

Biodiesel Production and Process Optimization

Rajarshi Kar, Oindrila Gupta, Mukundu Kumar Das

Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India

Abstract- "In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted.."

Rudolf Diesel.

In this project we have intended to prepare biodiesel from waste mustard oil. To make it economically feasible, a proper balance have to be struck between the raw material cost & the selling price of biodiesel as well as that of the byproduct glycerin. The variables affecting the yield and characteristics of the biodiesel produced from used frying oil were studied, the achieved results were analyzed and a set of recommendations were proposed.

Objective of the work:

To study the production of biodiesel from waste mustard oil and its process optimization

I. INTRODUCTION

Biodiesel refers to a vegetable oil- or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) with an alcohol.

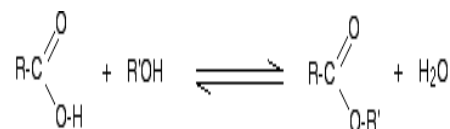
Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petro-diesel. Biodiesel can also be used as a low carbon alternative to heating oil.

Biodiesel is liquid which varies in color between golden and dark brown depending upon the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. Typical ethyl ester biodiesel has a flash point of about 130°C, biodiesel has a density of about 0.88 gm/cm³, less than that of water. A biodegradable transportation fuel that contributes no net carbon di oxide or sulfur emission to the atmosphere and is low in particulate emission. Ultra Low Sulfur Diesel fuel(ULSD) fuel, which is advantageous because it has virtually no sulfur content. Biodiesel has very good lubricating properties, significantly better than standard diesel which can prolong engine's life. As a result, Biodiesel can now compete with other alternative fuels and clean-air options for urban transit fleets and government vehicles across the country. It is safe, biodegradable and reduces air pollutants such as particulates, carbon monoxide and hydrocarbon. A variation in biodiesel energy density is more dependent on feedstock used than the production process.

II. REACTION INVOLVED

Esterification Reaction: The basic process of converting waste oil to biodiesel is called Esterification. Carboxylic acid reacts readily with alcohols in the presence of catalytic amount of mineral acids to yield compounds called esters. The process is called esterification.

The esterification reaction is both slow and reversible. The equation for the reaction between an acid RCOOH and an alcohol R'OH (where R and R' can be the same or different) is:



Transesterification

Triglycerides (1) are reacted with an alcohol such as ethanol/ methanol (2) to give ethyl/ methyl esters of fatty acids (3) and glycerol (4):

Animal and plant fats and oils are typically made of triglycerides which are esters containing three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol.

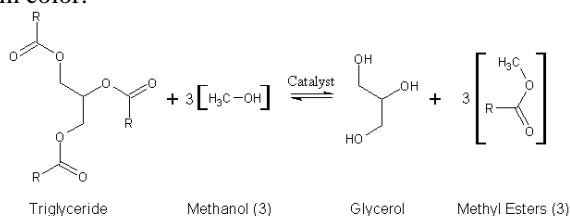
Normally, this reaction will precede either exceedingly slowly or not at all. Heat, as well as an acid or base are used to help the reaction proceed more quickly. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants but catalysts.

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). However, biodiesel produced from other sources or by other methods may require acid catalysis which is much slower. Since it is the predominant method for commercial-scale production, only the base-catalyzed transesterification process will be described below.

An example of the transesterification reaction equation, shown in skeletal formulas:

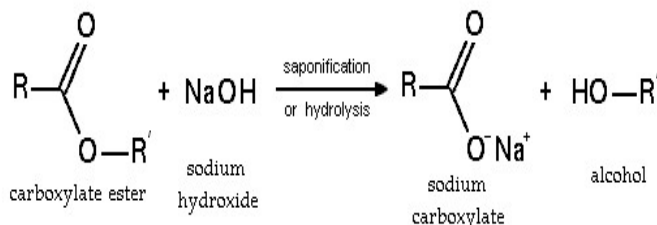
During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkali (NaOH, KOH, or Alkoxides). The main reason for doing a

titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. Empirically 6.25 g / L NaOH produces a very usable fuel. One uses about 6 g NaOH when the WVO is light in color and about 7 g NaOH when it is dark in color.



