

FUEL FROM OIL SEEDS: PRODUCTION AND ANALYSIS OF BIODIESEL DERIVED FROM VEGETABLE OILS

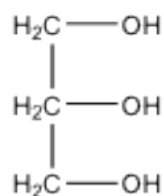
INTRODUCTION

Seed oils from soybean and canola plants are valuable commodities and have found widespread use and application as transportation fuels for economies worldwide. The first compression-ignition (diesel) engine was developed in 1893 by Rudolf Diesel. The first demonstration of this engine used liquid fuel derived from peanut oil as a feedstock and was displayed at the World Fair in Paris, France in 1900. Since that time, the use of oil derived from seed plants has fallen out of favor due to the introduction of refined petroleum diesel prepared from the distillation of crude oil. However, concerns over the continued availability of fossil fuels, in conjunction with a dramatic rise in greenhouse gases, have renewed interest in biorenewable resources.

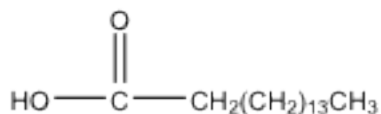
Diesel fuel contains a mixture hydrocarbons ranging from 8-21 carbon atoms and differs considerably from gasoline (mixture of C8 hydrocarbons). Gasoline is refined via fractional distillation of crude oil from 40-100°C, whereas diesel fuel is fractionally distilled between 200-350°C. Since it is composed of longer hydrocarbon chains, diesel has a lower flammability and explosivity relative to gasoline. Gasoline engines rely on a sparkplug to facilitate detonation of gasoline injected into a cylinder head whereas diesel engines do not use them and instead rely on much higher cylinder pressures to generate higher temperatures to achieve fuel detonation. Diesel engines typically yield better fuel economies than gasoline engines, but they suffer from the same emission problems associated with gasoline engines (volatile organic compounds, greenhouse gases, particulates, etc.). Diesel engines have traditionally suffered from increased particulate emissions compared with gasoline engines, although recent advances in catalysis and recycling of exhaust gases have nearly eliminated this occurrence. This phenomenon was mainly due to the low volatility of 'heavier' hydrocarbons in diesel fuel.

Oils and fats isolated from seed plants come to us mainly in the form of triglycerides. These are long fatty acid chains that are conjugated to a glycerol molecule (Figure 1). The first step in biodiesel synthesis is to hydrolyze the fatty acid-glycerol bond and create an intermediate free fatty acid (FFA).

FIGURE 1: CHEMICAL STRUCTURE OF GLYCEROL AND A REPRESENTATIVE FATTY ACID



GLYCEROL

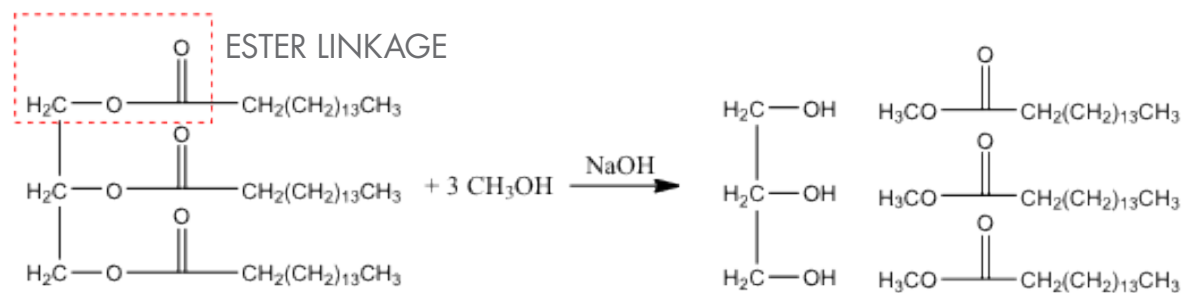


FREE FATTY ACID

FFA's are long chain hydrocarbon molecules terminated with a carboxylic acid functional group (-COOH). Longer chain lengths are associated with higher melting points and are therefore the main components of fats (solids), whereas shorter chain lengths are the main component of oils (liquids). This is the principle reason why oil seeds are nearly ideal for biodiesel fuel conversion, as the length of the FFA liberated from glycerol results in a product that has a lower melting point than fats or oils and therefore more suitable for use in a liquid fuel-combustion engine.

The intermediate FFA product must then be esterified with a methyl group to complete the conversion to a usable liquid fuel (Figure 2). FFA's cannot be used directly in most internal combustion engines as they readily undergo ionization to form salts that are typically solids under operating conditions. This will lead to 'gunking' and fouling of engine components (fuel pumps, filters, injector nozzles, etc.) Methyl ester fatty acids (MEFA) will not undergo ionization and therefore remain liquids up to the moment of ignition where they are combusted to form mainly carbon dioxide and water.

FIGURE 2. TRANSESTERIFICATION REACTION BETWEEN A TRIGLYCERIDE AND METHANOL. THE RESULTING PRODUCTS ARE GLYCEROL AND METHYL ESTER FATTY ACIDS (MEFA'S)



In this experiment, you will use oil derived from seed plants (canola and soy) to synthesize biodiesel fuel. You may also have used cooking oil (canola and soy) to use for biodiesel conversion. You will then analyze each fuel for yield, purity (freezing point test), combustibility, and particulate formation (during combustion).

