Transesterification of Oil – Making Methyl Ester

Introduction

Lesson Introduction

Vegetable oils and products synthesized from natural raw materials (either of vegetable or animal origin) are having a strong comeback in recent decades. One of the major reasons for the increased utilization of fatty chemicals for industrial use has been the ability to tailor the products to specific needs. Major areas of applications are in foods, soaps and detergents, cosmetics, pharmaceuticals, textiles and papers, oil field chemicals, fat-based emulsifiers, synthetic lubricants, metal working fluids, and last but not least, introduction into the transportation fuel sector as biodiesel.

Grades: 9-12

Time Needed: Three, 45-min class periods

Learning Objectives:

After completing this lesson, students will be able to:

1. Create a renewable biofuel
2. Identify products and reactants in Transesterification
3. Define Biorenewable
4. Compare and contrast diesel fuel and biodiesel fuel
5. Explain 5 benefits of biodiesel

Next Generation Science Standards (NGSS)

As a result of activities for grades 9-12, all students will learn content in these areas:

Topics

- **PS1:** Structure and Properties of Matter

Performance Expectation

- **HS-PS1-5:** Apply scientific principles and evidence to provide an explanation about the effects of changing the temperature or concentration of the reacting particles on the rate at which a reaction occurs
- **HS-PS1-7:** Using mathematical representations to support the claim that atoms, and therefore mass, are conserved during a chemical reaction
- **HS-ETS1-1:** Analyze a major global challenge to specify qualitative and quantitative criteria and constraints for solutions that account for societal needs & wants

Dimension

Practices:

- Developing & using models
- Planning & carrying out investigations
- Using mathematics & computational thinking
- Obtaining, evaluating, and communicating information

Disciplinary Core Ideas:

- **PS1:** Matter and its interactions

Cross-Cutting Concepts:

- Scale, proportion, and quantity
- Structure & function

Materials:

- ☐ (2) 20-32 oz (591-710 ml) beverage bottles with caps (sport and vitamin drinks, not water bottles)
- ☐ (1) Graduated beaker or measuring cup
- ☐ (1) Glass jar with a tight fitting lid to mix the methanol and sodium hydroxide (methoxide)
- ☐ (1) Large beaker or glass jar
- ☐ Aluminum foil or weighing boats
- ☐ Laboratory scale (0.1 g precision minimum)
- ☐ Disposable latex gloves
- ☐ Safety glasses or goggles
- ☐ Push pin
- ☐ Crock pot to warm the oil (140^0 F/60^0 C). **Use caution: the oil is HOT.** Place the oil in the crock pot to warm an hour before class. This can be done by a) placing the entire bottle of oil into the pot or b) aliquotting the oil into the 20 oz bottles and placing them in the pot.

Optional:

- ☐ Funnel or wire strainer
- ☐ #2 or #4 coffee filter
- ☐ Distilled water

Reagents

- ☐ Soybean oil (Wesson™ Vegetable Oil)
- ☐ Methanol (HEET™ gasoline additive) **CAUTION: Contents very flammable**
- ☐ Sodium hydroxide (NaOH, also known as “lye” or “caustic soda”)

Procedure:

Day 1

1. Wear safety glasses or goggles. When handling the sodium hydroxide, wear disposable gloves. When handling heated flasks, wear laboratory gloves.
2. Weigh out 2 grams of sodium hydroxide on a small piece of aluminum foil or weighing boat.
3. Weigh out 46 grams (60 ml) of methanol, HEET^{TM}, (SG 0.792) using a graduated beaker or measuring cup.
4. Mix the sodium hydroxide and methanol together in one of the bottles. Place the lid tightly on the bottle. Swirl and shake the methoxide mixture until the sodium hydroxide is completely dissolved, approximately 5 minutes. Alternative: let it sit overnight to finish dissolving.
5. Remove the bottle of Wesson^{TM} soybean oil from the crock pot and allow it to cool for 5 minutes. Weigh out 200 grams (210 ml) of oil into a 20 oz bottle.
6. Add the methanol/NaOH mixture to the 20 oz bottle containing the oil.
7. Place the cap tightly on the 20 oz bottle and shake vigorously for 30 seconds. Place the bottle back into the crock pot or water bath between shakings. This will help speed up the reaction. Let the mixture warm 2-3 minutes and shake again for 10 seconds. Repeat this for 15 minutes.
8. The mixture will thicken and darken, then becomes thinner than the original oil.
9. Let the bottle stand overnight.
10. The mixture will separate into two distinct layers. The clearer top layer is the methyl ester, and the darker bottom layer is the glycerol by-product of the Transesterification process.

