Biofuels from plant oils

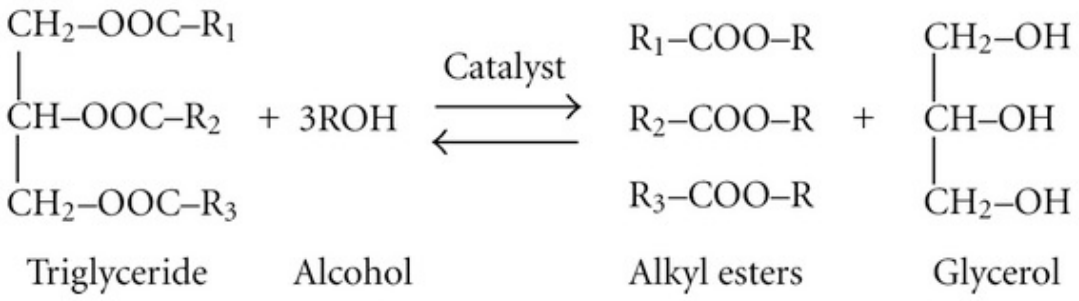
Focus question	How do plant oils become fuel?
Vocabulary	Transesterification, renewable diesel, biodiesel, petroleum diesel, miscible, glycerin, catalyst, ester, fatty acid chains, glycerol, hygroscopic

Diesel engines such as trucks, tractors, and heavy motors rely on No. 2 diesel for power. Diesel is commonly made from petroleum distillation. Renewable substitutes for fossil diesel are growing in popularity. These biofuels can be easily made from corn, soy, and other plant oils; animal fats; and waste grease through chemical reactions.

Biofuels refer to liquid or gaseous fuels commonly used for transportation. These are referred to by the United States Department of Agriculture as 'drop-in fuels', requiring no modification to engines. Biofuel derived from plant materials is among the most rapidly-growing renewable energy technologies. **Ethanol**, made mostly from corn starch from kernels using a process called fermentation, is by far the most significant biofuel in the United States. The remaining amount is **biodiesel**, which is made from vegetable oils (chiefly soy oil) as well as animal fats, waste oils, and greases. (ers.usda.gov/data-products/us-bioenergy-statistics/) Biomass-based diesel fuels include biodiesel and renewable diesel (eia.gov/energyexplained/biofuels/). Typically, 'biodiesel' is the term used for biomass-based diesel from soybean oil, while 'renewable diesel' refers to biomass-based diesel from corn oil.

Biomass-based diesel burns cleaner than petroleum and is derived entirely from biological sources. Environmental Protection Agency (EPA) research indicates that biomass-based diesel emits 11% less carbon monoxide and 10% less particulate matter than diesel. The Department of Energy and Agriculture found biodiesel reduces net carbon dioxide emissions by 78%. Unlike petroleum diesel, which contains sulfur and carcinogenic benzene, two components regulated by the EPA, biodiesel is nontoxic and biodegradable. They are completely **miscible** with petroleum diesel, which allows for easy blending. Biomass-based diesel can be combusted in any diesel engine, without needing to modify the engine.

Vegetable oils are triglycerides and they have a standard structure. A molecule of any given vegetable oil consists of two parts, a glycerol backbone and three distinct fatty acid chains that stem from the glycerol. Biodiesel is produced using the chemical process known as transesterification. **Transesterification** occurs when one type of ester, an oil molecule in this case, exchanges an R group with an alcohol. Today, we will be making biomass-based diesel with oil and methanol. We will also use a **catalyst**, potassium hydroxide, to speed up the reaction. The combination of catalyst and methanol is called methoxide. The end product is a combination of biomass-based diesel, unreactive methanol, glycerin, and soap.



Koohikamali, Sara & Tan, Chin & Ling, Tau. (2012). Optimization of Sunflower Oil Transesterification Process Using Sodium Methoxide. TheScientificWorldJournal. 2012. 475027. 10.1100/2012/475027.

The synthesis is a simple chemical reaction that produces biomass-based diesel and **glycerol**. The oil is mixed with methanol, while sodium or potassium hydroxide is added as a catalyst. The products separate into two layers with the biodiesel on top. The biodiesel is separated and washed, then it is ready for product evaluation.

