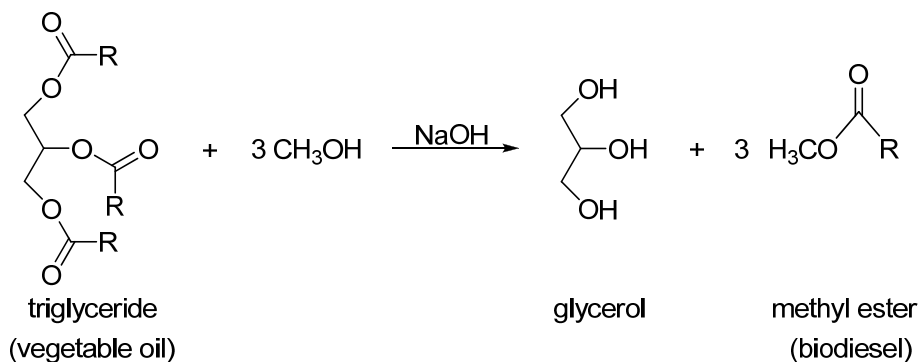


University of Wisconsin
Chemistry 116
Synthesis of Biodiesel*

Research into alternative fuel sources has become increasingly important as the supply of fossil fuel sources dwindles and the costs of fossil fuels increase. Energy sources such as solar energy, wind energy, hydroelectric energy, geothermal energy, and energy from biomass and biofuels are all renewable and environmentally friendly. Biodiesel is an example of a biofuel. Biodiesel differs from petroleum diesel in that it can be made from animal fat, waste vegetable oil (like from a fryer in a restaurant) or from virgin vegetable oil while petroleum diesel is made from petroleum (crude oil). Many different types of vegetable oil may be used; rapeseed and soybean oil are most commonly used, but peanut, coconut, safflower, corn, cottonseed, hemp, algae, jatropha, jojoba, and palm oil among others may also be used.

Biodiesel is made by the transesterification of triglycerides with methanol into methyl esters (biodiesel) and glycerol (waste product) under basic conditions. The R group represents a long chain fatty acid. The principle fatty acids in most vegetable oils are C16, C18, and C20 chains. You will use a GCMS (gas chromatograph-mass spectrometer) to identify the carbon chains in your biodiesel. Since the reaction is in equilibrium, a large excess of methanol is used to drive the reaction to the products. Once the reaction is complete it separates into two layers, with the denser glycerol in the bottom layer and the less dense methyl esters in the top layer.



The specific gravity (or relative density) of a given substance is the ratio of the density of the substance to the density of water (since it is a ratio, it is also unitless). The specific gravity of a substance can be used to determine its purity or to determine if it matches desired standards. Commercial grade grade biodiesel has a specific gravity between 0.86 – 0.90. Specific gravity is measured by a hydrometer; it has a weight at the bottom and a long stem on top. The solution to be measured is poured into a narrow cylinder and the hydrometer is placed in the solution. The distance the hydrometer floats above the solution is used to determine the specific gravity. In a solution with a lower specific gravity, the hydrometer sinks more while in a solution with a higher specific gravity, the hydrometer floats more. You will be constructing a hydrometer from a medicine dropper and calibrating it, then using the hydrometer to measure the specific gravity of your biodiesel.

You will use a soda can calorimeter to measure the enthalpy of combustion (ΔH_{comb}) of your biodiesel. The soda can will be filled with water (specific heat capacity = 4.184 J/g · K) and suspended over the biodiesel. A thermometer in the soda can will provide you with the

temperature change of the water. Remember that at a constant pressure, the heat content q will equal ΔH .

The enthalpy of combustion can be reported in either kJ/mol or kJ/g; the enthalpy of combustion for fuels is typically reported in kJ/g. Weighing the biodiesel before and after combustion will allow you to calculate the change in mass.

Since biodiesel is a mixture of many compounds, it will go through several stages before freezing. As the temperature lowers, the diesel will start to look cloudy; this is called the **cloud point**. As the temperature decreases further, the diesel will start to gel, which is called the **gel point**. Once diesel reaches the cloud point, it begins to clog up the fuel filters and injectors in an engine and prevents fuel from reaching the engine. You will measure the cloud and gel point of your biodiesel by placing it in an ice bath and observing the changes.

