Biodiesel

Learning Objectives:
- Enhance understanding of what biodiesel is and how it is made.
- Enhance understanding of biodiesel properties.
- Provide "hands-on" renewable biofuel production experience.
- Enhance appreciation for biodiesel's role in the emerging bioeconomy.

Learning Outcomes:
At the completion of this laboratory, participants will be able to:
- Define biodiesel.
- Describe the inputs & process of making biodiesel (transesterification).
- Calculate biodiesel yields.
- Describe and compare diesel, biodiesel and biodiesel blend properties.
- Explain the benefits and challenges of using biodiesel as a fuel.
- Explain the factors that affect production costs.

Pre-Lab

Background

Introduction
Fossil fuels (natural gas, coal, oil) are non-sustainable and non-renewable resources that society has become heavily dependent on. Petroleum (literally rock oil) is the source of gasoline and diesel, two common fuels that power automobiles. Prices of these petroleum-based fuels are rising due to their high demand and scarcity. In addition, the burning of these fuels increase society's ecological footprint and add to greenhouse gas emissions.

What is biodiesel?
Biodiesel is a fuel made from vegetable oil through a chemical reaction called *transesterification*. During transesterification, the -O-R group of an ester (R'COOR) and the -O-R" group of an alcohol (R"-OH) trade places, changing one *ester* (R'COOR) into another (RCOOR"). Vegetable oil is a triglyceride (also called a triacylglycerol), a glycerin (or glycerol) molecule connected via ester bonds to three fatty acid molecules (RCOOH). During the reaction, the fatty acids of the triglyceride molecule are cleaved and attach to the alkyl group (the part made of carbon and hydrogen) of the alcohol to form fatty acid alkyl esters (in our case, fatty acid methyl esters or FAMEs), which are biodiesel. To speed up the reaction, a base catalyst, typically sodium hydroxide (NaOH) or potassium hydroxide (KOH), is used. Animal fats are also triglycerides and therefore can also be made into biodiesel.

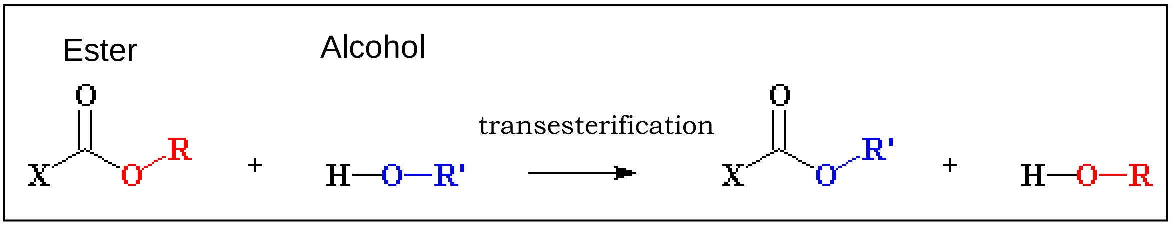


Figure 1: A general transesterification reaction.
Source: http://pslc.ws/macrog/kidsmac/glossary.htm

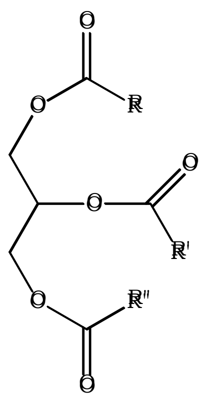


Figure 2:
Triglyceride structure: R, R' and R" are long alkyl (hydrocarbon) chains ranging from 12-20 carbons in length

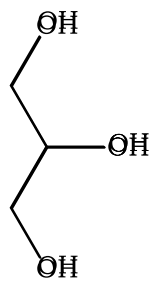


Figure 3:
Glycerol structure

The ester group in triglyceride will exchange places with the alcohol group in methanol or ethanol to form biodiesel. Biodiesel is a methyl or ethyl ester (depending on whether methanol or ethanol is used) of a long chain fatty acid hydrolyzed from triglyceride.

The chemical composition of diesel is about 75% saturated hydrocarbons (primarily paraffins including n-, iso-, and cyclo-paraffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging from approx. $C_{10}H_{20}$ to $C_{15}H_{28}$. and has a heat of combustion of 10,700 cal/g.

Biodiesel is produced from renewable sources such as new or used vegetable oils and animal fats, and is a cleaner-burning alternative to petroleum-based diesel fuel. Biodiesel has physical properties similar to those of petroleum diesel, but is non-toxic and biodegradable.

Average Density and Heating Value of Biodiesel and Diesel Fuel

Fuel	**Density, g/cm3**	**Net Heating Value Avg., Btu/gal.**	**% Difference vs. No. 2 Diesel Avg.**
No. 2 Diesel	0.850	129,500	
Biodiesel (B100)	0.880	118,296	8.65 %
B20 Blend (B20)	0.856*	127,259*	1.73 %*
B2 Blend (B2)	0.851*	129,276*	0.17 %*

Table 2. Selected Properties of Typical No. 2 Diesel and Biodiesel Fuels

Fuel Property	**Diesel**	**Biodiesel (B100)**	**Units**
Fuel Standard	ASTM D975	ASTM D6751	
Higher Heating Value	129,500	118,296	Btu/gal
Kinematic Viscosity @ 40° C	1.3 - 4.1	1.9 - 6.0	mm 2/s
Specific Gravity @ 60° C	0.85	0.88	kg/l
Density	7.079	7.328	lb/gal
Water and Sediment	0.05 max	0.05 max	% volume
Carbon	87	77	wt. %
Hydrogen	13	12	wt. %
Oxygen	0	11	
Sulfur	0.0015 max	0.0 to 0.0024	wt. %
Boiling Point	180 to 340	315 to 350	° C
Flash Point	60 to 80	130 to 170	° C
Cloud Point	-15 to 5	-3 to 12	° C
Pour Point	-35 to -15	-15 to 10	° C
Cetane Number	40 to 55	47 to 65	
Lubricity SLBOCLE	2,000 to 5,000	>7,000	grams
Lubricity HFRR	300 to 600	<300	microns

Source: U.S. Department of Energy, Biodiesel Handling and Use Guidelines (2nd Edition, March 2006)

Like petroleum diesel, biodiesel is used to fuel compression-ignition (diesel) engines. Low-level blends of biodiesel with petroleum diesel also provide benefits.