In industrial applications, the oil is then refined through a process that we cannot replicate in the lab. Biodiesel undergoes a refinery process similar to petroleum diesel. Renewable diesel results in biodiesel that is stable at low temperatures from a new process that creates a reaction with the feedstock and hydrogen called hydrotreating. Consequently, renewable diesel does not have hydrogen in it, whereas biodiesel does. Renewable diesel also has lower production volumes than biodiesel in the U.S.

Materials

- Methanol
- Sodium hydroxide or Potassium hydroxide
- Glass jar/lid
- 200 mL beaker
- Magnetic stir bar
- Hot plate/stir option
- Separatory funnel, 250 mL or pint-sized jar with lid
- Ring stand w/ring (not needed if using jars)
- Graduated cylinder
- Serological pump and pipettes
- Distilled water
- Weigh boats
- Scales
- Corn oil
- Vegetable (soybean) oil
- Other oils, if desired

Procedure

Part 1: Making renewable diesel (Day 1)

1. Under a fume hood, measure out 60 mL of methanol and add to glass jar, then seal jar quickly.
2. Weigh out 1.5 g of KOH (potassium hydroxide) and quickly add it to the jar of methanol. Seal jar immediately and shake to dissolve. Make sure to recap the KOH because it is hydroscopic. Your mixture is now called methoxide.
3. At the lab station, in a clean beaker, warm 150mL of oil sample to 50° C.
4. Add warmed oil sample to methoxide mixture in jar.
5. Add magnetic stir bar to the jar; loosely place lid back on jar; set stir to high speed and stir for 15 minutes. (Alternatively, tighten the lid, then shake vigorously for 15 minutes.)
6. Allow to sit for 24 hours.

Data for Part 1 (Day 1): visual observations from part 1 of Making renewable diesel

1. Immediately upon adding the methoxide, what did you notice about the oil? Was there a change in the color of the sample?

2. What did the solution look like after it began stirring?

Part 2 (Day 2)

Data from Washing renewable diesel

1. Now that the renewable diesel has rested for 24 hours, describe your sample.

2. Record the following characteristics of your biodiesel sample: color, consistency, and odor.

Initial removal of glycerin

1. Drain the glycerin from the renewable diesel into your jar. Using a graduated cylinder, record the amount of glycerin retrieved from sample. *Note: Crude renewable diesel contains impurities such as soap, incompletely transesterified glycerides, and methanol and must be cleaned/ washed prior to use).*

Wash and dry renewable diesel

1. Using a serological pipette, slowly add a total of 20 mL distilled water down the side of the jar.
2. Pick up the jar and gently rock back and forth for five minutes to wash the renewable diesel. (Do not shake!)
3. Let jar stand and wait 10 minutes for the mixture to separate into two layers. Pipette off the bottom “soapy” layer. Remove soap/glycerin waste into a waste flask or jar.

4. Using pH paper or probe, test the pH of the “soapy” layer and record below.
5. Repeat washing procedure steps 1–4 for a second washing.
6. Allow to settle overnight.
7. Measure the quantity of biodiesel in a graduated cylinder and record.
8. Calculate the percentage yield of your biodiesel production using the following equation:
   % yield = [volume biodiesel / (volume biodiesel + volume glycerin)] × 100%

Data

Oil	pH	Color	Odor	% Yield
Corn				
Soy				

Testing the biofuel

Various tests can be performed on the biofuel.

1. Cloud point test: Temperature tests can be easily done using small samples in eppendorf tubes, exposing them to refrigerator temperatures, freezer temperatures, and other temperatures in between to see if the sample clouds, which is an indication of portions of the mixture freezing. This would lead to poor performance. Students might brainstorm additives that could be used to keep the fuel from freezing without affecting performance.
2. Performance is a very important factor when creating a fuel. Putt putt boats may be used to test the length of time the fuel burns and speed.
3. A 3–27 Conversion Test may be performed to look for fall-out from the sample.
4. pH and density are two additional characteristics that may show differences in final products.

Reflection

1. What tests might you want to perform on your diesel fuel? (Think about various climate zones in the U.S.)

2. Is your biodiesel ready to put into an engine? If not, what other processes might be necessary before it is ready?

Rubric for self-assessment

Skill	Yes	No	Unsure
I can explain the difference between petroleum diesel, renewable diesel, and biodiesel.			
I can explain the process of transesterification.			