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PART 1: BIODIESEL SYNTHESIS FROM SEED OILS



Reminder: You need to follow proper personal safety which includes protective eye wear and gloves where appropriate.

1. Take a 50mL Erlenmeyer flask with a stir bar and add 14mL of methanol. Place the flask on a stir plate and set speed at a rate where it does not splash but stirs vigorously.
2. Slowly add 0.50g of NaOH to the mixture. Do not go over this mass and be sure to add it slowly.
3. Observe the NaOH become completely dissolved. Once this happens, sodium methoxide (NaOMe) has formed. This is a very strong and dangerous compound.
4. After the NaOMe is formed, pour 50mL of pure seed oil into a 250mL beaker and place the beaker and contents onto a magnetic stirring hot plate and warm it to 50°C. Turn on the stir feature (medium agitation) and add a stir bar to the beaker containing the oil. Turn off the heat when temperature is reached.
5. Slowly add the NaOMe to the warm seed oil with constant stirring. The solution will become cloudy. Stir the reaction for 20 minutes after the last drop of NaOMe is added.
6. After the reaction time is completed, transfer the contents of the beaker into centrifuge vials and cap them tightly. Label each vial with your name and the sample identity.
7. Place each vial into an empty slot in the centrifuge. Your instructor will direct you on how to operate the centrifuge, but aim for centrifuging the samples for about 2 minutes at 4000 rpm.
8. Using a pipet, discard the lower layer (glycerol, Unreacted NaOH, etc.). Collect and combine all of the biodiesel fractions from your centrifuge tubes and measure the mass and volume of your product in a graduated cylinder. Record these values and calculate your percentage yield.

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PART 2: PURIFICATION OF BIODIESEL FUEL

Biodiesel must be purified before it can be used as a fuel. The following outline utilizes a wet method or 'aqueous phase partitioning process' to purify the biodiesel fuel away from any contaminating residues (soaps, salts, glycerol, etc.). The biodiesel component is not water soluble, whereas most of the contaminants left behind are. We will take advantage of this difference in solubility character to clean up the biodiesel fuel.

1. Add your crude biodiesel to a 125ml Erlenmeyer flask. Add to it 5mL of 0.1M acetic acid and gently swirl the flask. Do not attempt to mix the material vigorously as this will result in the formation of an emulsion (aerated mixture of hydrophilic and hydrophobic components. Think salad dressing). After a minute or so of gentle swirling of the flask, you should let it settle for a few minutes in order for two layers to develop.
2. Tip the flask at a 45° angle and use a pipet to collect the bottom layer (aqueous layer) and discard it.
3. Add 5ml of distilled water to the crude biodiesel fraction and repeat the gentle swirling action and collection of the bottom water layer as outlined in steps 1 + 2.
4. Observe your biodiesel after sitting for 2 days and uncover the flask. Place your purified biodiesel on a hot plate and heat it to 80°C for 10-15 minutes to evaporate any remaining water. This operation should be done in the hood.

**PART 3: BIODIESEL ANALYSIS
FREEZING POINT**

1. Biodiesel will 'gel' at very low temperatures. Take 1-2mL of your purified and dried biodiesel fuel and place it into a test tube.
2. Prepare an ice-salt water bath by taking 100mL of ice and adding it to one or two tablespoons of salt. Stir.
3. Place the tube into the ice-salt water bath for 10-15 minutes.
4. Record your observations and temperature of the fuel after the time period is up. Did your biodiesel gel? If not, why do you suppose it didn't? Repeat with a sample of petroleum diesel.

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PART 3: BIODIESEL ANALYSIS COMBUSTION TEST

1. Obtain two cotton swabs. Load one cotton swab with biodiesel and the other with the starting seed oil that you chose at the beginning of the experiment. To load a cotton swab, dip it in the liquid and let it soak for a few seconds. Then lift it out and let it finish dripping before proceeding.
2. In the fume hood, light the two cotton swabs.
3. Make observations on the color of the flame, the time it took to start combustion, and the presence of any soot or particulates that form during the combustion reaction. Document how many seconds it takes for each swab to self-extinguish.

PARTICULATES TEST

1. Obtain the mass of a dry piece of round filter paper. Clip it into an inverted plastic funnel that is connected to a suction apparatus.
2. Obtain a cotton swab and load it with your synthesized biodiesel fuel.
3. Ignite the sample and immediately place it below the conical funnel containing the dried filter paper while the suction device is turned on. Do not place the burning swab so close to the filter and funnel so that the filter paper ignites or chars. Keep the tip of the flame about 3-5 inches from the base of the funnel.
4. Continue collecting the particulates as they form in the suction funnel until the cotton swab self-extinguishes.
5. Turn off the suction apparatus and carefully remove the filter paper and invert it without losing any particulate solids that are trapped in it. Obtain the weight of the filter paper + particulates and subtract it from the mass of the original filter paper. This mass represents the amount of particulates formed during combustion of your fuel.
6. Repeat this procedure with a sample of petroleum diesel and the original oil used to make the biodiesel. Compare and contrast your results. Which fuel burned 'cleaner'?