Experimental Procedure

You will work in groups of two to collect data. However, each student must record data and observations in his or her own notebook. Discuss with your lab partner how the work in this laboratory period will be divided before beginning.

Use the outline below to assess your progress during the laboratory period. If you find yourself falling significantly behind the schedule outlined below, inform your Lab Instructor.

- 1st Hour:*
1. Collect the required materials for the synthesis of biodiesel.
 2. Mix the reagents and allow the reaction to stir for 45 minutes.
**The GCMS takes about 15 minutes to run. We will begin taking turns on the instrument as soon as the synthesis is done.
 3. Construct and calibrate hydrometer.
- 2nd Hour:*
1. Determine enthalpy of combustion of biodiesel.
 2. Determine specific gravity of biodiesel.
- 3rd Hour:*
1. Determine the cloud/gel point of biodiesel and petroleum diesel.
 2. Determine approximate fatty acid composition of biofuel using GCMS data.

Equipment and Reagents

- 0.675M sodium methoxide
- absolute methanol
- vegetable oil
- pH paper
- dropper
- lock washer
- wick
- wick holder
- soda can calorimeter
- large watch glass
- matches
- 50 mL volumetric flask
- 5 and 10 mL volumetric pipets
- ruler
- rock salt (sodium chloride)
- ice

A. Synthesis of Biodiesel

Weigh a dry, clean 125 mL Erlenmeyer flask and stir bar. Measure 50 mL of vegetable oil and place in empty Erlenmeyer flask; reweigh flask, stir bar, and vegetable oil to determine the mass of vegetable oil. Place the flask on a stir plate and heat to 55 – 60° C. Add 10 mL of 0.675M sodium methoxide solution to vegetable oil. **Sodium methoxide is a strong base; use extreme caution with solution.** Make sure the solution is stirring fast enough to mix properly. Stir the reaction for 45 minutes keeping the temperature between 55 – 60° C. Turn the hot plate off when you reach ~52 or 53 °C. You can turn it back on as needed throughout the synthesis. **Do not allow the reaction to go above 60 °C.** Remove the flask from the stir plate and place on bench top to cool for 10 minutes. Place flask in an ice bath for 5 – 10 minutes until the biodiesel and glycerol separate into two layers and the glycerol layer has solidified. Weigh a dry, clean 125 mL Erlenmeyer flask. Very carefully pour the biodiesel into the clean flask, making sure to leave the glycerol layer and the stir bar in the reaction flask. Weigh the flask with the biodiesel and determine the mass of biodiesel produced. Using the pH paper, determine the pH of your biodiesel.

B. Measuring the Specific Gravity

Constructing your Hydrometer

Fill the medicine dropper approximately half full of deionized water. Expel any water in the long stem. Place the lock washer on the hydrometer through the stem. Place approximately 25 mL absolute methanol in your 25 mL graduated cylinder. Place the medicine dropper, bulb end down, into the graduated cylinder. It will either sink or float. If it sinks, remove it from the methanol and expel water drop wise until it floats. Once it floats, add enough methanol to the graduated cylinder so it is full to the very brim. Adjust the amount of water in the medicine dropper drop wise until it barely floats with approximately 3 - 4 cm length of the stem sticking out of the methanol. Once you have the medicine dropper floating properly, it is ready to use as a hydrometer. Add methanol to the graduated cylinder until it is filled to the brim, then measure the height of the stem sticking out above the surface. The density of methanol and this measured height will be the first data point in a calibration curve.



Hydrometer in Use.

Solution Number	Volume of Water (mL)	Specific Gravity
methanol	0	0.792
1	5	0.826
2	10	0.853
3	15	0.882
4	20	0.910

Calibrating your Hydrometer

You will use four solutions of methanol and water of known specific gravity, along with your measurement of absolute methanol, to calibrate your hydrometer. The calibration solutions will be shared amongst the groups. The TAs will assign you a solution to prepare. The solutions are prepared using a 50 mL volumetric flask and 5 and 10 mL volumetric pipets. The water is pipetted into the flask and diluted to the 50 mL mark with methanol.

