SYNTHESIS OF BIODIESEL

AIM

1. To generate laboratory know-how for the process of production of biodiesel from the given oil feed stock
2. To perform basic mass and energy balance calculations for a large scale batch process
3. To analyze the economics of the process
4. To learn various fuel characterization techniques

APPARATUS

Oil bath, stirrer, chiller, mantle, condenser, reactor, baffle, temperature sensor, vacuum pump, separating funnel, round bottom flask, beakers, conical flasks, insulation, pipettes, burette, Biodiesel pilot plant model for understanding the process

CHEMICALS REQUIRED

Feed stock oil, Methanol, Conc. Sulphuric acid (98%), Sodium hydroxide (NaOH), Ethanol, Phenolphthalein, Potassium hydroxide (KOH).

THEORY

Biodiesel is a clean, renewable alternative fuel which is far more eco-friendly than diesel. The common sources of biodiesel are

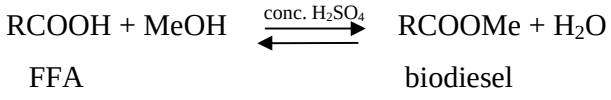
- Virgin oil feedstock; rapeseed and soybean oils.
- Waste vegetable oil (WVO)
- Animal fats
- Non edible oils like Jatropha, Neem Oil, Castor Oil
- Algae

Biodiesel is a mixture of esters of free fatty acids. Its colour varies between golden yellow and dark brown. It is immiscible with water, has high boiling point and high flash point. Biodiesel has better lubricating properties and much higher cetane ratings than today's lower sulfur diesel fuels. The calorific value of biodiesel is about 37.27 MJ/L. Pure Biodiesel is never used in a conventional diesel engine as it is not compatible with it. Hence it is blended

with diesel for usage in engines. Different blends of biodiesel available are B10, B20, B30, B100 and are named depending on the percentage of biodiesel in the blended mixture.

Refined oil contains a mixture of triglycerides, free fatty acids and small quantity of impurities. Triglycerides (TG) and free fatty acids (FFA) are converted to biodiesel through a series of steps which are as follows.

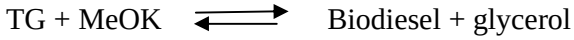
1) **Esterification**: This is an acid catalyzed process wherein the FFA present in the raw material is converted to biodiesel.



where R – long chain hydrocarbon

2) **Settling**: The catalyst added during esterification is separated along with methanol.

3) **Transesterification**: This is a base catalyzed process wherein MeOK is prepared and the TG present in the raw material is converted to biodiesel.



4) **Atmospheric distillation**: This is done to recover methanol from the transesterified product mixture.

5) **Settling**: Residue of the atmospheric distillation is settled to separate out glycerol and other impurities.

6) **Vacuum distillation**: This is used to purify the biodiesel obtained post settling.

3/27 Test-

3/27 test is performed to ascertain the completion of transesterification process.

Take 27 parts by volume of methanol and add 3 parts of the reaction mixture to it. Stir the mixture and allow it to settle for about 15 mins. If the reaction mixture almost dissolves in methanol, then the reaction is completed.

This test is based on the principle that biodiesel is soluble in methanol while TG is not.

PROCEDURE

1. FREE FATTY ACIDS (FFA) ANALYSIS:

1. Prepare around 0.01N (N) NaOH solution.
2. Take about 5-10 ml of ethanol in a beaker and add 2-3 drops of phenolphthalein indicator to it. Neutralize the ethanol with NaOH solution.
3. Add about 0.1-0.2 g of oil to the above solution. Note the exact weight (w) of the added oil carefully.
4. Again add a couple of drops of phenolphthalein to it and titrate the oil-ethanol solution.
5. Note the volume of NaOH required to neutralize only the oil. Let this be 'x' ml.
6. Wt % of FFA(Mol. Wt.-276) = (x*N*100*276)/(1000*w)

2. ESTERIFICATION PROCESS:

1. Take 200 g of given oil in a reactor.
2. Add methanol in 1:30 molar ratio to FFA.
3. Add H_2SO_4 1% by wt (g) of the above mixture.
4. Attach a vertical condenser in one of the necks of the reactor.
5. Ensure that the lid and openings are tightly closed so that there is no loss of methanol vapours.
6. Note the temperature with the help of given temperature sensor and maintain the temperature of the reaction mixture between 65^oC-70^oC.
7. Track the progress of the reaction by taking a sample every half an hour and performing FFA analysis. If FFA<1%, stop the reaction.

3. SETTLING PROCESS:

1. Keep the above reaction mixture for settling in a separating funnel till two separate layers are obtained (for about 1 hr).
2. Separate bottom layer (oil + esterified FFA) and top layer (methanol + H_2SO_4) and weigh them.
3. Perform transesterification of the bottom layer.