The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure

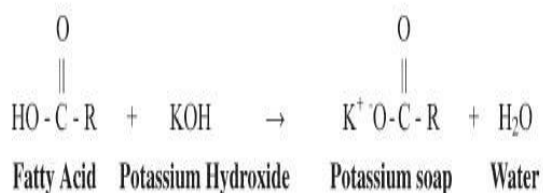
Ester Hydrolysis



Soap Forming Reaction

Acid Catalyzed Pretreatment

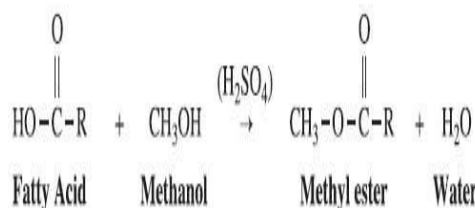
Special processes are required if the oil or fat contains significant amounts of FFAs. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to these feedstocks, the free fatty acids react with the catalyst to form Soap and water as shown in the reaction below:



Fatty Acid Potassium Hydroxide Potassium soap Water

Up to about 5% FFAs, the reaction can still be catalyzed with an alkali catalyst but additional catalyst must be added to compensate for that lost to soap. The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap inhibits separation of the glycerol from the methyl esters

and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters as shown in the following reaction:



Fatty Acid Methanol Methyl ester Water

This process can be used as a pretreatment to convert the FFAs to methyl esters and thereby reduce the FFA level. Then, the low FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters. As shown in the reaction, water is formed and, if it accumulates, it can stop the reaction well before completion. Removal of this alcohol also removes the water formed by the esterification reaction and allows for a second step of esterification or proceeding directly to alkali-catalyzed transesterification. Note that the methanol-water mixture will also contain some dissolved oil and FFAs that should be recovered and reprocessed. Soapstock, a mixture of water, soaps, and oil, is dried, saponified, and then esterified with methanol or some other simple alcohol using an inorganic acid as a catalyst. The procedure relies on a large excess of alcohol and the cost of recovering this alcohol determines the feasibility of the process.

When oils with free fatty acids are used, free fatty acids will be turned into soaps by the alkali catalyst. As a result, the yield of biodiesel is lowered for those oils, and the soap needs to be removed. The process used cleaning the biodiesel is known as "washing", in particular used for removing soaps. This process involves either bubbling water up through the biodiesel (after glycerin separation), or mixing water down on the top and letting it flow down through the biodiesel. Water pulls the soaps out of biodiesel as it passes through. The water eventually settles to bottom, and can be separated readily from the biodiesel.

Process Details

- **Feedstock:** Waste Mustard Oil
- **Chemicals Required:** Sodium hydroxide as a catalyst for transesterification reaction, Ethanol as a reagent, distilled water.
- **Equipments used:** A batch reactor with condenser, a stirrer, clamp, a heater, Digital temperature indicator (0 – 250 °C), Thermometer (0 – 250 °C) x 2 nose, Beaker (1 L capacity) x 2 nos, Cylinder (1 L capacity) x 2 nos, Conical flask (100 cm³) x 2 nos, Flash distillation apparatus with mantel heater for 1 L flask, Separating funnel Iron stand with ring holder (2 nos.), Rubber tube (½ inch dia.) x 1 roll (50m), measuring cylinder. Pipette, glass rod, PET bottles for biodiesel storage, a batch distillation unit, PH strip, filter paper.

➤ **Making a small batch biodiesel using Waste Mustard Oil:**

- Filter and dewater waste mustard oil by using filter paper since it may contain contaminants which oil acidic(rancid).
- Waste mustard Oil (3L) is heated to 50-60 °C for 10 minutes and then cooled.
- Firstly, 30grms of sodium hydroxide is mixed slowly with alcohol in a three-necked round bottom flask, stirring continuously.
- Oil is poured slowly in the prepared Sodium ethoxide mixture with continuous stirring and then heated at 50-60 °C for about 90 minutes.
- The alkalinity of the oil is measured by using pH strip during reaction. The color of the Ph strip shows the mixture is alkaline.
- Now the whole system should be cooled and the mixture allowed settling for at least 12 hours. But we kept it for three days.
- At the end of three days, the mixture separated to impure Biodiesel (upper layer) and impure Glycerin (lower layer) using a separating funnel.
- The separated layer of Biodiesel is then fed to a batch distillation unit for the recovery of ethanol and water. The temperature is maintained around 105 °C.
- The residue (biodiesel + soap) collected is taken in a beaker.
- The impure Biodiesel is washed with water. Two layers are formed, upper layer being Biodiesel and the lower layer being water.
- Now the Biodiesel is separated from the water by a separating funnel.
- This Biodiesel may contain a small percentage of water and so it is then dried by passing through silica gel.
- The impure Glycerin (colored) is treated with activated carbon and then filtered through a Buchner funnel.
- The amount of Biodiesel, Alcohol (recovered) and Glycerin are measured and noted.

III. BIODIESEL FROM WASTE MUSTARD OIL:
PROCESS STEPS

Heating of Oil

In order to speed up the reaction, the waste mustard must be heated. The ideal temperature range is 50° C to 60° C. Heating with electric elements is usually the easiest way to bring the oil up to temperature. Heat the oil first to remove any water content. Waste oil will probably contain water, which can slow down the reaction and cause saponification (soap formation). The less water in the oil the better. So waste mustard oil is heated to 50-60°C for 10 minutes and then cooled.

Proportion of Mustard oil, Sodium Hydroxide (alkali catalyst) and Ethanol taken are as follows:

Mustard Oil: Volume (3 L) * Density (910 g/L) = 2730 g
Sodium Hydroxide : 1% of Oil = 1% of 2730 g

= 27.3 g
~ 300 g

Ethanol: 3 moles of 100% C₂H₅OH per mole of oil
= (3 * 138) g
= 414 g

So, for 90% alcohol, amount taken = (414/.90) g
= 460 g
~ 500g

Mixing of ethanol and catalyst

The purpose of mixing ethanol and the catalyst (NaOH) is to react the two substances to form ethoxide. Firstly, NaOH is mixed slowly with alcohol in a three-necked round bottom flask, stirring continuously. NaOH does not readily dissolve into ethanol. It is best to turn on the mixer to begin agitating the ethanol and slowly pour the NaOH in. When particles of NaOH cannot be seen, the ethoxide is ready to be added to the oil. This can usually be achieved in 20 –30 minutes.

Heating and mixing

Oil is poured slowly in the prepared Sodium ethoxide mixture with continuous stirring and then heated at 50-60 °C for about 90 minutes. A full speed propeller coupled to an electric motor works fine as a mixer. Too much agitation causes splashing and bubbles through vortexing and reduces mix efficiency. There should be a vortex just appearing on the surface. Adjust the speed, or the pitch or size of the stirrer to get the right effect. The transesterification process separates the ethyl esters from the glycerin. Now the whole system should be cooled and the mixture allowed settling for at least 12 hours. But we kept it for three days.

Settling and separation

The ethyl esters (biodiesel) will be floating on top while the denser glycerin will have congealed on the bottom of the container forming a hard gelatinous mass. Then carefully decant the biodiesel. This can be done by draining the reactants out of the bottom of the container through a transparent hose. The semi-liquid glycerin has a dark brown color and the biodiesel is honey-colored. Keep a watch on what flows through the sight tube. When the lighter-colored biodiesel appears divert it to a separate container. If any biodiesel stays with the glycerin it is easy to retrieve it later once the glycerin has solidified. If you left the mixture in the tank until the glycerin gelled, reheat the tank just enough to liquify the glycerin again.

The separated layer of Biodiesel is then fed to a batch distillation unit for the recovery of ethanol and water. The temperature is maintained around 105 °C. The impure Biodiesel is washed with water. Two layers are formed, upper layer being Biodiesel and the lower layer being water.

Now the Biodiesel is separated from the water by a separating funnel. This Biodiesel may contain a small percentage of water and so it is then dried by passing through silica gel.

Draining of Glycerol

After the transesterification reaction, one must wait for the glycerol to settle to the bottom of the container. This happens

because Glycerol is heavier than biodiesel. The settling will begin immediately, but the mixture should be left a minimum of eight hours (preferably 12) to make sure all of the Glycerol has settled out. The Glycerol volume should be approximately 20% of the original oil volume. The impure Glycerin (colored) is treated with activated carbon and then filtered through a Buchner funnel. Volume of glycerin obtained near about 690ml.

Soap residue:

Suspended in the biodiesel will also be some soapy residues. These are the result of Na⁺ ions from the NaOH reacting with water created when the ethanol bonds with the ester chains along with any other water that was suspended in the oil. If the reaction produces more than the usual amount of soap, this happens when NaOH comes into contact with water before it has a chance to react with the oil. In this case the excess water should have been boiled off.

The part of the process where it is vital to keep all water out of the reaction is when making the sodium ethoxide. Keep the vessels NaOH comes in contact with as dry as possible. The chances of a good clean splitting of ester from glycerin with little soap by-product are much better on a warm dry summer day than on a damp winter day.

Washing Biodiesel

The purpose is to wash out the remnants of the catalyst and other impurities. There are three main methods:

- Water wash only (a misting of water over the fuel, draining water off the bottom)
- Air bubble wash (slow bubbling of air through the fuel)
- Air/water bubble wash (with water in the bottom of the tank, bubbling air through water and then the fuel)

Which method works the best is dependent on the quality of the fuel. Washing Biodiesel with water is the oldest and most common method of cleaning biodiesel. Raw unwashed biodiesel is about 3% ethanol. Ethanol is a solvent; it captures soap and other impurities and holds them dissolved in the biodiesel. Water soaks up that ethanol, releasing impurities to be washed away with water. Water washing is the most flexible way to purify biodiesel.

The process of washing biodiesel involves mixing it with water. Water is heavier than biodiesel and absorbs the excess alcohol, sodium hydroxide, and soap suspended in it. After washing and settling, the water and impurities in the water can be drained from the bottom of the container. Several water cycles are generally needed. The first water drained off the bottom of the biodiesel will be milky, and the final wash water drained off will be clear. Excess sodium hydroxide in biodiesel will form soap when mixed with water, and it takes a while for the soap to settle out.

Depending on the method use, it takes roughly as much as biodiesel for a wash cycle. Initial washing must involve gently mixing the formation of soap that will take time to settle out. However, you want the mixing to be thorough and for the water to be dispersed throughout the biodiesel oil. Mustard oil based will

have better cold weather flow characteristics than from coconut oil or animal fat.

IV. OBSERVATION AND RESULTS

Amount of waste mustard oil taken = 3liter

Mustard oil density = 910g/l=2730g

Amount of catalyst (NaOH) taken = 30g

Amount of ethanol = 500ml

pH of mixture = 7(indicates alkalinity)

Volume of impure biodiesel after reaction (V1) = 2800ml (94%)

Amount of ethanol loss due to vaporization = 20ml

After Flash distillation,
 Amount of ethanol recovered (V2) = 30ml

Volume of unwashed biodiesel (V3) = 2800ml

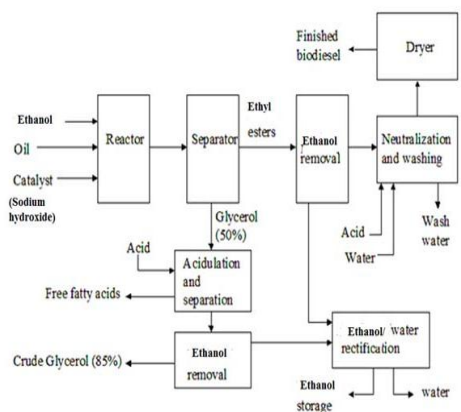
Volume of pure biodiesel = 2750ml

Comparative Study:

Characteristics	Diesel	Biodiesel
Color	Golden	Golden and dark brown
Density, kg/m ³	0.84	0.88
Flash point, °C	60 to 80	130
Fire point, °C	78	138
Viscosity, mm ² /s@40°C	1.3-4.1	1.5-4.0
Aniline Point, °C	42	54
Pour point, °C (summer)	18	10
Calorific Value, MJ/L	38.3	36
Boiling Point, °C	180 to 340	315 to 350

Comparative study between diesel and biodiesel

Figure: Process Flow Chart for Production of Biodiesel And By- product from waste Mustard Oil



Biodiesel: Physical Characteristics

Properties	Values
Color	Golden & Dark Brown
Specific Gravity	0.88
Aniline Point °C	54 °C
Diesel Index	43
Cetane Number(CN)	40
Flash Point °C	130 °C
Fire Point °C	138 °C
Kinematic Viscosity @40°C	1.5 to 4.0
Gross calorific value	10800

American Petroleum Institute (API) gravity

$$API\ gravity = \frac{141.5}{SG} - 131.5$$

Diesel Index (DI) = (Aniline point °F*degree API)/100

Cetane Number = Diesel Index - 3

Gross Calorific Value = 12400 - 2100 * ρ²

where ρ is the density

Suggestion for future work

Biodiesel is not yet cost competitive with petroleum diesel. In order to become more competitive, it is crucial to lower the production costs associated with biodiesel. The cost of raw

material consists of as much as 70-95% of the total production cost of biodiesel. The raw materials include oil, alcohol and a catalyst. In order to reduce the production cost, it is most beneficial to use waste cooking oil, as this is readily available and at a low price. Waste mustard oil presents problems in the form of excess water and free fatty acid composition of the oil

The best catalyzed transesterification of waste mustard oil with ethanol is most economic decision. An alkali catalyzed reaction allows for a low temperature and pressure with high conversion. An alkali catalyzed reaction would require an esterification pretreatment step in order to reduce the concentration of free fatty acids and dewatering process in order to create biodiesel suitable for vehicle consumption.

The problem of solidifying the biodiesel from waste vegetable oil in cold weather conditions should be rectified in future work by some kind of additives which are cheaply available in the market

The Future of Biodiesel fuel

BIO-DIESEL is diesel made from animate source (using plant oil and animal fats). Bio-diesel is basically comprised of short-alkyl esters, made from animal fats and plant seeds.

With increase in the demand of petroleum products the prices of petrol & diesel are increasing world wide. This trend is expected in years to come as the resources are also depleting. Hence alternative sources of energy for running our generators, automobiles etc. are being considered world wide.

The possibility of obtaining oil from plant resources has aroused a great interest and in several countries, vegetable oil after esterification being used as 'Biodiesel'.

Biodiesel is a nontoxic, biodegradable replacement of the petroleum diesel. The vegetable oils are treated with alcohol ethanol or methanol and alkali. The products of the reaction are Biodiesel and glycerol. Chemically biodiesel is monoalkyl esters of long chain fatty acid and its properties are similar to petrodiesel. The biodiesel can be used as 20% blend with petrodiesel in existing engines without any modification. Both the edible and non edible vegetable oils can be used as the raw materials for the biodiesel. Considering the cost and demand of the edible oils the non edible oils may be preferred for the preparation of biodiesel in India.

Biodiesel is a substance that preserves air quality. This type of fuel is designed to enhance the richness of a diesel automobile. Various organizations are setup to control air pollution and find new sources of fuels for vehicles. Not only does biodiesel help the environment, it also assists people is using a lower cost means of transportation. It is a more harmless method than the now used petroleum diesel. Biodiesel is created from nature oils and fats that can be gathered from anyone's gardens.

The future of biodiesel is growing. More companies are offering this solution to the consumers. At this stage, only diesel powered automobiles can use the new fuel. This is expected to change in the upcoming years. The mounting concern of off-shore oil as well as the environmental issues has groups in an uproar. Already there are several types of companies using biodiesel as their main source for transportation.

Biodiesel fuel also has its own advantages and disadvantages. The biggest advantage of biodiesel is that it can

play a significant role in reducing the harmful carbon dioxide emissions. However, there do exist some drawbacks of biodiesel which may become a hindrance in the introduction of biodiesel as an alternative to the harmful carbon emitting fossil fuels. Biggest advantage of biodiesel fuel is that it is non toxic and biodegradable, which makes it one of the most environment friendly alternative of power generation.

After completion of our actual experiment in the biodiesel production, we have obtained our desired compatibility with petroleum diesel. The flash point, pour point, calorific value, fire point, kinematic viscosity, density etc has been satisfactory taking into consideration the possibility of errors here. So our observation is compatible within the limits of experimental errors

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AUTHORS

First Author – Rajarshi Kar, Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India, Email: rajarshi.kar6@gmail.com

Second Author – Oindrila Gupta, Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India, Email: oindrila.gupta@gmail.com

Third Author – Mukundu Kumar Das, Chemical Engineering Department, Heritage Institute of Technology, Kolkata, India