Day 2

1. Carefully pour off the top layer (methyl esters) of the mixture, using a decanting method, into a container provided by your teacher/instructor. If you are continuing to the next day optional section, pour off the top layer into a clean 20 oz bottle.

   Alternative: Take a push pin and punch a hole in the bottom of the bottle. Allow the bottom layer (glycerol) to drain completely. You can control the rate at which the fluid drains by placing the cap back on the bottle. A tight cap will stop the draining.

   Place a piece of tape over the hole and proceed to the next step.

Optional:

2. Carefully pour off the top layer (methyl esters) of the mixture into a clean 20 oz bottle. See procedure above.
3. “Wash” the methyl esters to remove any remaining methanol and soap.
    a. Measure an amount of distilled water that is equal to one-half the volume of the recovered methyl esters.
    b. Add the distilled water to the recovered methyl esters and gently rock the bottle 3-5 minutes. Don’t shake it, or you will create an emulsion that will take a long time to separate.
    c. Allow the methyl esters and water to separate for 10 minutes.
    d. Drain the bottom (glycerol) layer of the mixture by poking a hole in the bottom of the bottle (see step 11 alternative) or pull the tape from step 11 procedure off the bottom of the bottle and loosen the cap. The top layer of the mixture contains the methyl esters.
    e. Do a second washing, repeating steps 13a through 13c.
4. Let the mixture sit overnight.

Day 3

1. Construct a filtering system by placing a coffee filter in a funnel or wire strainer. Position it over a beaker/jar to drain.
2. Drain off the bottom layer that contains glycerol (see step 11 alternative). Pour the top layer of the mixture that contains the methyl esters through the coffee filter system and allow it to drain.
3. When finished, pour the methyl esters into the container provided by the instructor. The liquid, biodiesel, will be used to run a diesel engine in another class period.

Sample questions and assessments with biorenewable fuels

General:

1. Using the information below and assuming the soybeans are composed of protein, oil and hulls, how much would a bushel of soybeans weigh?

   Soy protein = 48 lbs
   Soy oil = 11 lbs
   Soy hulls = 1 lbs

2. A farmer has 80 bales of switchgrass with an average volume of 1.85m^3 loaded on a flatbed of a semi. Each bale can deliver 3.6 GJ/m^3 of energy. How many joules of energy would this semi load of switchgrass potentially produce?

3. If the farmer above can harvest 200 bales from 10 acres of land. How much energy is produced per acre?

4. The same farmer is willing to sell each bale for $55.
   a. How much money will the farmer receive for the semi load of switchgrass?
   b. How much does each joule of energy cost at this point?

5. How many barrels of crude oil would be saved by this one semi load of switchgrass given there are 5.8×10^6 BTUs in a barrel?

6. Given 80% efficiency in production, how many gallons of ethanol will the semi load of switchgrass in question 5 produce?

Biodiesel:

1. Petroleum diesel contains 1.29×10^5 BTU/gal compared to 1.18×10^5 BTU/gal for biodiesel. How many gallons of B100 biodiesel does it take to get the same number of BTUs?

2. If standard #2 petroleum diesel cost $2.75/gal, what would biodiesel have to sell for to get the same amount of BTUs in 10 gallons of petroleum diesel?

3. Forty billion gallons of petroleum diesel is consumed in the United States each year. If the United States would legislate that all diesel be B20,
   a. How many acres of soybeans (a favorite oil) would have to be grown to meet this requirement?
   b. Could the United States realistically meet this goal?
   c. How could Iowa's soybean crop contribute and/or be affected?
   d. Explain/discuss in your group/class the pros and cons of your answers b and c.

Research and Experimental Design

Do some research to find out how many gallons of oil soybeans produce per acre, what the efficiency of biodiesel production is and how many acres of soybeans are grown in US?

