Biodiesel: Making Renewable Fuel from Waste Oils

Introduction

Biodiesel is a renewable fuel made from any biologically based oil, and can be used to power any diesel engine. Now accepted by the federal government as an environmentally friendly alternative to petroleum diesel, biodiesel is in use throughout the world. Biodiesel is made commercially from soybeans and other oilseeds in an industrial process, but it is also commonly made in home shops from waste fryer grease. The simple chemistry involved in small-scale production can be easily mastered by novices with patience and practice. In this exercise, students will learn the process of making biodiesel and practice some analytical techniques.

Dr. Rudolf Diesel first demonstrated his diesel engine to the world running on peanut oil in the early 1900’s. The high compression of diesel engines creates heat in the combustion cylinder, and thus does not require a highly flammable fuel such as that used in gasoline engines. The diesel engine was originally promoted to farmers as one for which they could “grow their own fuel”. Diesels, with their high torque, excellent fuel efficiency, and long engine life are now the engine of choice for large trucks, tractors, machinery, and some passenger vehicles. Diesel passenger vehicles are not presently common in the United States due to engine noise, smoky exhaust, and cold weather starting challenges. However, their use is quite normal in Europe and Latin America, and more diesels are starting to appear in the US market.

Over time, the practice of running the engines on vegetable oil became less common as petroleum diesel fuel became cheap and readily available. Today, people are rediscovering the environmental and economic benefits of making fuel from raw and used vegetable oils. Fuel made from waste fryer grease has the following benefits when compared to petroleum diesel:

Using a waste product as an energy source
Cleaner burning: lower in soot, particulate matter, carbon monoxide, and carcinogens
Lower in sulfur compounds: does not contribute to acid rain
Significant carbon dioxide reductions: less impact on global climate change
Domestically available: over 30 million gallons of waste restaurant grease are produced annually in the US

In addition, use of well-made biodiesel fuel can actually help engines run better. Petroleum diesel fuels previously relied on sulfur compounds in the oil to keep engines lubricated. However, sulfur tailpipe emissions are a significant contributor to the formation of acid rain, so regulators have forced the reduction of sulfur in diesel fuel. Biodiesel made from vegetable oil has a better lubricating quality and can help solve engine wear problems without increasing acid rain. For this reason, use of Biodiesel is already common in trucking fleets across the country.
Biodiesel can be readily mixed with diesel fuel in any proportion. Mixtures of biodiesel and diesel fuel are commonly referred to by the percentage of biodiesel in the mix. For example B100 contains 100% biodiesel, B20 contains 20%. Biodiesel can be run in any unmodified diesel engine. Biodiesel is less flammable than diesel. It will gel at a higher temperature (typically around 20F) and thus should be mixed with petroleum fuel in cold weather.

Making Biodiesel Fuel

The process of converting vegetable oil into biodiesel is known as transesterification, which is similar to saponification, the process for making soap. Vegetable oil molecules are triglycerides: they are made up of a heavy glycerol molecule, and three lighter fatty acid chains called esters. Glycerol is too thick to burn properly in a diesel engine at room temperatures, while esters make an excellent combustible material. Thus, the goal is to separate the esters from the glycerol. In this reaction, the vegetable oil molecules are cleaved apart with the catalyst Sodium Hydroxide (Lye), which is a strong base. Then the esters are combined with methanol to become methyl esters, otherwise known as biodiesel. For every liter of vegetable oil, the reaction uses 220 milliliters (22% by volume) of methanol, a powerful alcohol. New oil requires 4 grams of lye per liter of oil, whereas used oil will require somewhat more. The quantity of lye will vary depending upon the quality of our vegetable oil, and will need to be determined by chemical analysis. Students will first practice making fuel from new vegetable oil, which requires a known amount of lye for the reaction. In the second step, students will determine the quantity of lye needed for different used vegetable oils and test the analyses by making fuel from those oils.

SAFETY NOTES! Methanol and lye are dangerous substances and should be handled with caution! Methanol is poisonous to skin, and its fumes are highly flammable. Lye is a strong skin irritant and can cause blindness! Always wear gloves and goggles when working with these chemicals, and keep any sparks or flame away from methanol containers. Work under a chemical hood or other well ventilated space.