4. TRANSESTERIFICATION PROCESS:

1) **Preparation of Potassium methoxide** (MeOK) - Add KOH 1% by wt. (w.r.t. oil) and methanol in a 1:9 molar ratio to oil in the reactor and heat to 70^0C for 15-20 min.
2) Add the reaction mixture (oil + Esterified FFA) to the above MeOK mixture.
3) Attach the vertical condenser to one of the necks of the reactor.
4) Note the temperature with the help of given temperature sensor and maintain the temperature of the reaction mixture between 65^oC-70^oC.
5) Track the completion of the reaction by performing 3/27 test after 3 hrs.

5. ATMOSPHERIC DISTILLATION - METHANOL RECOVERY:

1) The transesterified mixture is subjected to atmospheric distillation to recover methanol.
2) Weigh the recovered methanol.

6. SEPARATION PROCESS:

1. Allow the mixture to settle in a separating funnel for 2-2.5 hrs.
2. Separate the top layer (Crude Biodiesel) and bottom layer (Water + Potassium hydroxide + Glycerol) and weigh them.

7. BIODIESEL PURIFICATION—VACUUM DISTILLATION:

1) The above top layer is subjected to vacuum distillation (750 mm Hg gauge pressure).
2) Add the porcelain chips to the round bottom flask.
3) Start heating after the applied vacuum is achieved.

NOTE:

1) For esterification and transesterification steps, ensure that
    a. All the openings in the reactor are properly closed and tightly sealed.
    b. Silicon fluid is present in the temperature sensor pocket.
    c. Baffle is present in the reactor.
    d. Stirrer speed and its distance from the base of the reactor should be such that there is no splashing.

2) During distillation, ensure that
    a. The round bottom flask is properly insulated.
    b. The heating rate does not exceed 40 units in the heating mantle.
    c. The chiller is maintained at a temperature of about $20^{o}C$.
    d. The condenser is operated in counter current flow.
3) During settling, the separating funnel should be closed with a glass cork.

OBSERVATIONS AND CALCULATIONS

Esterification:

Amount of Oil:

Amount of Methanol:

Amount of H_2SO_4 :

a) Esterification:

Sr. no.	Time (min)	Wt of sample (w) Gms	Initial burette reading (1) ml	Final burette reading (2) ml	Volume of NaOH (1)-(2) ml	FFA %
1	0					
2	30					
3	60					
4	90					
5	120					
6	150					
7	180					

Start Time: End Time: Total Time Taken:

RESULT:

Overall yield of reaction and weight of biodiesel obtained:

QUALITY CONTROL TESTS

AIM:

To study the quality control tests of biodiesel to determine:

a) Flash Point

b) Kinematic Viscosity

c) Density

d) Cloud point

e) Pour point

f) pH

FLASH POINT

APPARATUS:
Open cup apparatus, biodiesel sample, temperature indicator, matchsticks.

THEORY:
The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture with air. It is used in safety regulations to determine flammable and combustible materials.

Every flammable liquid has a vapour-pressure which increases as the temperature increases. As the vapour pressure increases, the concentration of evaporated flammable liquid in the air increases. Each flammable liquid requires a different concentration of its vapour in air to sustain combustion .So the flash point is the lowest temperature at which there can be enough flammable vapour to ignite, when an ignition source is applied.

PROCEDURE:
The sample is kept in the open cup attached with a temperature indicator and is heated. At regular temperature intervals a flame is brought over the biodiesel surface. The lowest temperature at which the vapours above liquid catch fire is the flash point of the liquid.

PRECAUTION:
The ignition source should not come in contact with the fuel.
Do not continue the experiment above the observed flash point.

VISCOSITY

APPARATUS:
Ostwald's U-tube viscometer, biodiesel sample, stop watch.

THEORY:
Viscosity is the ratio of viscous force to the internal force. Kinematic Viscosity is the ratio of absolute viscosity to density. It is important for the estimation of optimal storage, handling and operating conditions.
Viscometer is an instrument used to measure the kinematic viscosity of a fluid. The time taken for the level of the liquid to pass between these marks is proportional to the kinematic viscosity.

PROCEDURE:

Calibration of Viscometer
The time taken for a fixed volume of water to flow under gravity through the capillary of the viscometer between the two marked points is noted. Take at least four readings and take their average.
The kinematic viscosity of water is known at that particular temperature from standard tables
The same experiment is repeated for biodiesel and the average time is noted. Using the time taken for water and kinematic viscosity of water the kinematic viscosity for biodiesel is calculated.

PRECAUTIONS:
The viscometer should not be disturbed during the course of experiment.

DENSITY

APPARATUS:
Specific gravity bottle, biodiesel sample.

