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CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

ENERGY PRODUCTION FROM WASTES THROUGH TRANSESTERIFICATION-2

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Contents

- What is transesterification ?
- Organic wastes for transesterification
- Production of bio oil from oil seeds and its major composition
- Need of upgradation of bio oil to bio diesel
- Bio diesel properties
- Upgradation flowsheets
- Steps for upgradation
- Biodiesel production from mixed waste pant oil
- Combustion of bio oil/bio diesel in diesel engine

Steps for upgradation

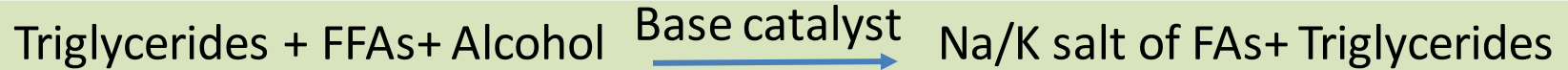
- The complete process for the production of methyl ester from plant oil and other feedstocks therefore involves basically five steps:
 - Acid esterification
 - Transesterification
 - Methanol recovery
 - Biodiesel refining
 - Glycerin refining

Pre treatment



Acid Esterification (AE)

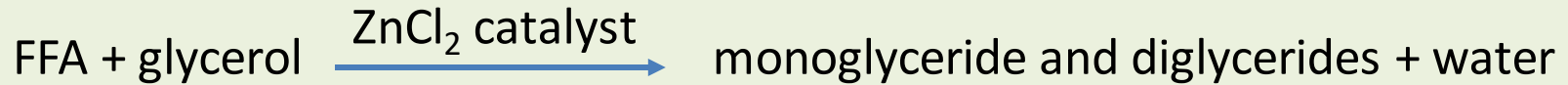
- Free fatty acids (FFAs) in biodiesel feedstocks react with alkali catalysts like NaOH and KOH and form soaps, which reduce the oil properties of the biodiesel.



- Low levels of FFAs (upto 4%) can be managed by using additional catalyst and allowing soap formation. NaOH $[\% \text{FFA}](0.144) + 1 \%$; KOH: $[\% \text{FFA}](0.197)/0.86 + 1 \%$; Sodium methoxide: $[\% \text{FFA}](0.190) + 0.25 \%$.
- Feedstock containing $> 4 \%$ FFAs (Animal fats and recycled greases) are first filtered and then pre-processed to remove water and other contaminants such as unwanted solids. The pretreated oil is then fed to the acid esterification process. Most plant oils and some food-grade animal fats do not require AE, ($\text{FFA} < 4 \%$).
- The sulfuric acid, is dissolved in methanol and then mixed with the pretreated oil. The mixture is heated and stirred, and the FFAs are converted to biodiesel. Once the reaction is complete, it is dewatered and fed to the transesterification process.

Alternative method to remove/ manage free fatty acids (FFAs)

- **Enzymatic methods** – Very costly, not a popular choice.
- **Glycerolysis** – Glycerol is added to high FFA feedstock with catalyst (ZnCl_2) at 200°C , which converts FFAs to monoglycerides and diglycerides.



- Water is vented as it is formed. Requires high temperature and slow process.
- **Acid catalysis followed by base catalysis**- Acid catalysis for conversion of FFAs to methyl esters, until $\text{FFA} < 0.5\%$ followed by addition of methanol and base catalyst to finish the reaction
- Acid such as H_2SO_4 catalyzes both esterification and transesterification reactions. Esterification of FFA is fast (1 hour) but transesterification is slow (2 days) at 60°C .

Conversion of FFA

The conversion of FFAs can be determined from the following Equation

$$\eta(\%) = \frac{S_0 - S_i}{S_0}$$

Where S_0 is initial acid value and S_i is the acid value at some reaction time

Determination of acid value : Known amount of sample is added to some amount of neutralized ethanol and is fully dissolved by heating. Phenolphthalein (0.5 mL) is used as an indicator. The sample is then titrated with standard KOH solution.

The acid value is calculated as

$$S = \frac{56.1 \cdot V \cdot c}{m}$$

where S is the acid value (mg KOH/g WCO); c is the concentration of the KOH used for titration (mol/L); V is the volume of KOH employed for titration (mL); m is the mass of the sample taken to be analyzed (g).

