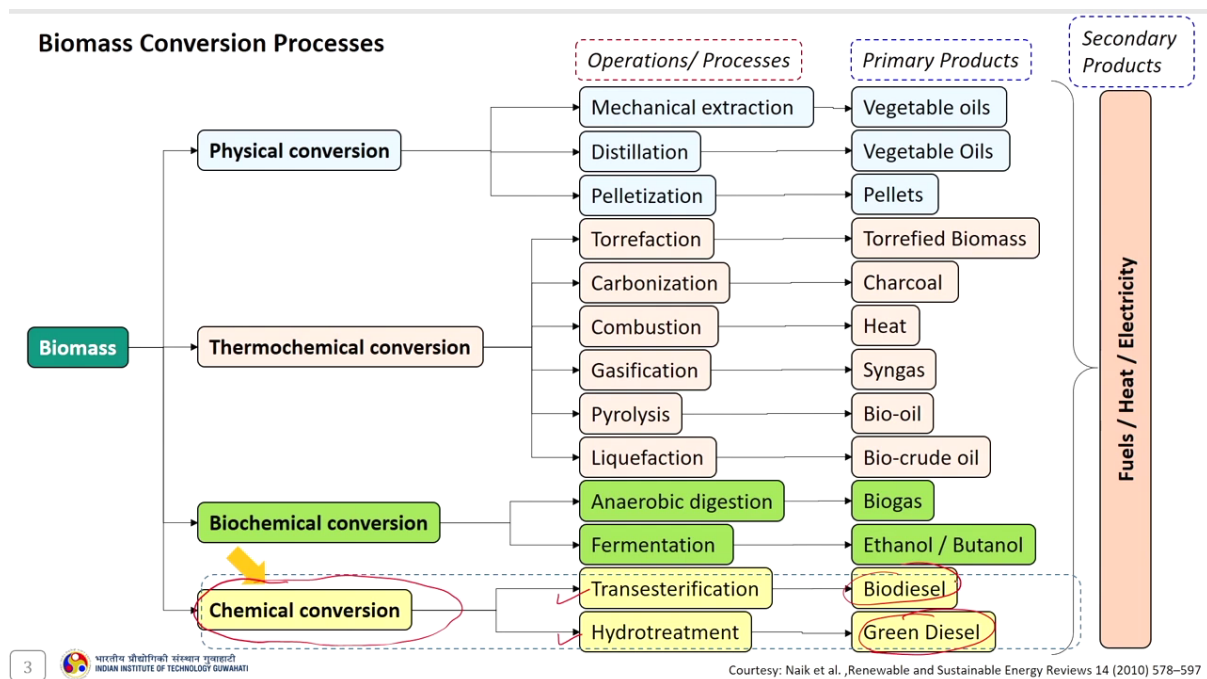
Lecture 24

Chemical Conversion Processes - Types of Feedstock and Pretreatment

Good morning everyone.

Welcome to this first lecture of the module 6. In this lecture, we will discuss different chemical conversion processes that is types of feedstock which are used for the chemical conversion processes, biodiesel production and the extraction processes.

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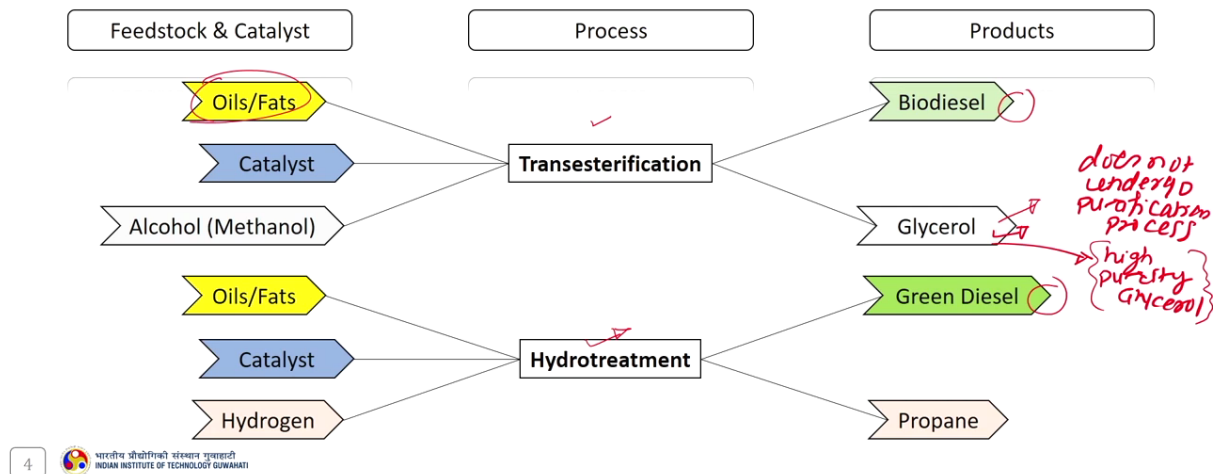


Among these different biomass conversion processes so far we covered thermochemical conversion and the biochemical conversion processes. However, in this module the main focus is on the chemical conversion process that is if you can see here in this chart. So, in this module, we will discuss about the different chemical conversion processes that are transesterification and hydro treatment to produce biodiesel and green diesel as a biofuel.

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Chemical Conversion Processes

- The chemical conversion of biomass refers to the use of chemical agent to convert biomass into biofuels.
- The most common chemical conversion process are : transesterification and hydrotreatment.



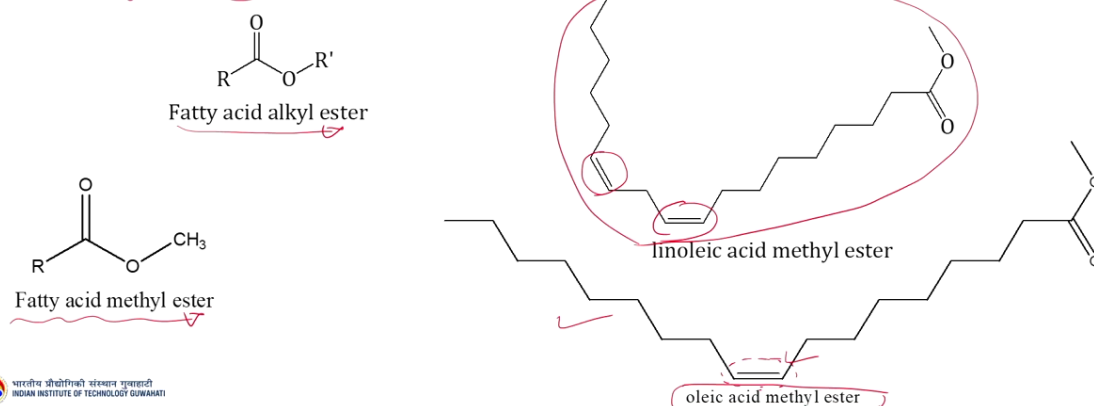
Chemical conversion processes. So, the chemical conversion of the biomass refers to the use of chemical agent to convert biomass into the biofuel. And if you look at this schematic here, so from this schematic it appears that different conversion routes are available for the production of the biodiesel and green diesel from the various feedstock material such as oils and fats. However, the crude glycerol produced during the biodiesel synthesis process has limited uses if it does not undergo the purification process.

The effective use of this crude glycerol obtained during the biodiesel production process is important to improve the economic sustainability of the biodiesel industry while reducing the environmental impact which is caused by this generated waste. Glycerol with high purity has a wide application in various industries such as pharmaceutical, cosmetic and food industry. Similarly, the hydro treatment is another chemical conversion process which is available for the conversion of oils and fats. The product obtained during this process is termed as green diesel.

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Biodiesel

- **Biodiesel**, also known as fatty acid methyl esters or **FAME**, is a renewable fuel produced from animal fats or vegetable oils (edible and nonedible) through the esterification and transesterification process.
- Biodiesel is made by alcoholizing the vegetable oils with a simple alcohol such as methanol, ethanol, propanol, butanol, or amyl alcohol in the presence of a catalyst.