Research and design a method to test the biodiesel you produced to petroleum based biodiesel or to other student produced biodiesel. Be sure to follow the scientific method, and determine what variable you are going to quantify in order to evaluate your results.

History:

The concept of using vegetable oil as an engine fuel likely dates to when Rudolf Diesel (1858-1913) developed the first engine to run on peanut oil, as he demonstrated at the World Exhibition in Paris in 1900.

Rudolf Diesel

Source: www.chemistry.org/portal/a/c/s/1/feature_tea.html

Rudolf Diesel firmly believed the utilization of a biomass fuel to be the real future of his engine. He wanted to provide farmers the opportunity to produce their own fuel. In 1911, he said, "The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries which use it."

> *"The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become, in the course of time, as important as the petroleum and coal tar products of the present time."*
> *Rudolf Diesel, 1912*

Unfortunately, Rudolf Diesel died in 1913 before his vision of a vegetable oil powered engine was fully realized. At the time of Diesel's death, the petroleum industry was rapidly developing and producing a cheap by-product called "diesel fuel" that would power a modified "diesel engine". Thus, clean vegetable oil was forgotten as a renewable source of power. Modern diesels are now designed to run on a less viscous (easier flowing) fuel than straight vegetable oil, but, in times of fuel shortages, cars and trucks were successfully run on preheated peanut oil and animal fat.

In the mid 1970's, fuel shortages spurred interest in diversifying fuel resources, and thus biodiesel as fatty esters was developed as an alternative to petroleum diesel. Later, in the 1990's, interest rose due to the large pollution reduction benefits coming from the use of biodiesel. Today's diesel engines require a clean-burning, stable fuel that will operate under a variety of conditions. The resurgence of biodiesel has been affected by legislation and regulations in all countries. Many of the regulations and mandates center on promoting a country's agricultural economy, national security, and reducing climate pollution/change.

What is Biodiesel?

Biodiesel is simply a liquid fuel derived from vegetable oils and fats, which has similar combustion properties to regular petroleum diesel fuel. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. Biodiesel is biodegradable, nontoxic, and has significantly fewer emissions than petroleum-based diesel when burned.

Biodiesel is an alternative fuel similar to conventional or "fossil/petroleum" diesel. The process used to convert these oils to biodiesel is called transesterification. This process is described in more detail below. The largest possible source of suitable oil comes from oil crops such as soybean, rapeseed, corn, and sunflower.

At present, oil straight from the agricultural industry represents the greatest potential source, but it is not being used for commercial production of biodiesel simply because the raw oil is too expensive. After the cost of converting it to biodiesel has been added, the price is too high to compete with petroleum diesel. Waste vegetable oil can often be obtained for free or already treated for a small price. One disadvantage of using waste oil is it must be treated to remove impurities like free fatty acids (FFA) before conversion to biodiesel is possible. In conclusion, biodiesel produced from waste vegetable/animals oil and fats can compete with the prices of petroleum diesel without national subsidies.

Sources

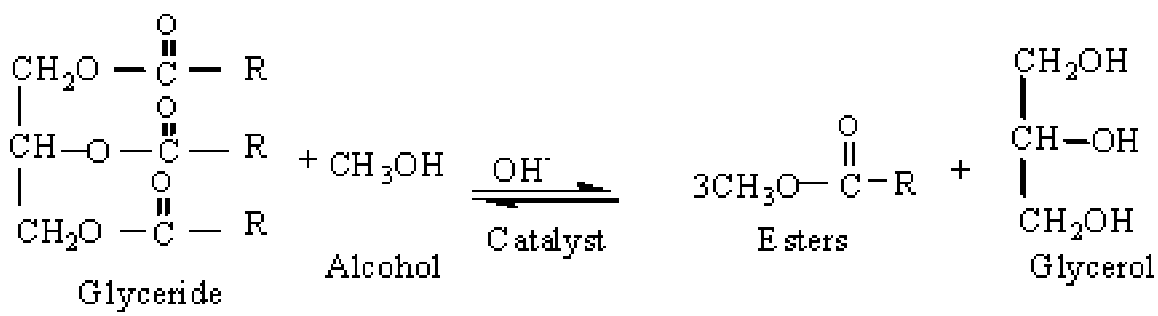
Adapted from the Biotechnology Outreach Education Center: Office of Biotechnology: Iowa State University, Ames Iowa: Mike Zeller author. Web site: www.biotech.iastate.edu/outreach.html

Making Biodiesel: Transesterification

Transesterification of natural glycerides with methanol to methylesters is a technically important reaction that has been used extensively in the soap and detergent manufacturing industry worldwide for many years. Almost all biodiesel is produced in a similar chemical process using base catalyzed transesterification as it is the most economical process, requiring only low temperatures and pressures while producing a 98% conversion yield. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base, with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can, in turn, affect the characteristics of the biodiesel.