THEORY:
Density is the ratio of mass to the volume. Pycnometer or specific gravity bottle is a small bottle or flask used to measure the specific gravities of liquids. These bottles are of known volume.

PROCEDURE:
The specific gravity bottle is filled with biodiesel up to the brim. Then the extra liquid is made to overflow as the lid is put. The bottle is thoroughly wiped. The bottle is weighed and weight of sample is found as the weight of empty bottle is known. The density is now calculated as the volume is known.

CLOUD POINT AND POUR POINT

APPARATUS:
pH meter, double glass tube with cork, ice , thermometer , beakers,$CaCl_2$, biodiesel, distilled water.

THEORY:
The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance. cloud point refers to the temperature below which wax in diesel or biowax in biodiesels form a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines.
The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed conditions. It is a rough indication of the lowest temperature at which oil is readily pumpable.

PROCEDURE:
1. Fill the double glass tube with Biodiesel up to the half way level.
2. Insert a thermometer in the tube so that its tip is completely immersed.
3. Prepare a mixture of ice and calcium chloride in a container, and put the double glass tube in the container
4. Remove the double glass tube at regular intervals of time and observe its contents, note the temperature at which you first observe a cloudy appearance. This temperature is the cloud point.
5. Continue the experiment, now observe the flow characteristics of the mixture by tilting the glass tube slightly, the temperature at which the contents stop flowing is the pour point.

pH DETERMINATION OF BIODIESEL

APPARATUS:
pH meter, buffer solutions, distilled water.

THEORY:

The pH value is an important quality criterion for all Bio-fuels. The more acidic the bio-diesel, more is the damage caused to the engine.

PROCEDURE:

1) Water and Bio-diesel are taken in 1:1 ratio by volume and heated at 70°C with continuous stirring for about 15 minutes.

2) Then the mixture is left for settling. After settling, water is collected and taken for pH measurement.

3) Before measuring the pH, the pH-meter is calibrated against two standard buffer solutions of values 4 & 9 respectively.

4) After calibration the probe of the meter is washed with distilled water and then cleaned using tissue paper.

5) Now the meter is dipped in distilled water. If it shows a value of 7 then further measurements are carried out else recalibration is done. While taking the reading, we should wait for steady state value.

6) Now the meter is dipped in the water sample collected after settling and the pH value is noted down 3 readings are taken and its average is taken as the final value.

PRECAUTIONS:

1) Before making any new measurement meter should be washed with distilled water.

2) After the experiments are done, the meter should be kept dipped in distilled water(pH7)

Calorific Value

Apparatus: Bomb calorimeter (Make: IKA C200), oxygen filling station (IKA C248), oxygen, decomposition vessel (C5010), weighing balance, cold water etc.

Theory:

Combustion is carried out in a calorimeter under specific conditions. The decomposition vessel is filled with a weighed fuel sample, the fuel sample is ignited and the temperature increase in the calorimeter measured. The specific calorific value of the sample is calculated as follows:

$$Ho = (C \times DT - Q_{External1} - Q_{External2}) / M$$

Where,
M = Weight of fuel sample
C = Heat capacity of calorimeter system. (decomposition vessel)
DT = Calculated temperature increase of water in inner vessel of measuring cell
$Q_{External1}$ = Correction value for the heat energy generated by the cotton thread as ignition aid
$Q_{External2}$ = Correction value for the heat energy from other burning aids

Procedure:

1) Take 0.5 – 1.00 gm of sample in a crucible.
2) Place the crucible in a decomposition vessel. (SS vessel).
3) Attach the burning thread between electrical igniter and sample.
4) Close the decomposition vessel and fill with 99.95 % pure oxygen. The pressure of the oxygen should be maximum 30 bar.
5) Place the decomposition vessel in calorimeter system and start analysis. The water required in the system should be maintained at 25 Deg.C.
6) It takes 17 min to complete the measurement and result will be displayed at the end of analysis.
7) After every measurement, clean the decomposition and crucible with water (sometime with acetone) and tissue paper.

Precautions:

1) It is essential that the sample fully combusts to ensure correct determination of calorific value. After each experiment check the crucible and the entire solid residue for signs of incomplete combustion.
2) The sample weight should be such that the temperature rise during the measurement is below 4 K. In other words, the calorific value of the weighted sample should not exceed 40,000J.
3) This instrument is used to determine the calorific value of solid and liquid materials.
4) For measurement of unknown samples, leave the room or keep safe distance from the calorimeter.

RESULTS:

a) Flash point:

b) Kinematic viscosity:

c) Density:

d) Cloud point:

e) Pour point:

f) pH:

g) Calorific value:

This lab experiment is designed and formulated by the Biosynth team that is working on a institute sponsored project on the production and utilization of biodiesel - a renewable energy source.