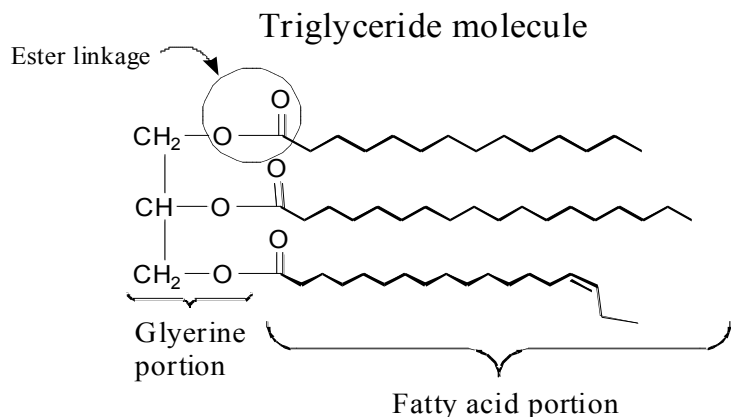


# Biodiesel Synthesis

## 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.

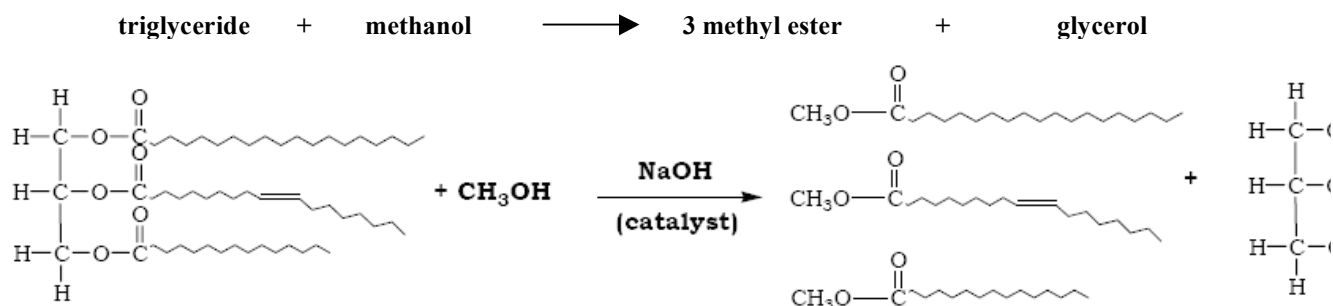
In this experiment you will synthesize biodiesel fuel from vegetable oil. Oils (called triglycerides or triacylglycerols) have a glycerine backbone joined by ester linkages to three fatty acid chains. The chemical structure below shows the different areas within a typical oil (triglyceride) molecule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



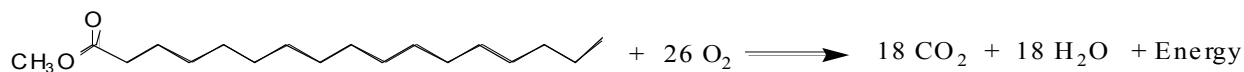
The triglycerides components of some common 'oils' are shown on page 1166 of your Bruice text. Note that different oils (canola, olive, soybean, etc.) differ in the percent composition of fatty acid chain lengths. **There is a larger list of oils and their composition at <http://www.scientificpsychic.com/fitness/fattyacids1.html>.**

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. Warm up 10 mL of 100% pure vegetable oil to about 60°C in a 100 mL beaker. Warming the oil up is not necessary, but increases the reaction rate.
2. Transfer about 2 mL of sodium methoxide solution (be sure the solution is well mixed – should appear cloudy) to a 50 mL beaker with a magnetic stirrer. Stirring gently, add the warm oil. Cover with watch glass and turn up stirrer to position 7 or 8. Stir for about 30 minutes.
3. Transfer the contents of the beaker into 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.
4. Using a transfer pipet, carefully draw off the top layer of biodiesel. Make sure not to get glycerol (bottom darker layer) in the biodiesel.

5. 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  $\text{CDCl}_3$  (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). Note the number on the vial. Cap and return the vial to your instructor. Your sample will be analyzed by the autosampler within the next two days.

Pre-laboratory Questions (Answer on a separate sheet and turn in before the start of lab):

1. What is the chemical name for an oil molecule?

Post-laboratory Questions:

1. Why did the two products of this experiment (glycerol and biodiesel) separate?
2. How many molecules of biodiesel are produced for each molecule of oil?
3. One argument for using biodiesel is that the net amount of  $\text{CO}_2$  released into the atmosphere is claimed to be zero (or near zero). How can this be, given that the combustion of biodiesel released  $\text{CO}_2$  (see reaction equation of previous page)?