During the esterification[A1] process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong base like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol. In most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide has been found more suitable for the ethyl ester biodiesel production, but either base can be used for methyl ester production.

The figure below shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction, so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.



Source: www.esru.strath.ac.uk/EandE/Web_sites/02-03/biofuels/what_biodiesel.htm

The products of the reaction are the biodiesel itself and glycerol.

A successful transesterification reaction is signified by the separation of the methyl ester (biodiesel) and glycerol layers after the reaction time. The heavier co-product, glycerol, settles out and may be sold as is or purified for use in other industries, e.g. pharmaceutical, cosmetics, and detergents.

After the transesterification reaction and the removal of the crude heavy glycerin, the product left is a crude biodiesel. This crude biodiesel requires some purification prior to use.

Biodiesel has a viscosity similar to petroleum diesel and can be used as an additive in formulations of diesel to increase the lubricity. Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most modern diesel engines. Biodiesel will degrade natural rubber gaskets and hoses in vehicles (mostly found in vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with Viton type seals and hoses, which are nonreactive to biodiesel. Biodiesel's higher lubricity index compared to petroleum diesel is an advantage and can contribute to longer fuel injector life.

Biodiesel is a better solvent than petroleum diesel and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petroleum diesel. Fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made, as biodiesel “cleans” the engine in the process. It is, therefore, recommended to change the fuel filter within 600-800 miles after first switching to a biodiesel blend.

Biodiesel's commercial fuel quality is measured by the ASTM standard designated D 6751. The standards ensure that biodiesel is pure and the following important factors in the fuel production process are satisfied:

- Complete reaction
- Removal of glycerin
- Removal of catalyst
- Removal of alcohol
- Absence of free fatty acids
- Low sulfur content

Biodiesel is, at present, the most attractive market alternative among the non-food applications of vegetable oils for transportation fuels. The different stages in the production of plant/seed oil methyl ester generate by-products, which offers further outlets. Oil cake, the protein rich fraction obtained after the oil has been extracted from the seed, is used for animal feed. Glycerol, the other important by-product, has numerous applications in the oil and chemical industries such as the cosmetic, pharmaceutical, food, and painting industries.

Benefits/Advantages of Biodiesel:

Biodiesel is biorenewable, meaning feedstocks to make biodiesel can be renewed one or more times in a generation.

Biodiesel is carbon neutral. Plants use the same amount of CO_2 to make the oil that is released when the fuel is burned.

Biodiesel is rapidly biodegradable and completely nontoxic, meaning spillages represent far less risk than petroleum diesel spillages.

Biodiesel has a higher flash point than petroleum diesel, making it safer in the event of a crash.

Blends of 20% biodiesel with 80% petroleum diesel can be used in unmodified diesel engines. Biodiesel can be used in its pure form but may require certain engine modifications to avoid maintenance and performance problems.

Biodiesel can be made from recycled vegetable and animal oils or fats.

Biodiesel is nontoxic and biodegradable. It reduces the emission of harmful pollutants, mainly particulates, from diesel engines (80% less CO_2 emissions, 100% less sulfur dioxide). But emissions of nitrogen oxide, the precursor of ozone, are increased.

Biodiesel has a high cetane number of above 100, compared to only 40 for petroleum diesel fuel. The cetane number is a measure of a fuel's ignition quality. The high cetane numbers of biodiesel contribute to easy cold starting and low idle noise.

The use of biodiesel can extend the life of diesel engines because it is more lubricating and, furthermore, power output is relatively unaffected by biodiesel.

Biodiesel replaces the exhaust odor of petroleum diesel with a more pleasant smell of popcorn or French fries.