Ding et al., 2012, Energies, 5, 2683-2691



Transesterification

- The plant oil, which contains less than 4% free fatty acids, is first filtered and then pre-processed to remove water and other contaminants.
- The pretreated oil is then fed directly to the transesterification process along with any products of the acid esterification process.
- The catalyst, potassium hydroxide, is dissolved in methanol and then mixed with the pretreated oil. Heterogeneous catalyst can also be used.
- If an acid esterification process is used, then additional alkaline catalyst must be added to neutralize any excess acid remaining from that step.
- Once the reaction is complete, the major co-products, biodiesel and glycerin, are separated into two layers.



Factors affecting transesterification process performance

- Reaction temperature
- Reaction-time
- Alcohol to oil mole ratio
- Catalyst concentration
- Free fatty acids content
- Mixing
- Water content
- Types of alcohol
- Catalyst types



Some heterogeneous catalysts for bio diesel production

Feed stocks	Solvent used	Catalyst	Operating conditions				Yield (%)
			Temp (°C)	Alcohol oil ratio	Catalyst loading wt%	Reaction time (h)	
Sunflower oil	Methanol	SrO	65	12:1	3	0.5	90
Soybean oil	Methanol	K_2CO_3/TiO_2 (Ti:K = 0.65:1)	60	12:1	6	2	25.15
Babassu coconut oil	Methanol	Amberlyst-15: Sulfonated ion exchange resin	60	100:1	-	8	80
Waste cooking oil	Methanol	Sulfonated carbon based catalyst	80	30:1	10	4	92

- **Methanol recovery**

- The methanol is usually removed immediately after the biodiesel and glycerine have been separated. This is done to prevent the reaction from reversing itself. Recovered methanol is cleaned and recycled back to the beginning of the process.

- **Biodiesel refining**

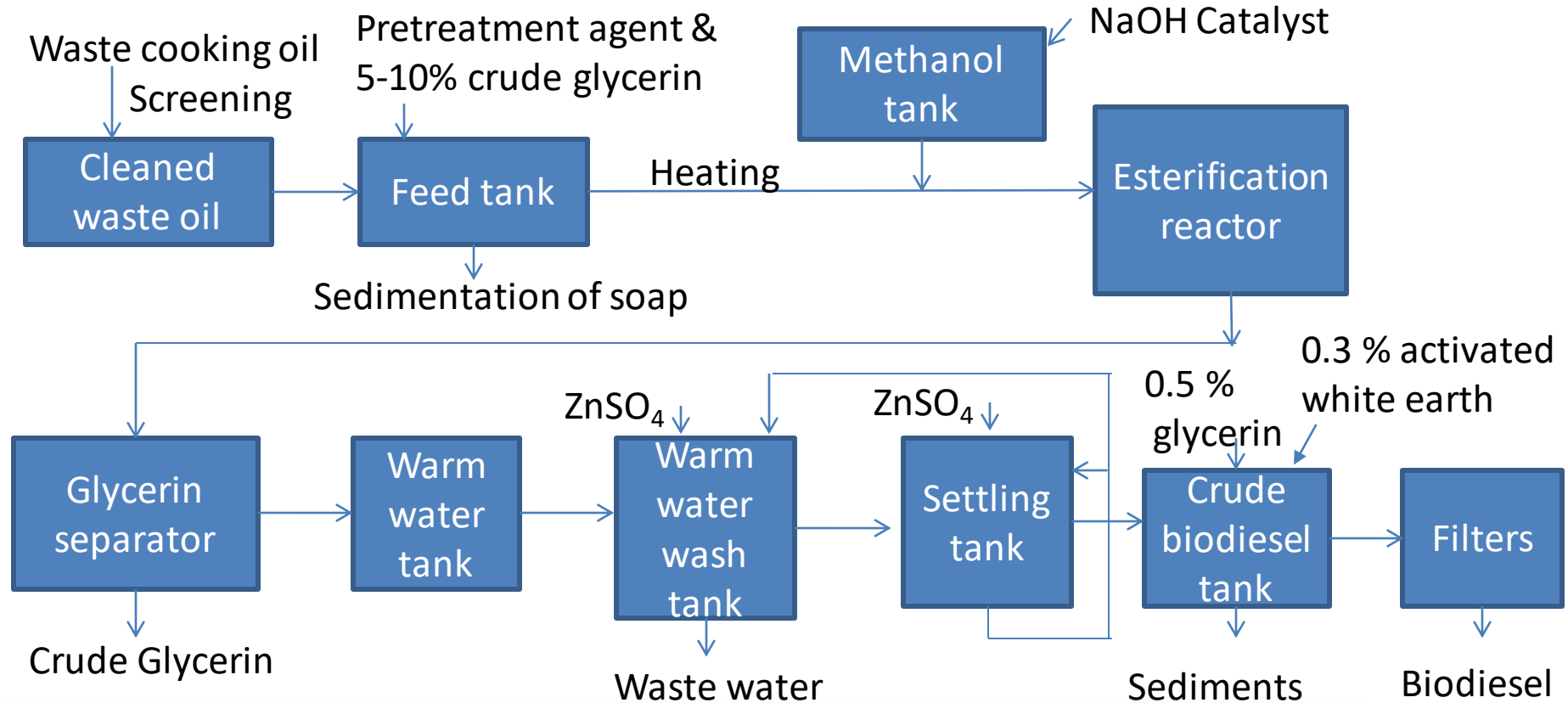
- Once separated from the glycerin, the biodiesel goes through a series of cleaning-up or purification steps to remove excess alcohol, residual catalyst and soaps.
- These consist of multistage washings with clean water.
- The product biodiesel is then dried and sent to storage.
- It can be further refined through an additional distillation step to produce a colorless, odorless, zero-sulfur, and premium quality biodiesel.