So, let us first discuss about the biodiesel. Biodiesel is also known as a fatty acid methyl ester and commonly referred as FEM is a renewable fuel produced from the animal fats or vegetable oils which are mostly edible or non-edible oils through the process of esterification and transesterification. And this biodiesel is made by alkalizing the vegetable oils with simple alcohol such as methanol, ethanol, propanol, butanol or amyl alcohol in the presence of catalyst.

And this structure here it represent the fatty acid alkyl ester structure and in case if the methanol is used as a alkalizing agent then it produces fatty acid methyl ester as a product. And this represents the structure of linoleic acid methyl ester containing two double bonds and this structure it represent the oleic acid methyl ester with single double bond. And it is also termed as the unsaturation contained in the given sample.

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Biodiesel Production Process

A typical process for biodiesel (FAME) production from oily feedstock includes following steps:

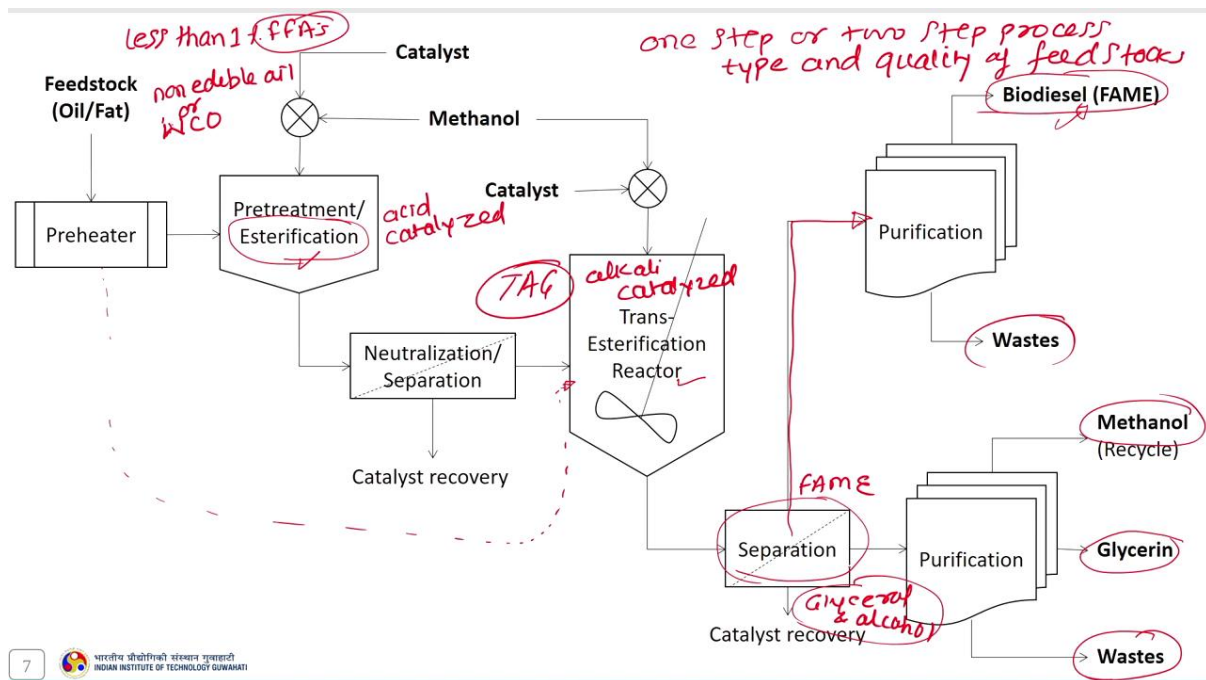
- ✓ (1) Esterification reaction of free fatty acids (FFAs) with acid catalyst,
- (2) Separation /neutralization of acid catalyst from the reaction mixture,
- (3) Transesterification of triacylglycerols (TAGs), FAME
- (4) Separation of the FAME (crude biodiesel) from the methanol/glycerol phase, and
- (5) Purification of crude biodiesel.

Also, the overall process includes the crude glycerol processing through acidification and separation of glycerol from alcohol.

This biodiesel production process includes several steps in which the esterification reaction of the free fatty acid with acid catalyst is the first step followed by the separation and the neutralization of the acid catalyst from the reaction mixture. And the resultant mixture is transesterified to produce FAME followed by the separation of FAME from methanol and glycerol phase and at the end purification of this crude biodiesel.

Also the overall process of biodiesel production includes the crude glycerol processing through acidification and the separation of glycerol from alcohol.

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This schematic here it represent the process arrangement of biodiesel synthesis from various oily feedstock materials and also includes the process selection for the biodiesel synthesis. So, this biodiesel production can be carried out as a one step or two step processes depending on the type and quality of feedstock.

When the oily feedstock such as refined vegetable oil contains less than 1 percent free fatty acids and no impurities then a alkali catalyzed transesterification process is applied. So, in that case directly alkali catalyzed transesterification process can be applied for the biodiesel synthesis. However when the oily feedstock such as non-edible oil or waste cooking oils containing high FFA, water and impurities are available as a feedstock material then a special attention in the process design and selection of the catalyst is required. In that case two step process is applied which include acid catalyzed pre-esterification followed by alkali catalyzed transesterification process to convert FFA and triacylglycerol into esters. Since both these reactions are reversible in nature that is esterification and the transesterification is applied.

Hence an excess alcohol is usually employed to force the reaction towards the methyl ester formation. The resultant product is allowed to separate into FAME and glycerol alcohol phase and the produce FAME is further purified to obtain a biodiesel. Similarly, the glycerol alcohol phase is purified to obtain glycerin and relatively a pure methanol.

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Types of Feedstock

Oils and fats extracted from various bio-based sources are directly or indirectly used as feedstock for biodiesel production.

Categories of suitable raw materials are as follows:

1. Edible vegetable oils : (1G feedstock)

Such as oils from rapeseed, palm, sunflower, soybean, etc.

2. Non-edible plant oils : (2G feedstock)

Oils from the seeds of castor, jatropha, jojoba, rubber, tobacco, pongamia, okra, wild safflower, sugar apple, etc.

3. Used/waste oils and animal fats :

Waste cooking oil (WCOs), waste animal fats (WAFs), grease, etc.

4. Oleaginous-microorganisms : (3G feedstock)

Microalgae (e.g. *Spirulina sp.*, *Chlorella sp.*); fungi (e.g. *Cryptococcus sp.*); bacteria (e.g. *E. coli*), etc.

After learning about the biodiesel synthesis process, let us discuss about the types of feedstock which are being used for the biodiesel production. Oils and fats extracted from various bio-based sources are directly or indirectly used as a feedstock material for the biodiesel synthesis.

And these raw materials are categorized as follows. That is edible vegetable oils also termed as first generation feedstock and it includes oils from rapeseed, palm, sunflower, and soybean oil. Non-edible plant oils termed as second generation feedstock include oil from non-edible seed that is castor, jatropha, jojoba, rubber seeds and etc. Similarly, the used and waste oil as well as the animal fat it includes the waste cooking oil, waste animal fats, grease etc. Similarly, the oleogeneous microorganism containing significant amount of the lipids are also considered as a raw material for the biodiesel production and are termed as third generation feedstock material which includes microalgae, fungi, bacteria.