B20 and B100: Alternative Fuels
The interest in biodiesel as an alternative transportation fuel stems mainly from its renewable, domestic production; it's safe, clean-burning properties; and its compatibility with existing diesel engines. Biodiesel can be legally blended with petroleum diesel in any percentage. The percentages are designated as B20 for a blend containing 20% biodiesel and 80% petroleum diesel, B100 for 100% biodiesel, and so forth. B100 and B20 or higher blends qualify for alternative fuel credits under the Energy Policy Act of 1992.

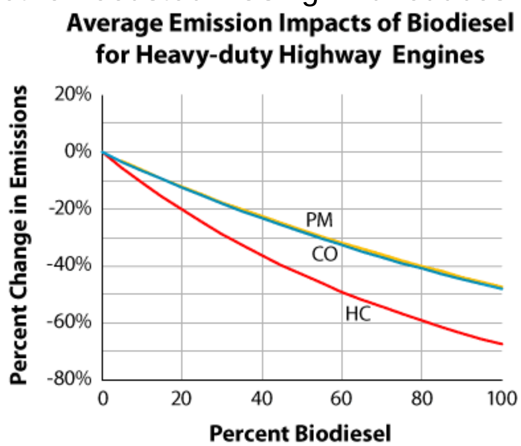
B100
B100 or other high-level biodiesel blends can be used in some engines built since 1994 with biodiesel-compatible material for parts such as hoses and gaskets. However, as biodiesel blend levels increase significantly beyond B20, a number of concerns come into play. Users must be aware of lower energy content per gallon and potential issues with impact on engine warranties, low-temperature gelling, solvency/cleaning effect if regular diesel was previously used, and microbial contamination. To avoid engine operational problems, pure biodiesel (B100) must meet the requirements of ASTM D6751-09, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. B100 use could also increase nitrogen oxides emissions, although it greatly reduces other toxic emissions. These issues can be addressed, but currently, B100 might be best used in professional fleets with maintenance departments.

B20
B20 is the most common biodiesel blend in the United States. Using B20 provides substantial benefits but avoids many of the cold-weather performance and material compatibility concerns associated with B100. B20 can be used in nearly all diesel equipment and is compatible with most storage and distribution equipment. B20 and lower-level blends generally do not require engine modifications. Because diesel engines are expensive, users should consult their vehicle and engine warranty statements before using biodiesel.

Biodiesel contains about 8% less energy per gallon than petroleum diesel. For B20, this could mean a 1 to 2% difference in the amount of fuel needed, but most B20 users report no noticeable difference in performance or fuel economy. Greenhouse gas and air-quality benefits of biodiesel are roughly commensurate with the blend; B20 use provides about 20% of the benefit of B100 use and so forth.

Environmental Benefits
In 2000, biodiesel became the only alternative fuel in the country to have successfully completed the EPA-required Tier I and Tier II Health Effects Testing under the Clean Air Act. These independent tests conclusively demonstrated biodiesel's significant reduction of virtually all regulated emissions, and showed biodiesel does not pose a threat to

human health. Biodiesel contains virtually no sulfur or aromatics, and use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter. A U.S. Department of Energy study showed that the production and use of B100, compared to petroleum diesel, resulted in a 78.5% reduction in carbon dioxide emissions because carbon dioxide released from biodiesel combustion is offset by the carbon dioxide sequestered while growing the soybeans or other feedstock. Using B20 reduces carbon dioxide emissions by 15%.



Since biodiesel is made from a renewable source, it has a favorable energy balance ratio. An energy balance ration compares the energy required to grow or extract, process, and distribute a fuel to the energy stored in the fuel. According to the USDA, biodiesel's ratio is 3.2. This means that for every unit of fossil-fuel-derived energy required to grow (fertilizers, feedstock, and pesticides), process (think harvest and extract) and transport (from field to refinery to fuel station) biodiesel, there are at least 3.2 units of energy contained in the fuel. By contrast, corn ethanol has an energy balance ratio of 1.34, and petroleum diesel's ratio is negative (-0.84) as is gasoline! (Tickell, 2006).

Safety Benefits
Biodiesel is nontoxic, so it causes far less damage than petroleum diesel if spilled or otherwise released to the environment. It is also safer than petroleum diesel because it is less combustible. The flashpoint for biodiesel is higher than 150°C, compared with about 52°C for petroleum diesel. Biodiesel is safe to handle, store, and transport.

Energy Security Benefits
With agricultural commodity prices approaching record lows, and petroleum prices approaching record highs, more can be done to utilize domestic surpluses of vegetable oils while enhancing our energy security. Because biodiesel can be manufactured using existing industrial production capacity, and used with conventional equipment, it provides substantial opportunity for *immediately* addressing energy security issues. If the true cost of using foreign oil were imposed on the price of imported fuel, renewable fuels, such as biodiesel, would likely be the most viable option. For instance, in 1996, military costs of securing foreign oil were estimated at $57 billion annually. Foreign tax credits accounted

for another estimated $4 billion annually and environmental costs were estimated at $45 per barrel.

Economic Benefits

The biodiesel industry has contributed significantly to the domestic economy. The 51,893 jobs that are currently supported by the US biodiesel industry reflect the beginning of the industry's potential to create jobs and economic growth in the US economy. Biodiesel has added $4.287 billion to the Gross Domestic Product (GDP) and has the potential to support more than 78,000 jobs by 2012. A stable, thriving biodiesel industry is necessary if the U.S. is to eventually benefit from the commercial scale production of algal-based biofuels. The National Biodiesel Board estimates that for every 100 million gallons of biodiesel that is produced from algae, 16.455 jobs will be created and $1.461 billion will be added to the GDP.

Quality Benefits

Biodiesel is registered as a fuel and fuel additive with the EPA and meets clean diesel standards established by the California Air Resources Board (CARB). B100 has been designated as an alternative fuel by the U.S. Department of Energy and the U.S. Department of Transportation. Moreover, in December 2001, the American Society of Testing and Materials (ASTM) approved a specification (D675) for biodiesel fuel. This development was crucial in standardizing fuel quality for biodiesel in the U.S. market. The biodiesel industry also utilizes a voluntary quality management certification program for biodiesel producers, marketers, and laboratories called the BQ-9000 Program. The BQ-9000 Program combines internationally accepted quality management principles with the ASTM biodiesel fuel specification to help ensure that customers and end users get the highest quality fuel possible. The National Biodiesel Accreditation Commissions issues 'BQ-9000 Marketer,''BQ-9000 Producer,' and 'BQ-9000 lab' certifications for biodiesel marketers and/or producers and biodiesel testing laboratories that have met all requirements of quality management system certification program.

EPAct Benefits

Effective November 1998, Congress approved the use of biodiesel as an Energy Policy Act (EPAct) compliance strategy. The legislation allows EPAct-covered fleets (federal, state, and public utility fleets) to meet their alternative fuel vehicle purchase requirements simply by buying 450 gallons of pure biodiesel and burning it in new or existing diesel vehicles in at least a 20% blend with diesel fuel. The Congressional Budget Office and the U.S. Department of Agriculture have confirmed that the biodiesel option is the least-cost alternative fuel option for meeting the Federal government's EPAct compliance requirements.

Engine Operation Benefits

Biodiesel improves fuel lubricity and raises the cetane number (performance rating) of the fuel. Diesel engines depend on the lubricity of the fuel to keep moving parts from wearing prematurely. Federal regulations reduced sulfur in diesel fuel to 15 ppm a few years ago, which resulted in reduced lubricity of petroleum diesel. Diesel specification

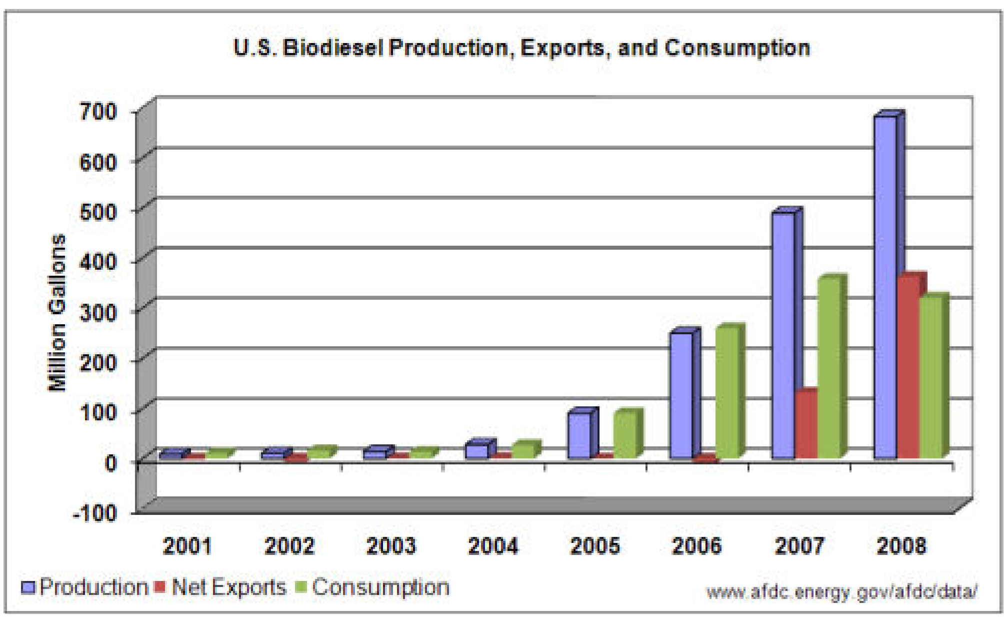
ASTM D975 was modified to require lubricity; biodiesel provides adequate lubricity to meet this requirement at blends as low as 1%.

Production Costs
The cost of producing biodiesel depends on a number of factors, including the following:

- Feedstock used in the process
- Capital and operating costs of the production plant
- Current value and sale of byproducts, which can offset the per-gallon cost of production
- Yield and quality of the fuel and byproducts

The overall cost of biodiesel production depends mainly on the feedstock used and its price; the prices of most feedstocks are subject to market fluctuations, which can also make biodiesel production costs vary over time. Although the price of conventional diesel is not a direct component of production costs, it provides the baseline against which to compare the cost.

Domestic biodiesel production has increased dramatically over the past decade; however, consumption has not increased at the same rate. Exports increased, mostly to Europe, due to favorable U.S. currency rates and European biodiesel use requirements. European and domestic policy changes may impact U.S. biodiesel exports in the near term. Current research is focused on developing algae as a potential feedstock because it is expected to produce high yields from a smaller area of land than vegetable oils.



Pre-Lab Tasks

1. What is biodiesel?

2. What are the ingredients used to make biodiesel?

3. Describe in your own words the process used to make biodiesel?

4. In which circumstances can biodiesel be used?

5. What are some advantages to using biodiesel? What are some disadvantages?

6. In 2009, $100 billion/yr. was spent by the U.S. on imported oil. The population of the U.S. was 305 million. What was cost per person? Per 4-5 person household?

7. A “good” size biodiesel plant produces approximately 30 million gallons (MMG) of biodiesel/year. Determine the land area (in acres) necessary to supply various feedstocks for such a plant using the data below:

Feedstock Source (method)	Wet Yield (MT/ha)	Harvest Moisture (%)	Oil Content (%)	Extraction efficiency (%)	Area Needed (acres)
Soybean (solvent)	3.9	10%	19.1 @ 13% moisture	96	
Soybean (expeller)	3.9	10%	19.1 @ 13% moisture	74	
Palm Oil	10	n/a	23 %	85	
Canola or Rapeseed	2.5	10%	43 @ 8.4% moisture	96	

Units of measure:	Assumptions:
MT = megaton (10^6),	1MT= 2200 lbs
ha = hectare, ac = acre	1ha = 2.471 ac
	biodiesel density = 7.34 lb/ gal or 0.88 g/cm^3
	100 kg oil yields approximately 100 kg biodiesel

First calculate oil content based on harvest moisture: $X_2 = X_1 (100\text{-}M_2)/(100\text{-}M_1)$
(M_1 = moisture content 1, M_2 = moisture content at state 2, X_1 = percent at moisture content M_1, X_2 = percent at moisture content M_2)

For example: if harvest moisture is 10%, and oil content is 25% at 15 % moisture, then the oil percentage at harvest = 25 (100-10) / (100-15) = 26.5%

Biodiesel Production & Testing

<u>Safety Checklist</u>

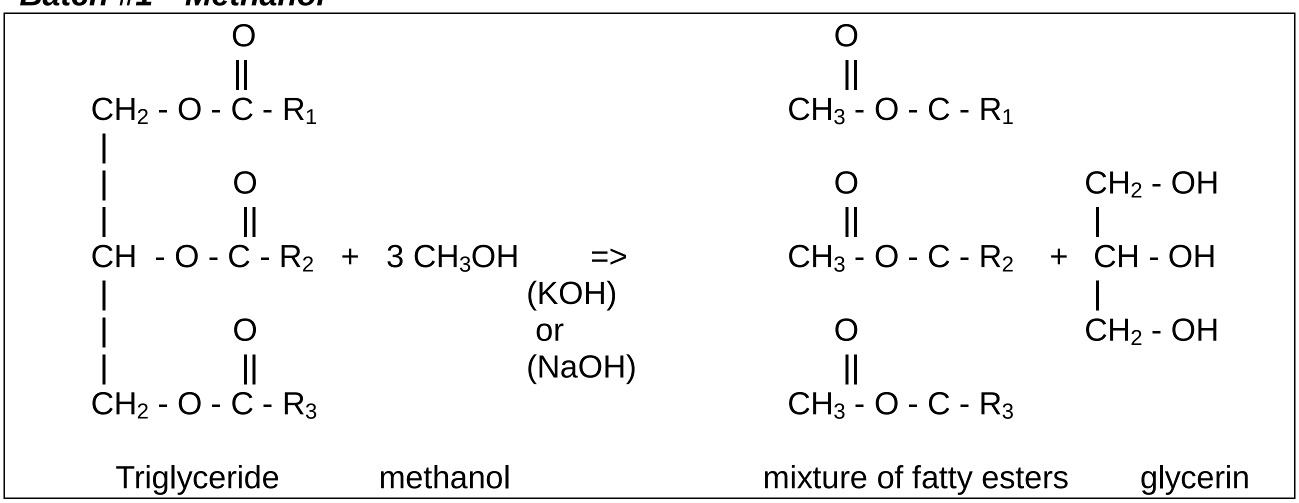
o Proper attire is worn (long pants and closed-toe shoes).
o Food and drinks are stored and consumed outside the laboratory.
o Lab coat and safety glass are worn.
o Latex or nitrile gloves are used when handling samples and chemicals.
o Insulated gloves are used when handling hot materials.
o Chemical aprons are worn when handling methanol or sodium hydroxide.

<u>Problem Statement</u>

In the top secret laboratory in the BRL, you will utilize the following procedure to make 3 "special" batches of biodiesel. You will then use your biodiesel to generate electricity with generator. Additional properties testing of the biodiesel will also be required to determine performance under "extreme" conditions as a fuel.

<u>Biodiesel Production</u>

Batch #1—Methanol



Known: The average molecular weight of soybean oil (as triolein) is 885.46g /mol.

Determine the molecular weight for methanol CH_3OH: _________ g.
Determine the molecular weight of glycerin: __________g.

On a weight basis, how much biodiesel will you produce?

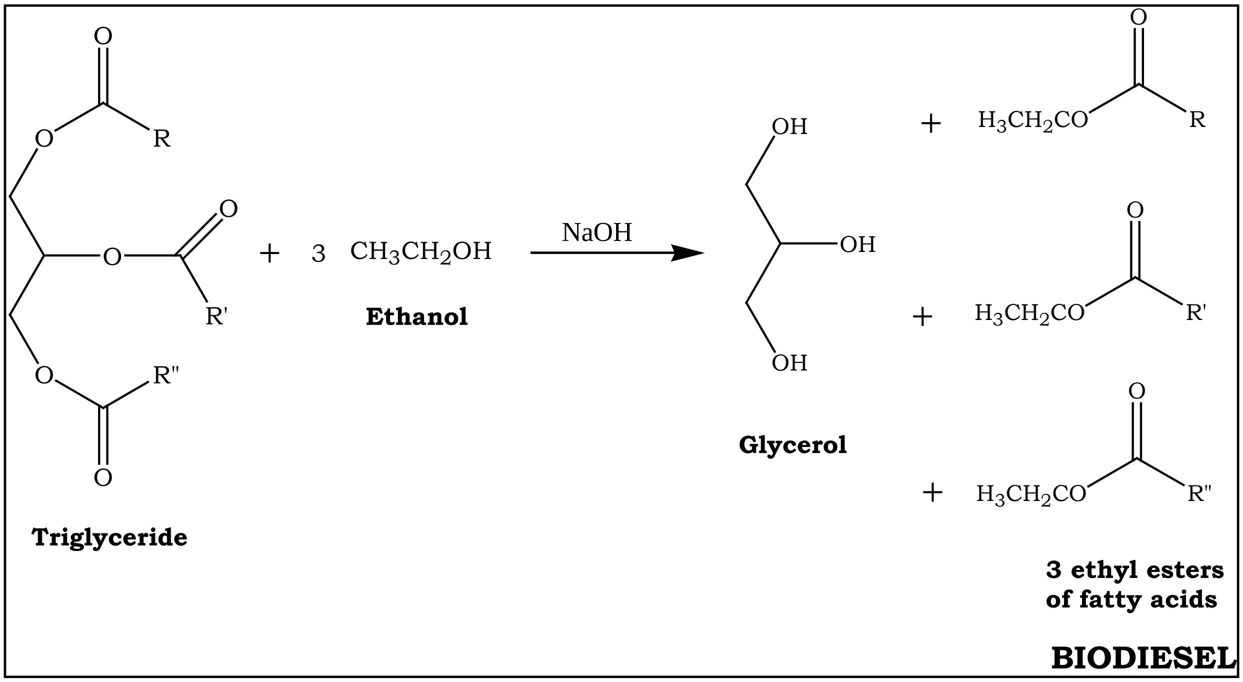
885.46g triglyceride + 96 g methanol → _____g fatty esters + 92g glycerin

If this lab uses 200g of soybean oil, how much methanol will be needed? _______g.

In production about 60%-200% of excess methanol is added to ensure the reaction goes to completion and methanol can be recovered.

How much methanol is needed to provide a 200% excess? _______g.

Batch #2 – Ethanol



Known: The average molecular weight of soybean oil (as triolein) is 885.46 /mol.

Determine the molar weight for ethanol CH_3CH_2OH: ___________g

According to the above "formula" for biodiesel, we need to multiply the ethanol molar weight x 3 = _________g.

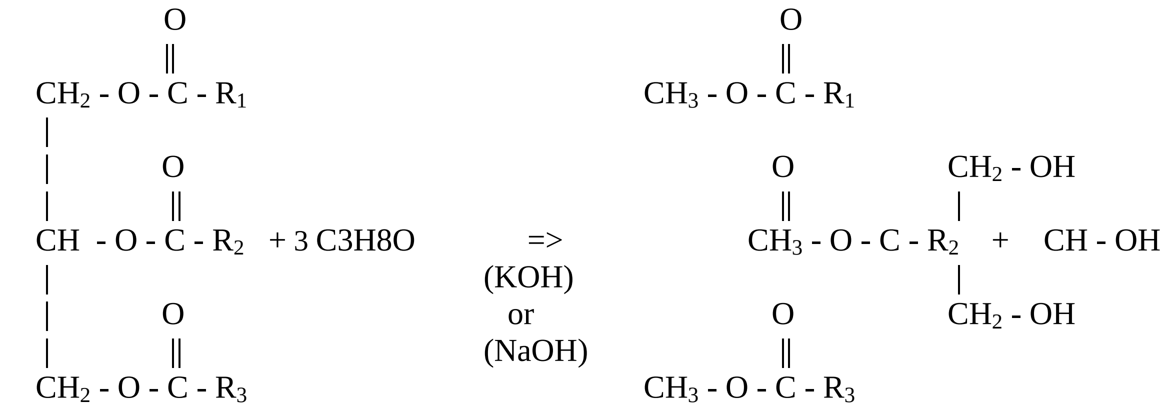
On a weight basis how much biodiesel will you produce?

885.46g Triglyceride + 138g ethanol ⇨ ________g fatty esters + 92g glycerin

Determine: In our lab we will use 200g of soybean oil, how much ethanol will be need? ________g.

Determine: In order increase the reaction, we will multiply the ethanol by 200%.....how much will we need? _________g

Batch #3 – Isopropyl alcohol (IPA)



Triglyceride | isopropyl alcohol | mixture of fatty esters | glycerin

Known: The average molecular weight of soybean oil (as triolein) is <u>885.46 /mol.</u>

Determine the molar weight for IPA C_3H_8O: _______g.

According to the above “formula” for biodiesel, we need to multiply the ethanol molar weight x 3 = _______g.

On a weight basis to make biodiesel, we would need how much ethanol?

885.46g Triglyceride + 180g IPA ⇨ ______g fatty esters + 92g glycerin

Determine: In our lab we will use 200g of soybean oil, how much IPA will be need? _________g.

Determine: In order increase the reaction, we will multiply the IPA by 200%.....how much will we need? ________g.

Pre-experiment Checklist

Each team of 2-4 has:

- 400-500 ml Erlenmeyer flasks /beakers
- 250-500 ml Erlenmeyer flasks/beakers
- 500-ml separatory funnel
- small beakers
- 2 thermometers (200°F max.)
- combination hot plate / magnetic stirrers
- 2 magnetic stir bars and magnetic wands

The following are available:

- tongs / laboratory gloves for handling hot flasks
- aluminum foil or weigh boats
- balance (0.1 g precision minimum)
- graduated cylinders
- soybean oil
- alcohols: methanol, ethanol, IPA
- sodium hydroxide (NaOH; also known as “lye” or “caustic soda”)

Procedure

Batch #1 Methanol

1. Weigh out 2.0 g of sodium hydroxide on a small piece of aluminum foil or weigh boat using balance.
2. Place 250 ml flask on balance and tare.
3. Add pre-determined amount of team’s alcohol for each batch to flask.
4. Add a magnetic stir bar to the methanol flask. Add the sodium hydroxide to the methanol. Place on the stirring hotplate (no heat) and stir to dissolve the sodium hydroxide completely, approximately 5 minutes.
5. Use a magnetic wand to remove the stir bar. Set methanol/NaOH flask aside.
6. Add 200 g of soybean oil to 500 ml flask.
7. Add magnetic stir bar to oil flask and heat flask up to a temperature of 60°C (140°F) on hot plate while stirring vigorously. Note: hotplate takes time to heat up and then retains heat for a long time.
8. Once the oil reaches temperature, slowly add the methanol/NaOH mixture.
9. Stir throughout the reaction (about 1 hr) with the stir bar.
10. The mixture will thicken and darken, then become thinner than the original oil.
11. Watch the temperature to ensure that it does not exceed 60ºC (140°F). Do not use the thermometer as a stirring rod.

12. After one hour, turn off the hot plate and stirring. Remove stir bar using magnetic wand.
13. Pour the mixture into the 500-ml separatory funnel. Allow the mixture to settle for at least 10-15 minutes. The bottom layer contains glycerin and some soap; the top layer is the biodiesel (fatty acid methyl esters or fatty acid ethyl esters).
14. Drain the bottom liquid (glycerin and soap) into a small beaker.
15. After separation has been completed, “wash” the biodiesel with distilled water to remove any remaining alcohol and soap.
    a. Spray a small amount of distilled water into the separatory funnel (about 10 initial squirts/sprays of water into the separatory funnel, about 10-20%/vol.).
    b. Wait about 5 minutes and observe the separation of the “white/milky”, soapy bottom layer from the top biodiesel layer.
    c. Separate this “milky” soap bottom layer from the biodiesel top layer into a clean beaker (this can be disposed of down the drain). Get as much of the bottom layer as possible.
16. Now “dry” the biodiesel to remove the excess water from washing.
    a. Pour the biodiesel remaining in the separatory funnel into a 400ml beaker and place on top of the stirring hotplate.
    b. Add a magnetic stir bar and a thermometer.
    c. Slowly heat to 105ºC, and keep at this temperature ~30 minutes or until the biodiesel becomes clear (the cloudiness will gradually disappear as water evaporates).
    d. Turn off the hotplate and allow biodiesel to cool. Remove the stir bar with the magnetic wand.
    e. We will use the use the results of your data analysis below to select a biodiesel sample to put into the generator and you can enjoy the benefits of your fuel by powering an appliance!

Batch #2 Ethanol (EtOH)

1. Weigh out 2.0 g of sodium hydroxide on a small piece of aluminum foil or weigh boat using balance.
2. Place 250 ml flask on balance and tare.
3. Add pre-determined amount of team’s alcohol for each batch to flask.
4. Add a magnetic stir bar to the ethanol flask. Add the sodium hydroxide to the ethanol. Place on the stirring hotplate (no heat) and stir to dissolve the sodium hydroxide completely, approximately 5 minutes.
5. Use a magnetic wand to remove the stir bar. Set ethanol/NaOH flask aside.
6. Add 200 g of soybean oil to 500 ml flask.
7. Add magnetic stir bar to oil flask and heat flask up to a temperature of 50-60°C (130-140°F) on hot plate while stirring vigorously. Note: hotplate takes time to heat up and then retains heat for a long time.
8. Once the oil reaches temperature, slowly add the ethanol/NaOH mixture.
9. Stir throughout the reaction (about 1 hr) with the stir bar.
10. The mixture will thicken and darken, then become thinner than the original oil.

11. Watch the temperature to ensure that it does not exceed 60ºC (140°F). Do not use the thermometer as a stirring rod.
12. After one hour, turn off the hot plate and stirring. Remove stir bar using magnetic wand.
13. Pour the mixture into the 500-ml separatory funnel. Allow the mixture to settle for at least 10-15 minutes. The bottom layer contains glycerin and some soap; the top layer is the biodiesel (fatty acid methyl esters or fatty acid ethyl esters).
14. Drain the bottom liquid (glycerin and soap) into a small beaker.
15. After separation has been completed, “wash” the biodiesel with distilled water to remove any remaining alcohol and soap.
    a. Spray a small amount of distilled water into the separatory funnel (about 10 initial squirts/sprays of water into the separatory funnel, about 10-20%/vol.).
    b. Wait about 5 minutes and observe the separation of the “white/milky”, soapy bottom layer from the top biodiesel layer.
    c. Separate this “milky” soap bottom layer from the biodiesel top layer into a clean beaker (this can be disposed of down the drain). Get as much of the bottom layer as possible.
16. Now “dry” the biodiesel to remove the excess water from washing.
    a. Pour the biodiesel remaining in the separatory funnel into a 400ml beaker and place on top of the stirring hotplate.
    b. Add a magnetic stir bar and a thermometer.
    c. Slowly heat to 105ºC, and keep at this temperature ~30 minutes or until the biodiesel becomes clear (the cloudiness will gradually disappear as water evaporates).
    d. Turn off the hotplate and allow biodiesel to cool. Remove the stir bar with the magnetic wand.
    e. We will use the results of your data analysis below to select a biodiesel sample to put into the generator and you can enjoy the benefits of your fuel by powering an appliance!

Batch #3 Isopropyl (IPA)

1. Weigh out **11.35** g of sodium hydroxide on a small piece of aluminum foil or weigh boat using balance.
2. Place 250 ml flask on balance and tare.
3. Add pre-determined amount of team’s alcohol for each batch to flask.
4. Add a magnetic stir bar to the IPA flask. Add the sodium hydroxide to the IPA. Place on the stirring hotplate (no heat) and stir to dissolve the sodium hydroxide completely, approximately 5 minutes.
5. Use a magnetic wand to remove the stir bar. Set IPA/NaOH flask aside.
6. Add 200 g of soybean oil to 500 ml flask.
7. Add magnetic stir bar to oil flask and heat flask up to a temperature of 60°C (140°F) on hot plate while stirring vigorously. Note: hotplate takes time to heat up and then retains heat for a long time.
8. Once the oil reaches temperature, slowly add the IPA/NaOH mixture.
9. Stir throughout the reaction (about 1 hr) with the stir bar.

10. The mixture will thicken and darken, then become thinner than the original oil.
11. Watch the temperature to ensure that it does not exceed 60ºC (140°F). Do not use the thermometer as a stirring rod.
12. After one hour, turn off the hot plate and stirring. Remove stir bar using magnetic wand.
13. Pour the mixture into the 500-ml separatory funnel. Allow the mixture to settle for at least 10-15 minutes. The bottom layer contains glycerin and some soap; the top layer is the biodiesel (fatty acid methyl esters or fatty acid ethyl esters).
14. Drain the bottom liquid (glycerin and soap) into a small beaker.
15. After separation has been completed, “wash” the biodiesel with distilled water to remove any remaining alcohol and soap.
    a. Spray a small amount of distilled water into the separatory funnel (about 10 initial squirts/sprays of water into the separatory funnel, about 10-20%/vol.).
    b. Wait about 5 minutes and observe the separation of the “white/milky”, soapy bottom layer from the top biodiesel layer.
    c. Separate this “milky” soap bottom layer from the biodiesel top layer into a clean beaker (this can be disposed of down the drain). Get as much of the bottom layer as possible.
16. Now “dry” the biodiesel to remove the excess water from washing.
    a. Pour the biodiesel remaining in the separatory funnel into a 400ml beaker and place on top of the stirring hotplate.
    b. Add a magnetic stir bar and a thermometer.
    c. Slowly heat to 80ºC, and keep at this temperature ~30 minutes or until the biodiesel becomes clear (the cloudiness will gradually disappear as water evaporates).
    d. Turn off the hotplate and allow biodiesel to cool. Remove the stir bar with the magnetic wand.
    e. We will use the use the results of your data analysis below to select a biodiesel sample to put into the generator and you can enjoy the benefits of your fuel by powering an appliance!

Data Analysis

Watch what happens during the transesterification and record your observations. Walk around and look at other biodiesel stations. As a group, identify the best looking biodiesel sample. Is it methanol or ethanol? This best sample will be used for producing power in the biodiesel generator. The others will be used for further biodiesel properties testing.

<u>Biodiesel Determination of Free and Total Glycerin, etc. (Bonanza Mini-Analyzer)</u>

Biodiesel Density and Freezing Point

Background

Your team will determine two very important biodiesel fuel properties, density and freezing point, of 5 biodiesel samples using a graduated cylinder, balance, beakers, test tubes/glass containers, rock salt, water, ice and thermometers. You will compare this to pure soybean oil.

Pre-experiment Checklist

- Samples are available for analysis: Optional based on availability
  - biodiesel #2 from production procedure (methanol and/or ethanol)
  - Biobus waste grease biodiesel
  - REG soybean biodiesel
  - REG animal fat biodiesel
  - REG combination biodiesel
  - soybean oil

Procedure-follow for all 6 samples

1. Weigh an empty graduated cylinder on a balance. Record the mass in grams.
2. Transfer approximately 20 mL of biodiesel into the graduated cylinder and record exact volume.
3. Weigh the graduated cylinder with the biodiesel on the balance and record mass.
4. Determine the mass of the biodiesel by difference.
5. Calculate the density of the biodiesel in g/ml (density = mass/volume).
6. If glycerol's density is 1.26 g/mL (greater than that of biodiesel), why does it sink to the bottom of the separator funnel/beaker?
7. Transfer the biodiesel samples evenly into a test tube, and set in the blue test tube rack.
8. Repeat steps 1-7 for all biodiesel and oil samples.
9. Set up an ice bath by dissolving some rock salt in ice water in 100 ml or larger beaker.
10. Place a thermometer into each test tube/glass container, and place into ice bath.
11. At 1 minute intervals, record the temperature and physical state of the biodiesel.
12. When the biodiesel appear "cloudy, record the time & temperature.
13. When the biodiesel begins to "gel", record the time & temperature.
14. If the biodiesel solidifies (freezes), record the time & temperature.
15. Stop monitoring if biodiesel does not freeze and the temperature has dropped below -20ºC.
16. Remove the test tubes from the ice bath and place in the test tube rack at room temperature.
17. Monitor the time & temperature at which the biodiesel melts, specifically when the solid or gelled biodiesel is returns to liquid state and seems to clarify in appearance.

Data Analysis

Which biodiesel sample(s) froze first in the ice bath? What was the temperature? Did any of the samples not change below -20ºC? Which melted/liquefied first? What was the temperature? Which would you want to “sell” as a winter fuel in Iowa?

Energy Content Determination (HHV)

Background

Your team will measure the higher heating value (HHV) of the five biodiesel samples using the Parr 6400 bomb calorimeter and pure soybean oil.

Pre-Experiment Checklist

- Samples are available for analysis
  - biodiesel #2 from production procedure
  - Biobus waste grease biodiesel
  - REG soybean biodiesel
  - REG animal fat biodiesel
  - REG combination biodiesel
  - Pure soybean oil

Procedure-follow for all 6 samples

1. Follow procedure for bomb calorimeter outlined in Biomass Properties Lab Handout.
2. Determine units to use on the calorimeter (review pre-lab material).
3. Analyze 2 replicate of 0.6 g samples of each type of biodiesel.
   a. Have 2 team members prepare one sample at a time, and place in the bomb for energy content determination, and then while awaiting the final result they can also prepare the duplicate sample.
   b. Record the energy content of each sample, and then clean out the cup, etc. and prepare for the second sample of this biodiesel type.

Data Analysis

1. Determine the average energy content for each type of biodiesel and the soybean oil. Compare the energy values.
2. Review the data provided in the pre-lab and in the biomass properties lab and the text. Where does your data fall in relation to the published results?

Optional – Biodiesel pH

Background

Many people have reported problems with trying to "read" the pH of biodiesel by putting the pH probe straight into the biodiesel. The pH scale commonly used (pH = 0-14) is a measurement for aqueous solutions. Although biodiesel can hold a tiny amount of water, for all practical purposes, biodiesel is a non-aqueous solution, so pH cannot be determined the traditional way. Water must be added to measure the relative concentration of acidic and basic ions (included as part of the soap impurity) present in the biodiesel. Soap is the salt of a weak acid and a strong base. When biodiesel is mixed with water, some of the soap is washed out of the biodiesel into the water. The pH of the wash water should always be above 7 to start. As the biodiesel is further “washed”, the pH of the wash water should continue to fall until it reaches the pH of the water being used to wash. It may be beneficial to leave a little bit of soap in the biodiesel so that any water will be basic (caustic) rather than acidic. Acid will attack steel but base does not, and the expensive parts of a diesel's fuel system are made from steel.

Procedure

1. Put similar amounts of biodiesel and water in a container and shake hard for a few seconds.
2. After biodiesel and water layers separate, measure the pH of the water.

Optional - Oil/Biodiesel Viscosity Test with 'Falling Ball' Method

Background

Your team will determine one of the important biodiesel properties, i.e. viscosity of available biodiesel samples. Viscosity can be generally described as "stickiness" of a fluid, being expressed with unit of centipoise (cP) or centistokes (cSt). Viscosity of a fuel is very important because it affects atomization of the fuel being injected into the engine combustion chamber. A small fuel drop is desired, so that complete fuel combustion occurs. A high viscosity fuel, such as raw vegetable oil, will produce larger drop of fuel in an engine combustion chamber, which may not burn as clean as fuel that produces a smaller droplet. Unburned oxidized fuel will build up in the engine around valves, injector tips and on piston sidewalls and rings, eventually resulting in broken rings in few cases. Hence, it's essential to ensure the biodiesel produced could match the ASTM standard of viscosity for biodiesel in market, so that it's engine- and environmental friendly.

Pre-experiment Checklist

- Oil or biodiesel samples
- 100ml graduated cylinder
- Marble
- Ruler
- Stopwatch
- Calculator

Procedure

Measuring Ball Density

1. Measure the diameter of a marble with Vernier Caliper in centimeter (cm). Calculate the radius of marble in cm, and volume of the marble in cm^3. (Radius, r = d/2, Volume = $4/3*\pi*r^3$)

2. Weigh the marble in grams (g). Calculate the density of the marble in g/cm^3. (Density = mass/volume)

Measuring Biodiesel Density

3. Weigh an empty 100ml graduated cylinder on a balance. Record the mass in grams (g).

4. Transfer approximately 100ml of oil/biodiesel into the graduated cylinder and record the exact volume.

5. Weigh the graduated cylinder with the oil/biodiesel on the balance and record mass.

6. Determine the mass of the oil/biodiesel by difference.

7. Calculate the density of the oil/biodiesel in g/ml. (Density = mass/volume)

Measuring Velocity of Dropping Ball

8. Use a marker pen to draw a horizontal line across '90ml' level. This will serve as starting point of dropping ball to start the stopwatch.

