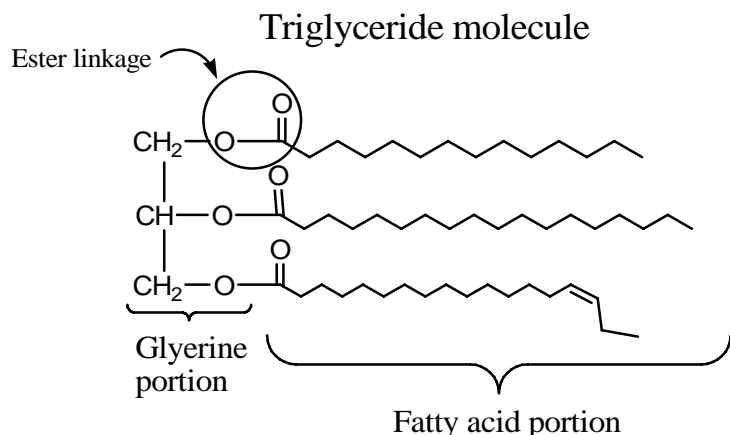


Biodiesel Synthesis

Introduction

The United States is the largest single consumer of fossil fuels in the world. Each year, the U.S. consumes 125 billion gallons of gasoline and 60 billion gallons of diesel fuel. With our current energy consumption and the possibility of a world-wide decline in oil production in the near future, the desire to find alternative feedstocks for our energy needs is increasing. One such alternative feedstock is vegetable oil. Vegetable oil offers the benefits of a more environmentally sensitive synthetic route for obtaining diesel fuel. This fuel source is commonly known as biodiesel, and can be synthesized on an individual vehicle level or on an industrial scale. The methods behind biodiesel synthesis have been known for decades. In recent years, however, there has been significant interest in the production of biodiesel from food industry waste oils. Every year, fast food restaurants in the U.S. produce over 3 billion gallons of used cooking oil. Since many gallons of this used oil inevitably end up in landfills and sewers, the production of biodiesel from waste oil has the potential to significantly reduce environmental impact.

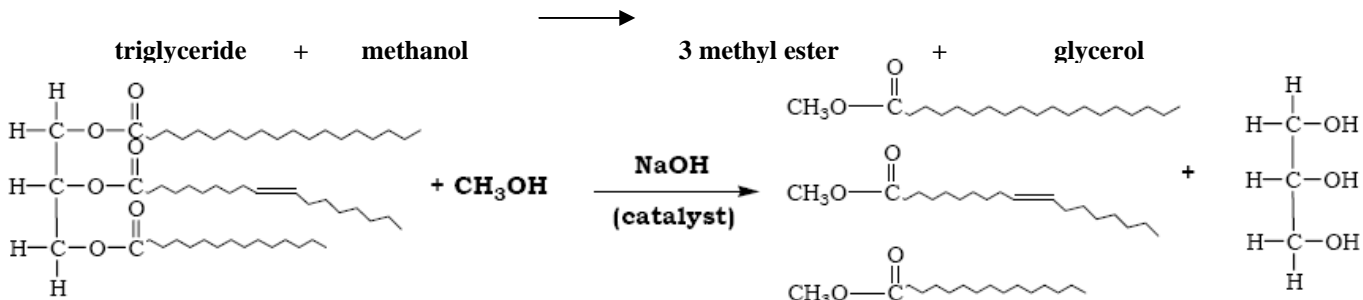
In this experiment you will synthesize biodiesel fuel from vegetable oil. Oils (called triglycerides or triacylglycerols) have a glycerine backbone joined by ester linkages to three fatty acid chains. The chemical structure below shows the different areas within a typical oil (triglyceride) molecule with one of the three ester linkages circled. The fatty acid portions may vary in length between C12 and C18.



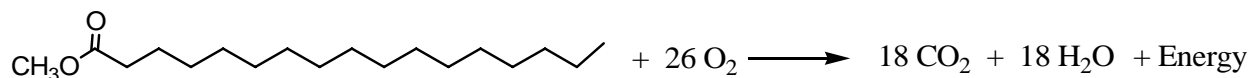
The triglycerides components of some common 'oils' are shown on page 1166 of your Bruice text. Note that different oils (canola, olive, soybean, etc.) differ in the percent composition of fatty acid chain lengths. There is a larger list of oils and their composition at <http://www.scientificpsychic.com/fitness/fattyacids1.html>.

The reaction to form biodiesel from a triglyceride is known as a transesterification reaction (see page 744 of the Bruice text). Transesterification is the process of transforming one type of ester into another type of ester. The reaction is catalyzed by the presence of the strong base, NaOH.

In the first step of the reaction, the NaOH reacts with methanol in an acid base reaction. The products of this first step of the reaction are a very strong base, sodium methoxide, and water. In the second step, the sodium methoxide breaks the glycerine section from the fatty acid section. The separation of the glycerine portion leads to the formation of three methyl esters (the biodiesel) and glycerol. The NaOH is regenerated as a product in the reaction. The biodiesel and glycerol are immiscible and will separate to form two layers. The glycerol layer will also contain NaOH and excess methanol. The separation of the biodiesel and glycerol layer is fortuitous in that we can easily separate and isolate our biodiesel product from the remaining product mixture. The general reaction is shown on the next page.