Measuring the Height of the Hydrometer

Fill a graduated cylinder with the solution you prepared and gently place your dry hydrometer into the graduated cylinder. Add more of the solution until the cylinder is filled to the brim. Tap the hydrometer gently once or twice to make sure it bobs freely. Use a ruler to carefully measure the height that your hydrometer stem sticks out of the liquid. Record the values to the nearest millimeter (mm). Tap the hydrometer gently and repeat the measurement. This measurement is tricky because it must be made from the liquid surface to the end of the hydrometer stem. The height variations between the solutions are small, so measure the heights carefully and then record the average of the readings in your notebook. Remove the hydrometer from the solution and wipe it off. You will be sharing solution numbers 1-4 with other groups in your lab. *Do not discard the solution! Invite other groups to use your cylinder to calibrate their hydrometers.* Repeat the measurement procedure for each solution in the table. Construct a graph of hydrometer height vs. the specific gravity.

Repeat the above procedure to measure the height of the hydrometer in the biodiesel and calculate its specific gravity.

C. Cloud/Gel Point

Place some ice in a beaker large enough to fit the 25 mL Erlenmeyer flask. For approximately every 100 mL of ice in the beaker, add approximately 33 g of rock salt. Stir briefly to ensure the ice and salt are mixed. Place your remaining biodiesel in a 25 mL Erlenmeyer flask. Place the flask in the salt/ice bath. Swirl the flask and carefully observe the biodiesel. Record the temperature of the cloud point. The cloud point is rather difficult to observe, but the solution will go from clear to cloudy. Continue to

swirl the flask in the salt/ice bath until the gel point is observed. At the gel point, the biodiesel will start to clump up and form a gel. Record the temperature of the gel point. Repeat the procedure for the petroleum diesel.

D. Enthalpy of Combustion

Measure out 100 mL of deionized water and place in the soda can calorimeter. Measure the temperature of the water. Insert a glass stir rod into the holes in the calorimeter and suspend the calorimeter from a ring clamp. Obtain a wick in a wick holder and place it in a clean, dry evaporating dish. Add a few mLs of biodiesel (less than 4 mL), making sure you wet the wick. Weigh the evaporating dish with the wick and the biodiesel. Place the evaporating dish on your stir plate in your student hood (make sure the stir and heat function are off and that the stir plate is at room temperature). Place a wire triangle under the evaporating dish to provide extra stability to avoid the dish accidentally tipping over. Carefully light the wick and lower the soda can so it is directly over the flame. Allow the biodiesel to burn until the temperature of the water in the calorimeter has changed by at least 10 degrees Celcius. Place the large watch glass on the evaporating dish to extinguish the flame. Measure the final temperature of the water in the calorimeter. Once the evaporating dish has cooled, weigh it. Calculate the enthalpy of combustion of biodiesel. If time permits, you may want to repeat this procedure and report an average value for the enthalpy of combustion.



Example of Calorimeter Setup.

D. GCMS Determination of Fatty Acid Composition

With the help of the TA, inject about 1 μL of your biofuel into the GC. The separation takes about 15 minutes to complete. For the GC separation, the polar column is held at a constant temperature of 200°C. When the run is complete, integrate the areas of your peaks and compare to the GCMS run of the methyl ester standard mix. The methyl ester standard mix is 20% in each of the methyl esters derived from the following acids: C16:0 palmitic acid, C18:0 stearic acid, C18:1 oleic acid, C18:2, linoleic acid, and C18:3 linolenic acid. Use the areas of the peaks to determine the relative fatty acid composition of your fuel. Compare to the expected ratio for the vegetable oil you used.

Safety and Disposal Sodium methoxide (NaCH_3O) is a base and will cause burns to the skin. In the event of skin contact with sodium methoxide, wash the affected area with cold water for 5 minutes and notify your TA.

Caution should be taken when using an open flame. Make sure all flammable materials (chemicals, especially methanol, papers, paper towels, etc.) are moved away from the area.

Dispose of pure methanol, glycerol, and methyl ester products (biofuel) in the organic waste container. Dispose of the methanol/water solutions and excess sodium methoxide solutions down the sink with plenty of water. Consult your TA if you are not sure about disposal of a particular material.

Lab Report Your TAs will provide you with details of the report format.

* This experiment was adapted from experiments written by Jeanine Batterton, Chad Wilkinson, José Laboy, Jamie Ellis, and Megan Jacobson. Copyright © 2009 by the Department of Chemistry, University of Wisconsin-Madison