Glycerine refining

- The crude glycerine from the transesterification process may be recovered or used in a fuel blend for steam production.
- The crude glycerine contains unreacted catalyst and soaps that must be neutralized with an acid.
- The water and alcohol are also removed to produce 50%-80% crude glycerin.
- The remaining contaminants include unreacted fats and oils.
- In large biodiesel plants, the glycerin can be further purified through a series of unit operations to produce a product of 99% or higher purity.
- This purified product is suitable for use in the pharmaceutical and cosmetic industries.





Pre treatment of waste mixed oils

- Waste plant oils recovered from restaurants and other sources is fed into a vessel with metal filter to remove undesirable materials.
- The filtered oil accumulates at the bottom of the vessel and is transferred by a gear pump to the Feed Tank.
- The Feed Tank is then heated to 50⁰-60⁰C.
- A pre-treatment agent and 5-10% crude glycerin are added to prevent solidification of the oil and hasten the precipitation and sedimentation of soap particles.
- The mixture is agitated for about 20 minutes and then settled for about one hour.
- The soap sediment is removed from the bottom of the tank and the pre-treated oil is fed into the esterification reactor.



Esterification process and biodiesel recovery

- Methanol and caustic soda, as catalyst, are mixed together in the methanol tank.
- Normally, the amount of caustic soda is about 4.7% of that of methanol, which is sufficient to raise the temperature of the mixture in the methanol tank to 50°C , still below the boiling temperature of methanol of 65°C .
- This mixture is pumped to the continuous esterification reactor to mix and react with the pre-treated feed oil.
- Feed oil is first preheated to 70°C by passing it through a tube coil heater before it enters the esterification reactor.



- The preheated feed oil and the solution from the methanol tank are mixed through a line mixer and then reacted inside the continuous tube esterification reactor where the retention time is around 30 minutes and the temperature is kept under 60°C.
- The reaction products are sent to the glycerin separator where crude glycerin, which contains residual soap and methanol, is separated.
- The crude biodiesel is sent to the **warm water tanks** and the **warm water wash tank** (heated and equipped with an agitator) for further treatment and refining.
- Zinc sulfate is added to the crude biodiesel in the **warm water wash tank** to destroy the emulsion and precipitate residual soap.
- The mixture then goes to the **warm water separator** where the impurities are separated from the supernatant crude biodiesel, which looks whitish and muddy due to residual water contaminants in emulsion.

- This crude biodiesel is sent to the **settling tank** to remove the contaminants. The recovered water from the **settling tank** is treated under vacuum to remove contaminants and then recycled back into the **warm water wash tank**.
- The crude biodiesel is further treated in the **crude biodiesel tank** by the addition of 0.5% glycerin as de-watering agent and 0.3% activated white earth as sedimentation agent (agitated for 15 minutes and settled overnight).
- The sediments are removed from the bottom and the treated supernatant is further refined through filtration in the **filtration tank**.
- Further cleaning is attained by a second stage filtration in a **paper filter**.
- The refined biodiesel product is then placed in regular drums ready for delivery and use.

Glycerine recovery

The crude glycerine from the **glycerin separator** is stored in a **neutralization tank**, which is glass-lined and equipped with a closed-type agitator.

It is heated under normal pressure to distil out the methanol, which is recovered from the condenser located at the top of the **neutralization tank**.

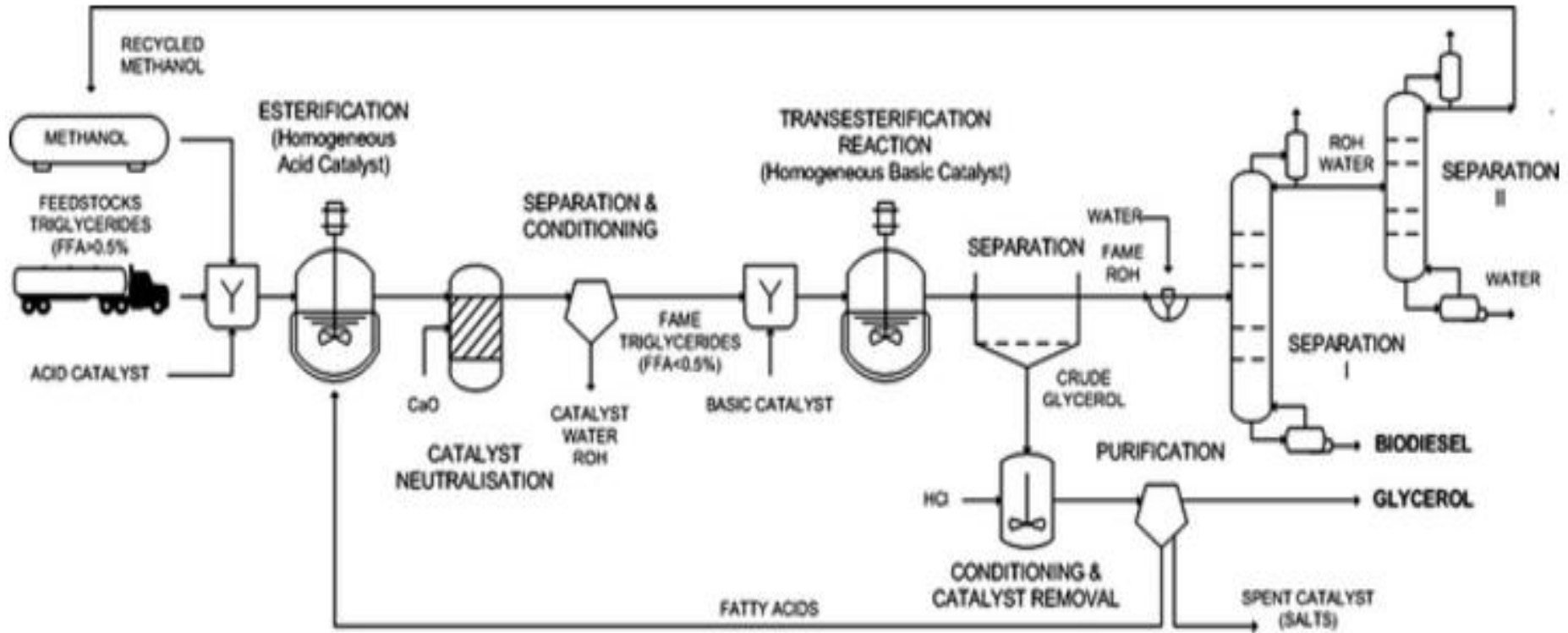
The remaining crude glycerine is neutralized by the addition of hydrochloric acid and the residual soap is converted into oil, which is removed from the upper layer.

Crude glycerine is taken from the bottom of the **neutralization tank** and pumped first to the **crude glycerin tank** and then to the **crude glycerin concentrator** for further treatment.

The crude oil that is skimmed off from the **neutralization tank** is burned as fuel for heating the **vacuum distillation unit**.