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Properties of few selected non-edible seed oil samples

Oil Properties \ Species	Karanja	Jatropha	Cotton	Rubber	Polanga
Fatty acid composition (%)					
Palmitic acid C16:0	11.65	16.00	11.67	10.20	12.01
Steric acid C18:0	7.50	6.50	0.89	8.70	12.95
Oleic acid C18:1 <i>C=C</i>	51.59	43.50	13.27	24.60	34.09
Linoleic acid C18:2 <i>2 double bonds</i>	16.46	34.40	57.51	39.60	38.26
Linolenic acid C18:3	2.65	0.80	-	16.30	0.30
Physico-chemical properties					
Specific gravity (-)	0.913	0.920	0.912	0.910	0.896
Viscosity @ 40 °C (cSt)	28	18	50	66	72
Flash point (°C)	205	174	210	198	221
Calorific value (MJ/kg)	34.0	38.5	39.6	37.5	39.2
Acid value (mg KOH/g)	5.0	3.8	0.1	34.0	44.0

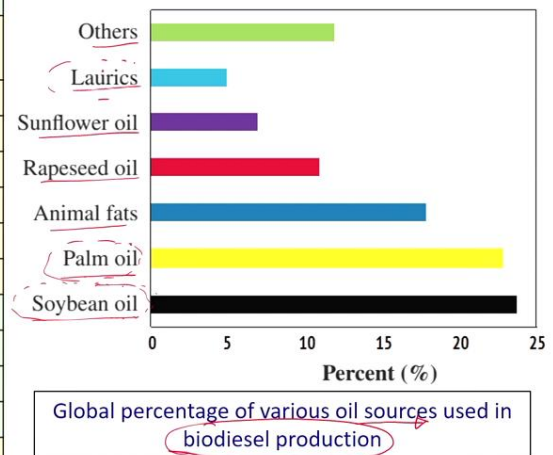
As discussed before these oily feedstocks are derived from various different bio-based sources and also various different technologies are used to produce these oily feedstock material. As a result there is a significant variation in their properties. For example the comparison of the fatty acid composition it indicates that some seed oil contains significant amount of the monounsaturated fatty acids in its composition. Monounsaturated fatty acid means the fatty acids those that have only one unsaturation in their structure and that is a single double bond in its structure, while other oils shows significant amount of the polyunsaturated fatty acid content in its composition. Although this oil also has quite significant number of monounsaturated fatty acid content but the polyunsaturated fatty acid content is significantly high compared to that of the monounsaturated fatty acid content.

And the polyunsaturated fatty acids are the acids that contain more than two double bonds in its structure. And if you look at this particular number here, it indicates two double bonds in its structure. Whereas this number here it indicates the single double bond in its structure and the linolenic acid contains three double bonds in its structure. However, the percentage of linolenic acid is relatively less in the given feedstock. Similarly the comparison of the physicochemical properties of this oil indicates that some oil has higher viscosity and higher acid value compared to other oils.

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Globally used biodiesel feedstock

Country	Major Raw Materials (or Feedstock)
India	Waste oil, Animal fat, Jatropha oil, Karanja oil, Mahua oil
China	Jatropha oil, Waste oil
Thailand	Palm oil, Jatropha oil, Coconut oil
Malaysia	Palm oil
Russia	Rapeseed oil, Soybean oil, Sunflower oil
Japan	Waste oil
Korea	Waste oil
Mexico	Animal fat, Waste oil
Canada	Canola oil, Animal fat
USA	Soybean oil, Waste oil
Brazil	Soybean oil, Palm oil, Caster oil, Cotton oil
European countries	Rapeseed oil, Sunflower oil, Waste oil, Animal fat
Australia	Waste oil, Animal fat



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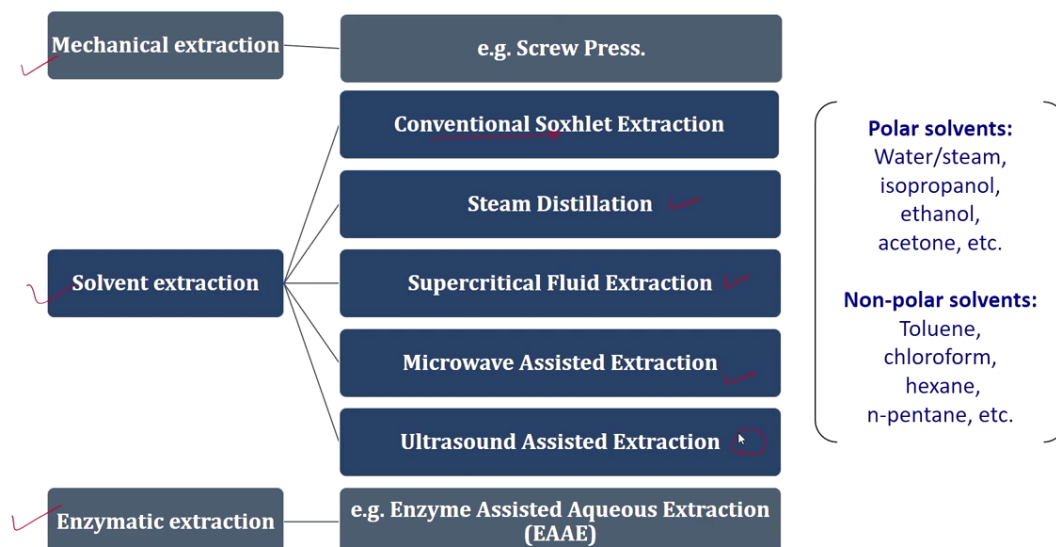
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Courtesy: Ingole, Nano and Biocatalysts for Biodiesel Production, Wiley 2021

And this chart here it indicates the global percentage of the various oil sources used in the biodiesel production which includes soybean oil, palm oil, animal fats, rapeseed oil, sunflower oil, lorax and others. However, the percentage of soybean oil used in the biodiesel production is relatively high followed by the palm oil and the lowest is lorax. Similarly this table here it gives details about the country specific feedstock for the biodiesel production.

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Extraction of Oils and Fats



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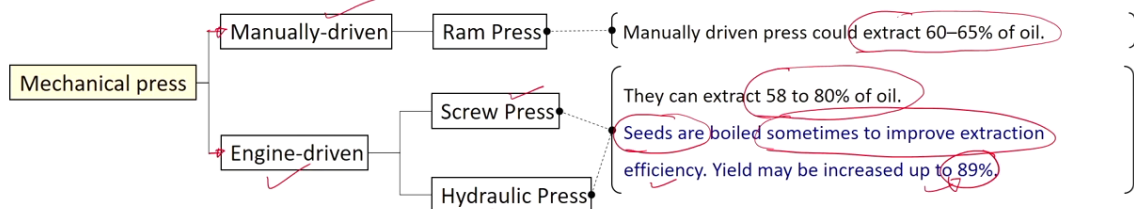
After learning about the globally used feedstock material for the biodiesel production, let us discuss about the different technologies which are used to produce this oily feedstock materials. Different technologies which are used for the extraction of the oil include the mechanical extraction, solvent extraction and enzymatic extraction.

However, the solvent extraction techniques are sub classified as conventional Soxhlet extraction technique, steam distillation, supercritical fluid extraction, microwave assisted extraction and ultrasound assisted extraction which includes polar solvent and non-polar solvent as a medium for the extraction of oily material from the biomass matrix.

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① Mechanical extraction

- The most commonly used method for oil extraction is mechanical pressing.
- *In mechanical press, cell wall fractures and oil squeezed out, by applying mechanical force on the seeds.*
- Presses can be driven manually (ram press) or by an engine. Engine-driven screw press is more efficient.
- Extraction could be performed as batch or continuous process.
- In general, batch process is more efficient since the larger amount of oil can be extracted.



Disadvantages: Mechanical pressing alone does not remove all the oil from the seed. Chemical extraction method is used to remove the remaining oil that mechanical press cannot.

And the most commonly used method for the oil extraction is mechanical pressing. In mechanical pressing, cell wall fractures and oil squeeze out by applying mechanical force on the seed samples. Now, if you look at this particular chart here, these mechanical press methods are of two types that is manually driven and engine driven. However, the engine driven screw press method is more efficient in terms of oil extraction.

And the extraction it could be performed as batch or the continuous process. However, the batch process is more preferred option because it gives more efficiency since the large amount of the oil can be extracted using a batch mechanical process. And this schematic here,

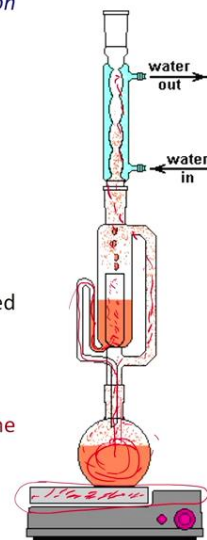
it represent the classification of the mechanical method that is manually driven and engine driven. In case of the manually driven method, it could extract around 60 to 65% of the oil whereas the engine driven method is sub classified into screw press and hydraulic press method. And this method extract around 58 to 80% of the oil and in some cases, the seeds are boiled to improve the extraction efficiency.