Biodiesel is a fuel, which means that it produces energy through combustion with oxygen (as does regular diesel). The combustion reaction is shown below:



Note that in the combustion reaction each carbon contained in biodiesel is converted to carbon dioxide. As each carbon is oxidized to carbon dioxide it will release about 850 kJ per mole. The more carbons, the more energy produced upon combustion.

Vegetable oil itself is also a fuel and can undergo combustion with oxygen. If this is so why do we need to convert the vegetable oil (triglycerides) to the methyl esters—why not just burn vegetable oil? The reason is due to the viscosity of the triglycerides. Viscosity is the internal friction or stickiness of a liquid. A viscous material is ‘thicker’ and does not flow quickly (i.e., syrup is a viscous liquid). See <http://www.brevardbiodiesel.org/viscosity.html> for a comparison. The viscosity of vegetable oil will present a problem in that its stickier nature will prevent it from flowing easily through the fuel pump systems of an engine. Since viscosity is generally inversely proportional to temperature, at lower temperatures the viscosity problem is enhanced. Unlike the triglycerides, methyl esters (biodiesel) are less viscous and will easily flow through the fuel system of an engine, though there is some controversy over the type and percentage of biodiesel that can be used in a standard diesel engine due to issues with gelling of the fuel. See <http://www.ag.ndsu.edu/pubs/ageng/machine/ae1305w.htm#cold> for specific numbers.

Experimental Procedure

Note: The following procedure is for synthesizing a biodiesel mini-batch from 100% pure unused vegetable oil. This method can easily be modified for other oils such as canola, olive, soybean peanut etc. You may bring an oil of your choice from home.

1. Prepare a warm water bath in a 250 mL beaker. Use about 50 mL of water and heat the water to 55-60°C. (Do not go over 60° during the reaction period.)
2. Weigh a 25-mL round-bottom flask. Add 10 mL of 100% pure vegetable oil to flask and reweigh to get the weight of the oil. Transfer 2 mL of sodium methoxide solution (be sure the solution is well mixed – should appear cloudy) to the flask. Place a magnetic stir bar in the flask and attach the flask to a water condenser using a cap and an O-ring. (You do not need to run water through the water-condenser.) Clamp the condenser so that the round bottom-flask is close to the bottom of the beaker.
3. Turn on the magnetic stirrer to the highest level possible (may not be the highest setting on the stirrer). Stir for 30 minutes.
4. Transfer the contents of the flask to a 15 mL plastic centrifuge tube. The mixture will separate into two different layers. The glycerol will sink to the bottom, and the methyl ester (biodiesel) will float to the top. Allow the mixture to sit for about 15 minutes, and then place it in a centrifuge and spin for another 5 minutes (don't forget to counterbalance the centrifuge). If the layers have not separated, continue to centrifuge for another 5 minutes.
5. Using a transfer pipet, carefully draw off the top layer of biodiesel and transfer to a 50-mL beaker. Make sure not to get glycerol (bottom darker layer) in the biodiesel. (**Note:** Normally we remove the bottom layer first when we want the top layer. This time we are removing the top layer to make sure that we don't contaminate the biodiesel with the bottom layer. You should leave a little of the biodiesel behind to make sure you don't contaminate it.)
6. Place the beaker of biodiesel on a hot plate and insert a thermometer into the biodiesel, holding the thermometer in place with a clamp. Heat the biodiesel at about 70°C for 15 -20 minutes to remove methanol.
7. Weigh the biodiesel. Use the IR, NMR and GCMS to identify your products.

For the IR spectrum, your instructor will show you how to operate the machine. Look for presence of a carbonyl group and OH group (due to methanol or glycerol impurity).

For the NMR spectrum, add 3-4 drops of your sample to an NMR tube and then add 0.7 mL of CDCl_3 (deuteriochloroform, a common NMR solvent). On the website there is an NMR spectrum of pure vegetable oil. Compare your spectrum to this to determine if you produced biodiesel.

For the mass spectroscopy, place 4 mL of methylene chloride and 1 drop of your product into the special mass spec vial provided by your instructor (Your instructor will tell you how to label the

vial). Cap and return the vial to your instructor. Your sample will be analyzed by the auto-sampler within the next two days.

8. Calorimetry—obtaining the heat of combustion (energy output) of your Biodiesel fuel.

Burning your biodiesel will produce a specific amount of energy (as shown on the combustion reaction on the previous page). We will measure this energy output of your biodiesel using a Calorimeter. By Burning a specific weight of your biodiesel and measuring the temperature increase of the calorimeter we can calculate the heat of combustion (amount of heat/gram) of biodiesel. The formula is given below:

$$H_g = \Delta t W/m$$

H_g is heat of combustion per gram

Δt is the temperature rise in the calorimeter

W is the 'energy equivalent of the calorimeter' which is 2426 calorie/ $^{\circ}C$

m is the mass of your fuel in grams

The heat of combustion for heptane, a common component in regular gasoline was measured to be 11830 cal/g. Can your biodiesel do better than this?