Other cautions: Biodiesel fuel made in a school lab is experimental in nature, and should be burned in diesel engines at the users own risk. While well made fuel will not harm a diesel engine, interested students are advised to read further on the subject before actually testing biodiesel in an engine. Do not remove biodiesel fuel from the laboratory classroom.
Procedure: Read over all instructions before you begin

Part 1: Making Fuel From New Vegetable Oil.
1. Put on your gloves and goggles. Everyone must wear protective gear!
2. Measure out 500 ml of new vegetable oil and pour it into a large beaker.
3. Heat 500 ml of new vegetable oil to 50°C on a hotplate using a stirrer. One person in your group should watch the temperature closely so the oil does not overheat.

Perform the following two steps under the chemical hood in laboratory.
4. Measure 110 ml of methanol in a graduated cylinder and pour into your mixing bottle. Cap the methanol bottle and your mixing bottle tightly.
5. Weigh out 2.0 grams of sodium hydroxide (lye) and add to the methanol in your mixing bottle. Cap the bottle and swirl gently for a few minutes until all of the lye dissolves. You now have sodium methoxide in your bottle, a strong base. Be careful!
6. When the lye is dissolved and the oil is up to 50°C, add 500 ml of warm oil to the methoxide and cap the bottle tightly. Invert the bottle once over a sink to check for leaks.

Caution: Be certain that the oil is not over 60°C, or the methanol may boil.

7. Shake the bottle vigorously for at least one minute, then allow your reaction to settle.
8. Over the next 30-60 minutes, you should see a darker layer (glycerol) forming on the bottom of the bottle, with a lighter layer (biodiesel) floating on top. Complete settling of the reaction will require several hours to overnight. Move on to the next step of the exercise while your biodiesel is settling.

Data Analysis Part 1: You may type answers to these questions and attach them to your lab notebook.

1. If the base rate for Sodium Hydroxide (lye) is 4.0 grams per liter of oil, why did you only use 2.0 grams for this batch?

2. How much lye would be used to convert 50 liters of new oil?

3. For a given quantity of new oil, what variables could be changed to effect the reaction?
Part 2: Testing Waste Oil by Titration to Determine the Quantity of Lye

As vegetable oil is used for frying foods, the high heat, water, and food products in the fryer can degrade the oil into various byproducts. One byproduct is the development of free fatty acids in the oil. These acids will act to neutralize some of the lye used in the biodiesel reaction. Since the reaction requires 4 grams of catalyst for every liter of oil, we will need to add extra lye to make up for that neutralized by the free fatty acids. More heavily used oil will tend to be more acid, and thus require larger quantities of lye than lightly used oil. It is important when making biodiesel to use the proper amount of lye for a given oil. Too much lye can result in a solid soap forming in the reaction vessel, and too little lye will result in an incomplete reaction and poor quality fuel. The exact amount of extra lye required is determined by a process called titration. To perform the titration, a known solution of lye is added to a sample of used oil in measured amounts, until a desired pH shift is seen. Because it is difficult to measure the pH of oil, the oil will first be dissolved in isopropyl alcohol to make testing easier. For this exercise, you will determine the quantity of lye needed to make biodiesel from two different oils: one that is heavily used and one that is lightly used.

1. Obtain a sample of used vegetable oil from two different sources. Preferably one will be more heavily used than the other. Label the lightly used oil as sample A, and the heavily used oil as sample B.

2. Using a pipette, syringe, or graduated eyedropper, measure 1.0 ml of oil from one sample into a small mixing beaker. Make a note in your lab book of which oil you are using first: lightly used (A) or heavily used (B).

3. Measure 10 ml of isopropyl alcohol using a graduated cylinder, add this to the oil, and swirl to mix.

4. Test the pH of the oil-alcohol solution using a pH strip.

5. Using a different pipette, add lye-water (from a stock 1% solution of NaOH in distilled water) to the oil-alcohol solution in 0.5ml increments. Add the lye-water carefully so that you are sure to only add 0.5 ml at a time.

6. After each 0.5ml addition of lye-water, recheck the pH with a pH strip. Record the number of 0.5ml additions you make on a tally sheet!

7. Continue adding lye-water until the pH of the solution reaches approximately 8.5. At this point, count the number of ml of lye-water that you added. (Ex. if you added ½ ml of lye-water three times, you added a total of 1.5 ml of lye-water).