And in that case, the yield may increase up to 89%. And this is the advantage of the engine driven method where a small pre-treatment with the seed results into increase oil yield and it may go up to even 89%. However, this method has certain limitation because the mechanical pressing alone, it does not remove all the oil from the seed. And the chemical extraction method is used to remove the remaining oil that the mechanical press could not. And this is the major limitation of the mechanical pressing method.

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② Conventional Soxhlet Extraction

- It is a basic technique for the extraction of fat and oils from seed matrix, primarily based on the selection of solvent, and involves the use of heat (invented in 1879).
- Solvents used for oil/fat extraction:
 - Polar solvents: Isopropanol, ethanol, acetone, etc.
 - Non-polar solvents: Toluene, chloroform, hexane, n-pentane, etc.
- Soxhlet extraction, which has been the oldest method of extraction, is the most referred technique for evaluating the performance of other solid-liquid extraction methods.
- **Disadvantage:** Extraction time and the requirement of a large amount of solvent are the major limitations of Soxhlet extraction technique.



Next is conventional software extraction method. Now if you look at this particular diagram here, it shows the principle of software extraction from a given biomass material. So it is a basic technique for extraction of fats and oil from the seed matrix and it is primarily based on the selection of solvent and also involves the heat. Solvent used for the oil and fat extraction includes the polar solvent that is isopropanol, ethanol, acetone or non-polar solvent like toluene, hexane, chloroform and n-pentane. So in this case, the biomass material is placed in

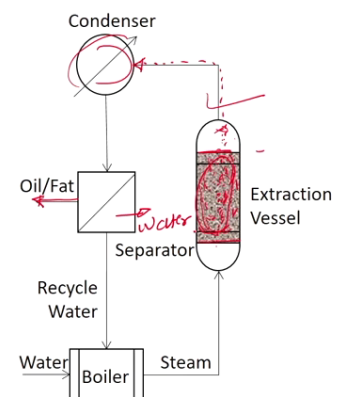
the thimble here and the appropriate solvent that is either polar or non-polar solvents is used for the extraction purpose.

With the suitable heat source, the solvent is vaporized and it is condensed and dropped over this biomass material. And solvent along with the extracted component is siphoned through this particular capillary inside this vessel. This solvent extraction has been the oldest method for the extraction of oils and fats and it is the most referred technique for evaluating the performance of the other solid liquid extraction method as well. However, this particular technique also has certain limitations. Because as you can see here the operation, it takes relatively longer time and also required significant amount of the solvent for the extraction of oils and fats and that is the major limitation of the solid extraction technique.

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③ Steam Distillation

- Oil extraction through steam distillation works by passing steam through the oil-bearing biomass, where the steam acts as a solvent that dissolves/ breaks the pores to release and carry away oil from the biomass matrix.
- After extraction, the steam is condensed to separate crude oil & water.
- Steam distillation is effective extraction method for plant oil that cannot withstand high temperature due to its volatility or oxidation stability. Oil extracted by steam distillation shows low thermal degradation property.
- **Disadvantages:** The long period between the starting of the process and production of oil, as time and energy is wasted through the wetting process. Also it has high capital and operation cost. Thus, steam distillation extractions are carried out for high value oil only.



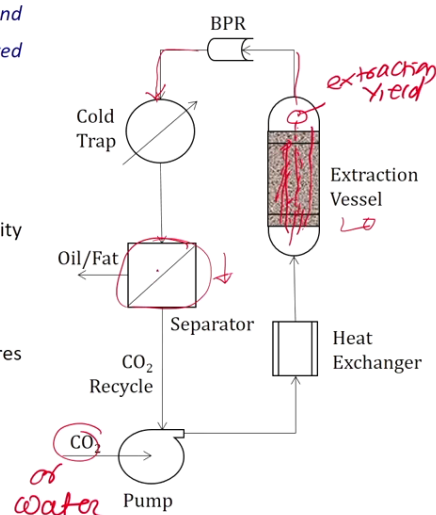
Next is the steam distillation method. So in this method, the oil extraction through steam distillation works by passing the steam through the oil bearing biomass which is packed in this extraction vessel here where the steam act as a solvent that dissolves and breaks the pores to release and carry away oil from the biomass matrix. After extraction, the steam is condensed to separate the oil or fat from water. And this is a very effective method for the plant oil that cannot withstand high temperature due to its volatility or oxidation stability. Oil extracted by this steam distillation shows low thermal degradation properties.

The limitation of this steam distillation method is the long period between starting of the process and the production of oil, as the time and energy is wasted through the wetting process. Because in this process the time and energy it goes waste through wetting this process here in this particular extraction vessel. Also it has high capital and the operation cost, thus steam distillation extractions are carried out only for high value oils. Because significant amount of the time and energy goes waste while wetting this sample here in the extraction vessel. And thereafter the real extraction of the oil takes place along with the flow of the steam through the extraction vessel.

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④ Supercritical Fluid Extraction (SFE)

- In SFE, a solvent (such as water, CO₂, etc.) at/above its critical temperature and pressure allowed to pass through biomass matrix to extract desired compounds.
- Under supercritical conditions the solvent shows unique properties:
 - **Density** ranging between that of gases and liquids, allowing high diffusivity and solubility.
 - **Solvent power** allows to dissolve both polar and nonpolar molecules.
 - **Low surface tension & viscosity** allows penetration through small pores thereby enhancing extraction of molecules.
 - **Selectivity** can be achieved by changing T & P, or using co-solvents.
 - **Ease of separation** of solvent from product by simply reducing T & P.



Another important method for the extraction of the oil is supercritical fluid extraction. In supercritical fluid extraction process a solvent such as CO₂ or water at above its critical temperature and pressure allowed to pass through this biomass matrix to extract the desired compounds. Under supercritical condition this solvent shows unique properties in the sense the density of the solvent under the supercritical condition varies between that of the gas and liquids and allowing high diffusivity and the solubility through this biomass matrix. Similarly the solvent power it allows to dissolve the both polar and non-polar molecules in the supercritical solvent. Low surface tension and the viscosity it allows the penetration of solvent through the small pores of the biomass and thereby enhances the extraction yield.

Selectivity this can be achieved by tuning the temperature and pressure or using the co-solvent. The ease of separation of solvent from the product by simply reducing the temperature and pressure that means the solvent and the product mixture can be easily separated by reducing its temperature and pressure to ambient condition. As we know the CO_2 is at gaseous state at ambient condition and hence it will release out from the product matrix and will get relatively a pure product in a separator.

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- CO_2 is most commonly employed solvent in SFE, because:
 - It has low critical temperature and pressure condition.
 - It is also inexpensive, incombustible, and non-toxic.
 - It can be easily removed from the extracted oil.
 - It is adaptable with co-solvent such as methanol and ethanol to extract oil from different biomass.
- **Advantages:**
 - SFE has been found to give a higher yield compared to other extraction techniques.
 - The oil extracted has a lower viscosity than other techniques.
 - SFE offers higher selectivity in extraction and flexibility of operating parameters.
 - e.g. Unsaturated fatty acids can be selectively extracted through the addition of alcohol as co-solvent.
 - SFE is diffusion-based process, therefore, significantly faster compared to other extraction methods.
- **Disadvantages:** Incompatibility of solvents with some biomass components; High-pressure operations; Higher capital and operational cost.

As we discussed CO_2 is the most commonly employed solvent in the supercritical fluid extraction technique, because it has relatively a low critical temperature and pressure condition. It is also inexpensive, incombustible and non-toxic in nature.

It can be easily removed from the extracted oil as I mentioned just before, that once the temperature and pressure is reduced and brought to a ambient condition then the CO_2 can be easily removed from the extracted oil as the CO_2 is at its gaseous state at ambient condition. It is adaptable with the co-solvent also such as methanol, ethanol to extract the oil from different biomass samples. Advantage of this technique is it has been found to give a higher yield compared to that of the other extraction techniques. And the oil extracted has lower

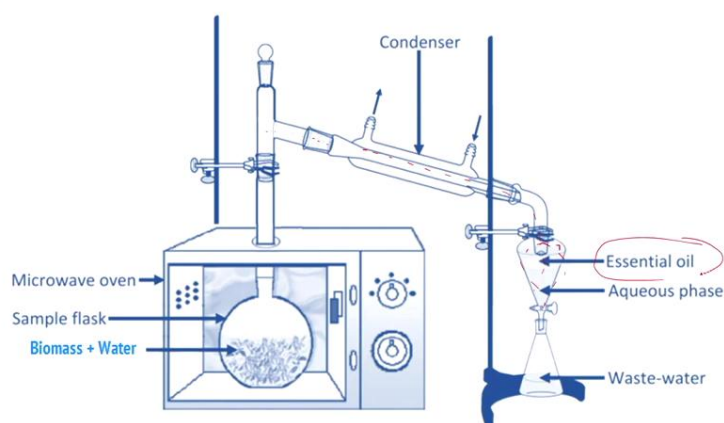
viscosity than extracted using the other techniques. Similarly, this particular process offers higher selectivity in the extraction and flexibility of the operating parameters.

