The Synthesis of Biodiesel from Vegetable Oil

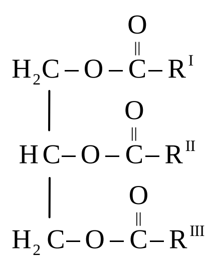
Introduction

The use of reclaimed vegetable oil from restaurants, for use as a fuel for road vehicles, has received a lot of attention in recent years. Used vegetable oils contain solids and free fatty acids due to oil breakdown during the frying process. Normally, the used oil must be filtered and the quantity of the free fatty acids must be determined so that the chemicals necessary for the breaking down of the cooking oil can be calculated.

In this experiment the biodiesel will be made from fresh vegetable oil to avoid the solids and a titration to determine the mass of sodium hydroxide needed to react with the whole oil molecules.

The diesel engine was developed by Rudolf Diesel, a French thermal engineer, in 1893 with the first working prototype in 1897. A diesel engine works by creating heat by compressing air followed by the injection of fuel which burns, increasing pressure to drive the pistons. Early diesel engines were intended to run on peanut oil and were later adapted to run on the lower viscosity and cheaper petroleum diesel. Today, diesel engines are used in cars, buses and trucks. Biodiesel can be used directly in diesel engines or blended with petroleum based diesel fuel.

Vegetable oils are esters of glycerin, commonly called triglycerides, with different fatty acids with the structure:



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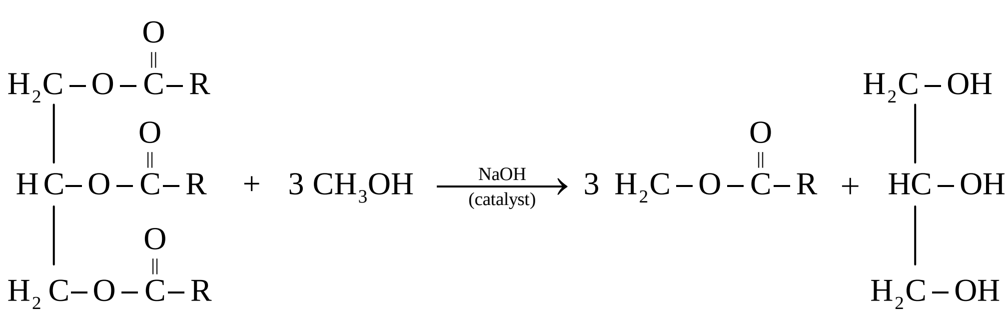
Where R^{I}, R^{II}, and R^{III} can be the same or different fatty acids. (See Table 1)

The preparation of the biodiesel is a transesterification reaction where the triglycerides are converted into simpler methyl esters of the fatty acids (the biodiesel).



Triglyceride methanol fatty acid methyl ester glycerin

Table 1. Fatty acid composition of some common edible fats and oils
Percent by weight of total fatty acids

Oil or Fat	Unsat./Sat. ratio	Saturated fatty acids					Mono unsaturated	Poly unsaturated	
		Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	*Palmitic Acid C16:0*	*Stearic Acid C18:0*	*Oleic Acid C18:1*	*Linoleic Acid (ω6) C18:2*	*Alpha Linolenic Acid (ω3) C18:3*
Canola Oil	15.7	-	-	-	*4*	*2*	*62*	*22*	*10*
Coconut Oil	0.1	6	47	18	*9*	*3*	*6*	*2*	-
Corn Oil (Maize Oil)	6.7	-	-	-	*11*	*2*	*28*	*58*	*1*
Cottonseed Oil	2.8	-	-	1	*22*	*3*	*19*	*54*	*1*
Flaxseed Oil	9.0	-	-	-	*3*	*7*	*21*	*16*	*53*
Grape seed Oil	7.3	-	-	-	*8*	*4*	*15*	*73*	-
Lard (Pork fat)	1.2	-	-	2	*26*	*14*	*44*	*10*	-
Olive Oil	4.6	-	-	-	*13*	*3*	*71*	*10*	*1*
Palm Oil	1.0	-	-	1	*45*	*4*	*40*	*10*	-
Palm Kernel Oil	0.2	4	48	16	*8*	*3*	*15*	*2*	-
Peanut Oil	4.0	-	-	-	*11*	*2*	*48*	*32*	-
Safflower Oil*	10.1	-	-	-	*7*	*2*	*13*	*78*	-
Sesame Oil	6.6	-	-	-	*9*	*4*	*41*	*45*	-
Soybean Oil	5.7	-	-	-	*11*	*4*	*24*	*54*	*7*
Sunflower Oil*	7.3	-	-	-	*7*	*5*	*19*	*68*	*1*