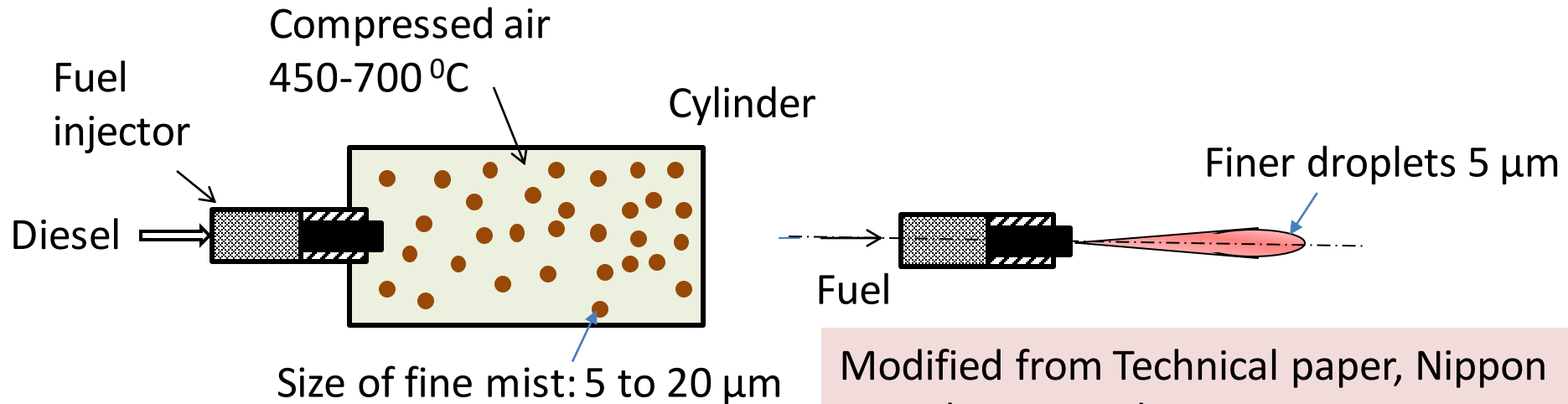
- The **crude glycerin concentrator** is equipped with steam-heated jacket and vacuum ejector to remove water from crude glycerin.
- The crude glycerin is then sent to a two-stage **vacuum distillation unit** where dissolved solids such as sodium chloride are removed (first stage) and 99.5% glycerin with a light yellow color is produced.
- This product is further refined in the **activated carbon treatment tank** to remove residual color.
- The amount of activated carbon needed to produce a product of acceptable quality is 2-3% of the amount of glycerin.
- The activated carbon is mixed with glycerin for 15 minutes at a temperature of 90⁰-100⁰C.
- The mixture is then passed through the **glycerin filter** to produce the final product of clear 99.5% glycerin.



Heterogeneous acid catalysts for biodiesel production: current status and future challenges, Juan et al, 2009, Green Chemistry, 11, 1285-1308 (with permission)

Combustion of bio oil/bio diesel in diesel engine

- When diesel fuel is injected into the cylinder, it normally produces fine mist ranging in size from 5 to 20 microns.
- The finer the mist and the more uniform the mist size, the better is the combustion inside the cylinder.



Modified from Technical paper, Nippon Ecosolutions, Ltd., Japan 2007

- Plant oils that are generally much more viscous than diesel fuel cannot be injected into the cylinders as effectively and efficiently as diesel fuel.
- And even if the plant oil can be successfully injected, the injector, which was carefully engineered to the specifications of the diesel fuel, cannot provide a fuel mist as fine as when plant oils are used.
- Larger fuel droplets result burning causing difficulty with starting and incomplete combustion, which leads to build-up of carbon residue.
- More deposits inside the engine, cause poor engine performance resulting from low compression due to sticking piston rings or coked valves.
- Deposits on the injector nozzle produce poor injection spray pattern resulting in even more incomplete combustion and possible piston damage due to increased heat on piston surfaces.

Modification in engine technology for handling viscous oil like bio oil

Twin Tank or Dual Fuel System

- The engine is started on the conventional diesel fuel and the waste heat generated by the engine is used to heat the plant oil.
- This avoids running viscous plant oil through a cold engine at start up.
- A temperature gauge in the fuel line determines when the plant oil is hot enough for the fuel supply to be switched to 100% plant oil. The fuel supply is switched by a three-way valve.
- Before shutting down for extended periods, the fuel supply is switched back to conventional diesel fuel and the engine is allowed to run for about 3 to 5 minutes so that any residual plant oil is flushed from the fuel system.
- The vehicle or engine is then ready to be restarted on diesel fuel.



Thanks