So as we discussed before, the operating temperature and pressure can be tuned to improve the selectivity of the process. For example, the unsaturated fatty acids can be selectively extracted through the addition of alcohol as a co-solvent in the range of 1 to 5%. Similarly, this is a diffusion based process therefore significantly faster compared to the other extraction methods. However, this particular process also has certain limitation that is incompatibility of solvent with some biomass components, high pressure operations, and higher capital and operational cost. These are basically the major limitation of SFE process.

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⑤ Microwave Assisted Solvent Extraction (MASE)

- Electrical energy is directly converted into thermal energy during microwave heating which is directed to the polar solvent to extract the oil from the biomass.



Another important technique which is used for the extraction of oil includes the microwave assisted solvent extraction. So, in this process electrical energy is directly converted into the thermal energy during the microwave heating and which is directed to the polar solvent to extract the oil from the biomass matrix. The solvent along with the extracted components are condensed and allowed to separate here to form aqueous phase and oily phase.

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- The differences between microwave heating and conventional heating are related to:
 - ⇒ the direction of mass and heat transfer in the heated material, and
 - ⇒ the temperature gradient across the heated material.
- **Advantages:**
 - ⇒ MASE is more efficient compared to conventional extraction methods.
 - ⇒ It has a very high extraction rate and oil yield.
 - ⇒ It requires less solvent and the process itself is very easy to control.
 - ⇒ It is energy efficient and it emits very little CO₂.
- **Disadvantages:** It is very susceptible to the presence of solid deposit, which obstruct heat and mass transmission. Also, it is not efficient for non-polar and volatile solvent.

The difference between this microwave heating and the conventional heating are mainly related to the direction of mass and heat transfer in the heated material and also the temperature gradient across the heated material. That is the main difference between the microwave heating and the conventional heating.

However, the advantage of this technique is it is more efficient compared to that of the conventional extraction method and it has very high extraction rate and oil yield. It also requires less solvent and the process itself is very easy to control. As a result, the extraction rate as well as the oil yield can be controlled very effectively in the microwave assisted extraction technique. It is energy efficient and emits very little carbon dioxide. However, the limitation of this technique includes it is very susceptible to the presence of solid deposits during the extraction process and which obstruct the heat and the mass transmission. And also it is not efficient for the non-polar and volatile solvents.

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⑥ Ultrasound Assisted Solvent Extraction (UASE)

UASE works through two phenomena:

(a) Electrical energy converted into acoustic energy:

- ⇒ Electrical energy converted into acoustic energy by an ultrasound source.
- ⇒ The vibration generated by this ultrasound source has a range between 18 kHz and 100 MHz.

(b) Electrical energy converted into heat energy:

- ⇒ When the target material absorbs the acoustic energy, it converts the energy into heat energy.
- ⇒ Cavitation occurs due to ultrasound heating, which cause shock waves creating hot spots of high temperature and pressure (high up to 4000 °C and 1000 bar, respectively).

- These phenomena assist the extraction of oil by disrupting or disintegrating the biomass matrix.

Next is the ultrasound assisted solvents extraction technique. And this particular technique it works through two phenomena where the electrical energy is converted into the acoustic energy by ultrasound source. And the vibration generated by this ultrasound source has a range between 18 kilohertz to 100 megahertz. Similarly this electrical energy is converted into the heat energy when the target materials absorb this acoustic energy it converts energy into the heat energy.

And the cavitation occurs due to this ultrasound heating which cause shock waves creating hot spots of high temperature and pressure in the range of up to like 4000 degree Celsius and 1000 bar. And this phenomenon assists the extraction of the oil by disrupting or disintegrating the biomass matrix which eventually results in the release of oil from the biomass matrix.

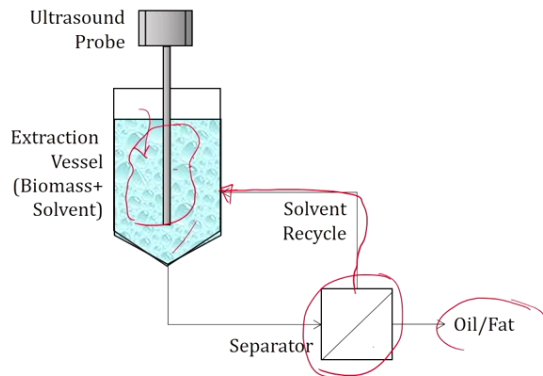
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- **Advantages :**

- High efficiency. ✓
- High extraction rate, and
- Low capital cost. &

- **Disadvantages :**

- Formation of free radicals under cavitation phenomena, which may react with oil.
- Thermal degradation or damage of the some fragile valuable compounds in an oil.
- High operating cost due to a high amount of solvent and multiple cycles to achieve optimal oil yield.



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The advantage of this technique includes high efficiency, high extraction rate and low capital cost. However, the free radicals formed during this cavitation phenomenon may react with the oil and that is the major limitation of this process. Similarly the thermal degradation or damage of the some fragile valuable compounds in oil may occur because of these high shock waves, high operating cost due to the high amount of solvent and the multiple cycles to achieve the optimal oil yield.

And these are the basic limitation of ultrasound assisted extraction technique. And this schematic here it shows the ultrasound assisted extraction phenomena here. So, in this vessel the biomass plus solvent mixtures are subjected for the extraction of the oil and after the extraction the material is allowed to separate into oil and the solvent phase. The solvent after separation is recycled back for the next cycle of extraction and the recover oil and fats are further process for the purification.

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⑦ Enzyme Assisted Aqueous Extraction (EAAE)

It primarily involves diffusing the ground biomass in aqueous solution of enzyme, where enzyme react to provide motive force to free the encapsulated oil from the biomass cells.

- **Advantages:**

- EAAE has great potential due to its environment-benign nature.
- No harmful chemical used. The residual biomass can be used as a protein rich animal feed or fertilizer.
- Superior quality oil as compared to other oil extraction methods.
- Oil contains a very low fraction of FFA and phospholipid. It has good oxidative stability.

- **Disadvantages:**

- Time consuming process; High cost of enzyme; Emulsification of extracted oil; High cost of downstream processing of the extracted oil involving centrifugation, demulsification, and residue drying.

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And the next process is enzyme assisted aqueous extraction technique. And this technique it primarily involves the diffusion of fine biomass particle in aqueous solution of enzymes where this enzyme reacts to provide a motive force to free the encapsulated oil from biomass cells. And the advantage of this technique is it has a great potential due to its environment friendly nature. No harmful chemicals used during the extraction process. And thus the residual biomass can be used as a protein rich animal feed or fertilizer, superior quality oil as compared to that of the other extraction methods. Even the oil obtained from this process contains very low fraction of FFA and phospholipids and it has a good oxidative stability as well.

The limitation its time consuming process, as we know the enzymatic reactions are literally a slow reaction. So, it requires literally more time to extract out the oil from the biomass matrix. Even the high cost of enzyme is another limitation of this process, emulsification of the extracted oil and high cost of downstream processing of the extracted oil which involves again the centrifugation, demulsification and residual drying. And these are the basic limitation of this process.

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Feedstock/Oil Pretreatment

- The feedstock usually contains unwanted components such as phosphatides, waxes, tocopherols, steryl glucosides, chlorophyll, colorants, and free fatty acids.
e.g. The presence of steryl glucosides in biodiesel result in significant low-temperature operability issues at temperatures above cloud point. Also, it cause engine failure due to fuel filter plugging.
- Therefore, pretreatments are performed on the feedstock to remove these impurities prior to the transesterification.
- Pretreatments involved in the biodiesel production process are filtration, winterization, degumming, demetallization, deacidification, bleaching, deodorization, etc.

After learning about the various extraction methods and the techniques, it is clear that the oil obtained at the end of this extraction processes is mostly a crude oil and hence the downstream processing of this extracted oil is essential to convert it into a usable form.

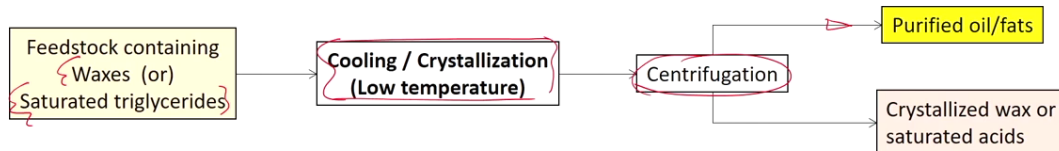
Because these feedstock usually contains unwanted components such as waxes, tocopherols, sterile glucosides, chlorophyll, colorant and free fatty acids. For example, if the extracted oil is directly used for the biodiesel synthesis process then the presence of this sterile glucoside in the biodiesel results in significant low temperature operability issues at temperature above cloud point. Also it causes engine failure due to fuel filter plugging. And thus the pre-treatments are performed on the feedstock to remove these impurities prior to the transesterification process. And these different pre-treatment techniques involved in the biodiesel production process are filtration, winterization, degumming, demetallization, deacidification, bleaching and deodorization.

Now let us discuss about this different pre-treatment techniques which are involved in the biodiesel production.

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① Winterization

- Some oils and fats contain waxes or saturated triglycerides. These high temperature melting compounds are removed by winterization.
- In the winterization process, oil is subjected to low temperatures (i.e. cooled) for a defined period of time in order to crystallize the saturated acids components, which are further separated by centrifugation.



- During the winterization the concentration of FFAs can be increased, so it is preferred to carry out winterization before deacidification (or esterification).
- Winterization step can also be performed during purification of biodiesels to improve cold flow properties.
- Winterization is a simple and cheaper method used to improve oils and biodiesels cold flow properties.

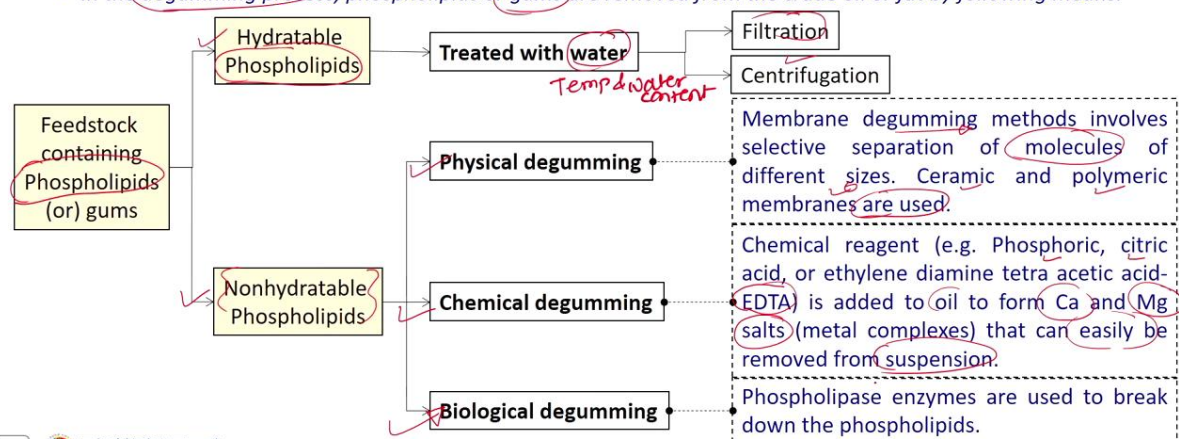
So let us discuss about the winterization. So the feedstock containing wax and saturated triglycerides are removed by winterization. In winterization process the oil is subjected to low temperature for a defined period of time in order to crystallize the saturated acid component and which are further separated by the centrifugation, so that relatively pure oil can be obtained. And during this winterization process the concentration of the FFS can be increased.

So, it is preferred to carry out the winterization before deacidification process that is before esterification. And this winterization step, it can also be performed during the purification of the biodiesel to improve its cold flow properties. Winterization it is a simple and cheaper method and hence it is used to improve the oil and biodiesel's cold flow properties.

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② Degumming

- Some vegetable oils contain high concentration of phospholipids, which may settle at the bottom in the tank due to their higher density after a long time period.
- In the degumming process, phospholipids or gums are removed from the crude oil or fat by following means.



Another important pre-treatment technique is a degumming. Because some feedstock may contain phospholipids which may settle at the bottom in the tank due to their high density.

And this may occur during the prolonged storage period of the oil. And hence this degumming process is used to remove these phospholipids or gums from the crude oil. Different techniques are available for the separation of phospholipids from crude oil and fats while the selection of this appropriate technique, it depends on the type of phospholipids that is hydratable or non-hydratable. The hydratable phospholipids can easily be removed by filtration or centrifugation after simple treatment of oil with the small amount of water. And the process is mostly affected by temperature and water content.

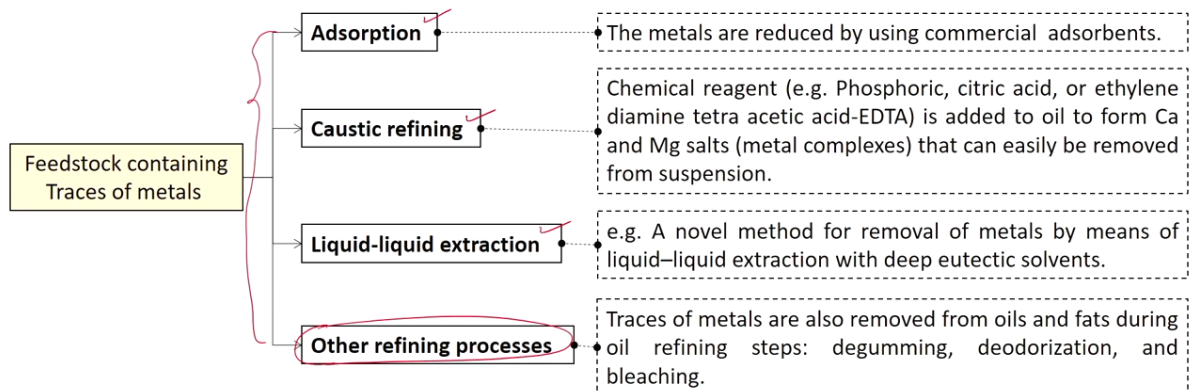
Similarly, the non-hydratable phospholipids can be separated from oils and fats by chemical degumming, physical degumming or biological degumming method. In case of physical degumming it involves the membrane separation method by selective separation of the molecules of different sizes. And usually the ceramic and the polymeric membranes are used for this degumming operation. Still in case of chemical degumming the chemical reagents such as phosphoric acid, citric acid or EDTA is added to oil to form calcium and magnesium salts so that it can easily be removed from suspensions. However, the biological degumming

method, it involves the phospholipase enzymes which are used to break down the phospholipids present in the oils or fats.

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③ Demetallization

- Traces of metals in oily feedstocks usually come from the source or processing equipment.
- Removal of metal content in oil/biodiesel is usually performed by adsorption, caustic refining, or liquid-liquid extraction followed by water washing steps.



Another important technique is a demetallization. In demetallization process a traces of metals present in the oily feedstock materials are removed using a preferred technique. And these traces of metals in oily feedstock usually come from source material or processing equipment. And various techniques are available for the removal of this metal content in oil or biodiesel, which includes adsorption, caustic refining, liquid-liquid extraction and other refining processes. So, the suitable techniques need to be used to remove this metal content from oil or biodiesel.

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④ Bleaching and deodorization

- Bleaching and deodorization of oil are not essential steps in the biodiesel production process.
- However, residual oils recovered from wastes generated in the vegetable oil refineries after bleaching and deodorization can be used as feedstock for biodiesel production.
- **Deodorization** involves the removal of volatile compounds (ketones and aldehydes) as well as some other compounds (pesticides and PAH) and is usually performed by steam distillation.
- **Disadvantage:** during this process different chemical reactions can occur that may destroy the structure of triglycerides; resulting in lowering the quality of oil.
- **Bleaching** is used to remove trace metals, soaps, and pigments from oil sample.

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Bleaching and deodorization: Bleaching and deodorization of the oil are not essential step in the biodiesel production process.

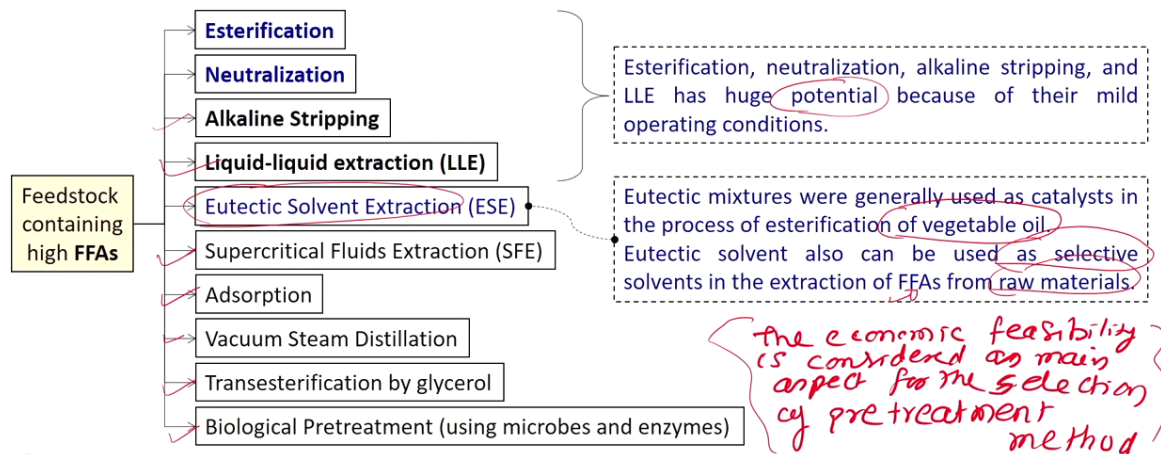
However the residual oil recovered from the waste generated in the vegetable oil refineries after the bleaching and the deodorization step can be used as a feedstock material for the biodiesel production. The waste generated in the vegetable oil refineries after the bleaching and deodorization operation contains significant amount of the oil. Hence this specific waste can be used as a potential raw material for biodiesel production. And this deodorization it involves the removal of the volatile compounds that is ketones and aldehyde as well as some other compound that is pesticide and pH and it usually performed by the steam distillation operation.

However, the limitation of this particular process is during this process different chemical reactions may occur and that may destroy the structure of the triglycerides and resulting in lowering the quality of oil. And this bleaching operation, it is used to remove the trace metals, soaps, pigments from oil sample.

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⑤ Deacidification (Esterification)

- A low quality feedstock with high FFA content prevents the conversion of triglycerides into FAME.
- The most commonly used deacidification methods are: **Esterification** (with acid catalysts) & **Neutralization**.



Next is deacidification or esterification. Deacidification normally performs with low quality feedstock with high FFA content. Because this high FFA content in the oily feedstock prevents the conversion of triglycerides into fame. And the most commonly used deacidification methods are esterification and neutralization.

However, some alternative methods of pre-treatment of low quality feedstocks are also available such as vacuum distillation, transesterification by glycerol, biological pre-determined, adsorption, supercritical fluid extraction, liquid-liquid extraction, eutectic solvent extraction and alkaline stripping. The economic feasibility is considered as main aspect for the selection of pre-treatment method. However, the economic feasibility is considered as main aspect for the selection of pre-treatment method. Because the esterification, neutralization, alkaline stripping and LLE has a huge potential because of their mild operating conditions. Whereas the eutectic mixture were generally used as a catalyst in the presence of esterification of the vegetable oil.

And this eutectic solvent also can be used as selective solvent in the extraction of FFA from the raw material. Therefore, the economic feasibility is considered as a main aspect for the selection of pre-treatment method.

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- The hydrolysis of triglycerides (by lipase action) leads to the formation of free fatty acids (FFAs).
- The free fatty acid (FFA) content and acid value (or acid number) are the measures of the amount of acidic substances present in the oil/fat sample.
- The **acid value** (AV) or **acid number** (AN) is defined as the amount of (milligrams) potassium hydroxide (KOH) required to neutralize the free fatty acids present in 1 g of oil or fat sample.
- It is determined by titrating a solution of the oil/fat in diethyl ether with alcoholic solution of KOH.

$$\text{Acid Value (AV)} = \frac{56.11 \times c_{\text{KOH}} \times V_{\text{KOH}}}{m_{\text{oil}}} \quad (\text{unit: mg KOH/g oil})$$

Where, c_{KOH} is concentration (Normality) of alcoholic KOH solution,

V_{KOH} is volume of titrant (KOH) used for the titration.

m_{oil} is the mass of oil sample

As we know the hydrolysis of this triglycerides by action of lipase enzyme leads to the formulae formation of the free fatty acids. And the free fatty acid content, that is also termed as the acid value, are the measure of number of acidic substances present in the oil or fat sample. And this acid value or the acid number, it is defined as the amount of potassium hydroxide required to neutralize the free fatty acids present in 1 gram of oil or fat sample.

And it is determined by titrating a solution of oil or fat sample in diethyl ether with alkali solution of potassium hydroxide. And this acid value is estimated using this equation here. This is the constant value multiplied by the concentration of alkali KOH solution into the volume of titrant used for the titration divided by the mass of the sample used for the titration. And its unity is milligram KOH per gram of oil sample or per gram of fat sample.

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- Acid value is expressed as mg/g, whereas the FFA content is expressed as a percentage (i.e. % g/g).
- AV is converted to FFA content as:

$$FFA(\%) = AV \times \frac{MW_{acid}}{10 \times MW_{KOH}}$$

- **Example:** If the AV of an oil containing oleic acid (MW=282.4) is 4 mgKOH/g, then express its FFA content.

$$FFA(\%) = 4 \times \frac{282.4}{10 \times 56.1} \approx 4 \times \frac{1}{2} = 2$$

4
FFA -

Therefore the FFA content of the oil is 2%

And this acid value is also expressed as milligram per gram whereas the free fatty acid content is expressed as percentage.

And this acid value can be converted into FFA as per the following equation. So, the FFA percentage is equal to the acid value into molecular weight of acid divided by 10 into molecular weight of KOH. So, to understand this conversion of acidic value into free fatty acid, let us try to take help of this simple example here. If the acid value of oil containing oleic acid is 4 milligram KOH per gram of oil sample then we need to just express its FFA content. So, in this case as we know, the FFA content can be represented using this equation here. So, acid value of the sample is known that is 4 and the molecular weight of the acid that is oleic acid is given as 282.4 and the molecular weight of KOH is 56.1.

So, once we substitute this value in this equation we will get the FFA percentage as 2 however the acid value was 4. So, normally the free fatty acid contents of any sample are considered as half of its acid value. So, for example if the acid value is 4 then its free fatty acid content is considered as 2.

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- Some feedstock oil/fat contains significant amounts of free fatty acid (FFA). e.g.,
 - Non-edible oils, crude vegetable oils, and waste cooking oils (WCO) typically contain 2–7% FFA.
 - Animal fats contain 5–30% FFA.
 - Whereas a low quality feedstock, such as trap grease, can contain FFA up to 100%.
 - Moisture or water present in the vegetable oils increase the FFA value.
- If an alkali catalyst is added to these feedstocks (i.e. direct transesterification), the FFA react with the catalyst to form soap and water:



Since some feedstock contain significant amount of the free fatty acid in its composition that is non-edible oils, crude, vegetable oils or we can say the waste cooking oils which typically contain around 2 to 7% of the free fatty acid in its composition. Similarly, the animal fats contain around 5 to 30% free fatty acids and low quality feedstock such as trap grease contains FFA up to even 100%.