Notes: Percentages may not add to 100% due to rounding and other constituents not listed. Where percentages vary, average values are used.
The symbol C10:0 or C18:2 tells the number of carbon atoms in the fatty acid and the number of carbon-carbon double bonds in the compound

Safety

Safety goggles must be worn at all times in the laboratory

Sodium Hydroxide is caustic both as a solid and in solution. Significant heat is released when the sodium hydroxide dissolves in water. In the event of skin contact, wash the affected area with copious amounts of water. Contact with the eyes can cause serious long-term damage. In the event of eye contact, go to the nearest eyewash and rinse the eyes for up to 15 minutes. Have all areas of contact evaluated by qualified medical personnel.

Methanol is flammable. Work with the methanol away from any ignition source. (NOTE: Hotplates can spark, unseen to the experimenter.) The flame above burning methanol is virtually invisible, so it is not always easy to observe a methanol flame. Methanol vapors are toxic, work in a well ventilated area.

When burning the biodiesel, work in a fume hood.

Disposal

All wastes from the reaction should be placed in a bottle labeled for vegetable oil, glycerin and methanol.

A separate container will be provided for collection of the biodiesel.

Materials Needed

Vegetable oil (soybean, peanut, cottonseed, coconut, or other oil of your choice)
Sodium hydroxide, NaOH, pellets
Methanol, CH_3OH, absolute
Sodium chloride, NaCl
Sodium sulfate, Na_2SO_4, anhydrous
Steel wool
125 mL Erlenmeyer flask
2 - 100 mL or 150 mL beakers
50 mL graduated cylinder
Thermometer, 110° or 120°C
Separatory funnel
Watch glass
Mortar and pestle
Vacuum filtration apparatus: side arm flask with Büchner funnel and filter paper
Magnetic stir bar
Stirring hot plate
pH paper
test tube, 12 x 75 mm
test tube rack
digital thermometer or Lab Pro with temperature probe

Procedure

Measure out 14 mL of methanol and put into the 125 mL Erlenmeyer flask.

Weigh out 0.50g of sodium hydroxide pellets. Crush these pellets in a clean, dry mortar and pestle. Transfer the crushed solid into the flask containing the methanol.

Place a stir bar into the flask, place it on a magnetic stirrer and stir for 5-10 minutes until the NaOH dissolves.

Measure out 60 mL of vegetable oil, determine the mass of the oil and add this to the reaction flask. Heat the flask and its contents to a temperature between 45° and 50°C for 20 to 30 minutes with continuous stirring such that the mixture does not separate into two layers.

While still warm, pour the mixture into a separatory funnel and allow to cool until the mixture separates into two layers. The upper layer will be the biodiesel and the lower layer will be mostly glycerin. Do not let it stand for too long as the lower layer may solidify.

Drain the lower layer into a 100 mL beaker. This solution contains glycerin, unreacted methanol, unreacted sodium hydroxide, a trace of water and salts. In a commercial process, the glycerin and methanol can be collected for reuse. In this experiment, it will be disposed in a waste container labeled for glycerin and methanol.

The top layer in the separatory funnel should be the biodiesel. It will be contaminated with traces of methanol, glycerin, unreacted sodium hydroxide, and some soap which is a byproduct of the reaction. (Soap is the sodium salt of a fatty acid.)

Wash the biodiesel by adding 10 mL of tap water to the separatory funnel. Gently swirl the mixture for about 1 minute to dissolve the methanol, glycerin, sodium hydroxide, and any soap. Do not shake the mixture vigorously as an emulsion may form.

Allow the mixture to separate. Drain of an discard the bottom layer. NOTE: If an emulsion forms, add 0.2 g of sodium chloride and swirl the mixture for 1 to 2 minutes. Allow the mixture to stand. Two layers should form. Drain off the lower layer and discard it in the waste container labeled for glycerin and methanol.

Drain the biodiesel layer into a clean, dry beaker. Vacuum filter the biodiesel using a Buchner filtration apparatus into a clean, dry side arm flask.

