Food or Fuel? (Teacher Notes)

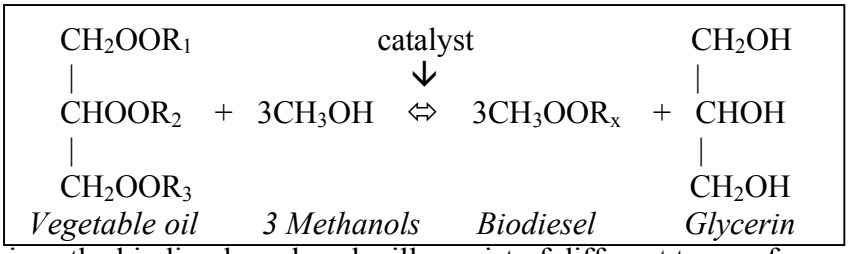
(The Chemistry and Efficiency of Producing Biodiesel)

Background on Biodiesel Production

(It is strongly suggested that the materials adapted for this background: http://www.unh.edu/p2/biodiesel/media/NHSTA-handout.doc be consulted as a one-stop resource for further detail in gathering lecture material).

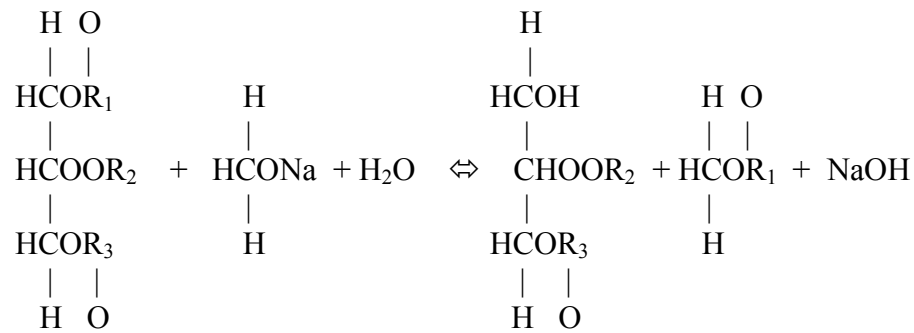
Vegetable oils and animal fats are triglycerides, containing glycerin. The biodiesel process turns the oils into esters, separating out the glycerin. The glycerin sinks to the bottom and the biodiesel floats on top and can be poured off.

The process is called transesterification, is show below. The reaction substitutes alcohol for the glycerin in a chemical reaction, using lye as a catalyst.



R_x is used since the biodiesel produced will consist of different types of mono-alkyl esters, because of the various fatty acids (R_1, R_2, R_3) in the vegetable oil. The reaction can proceed both ways, so it is necessary to add an excess of methanol to force the reaction to the right. Since it is not desirable to have free methanol in the biodiesel fuel, it is then necessary to recover the methanol either by water washing, or a pressure-condensing method. But, the glycerin must be removed first (and actually, most of the excess alcohol stays with the glycerin). If you remove the surplus methanol while the glycerin is still present with the biodiesel, the process will start gradually reversing – biodiesel and glycerin combining to re-make vegetable oil and methanol. The glycerin is more dense than the biodiesel, so it will gradually settle to the bottom in the reactor, simplifying separation.

Now, since we first react the catalyst with the methanol to form a methoxide (potassium or sodium methoxide), the reaction doesn't actually proceed exactly as shown above. If we use NaOH as our catalyst, it combines with methanol (CH_3OH) to form sodium methoxide ($NaO\text{-}CH_3$) and a water: $NaOH + CH_3OH \rightarrow NaOCH_3 + H_2O$. Sodium Methoxide is a quite hazardous material, so it is extremely important to handle it with care – it is explosive and toxic.



Step 1 – triglyceride turns to diglyceride, one methoxide joins freed fatty acid to make biodiesel

1. Notes on Chemicals Needed

The alcohol used can be either methanol, which makes methyl esters, or ethanol (ethyl esters). Most methanol comes from fossil fuels (though it can also be made from biomass, such as wood), while most ethanol is plant-based (though it's also made from petroleum). But the biodiesel process using ethanol is much more difficult than with methanol, strictly not for novices.

Methanol is also called methyl alcohol, wood alcohol, wood naphtha, wood spirits, methyl hydrate (or "stove fuel"), carbinol, colonial spirits, Columbian spirits, Manhattan spirits, methylol, methyl hydroxide, hydroxymethane, monohydroxymethane, pyroxylic spirit, or MeOH (CH3OH or CH4O) -- all the same thing. (But, confusingly, "methylcarbinol" or "methyl carbinol" is used for both methanol and ethanol.)