Moreover the moisture and the water present in the oil increases the FFA value. As we have just discussed before, the hydrolysis of triglycerides results into the formation of the FFA. So, if the moisture or the water is present in the vegetable oil then it may hydrolyze the triglyceride and convert it into the FFA. And in case the alkali catalysis is used directly to this feedstock for the transesterification process then this FFA reacts with the catalyst to form soap and water. And this is a saponification reaction where the fatty acids react with alkali catalyst to form soap and water, if the FFA contain is significantly high in the raw material.

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- When the FFA content is $>5\%$, the soap contributes to emulsification during the water wash. Thus, it inhibits the separation of the glycerol from the biodiesel (Knothe et al., 2005).
- Also, the higher the FFA content or acid value of the oil, lower is the transesterification reaction conversion efficiency.
- For better conversion efficiency in the transesterification reaction:
 - It is advisable that the oil should have an acid value (AV) lower than 1 mg KOH/g (Ingle, 2021).
 - All substances should be anhydrous to avoid further hydrolysis of triglycerides to free fatty acids (FFAs).

$$\text{FFA} = 0.5\%$$

Therefore, if the feedstock contain significant amounts of FFAs, it requires the esterification treatment to lower the FFA content.

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When the FFA content is greater than 5 percent then the soap contributes to emulsification during the water wash operation.

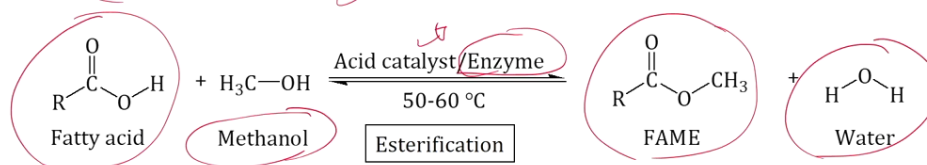
And thus it inhibits the separation of glycerol from the biodiesel. Therefore this FFA content need to be controlled during the biodiesel process, so that the emulsification will not takes place in the prepared sample. Also the higher FFA content or the acid value of the oil lowers the transesterification reaction conversion efficiency. Therefore, to achieve the better conversion efficiency in the transesterification reaction, it is advisable that the oil should have acid value lower than $1 \text{ mg KOH per gram of sample}$ or the oil should have FFA equivalent to 0.5 percent. And all other reactor used during this transesterification process should be unaddressed to avoid the further hydrolysis of the triglycerides to FFA.

And hence if the feedstock contains significant amount of the FFA then it requires the pre-treatment in the form of deacidification or the esterification to lower the FFA content of the crude oil.

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Esterification

- Esterification refers to the reaction of free fatty acids (FFA) with alcohol (usually methanol) in the presence of an acid catalyst (like sulphuric acid) to form esters and water.



- In general, the esterification is regarded as an **acid-catalyzed pretreatment step**.
- The esterification product must be dried to remove the water/moisture which can hinder transesterification.
- The esterified or deacidified oil containing triglycerides with acid value of <1 mg KOH/g, suitable for alkaline transesterification (Ingle, 2021).
FFA = 0.5%

So, as we discussed earlier this esterification process, it refers to the reaction of free fatty acids with alcohol in presence of acid catalyst like sulphuric acid as a catalyst to form esters and water. So, this reaction here it represent the conversion of free fatty acids in the crude oil by reacting with alcohol that is methanol in presence of suitable acid catalyst that is sulphuric acid catalyst. Or sometime it is carried out with the enzyme as well to form esters and water as a product. And this particular reaction is regarded as acid catalyst pre-treatment step in the biodiesel process.

And this esterification product, it must be dried to remove the water and the moisture which can otherwise hinder the transesterification process at a later stage. The esterified or the deacidified oil containing triglyceride with acid value less than 1 mg KOH per gram or as I mentioned FFA equal to 0.5% suitable for alkaline transesterification process to produce biodiesel.

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Conversion efficiency of Esterification reaction:

The conversion efficiency of the process can be calculated on the basis of acid value or the FFA content of the feed and product samples using the following equation:

$$\text{Conversion(\%)} = \frac{AV_{\text{feed}} - AV_{\text{prod}}}{AV_{\text{feed}}} \times 100$$

$$\text{Conversion(\%)} = \frac{FFA_{\text{feed}} - FFA_{\text{prod}}}{FFA_{\text{feed}}} \times 100$$

Where, AV_{feed} is acid value of the feed, and

AV_{prod} is the acid value of the product.

FFA_{feed} is free fatty acid content of the feed, and

FFA_{prod} is the free fatty acid content of the product.

So, to know the extent of the esterification reaction, the conversion efficiency of the esterification process, it can be calculated on the basis of acid value or the free fatty acid content of the feed or the product sample using this simple equation here. So, this represent the conversion percentage acid value of feed, minus acid value of the product, divided by the acid value of feed material into 100.

So, with the help of this equation we can calculate the conversion efficiency of the esterification process. Or instead of acid value if you know the free fatty acid content of the specific given sample then the conversion efficiency can also be calculated with the help of free fatty acid content. AV suffix feed it indicates the acid value of the feed. Similarly the acid value of the product is represented like this and this represents the free fatty acid content of the feed and the product sample.

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Example. Oil sample was esterified using methanol and acid catalyst to reduce its free fatty acid (FFA) content. To determine the acid value of feed and product oil sample, 10 g of each oil sample was titrated separately against 0.1 M KOH ethanolic solution (titrant). The amounts of titrant required to achieve the end point of titration were 32.1 mL and 1.8 mL for the feed and product sample, respectively. Calculate the conversion efficiency of the esterification process.

Solution:

$$\text{Acid Value (AV)} = \frac{56.11 \times c_{\text{KOH}} \times V_{\text{KOH}}}{m_{\text{oil}}} \quad (\text{unit: mg KOH/g oil})$$

Where, c_{KOH} is concentration (Normality) of alcoholic KOH solution,

V_{KOH} is volume of titrant (KOH) used for the titration.

m_{oil} is the mass of oil sample

$$AV_{\text{feed}} = \frac{56.11 \times 0.1 \times 32.1}{10} = 18 \text{ mg KOH/g oil}$$

$$AV_{\text{prod}} = \frac{56.11 \times 0.1 \times 1.8}{10} = 1 \text{ mg KOH/g oil}$$

So, to understand this concept of the conversion efficiency of the esterification process, let us try to solve one small example, here in which the oil sample was esterified using methanol and acid catalyst to reduce its free fatty acid content.

To determine this acid value of the feed and the product oil sample 10 gram of each sample was titrated separately against 1 molar KOH ethanol solution. And the amount of titrant required to achieve the end point of the titrations were 32.1 ml and 1.8 ml for feed and product sample respectively. So, with the help of this given data we need to calculate the conversion efficiency of the esterification process.

So, as we know the acid value of the sample can be estimated using this equation. So, in this equation we know the concentration of alcoholic KOH solution as well as the volume of titrant used for the titration and the mass of the oil used for the titration. As 10 gram of sample is used for the titration and the concentration is 0.1 molar ethanol alcoholic KOH solutions and for the feed the amount of titrant required was around 32.1.

So, after substituting this value in this equation here, we get the acid value of feed sample. Similarly, we can estimate the acid value of the product sample which comes out to be

around 1 milligram KOH per gram of oil. Whereas for the feed, the acid value is around 18 milligram KOH per gram of oil sample.

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To calculate the conversion efficiency of the esterification process:

$$\text{Conversion} = \frac{AV_{\text{feed}} - AV_{\text{prod}}}{AV_{\text{feed}}} = \frac{18 - 1}{18} = 0.944 = 94.4\%$$

Therefore, the conversion efficiency of the given esterification process is 94.4%.

So, once we know the acid value of feed and the acid value of the product then with the help of this given equation we can easily calculate the conversion efficiency of the esterification process. Because the acid value of the feed is known that is 18 and the acid value of the product is 1. So, after substituting this value here, the conversion efficiency comes out to be around 94.4%. So, similarly the conversion efficiency of given sample can be estimated, once we know the acid value of feed and the product sample.

This covers our discussion on the chemical conversion processes. In the next lecture that is the second lecture of the module 6, we will discuss the mechanism of transesterification process and the fuel characteristics of the biodiesel.

Thank you.