Remove any traces of water from the biodiesel by adding 0.5 g of anhydrous sodium sulfate. Swirl the mixture for 1 to 2 minutes. Pour the dried biodiesel into a clean, dry, weighed 50 mL graduated cylinder.

Determine the mass and the volume of the biodiesel.

Evaluation of the Biodiesel

Determination of pH

Add 5 drops of your biodiesel to 1 mL of distilled water and mix thoroughly. Using pH paper, estimate the aqueous pH of your biodiesel.

Freezing point

Biodiesel will “gel” at low temperatures. Transfer approximately 1 mL of your biodiesel to a small test tube. Place the test tube in a test tube rack and place it in the freezer for 15-20 minutes.

Your biodiesel should “gel” in this time. **If your biodiesel does not gel, repeat the drying step.**

Remove the sample from the freezer and immediately add a digital thermometer and record the temperature. Holding the test tube near its top, gently stir the gel with the thermometer and record the temperature when the sample has completely melted.

Clean the thermometer or temperature probe when done.

Combustion Test

Obtain a small wad of clean steel wool. Fluff the steel wool to the size of a ping pong ball. Place the steel wool on a watch glass and determine the total mass.

Place 5 – 10 drops of your biodiesel on the steel wool. Determine the mass of the biodiesel used.

Take the watch glass and steel wool to the fume hood. Ignite the sample with a match.

Record the time it takes for the sample to burn, the color of the flames, and if any smoke or soot is observed.

Does the burning biodiesel have any odor?

Allow the residue and watch glass to cool. Determine the residual mass of the biodiesel after combustion.

References

Harrison, Shallcross, and Henshaw, *Climate Change: Some Chemistry Experiments*, National Science Learning Centre, University of York, 2006

Costello, *Small Scale Biodiesel Production*, Chemistryland.com, web page updated 2011.

Meyer and Morgenstern, *Small Scale Biodiesel Production: A Laboratory Experience for General Chemistry and Environmental Science Students*, *Chem. Educator*, Vol. 10, No. X, 2005

Report Form

The Synthesis of Biodiesel from Vegetable Oil

Name ______________________________ Course/Section ____________

Partner's Name (if applicable) ________________________ Date ____________

Data and Results

Volume of vegetable oil used ________________ mL

Mass of vegetable oil used ________________ g

Volume of the dried purified biodiesel ________________ mL

Mass of the dried purified biodiesel ________________ g

% yield of biodiesel based on mass ________________ %

$$\%\ \text{yield} = \frac{\text{mass of dried biodiesel}}{\text{mass of oil used}} \times 100\%$$

Note: The theoretical yield of biodiesel is 70%

Color of the purified biodiesel ______________________

pH Test

Estimated aqueous pH of your biodiesel ________________

Freezing point

Temperature at which your gelled biodiesel "melted" ____________ °C

Combustion Test

Was the biodiesel easy to ignite?

What color was the flame of the burning biodiesel?

Did you observe any soot or smoke?

Did the burning biodiesel have an odor? If yes, describe it.

Time that your biodiesel sample burned___________________ min

Questions

1. Why do fatty acid esters (the biodiesel) and glycerin separate into different layers?

2. Why would the unreacted methanol and sodium hydroxide be more soluble in the glycerin layer rather than in the biodiesel?

3. Why has the biodiesel better physical properties than the starting vegetable oil for use in an engine?

4. Based on the pH of the biodiesel, do you think it has any corrosive effects on the engine or fuel system?

5. Look up the freezing point of the type of vegetable oil you used in this experiment. Compare that to the freezing point of your biodiesel.

6. Is biodiesel a practical fuel for the northern U.S. or Canada? What options are possible to improve the freezing point characteristics of biodiesel?

7. List four advantages of using biodiesel as a fuel.

8. Explain the difference between renewable and non-renewable resources.

9. In the commercial production of biodiesel, 1.20 x 10^3 kg of vegetable oil produces 1.1 x 10^3 kg of biodiesel. How does your yield compare to this?

10. Find the current price of biodiesel doing an Internet search. Compare that to the current price of diesel fuel made from petroleum. (Note: The retail cost of fuels includes state and national taxes.)

11. One argument against biodiesel being a "green" fuel is that combustion produces CO_2 which is a greenhouse gas. Is it possible to counter this argument from the standpoint of using renewable resources?