You can usually get **methanol** from bulk liquid fuels distributors (for large quantities). For small amounts, you can use DriGas fuel line antifreeze, one type is methanol (e.g. "HEET" in the yellow container), another is isopropyl alcohol (isopropanol, rubbing alcohol)→Per the advice on the Kitchen Biodiesel website, make sure to get the methanol type of DriGas because isopropanol does not work for making biodiesel. Methanol is also sold in supermarkets and chain stores as "stove fuel" for barbecues and fondues, but check the contents -- not all "stove fuel" is methanol, it could also be "white gas", basically gasoline. It must be *pure* methanol or it won't work for making biodiesel.

The **lye** catalyst can be either sodium hydroxide (caustic soda, NaOH) or potassium hydroxide (KOH). This lesson chooses to use NaOH because it is often easier to get and it's cheaper to use. With KOH, the process is the same, but you need to use 1.4 times as much (1.4025). Note: Experienced biodieselers making top-quality fuel usually use KOH, and so do the commercial producers. KOH can also provide potash fertilizer as a by-product of the biodiesel process.

You can get both NaOH and KOH from soapmakers' suppliers and from chemicals suppliers. NaOH is used as drain-cleaner and you can get it from hardware stores, but it has to be pure NaOH (not Drano or equivalent, no colored granules).

CAUTION:

Lye (both NaOH and KOH) is dangerous -- don't get it on your skin or in your eyes, don't breathe any fumes, keep the whole process away from food.. Lye reacts with aluminum, tin and zinc. Use HDPE (High-Density Polyethylene), glass, enamel or stainless steel containers for methoxide.

2. Lye

You need to be quick when measuring out the lye because it very rapidly absorbs water from the atmosphere and water interferes with the biodiesel reaction.

How much to use: For a 1L batch of biodiesel, NaOH must be at least 96% pure. Use exactly 3.5 grams. If you're using KOH it depends on the strength. If it's 99% pure (rare) use exactly 4.9 grams (4.90875). If it's 92% pure (more common) use 5.3 grams (5.33). If it's 85% pure (also common) use 5.8 grams (5.775). Any strength of KOH from 85% or stronger will do the job.

3. Mixing the methoxide

Methanol also absorbs water from the atmosphere so do it quickly and replace the lid of the methanol container tightly. Don't be too frightened of methanol, if you're working at ordinary room temperature and you keep it at arm's length, you won't be exposed to dangerous fumes.

Shake the container a few times -- swirl it round rather than shaking it up and down. The mixture gets hot from the reaction. If you swirl it thoroughly for a minute or so five or six times over a period of time the lye will completely dissolve in the methanol, forming sodium methoxide or potassium methoxide. As soon as the liquid is clear with no undissolved particles you can begin the process.

[Tip: The more you swirl the container the faster the lye will dissolve]. Experienced biodieselers comment that with NaOH it can take from overnight to a few hours to as little as half-an-hour with lots of swirling; but the micro-scaled version used in this lab will take 10-15 minutes. (Remind students not to be impatient and that it may take 5 or 6 swirls to get it to dissolve, wait for ALL the lye to dissolve). Mixing KOH is much faster, it dissolves in the methanol more easily than NaOH and can be ready for use in 10 minutes].

Some Additional Notes on Materials and Safety:

A few cautions: DON'T mix the methanol and NaOH (lye) in a plastic bottle (the student lab handout is suggesting pint-sized or smaller canning or jelly jars) as NaOH attacks some types of plastic. Once the methoxide is mixed, though, it is quite acceptable to mix your biodiesel in a plastic bottle.

DO NOT allow any WATER into any steps of this procedure.

Again, Do NOT store unused methoxide in plastic bottles. Some plastic will degrade over time when in contact with methoxide.

Methanol boils at about 65°C/148°F. DO NOT mix when the oil is above 60°C/140°F.

The Process Revisited:

If you would like to use a blender, here is a sample process. (The student lab handout processes by shaking.)

Use a spare blender you don't need or get a cheap secondhand one -- cheap because it might not last very long, but it will get you going until you build something better.

Check that the blender seals are in good order. Make sure all parts of the blender are clean and dry and that the blender components are tightly fitted.

Pre-heat the oil to 55 deg C (130 deg F) and pour it into the blender.

With the blender still switched off, carefully pour the prepared methoxide from the High density polyethylene (HDPE) container into the oil.

Secure the blender lid tightly and switch on. Lower speeds should be enough. Blend for at least 20 minutes.

4. Transfer

As soon as the process is completed, pour the mixture from the blender or the mini-processor into the 2-litre PET bottle for settling and screw on the lid tightly. (As the mixture cools it will contract and you might have to let some more air into the bottle later.)

5. Settling

Allow to settle for 12-24 hours.

Darker-colored glycerin by-product will collect in a distinct layer at the bottom of the bottle, with a clear line of separation from the pale liquid above, which is the biodiesel]. The biodiesel varies somewhat in color according to the oil used (and so does the by-product layer at the bottom) but usually it's pale and yellowish (used-oil biodiesel can be darker and more amber). The biodiesel might be clear or it might still be cloudy, which is not a problem. It will clear eventually but there's no need to wait.

Carefully decant the top layer of biodiesel into a clean jar or PET bottle, taking care not to get any of the glycerin layer mixed up with the biodiesel. If you do, re-settle and try again.

6. Analyzing the Product: (this section relates to Q#4 in the student handout)

After allowing the solution to sit for about ten minutes, the beginning of separation can be observed. However, after about eight hours the glycerin molecules will have mostly settled to the bottom of the container and the methyl esters (biodiesel) will be on top.

Student products should now have a bottle containing lighter colored biodiesel on top of a layer of darker “glop.” The biodiesel will be very cloudy, and it will take a day or two more for it to clear.

Typically the “glop” layer is about the same or a bit more than the amount of methanol used. Methanol makes up approximately 10% of the Biodiesel, but to force the reaction, an excess is generally added – usually totaling 20% of the volume of the oil (at a larger scale, well designed processors can use methanol recovery systems to recover this surplus methanol after the reaction, after removal of the glycerin).

For a reaction with one liter of oil; 200 ml of methanol is first mixed with 3.5 grams of NaOH, plus any additional NaOH in regards to the free fatty acid titration (only necessary if using used/waste vegetable oil).

Additional Resources

Websites:

- Biomass Glossary from the U.S. DOE's Energy Efficiency and Renewable Energy Information Portal
  http://www.eere.energy.gov/biomass/student_glossary.html
- The U.S. DOE's Alternative Fuels Data Center
  http://www.eere.energy.gov/afdc/fuels/biodiesel.html
- The National Biodiesel Board
  http://www.biodiesel.org/
- Howstuffworks segment on "How Biodiesel Works"
  http://auto.howstuffworks.com/biodiesel.htm
- BECON Biodiesel Education
  http://www3.me.iastate.edu/biodiesel/Pages/biodiesel1.html
- Colorado University's Biodiesel Chemistry presentation
  http://www.cu-biodiesel.org/webPRES/evan.htm

Interactive Excel Spreadsheet:

- Biodiesel-O-Matic.xls

In-depth information on washing fuel and further quality testing:

- Wash test:

This is the most useful all-round test, and it's very simple: Put 150 ml of unwashed biodiesel (settled for 12 hours or more, with the glycerin layer removed) in a half-liter glass jar. Add 150 ml of water, screw the lid on tight and shake it up and down violently for 10 seconds or more. Then let it settle. The biodiesel should separate from the water in half an hour or less, with amber biodiesel on top and milky water below. This is quality fuel, a completed product with minimal contaminants. Wash it, dry it and use it with confidence.

Wash-test with unwashed biodiesel -- left, after a violent 10-second shaking; right, biodiesel and water separated cleanly within minutes. The biodiesel will be cloudy, and the water can be milkier than this, but as long as it separates quickly and cleanly, it passes the test.

But if it turns into something that looks like mayonnaise and won't separate, or if it only separates very slowly, with a creamy white layer sandwiched between water and biodiesel, it's not quality fuel and your process needs improvement. Either you've used too much catalyst and made soap (better titration), or a poor conversion has left you with half-processed mono- and diglycerides, fuel contaminants that act as emulsifiers (better titration, try more methanol, better agitation, longer processing time, better temperature control), or both too much catalyst and poor conversion.

Whichever, you're headed for washing problems. Super-gentle washing techniques might avoid the problems, but you'll still be left with poor-quality fuel laced with contaminants that can cause injector coking and engine damage and they can't be washed out.

If you have an emulsion any thicker than the normal "paper thin" interface layer between oil and water, the batch should be retreated. Retreat as with virgin oil, with the standard 3.5 g of lye per liter of oil but using only 100 ml methanol per liter of oil.

Quality testing, continued.

Aleks Kac, a contributor to the "Journey to Forever" web forum, has provided the following information and some additional quality tests. An extension activity may be coordinated utilizing the following text to spur discussion about fuel quality and subsequent viability.

- "Diesel engines require fuel of a certain quality. You just can't pour poor-quality biodiesel into the tank and expect the engine to go on and on without problems. You have three very dangerous enemies: free glycerin, poorly converted oils/fats and sodium lye. Free glycerin and mono-, di- and triglycerides (poor ester conversion) will form gum-like deposits around injector tips and valve heads, sodium lye can damage the injector pump. The key to good fuel is to just do right and finish it! Use pure chemicals (sulfuric acid, sodium lye and methanol) and measure them accurately -- this will take care of poor conversion. A proper wash will get rid of any glycerin and neutralize the remaining lye.

7. Washing

If you would like to extend the lesson to complete a wash and pass through your own version of standards testing, proceed to www.biodieselcommunity.org/washingasmallbatch, for more information.