8. Calling the number of ml of lye-water that you added “X”, put that number into the following equation:
\[ X + 4.0 \text{ grams} = L \]

\[ L = \text{the total number of grams of lye needed to make biodiesel from 1 liter of this particular oil. Record this number in your lab book.} \]

9. Repeat steps 1 through 7 using a second batch of oil of different quality, and record the value for \( L \) in your lab book. Be sure to keep track of which value for \( L \) refers to which oil sample. You may want to repeat the titration for each oil to be sure of your results.

**If using phenol red instead of pH strips, follow these steps:**
1. Add 5 drops of phenol red to the beaker containing 10 ml of isopropyl alcohol and 1 ml of oil to be tested.
2. The solution will appear yellow at an acid pH, and will turn pink when the pH is between 8 and 9. Add lye-water in 0.5 ml increments, counting as you go, until the oil alcohol solution turns pink or purple and stays that way for 30 seconds or more.
3. The number of ml of lye-water it took to turn the solution pink is “\( X \)”. Refer to the equation above.

**Data Analysis Part 2:** You may type answers to these questions and attach them to your lab notebook.

1. Why is it necessary to perform a titration on used vegetable oil?

2. How much lye will be required to convert 1.0 liters of vegetable oil sample A to biodiesel? Sample B?

3. How much lye will be required for 0.5 liters of each oil: A? B?

4. When biodiesel brewers make large batches of fuel, they typically repeat the titration procedure several times per batch. Why do you think they would do this?

5. Which type of oil do you think requires more lye catalyst, lightly used or heavily used? Why?

6. Can you see any difference in color between the heavily used oil and lightly used oil?

In part 3, you will use the value for L that you determined in step 2 to make fuel from waste oil. This is basically a repeat of the procedure from part 1, except that you will be varying the quantity of lye for each batch.

1. Put on your gloves and goggles. Everyone must wear protective gear while handling chemicals!

2. Measure out 500 ml or more of each waste vegetable oil, and pour it into a large beaker. Mark each beaker “A” or “B” depending on the oil you are using. Obtain two mixing bottles and label one “A” and the other “B”

3. Heat 500 ml of each vegetable oil to 50°C on a hotplate using a stirrer. One person in your group should watch the temperature closely so the oil does not overheat.

4. Measure 110 ml of methanol in a graduated cylinder for each batch and pour into your mixing bottles. Perform this step and the next under the chemical hood. Cap the methanol and mixing bottles when you are finished.

5. Weigh out and add the correct amount of lye for each oil to your mixing bottles. Recap the bottles tightly. Gently agitate each bottle until the lye is dissolved.

6. When the oil samples are up to 50°C, add 500 ml of the proper oil to the each mixing bottle and cap them tightly. Be sure that the oil is not over 60°C to avoid boiling the methanol!

7. Invert the mixing bottle once over a sink to check for any leaks.

8. Shake the bottles vigorously for at least one minute. Allow your reactions to settle.

9. Leave the bottles to settle until next week.

10. Clean up your lab space.

Assessing Your Biodiesel (Week 2)

If your procedure worked correctly, there should be two distinct layers after settling. The darker layer at the bottom is a crude glycerin byproduct, and the lighter layer on top is biodiesel. If you pick up the settling bottle and rock it slightly from side to side, notice how the darker layer is thicker than the fuel floating on top. This higher viscosity of glycerin is one of the reasons that it isn’t suitable for use in a diesel engine at room temperatures. By removing the heavier, more viscous part of the oil, the esters pass through the engine’s injectors and combust that much easier.

It is common to see a whitish third layer floating between glycerin and the biodiesel. This soaplike material is a result of adding too much lye, or having water in the
oil. It should be discarded with the glycerin. Oil can be tested for water content by heating it to the boiling point of water (100° C) and watching for bubbles. After settling for a few days (or a week), biodiesel producers will decant the fuel off the top of the glycerin, pass it through a filter, and use it like diesel fuel in any diesel engine. Many fuel producers further refine the fuel by washing with water before use.

**Cleanup:** Biodiesel can be discarded with other chemical wastes from the school chemistry lab.

**LAB NOTES:**

Sources of Oils:

Data and Calculations: