Laboratory 5: Transesterification of Vegetable Oil and Alcohol to Produce Ethyl Esters (Biodiesel)

Topics Covered

- Transesterification of vegetable oils or animal fats as a reversible chemical reaction
- The role of catalyst in transesterification of vegetable oils or animal fats
- The use of ethanol (rather than the more common methanol) in biodiesel production
- The importance of temperature and agitation/mixing for the chemical reaction
- Side reactions competing with transesterification
- Separation of co-product glycerol

Equipment Needed (per pair or group)

- 250 mL flask or beaker, and small watch glass or stopper
- 125 mL Erlenmeyer flask and stopper
- Separatory funnel, 250 mL
- Stirring hot plate and 2 magnetic stir bars
- Thermometer
- Aluminum foil
- Weighing scale (readable to 0.01 g)

Reagents Needed (per pair or group)

- Ethanol (anhydrous, 100%)
- 1 gram potassium hydroxide
- 100 grams vegetable oil, tallow, or lard (food grade)

Background Information -- Transesterification

According to the current American Standards for Testing Materials (ASTM), biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines.

One process for making biodiesel is called transesterification. This is a chemical reaction in which 1 mole of triglycerides (vegetable oil or animal fats) reacts with 3 moles of alcohol to produce 3 moles of alkyl esters (biodiesel) and 1 mole of glycerol, a co-product. This is a reversible, equilibrium reaction and requires excess alcohol to push it toward the products side. Usually, 6 moles of alcohol are used per 1 mole of triglycerides. Le Chatelier's principle explains this behavior. This principle, named after Henry Le Chatelier, can be summarized as follows:

If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

Typically, a strong base such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used as the catalyst, which normally would not be consumed during this reaction and would end up in the glycerol layer. This is not always the case, as we will see later.

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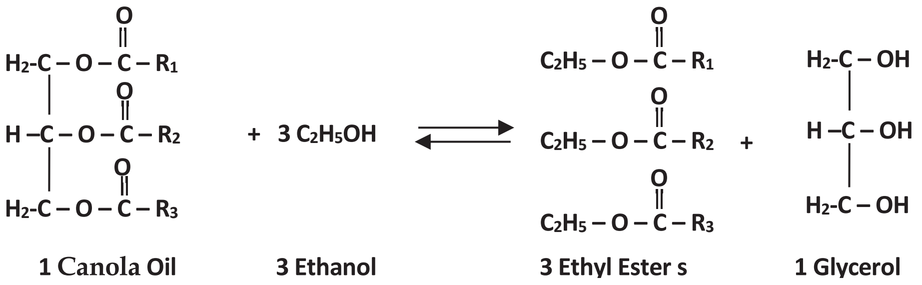
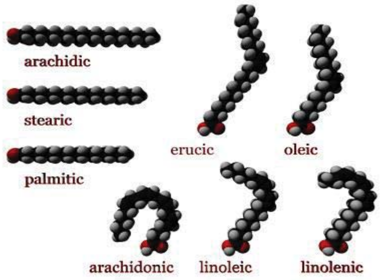
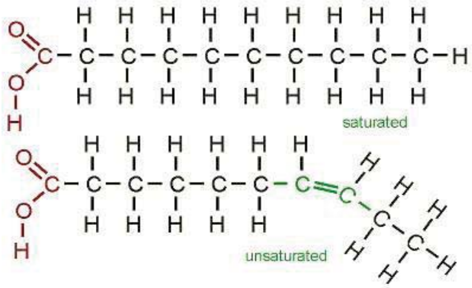


*Figure 1 - **The Transesterification Reaction***

A triglyceride is a molecule made up of three fatty acids attached to a glycerol backbone. Figure 1 shows a depiction of the reaction where the R's represent the fatty acids that make up a triglyceride. The three fatty acids on each molecule could be the same or they could be different. Each oil or fat has a unique fatty acid profile. Canola, for example, is high in oleic acid which is an 18 carbon chain with one double bond. It also contains linoleic acid as well as a number of other less prominent fatty acids.





The fatty acid makeup of the oil or fat is responsible for some of the properties found in the resulting biodiesel. The more *saturated* (no double bonds) the oil or fat is, the more stable the biodiesel (the less likely it is to go rancid). However, the cold flow properties tend to be poorer as the saturation increases. In other words, saturated fats tend to solidify at higher temperatures than do unsaturated oils.

These trends are reversed as the level of unsaturation (number of double bonds) increases. Notice, in the pictures to the left, that unsaturated fatty acids are bent, and therefore do not readily stack up to form a crystalline structure. These crystals are often associated with filter plugging during cold weather. On the other hand, the saturated fatty acids are straight and will stick together to form crystals at higher temperatures, causing biodiesel made from saturated fats to gel (and clog up the engine) even at temperatures significantly above freezing.

You can see in Figure 1 that it takes three molecules of ethanol for each molecule of triglyceride to satisfy a complete reaction. This would be a 3:1 molar ratio of alcohol to oil. Typically in practice, a 6:1 molar ratio is used to drive the reaction to the product side. What happens to the excess alcohol that was not used in the reaction? It is unused at the end of the process and separates partly with the fuel and partly with the glycerol. It can be recovered and reused through a process of distillation.

The transesterification reaction will proceed quickly at first and eventually slow down as it reaches equilibrium. At this point, there will be some unreacted glycerides left in the biodiesel. It is possible to improve the quality by removing the glycerin that has settled out and to run another reaction, thus pushing the equilibrium point further to the products side. For this lab, one reaction should be enough to get a good separation of the glycerin from the biodiesel.

Biodiesel can be made from a variety of feedstocks.

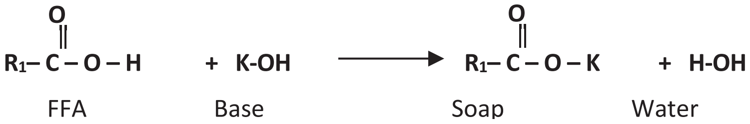
To calculate the mass of alcohol needed to achieve a 6:1 molar ratio, you will need the molecular weights of the triglycerides and the alcohol being used. In this example, canola oil and ethanol are the reactants.

It can be very difficult to calculate the molecular weight of a fat or oil, since they are made up of many different large molecules (trigylcerides), each with different fatty acids attached. For this exercise we will use a value of 877 g/mol for canola.

Ethanol is not completely soluble in fats and oils, so vigorous mixing is required. As the reaction proceeds the product (alcohol esters) acts as a co-solvent, making the two reactants miscible improving contact and interaction.

For most chemical reactions, temperature plays a major role. There is a rule of thumb that states "for every 10 °C rise in temperature the speed of the reaction doubles." To increase the reaction rate, it's relatively easy to increase the temperature. For an unpressurized reactor the temperature should not exceed the boiling point of the alcohol (78 °C for ethanol) for the obvious reason that the ethanol will boil away and the reaction will stop and in some cases reverse. A pressurized reactor, although requiring specialized construction, would allow for a higher temperature reaction and thus a faster reaction rate.

Sometimes an unfortunate side reaction called saponification occurs. This is the process of making soap. Whenever triglycerides (oils and fats), a strong base (sodium or potassium hydroxide), and water come together, soap is formed. Oils and fats used for cooking tend to oxidize due to high temperatures and contact with water. This can cause some of the fatty acids to break off the glycerol backbone and float free. These are referred to as *free fatty acids* (FFA) as shown in Figure 2. They will quickly react with the catalyst to form soaps, destroying some of the catalyst in the process. This reaction proceeds much faster than transesterification. In this case, extra catalyst will be needed to carry out the transesterification reaction. In the case of oils with very high FFA, an acid or enzyme catalyst has to be used to cause the *esterification* of the FFAs to biodiesel.



$$R_1-\overset{\overset{O}{\|}}{C}-O-H \;+\; K\text{-}OH \longrightarrow R_1-\overset{\overset{O}{\|}}{C}-O-K \;+\; H\text{-}OH$$

Figure 2 - ***The Saponification Reaction***

Why is this unfortunate? Soap is a long molecule that has a polar head and a non-polar tail. While polar substances are not usually soluble in non-polar solvents, and vice-versa (like dissolves like), soap has properties of both, making it a perfect substance to clean non-polar oil and grease off your hands using water. However, soap can complicate the separation of the non-polar esters from the polar glycerol, water and alcohol.

Normally, glycerol, water and alcohol are not very soluble in biodiesel. They tend to hang on to each other and separate quickly by gravity from the biodiesel due to their higher combined density. However, the more soap that is present, the more these compounds become soluble in each other. This makes it harder for them to separate, which causes a loss of yield (less biodiesel produced). If a small amount of water is added at the end of the reaction it can shift the phase equilibrium in favor of a more complete separation.

Pre-Lab Exercises

1. Log on to the triglyceride molecular weight calculator: http://www.cals.uidaho.edu/bioenergy/molecularCalculator.asp
2. Check the molecular weights of the fats and oils in the pull-down menu.
3. Compare the molecular weight of rapeseed oil to that of palm kernel oil. What differences do you see in the fatty acid make-up of these two? Why do think there is a big difference in molecular weights of these two triglycerides?

Safety Note: Because of the potentially dangerous chemicals used in this lab, everyone must wear safety glasses or goggles while working in the laboratory. Lab coats or aprons should be worn when pouring or mixing chemicals. If a fire occurs, leave the building immediately. Do not try to fight it!

Laboratory Procedure

The following procedure will be used to make a small batch of biodiesel

1. Calculate the molecular weight of ethanol.
2. Since we are using 100 g of oil, we can use the following relationship to calculate the ethanol needed for a 6:1 ratio of methanol moles to triglyceride moles:

$$\frac{100 \text{ g of oil}}{877 \text{ g/mol}} = \frac{X \text{ g of ethanol}}{6 * (46 \text{ g/mol})}$$

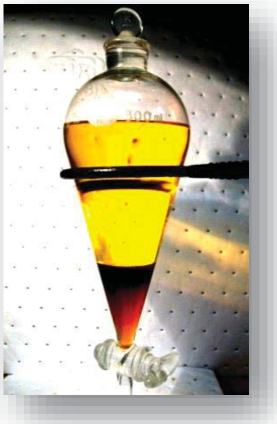
3. Following safe lab procedures, weigh out 1 g of potassium hydroxide into a 125 mL Erlenmeyer flask. Into this same flask add the calculated amount ethanol (from step b).

4. Add a magnetic stir bar, cover with aluminum foil or a watch glass, and place on a stirring hot plate. Mix until the KOH is completely dissolved. Set this aside and go to the next step.

5. Weigh an empty 250 mL Erlenmeyer flask and record the weight in table 1. Into this same flask weigh out about 100 g of the oil or fat to be converted to biodiesel. Again record the exact weight in table 1. Add a stir bar, put on a hot plate, and heat to around 60 °C.

6. Next, add the alcohol/catalyst mixture to the oil in the flask and cover with a watch glass or aluminum foil to keep the alcohol vapors from escaping. Stir this mixture at a moderate level for 60 minutes while holding the temperature at 60 °C.

7. Transfer the mixture to a separatory funnel and allow it to settle for 20 minutes.



8. Remove the glycerin (lower) layer; the upper phase is the biodiesel.

9. **Note**: If there is no phase separation after 5 to 10 minutes, it can be forced by the addition of water. Return the mixture to the 250 mL Erlenmeyer flask, and while stirring, add 15 mL of water and continue to stir for about 10 seconds. Then, return the mixture to the separatory funnel. This action will concentrate the polar molecules of water, ethanol and glycerol and allow them to settle along with a good portion of the soap.

10. Weigh a clean 250 mL beaker or 250 mL Erlenmeyer flask and record the weight in table 1. Next weigh the clean biodiesel and record that weight to be used for the yield calculation.

Observations

How quickly did the glycerol layer form in the bottom of the separatory funnel?

Did you have to add water to effect the separation?

What qualities does the biodiesel have compared to the starting material? (color, smell, viscosity)

What qualities does the crude glycerol have?

Data collection

Table 1

Category	Item	Variable	Quantity (g)
Oil	Flask weight	W_{ini}	
	Flask + sample	W_{end}	
	Net sample size	W_1	
Biodiesel	Flask weight	W_{ini}	
	Flask + sample	W_{end}	
	Net sample size	W_2	

Data processing

a. Calculate the percent yield on a weight basis:

$$\% \text{ Yield} = (W_2/W_1) \times 100$$

where: W_1 = the initial weight of oil or fat
W_2 = the final weight of the finished biodiesel

% Yield = ____________

b. Calculate the average molecular weight of the ethyl esters using the known MW's of oil, ethanol and glycerol and the relationship below:

$$MW_{oil} + 3 \times MW_{ethanol} = 3 \times MW_{ethyl\ ester} + MW_{glycerol}$$

Avg MW $_{\text{ethyl ester}}$ = ____________________