9. The bottom of cylinder will serve as ending point of dropping ball to stop the stopwatch.

10. Measure the height between calibrated starting point and ending point of dropping ball in cm.

11. Drop the marble into the oil/biodiesel. Once the marble reaches starting point, start the stopwatch.

12. Stop the stopwatch as soon as the marble reaches the ending point. Record the time in seconds.

13. Calculate the velocity of dropping marble in cm^3/s. (Velocity = height/average time)

Measuring Oil/Biodiesel Viscosity

14. Calculate the viscosity of the oil/biodiesel in centipoise (cP) using the following equation:

$$Viscosity\ (cP) = \frac{2 \times (density\ of\ marble - density\ of\ oil) \times g\ \times r^2}{9\ \times ball\ velocity}$$

, where *g* = gravitational acceleration = 980 cm/s^2
r = radius of marble, cm

Optional

15. If the sample is biodiesel, calculate kinematic viscosity of biodiesel (another way to express viscosity) in centistokes (cSt).

$$Kinematic\ Viscosity\ (cSt) = \frac{Viscosity\ (cP)}{biodiesel\ density\ (g/cm^3)}$$

16. Compare the value with ASTM standard of kinematic viscosity for biodiesel in market.

Data Analysis

	Source	Oil/Biodiesel I	Oil/Biodiesel II	Oil/Biodiesel III	Oil/Biodiesel IV	Oil/Biodiesel V	Oil/Biodiesel VI
Diameter of marble	cm						
Radius of marble (= diameter/2)	cm						
Volume of marble (= $1/3*\pi*r^3$)	cm^3						
Mass of marble	g						
Density of marble (= mass/volume)	g/cm^3						
Mass of empty graduated cylinder	g						
Mass of graduated cylinder with biodiesel	g						
Mass of biodiesel	g						
Volume of biodiesel	ml						
Density of biodiesel (= mass/volume)	g/ml						
Height between starting and ending point	cm						
Travelling time of dropping marble	s						
Velocity of dropping marble (= height/time)	cm/s						
Viscosity (in formula)	cP						
Kinematic Viscosity (= viscosity / density)	cSt						

Optional – Oil/Biodiesel Viscosity Test with "DIY Viscosimeter"

Background

Your team will make a "DIY Viscosimeter" to estimate the viscosity of biodiesel. Viscosity can be generally described as "stickiness" of a fluid, being expressed with unit of centipoise (cP) or centistokes (cSt). It's essential to ensure the biodiesel produced could satisfy the ASTM viscosity standard for biodiesel in market, so that it's engine- and environmental friendly. However, a precise lab-use viscosimeter is very expensive and not easily accessible, especially for public learning community interested in making biofuel and understanding more about its properties. Thus, "DIY Viscosimeter" made with few household items could help us to estimate roughly biodiesel viscosity with minimal costs.

Pre-experiment Checklist

- Empty plastic bottle (roughly 1.25L to 1.5L in size)
- 2mm copper pipe
- Drill & 2mm drill bit
- Biodiesel (about 1.5L to 2L)
- Retort stand and clamps
- A bucket
- Thermometer & two 1-Liter beakers
- Heat plate
- Stop-watch & calculator

Procedure

Making DIY Viscosimeter

1. Cut the bottom off the plastic bottle using scissors.

2. Remove the cap of the bottle and drill a hole on it.

3. Make sure the ends of copper tube are smooth and round with no burrs. Insert the copper tube into the hole for about 1cm.

4. Screw back the bottle cap. Test the DIY Viscosimeter by filling it up with water, and ensure there's no leakage around the cap. Replace the cap, if necessary.

5. Measure out and mark a vertical 10cm section on the side of the bottle. The line nearest the cut-off end of the bottle represents the start line, whereas the one nearest the cap represents the finish line.

Set-up DIY Viscosimeter

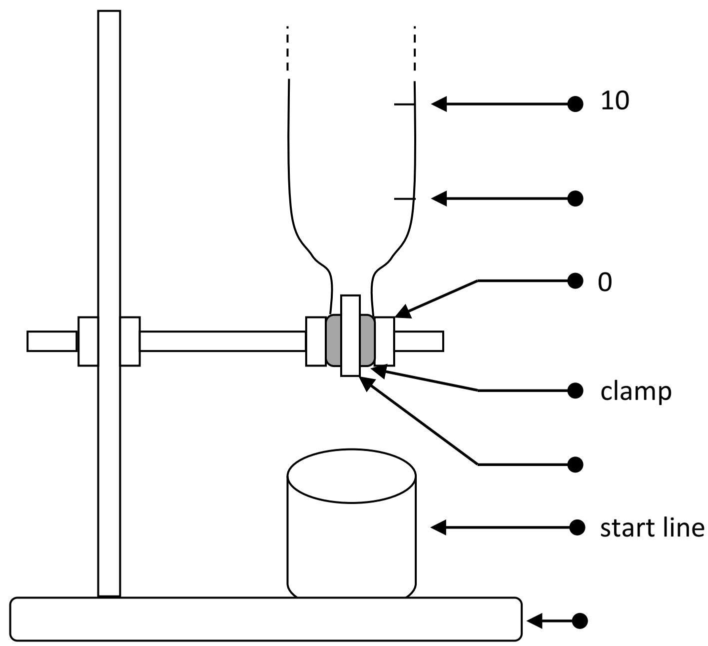


Figure 1. Set up of DIY Viscosimeter.

6. Set up the DIY Viscometer as shown in the Figure 1.

7. Place a bucket underneath the bottle, in order to contain flowing-out biodiesel.

Test Biodiesel Viscosity with DIY

8. Heat the biodiesel up to 40^{o}C. Once biodiesel reaches desired temperature, put one finger over the end of copper pipe and fill the plastic bottle with biodiesel to above start line. (NOTE: One person needs to support the stand or bottle to ensure the bottle is held perpendicular to the bucket, while the bottle is filled up with biodiesel.)

9. Remove the finger and allow the biodiesel to flow out. Once the biodiesel reaches the start line, start the stop watch.

10. Measure how long the biodiesel takes to get to the finish line. Repeat the measurement for at least two times to obtain accurate result. If this test is done properly, the results should be within a few tenths of a second of each other.

11. Divide the results in seconds by ten to find out how far the biodiesel travelled in one second. This will give you the value in centistokes, which is the standard measure of viscosity in fuel oil.

12. Compare the value with ASTM standard of kinematic viscosity for biodiesel in market.