Green Chemistry in the Curriculum: Biodiesel Module

Teacher's Guide to the Biodiesel Module

Module Layout and Preparation:
The module is designed to be a multi-component module with multiple lesson plans. Portions can be used as appropriate within the classroom. The following activities are outlined throughout this module:

Part 1. Physical Properties, Physical changes and Chemical Changes
- ***Activity 1-1:*** Determining the physical properties of vegetable oils.

Part 2. Preparation of Biodiesel.
- ***Activity 2-1:*** Titration of WVO.
- ***Activity 2-2:*** Synthesis of Biodiesel from WVO.
- ***Activity 2-3:*** Analysis of biodiesel.

Green Chemistry Principles:
The Biodiesel module demonstrates a number of Green Chemistry principles including:

Principle #1: Pollution Prevention – It is better to prevent waste than to treat or clean up waste after it is formed.
Principle #4: Safer Chemical Products – Chemical products should be designed to preserve efficacy of function while reducing toxicity.
Principle #7: Renewable Resources – A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.
Principle #10: *Design for Degradation* – Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

. **Learning Standards:**
High School Chemistry Learning Standards are identified throughout the biodiesel module. The module can be used in a variety of formats and to discuss many Learning Standards, including:

1. Properties of Matter
   a. Identify and explain physical properties (density, melting point, boiling point, etc.) and chemical properties (the ability to form new substances. Distinguish between chemical and physical changes.
2. Chemical Reactions and Stoichiometry
   a. Classify chemical reactions as synthesis (combination), decomposition,

single displacement (replacement), double displacement, and combustion.

3. Solutions, Rates of Reaction, and Equilibrium
    a. Calculate concentration in terms of molarity. Use molarity to perform solution dilution and solution stoichiometry.
    b. Identify the factors that affect the rate of a chemical reaction (temperature, mixing, concentration, particle size, surface area, catalyst).
4. Acids and Bases and Oxidation-Reduction Reactions
    a. Relate hydrogen ion concentrations to the pH scale and to acidic, basic, and neutral solutions. Compare and contrast the strengths of various common acids and bases.
    b. Describe oxidation and reduction reactions and give some everyday examples, such as fuel burning and corrosion.

Scientific Inquiry Skills Standards:

The hands-on approach to this module allows for the use of inquiry skills throughout. There are many instances where the skills can be applied. The inquiry skill standards identified include:

SIS1. Make observations, raise questions, and formulate hypotheses.
- Observe the world from a scientific perspective.
- Pose questions and form hypotheses based on personal observations, scientific articles, experiments and knowledge.

SIS2. Design and conduct scientific investigations.
- Articulate and explain the major concepts being investigated and the purpose of an investigation.
- Select required materials, equipment, and conditions for conducting an experiment.

SIS3. Analyze and interpret results of scientific investigations.
- Use results of an experiment to develop a conclusion to an investigation that addresses the initial questions and supports or refutes the stated hypothesis.
- State questions raised by an experiment that may require further investigation.

Teacher's Guide to the Biodiesel Module
Part 1. Physical Properties, Physical changes and Chemical Changes

Activity 1-1: Determining the physical properties of vegetable oils.

.**Learning Standard:** Properties of Matter
This is a simple way of visualizing physical changes of matter by investigating the difference in vegetable oils. Students are given 4 unknown oils, which are available at the supermarket and are asked to perform a test on the oils to determine the identity of the unknown. The coconut oil has a melting point close to room temperature and will solidify upon cooling slightly. Upon cooling all 4 oils over ice, the coconut oil will solidify first, followed by the peanut oil. The canola oil and soybean oil should both not solidify due to their melting points being below the freezing point of water. The concept of other distinguishing properties of the oils can then be discussed (density, color, etc.).

Helpful Tips:

- Coconut Oil will solidify at room temperature (melting point is 77°F). Before performing this experiment it can easily be melted by placing the container in warm water.
- All oils are available from the supermarket. Rapeseed oil is canola oil.

Required class time: One class period

Supplies needed:	***Fisher Catalog Number:***
• Coconut Oil	AC36547-5000 [CAS# 8001-31-8]
• Peanut Oil*	AC41684-5000 [CAS# 8002-03-7]
• Rapeseed Oil	ICN96005501 [CAS# 8002-13-9]
• Soybean Oil	S802371 [CAS# 8001-22-7]
• 25 mL Erlenmeyer flask (4/student)	S63268
• 250 mL Beakers (4/student)	S63326
• Ice	

* Be aware of peanut allergies and substitute oils as appropriate. *Do not use if there is a peanut allergy in your classroom.*

Teacher's Guide to the Biodiesel Module
Part 2. Preparation of Biodiesel.

The preparation of biodiesel is a multi-step process that includes 3 activities. It will require 3 class periods to complete. Activity 2-1 can be done by the instructor ahead of time OR if waste vegetable oil is NOT used, then this step can be skipped.

Activity 2-1: Titration of WVO.

.**Learning Standard:** Solutions, Rates of Reaction, and Equilibrium
The first activity for making Biodiesel is a titration exercise, which can be used to teach students about the concept of concentrations and molarity.
Waste vegetable oil (WVO) can be obtained from the cafeteria or a local restaurant that serves fried food if asked! Be sure to filter the solids from the vegetable oil before using. Due to the breakdown of the triglycerides during the frying process, it is necessary to first determine the content of free fatty acids in the WVO. You are able to do this ahead of time to save time in class. Or, alternatively, you can use this as a lesson with your students to learn titration techniques. It is an opportunity to talk about concentration and have them perform scientific calculations. Be sure to check their answers before moving on to Activity 2-2.

Helpful Tips:

- Vegetable oil purchased from the store can be used instead of waste vegetable oil. In this case, there are no free fatty acids and the amount of base required to hydrolyze the triglyceride can be calculated easily from the Activity 2-1 Worksheet.

Required Class time: One class period.
Time saver: Determine the free fatty acid content before class to save a class period.

Supplies needed:	***Fisher Catalog Number:***
• Buret, 10 mL	03-700A
• Ring Stand	S97616
• Buret Clamp	S48400
• 0.01M NaOH (5-7 mL/student)	SS284-1
• Graduated cylinder, 10mL	08-557-1A
• Isopropanol	AC42383-0010
• Erlenmeyer flask, 25 mL	07-250-087
• Autopipet (1 mL volume)	05-402-91
• Pipet tips	05-403-71
• Phenolphthalein indicator	S76958
• Distilled water	S80239

Activity 2-2: Synthesis of Biodiesel from WVO.

. **Learning Standard:** Chemical Reactions and Stoichiometry
This activity can be used for discussing synthesis and synthetic transformations. The process involves the use of a catalyst and therefore catalysis can be discussed. The nature of vegetable oil and diesel allows for many discussions when introducing organic chemistry concepts including hydrocarbons, functional groups (esters), fatty acids, etc.

The synthesis of biodiesel is fairly straightforward and can be done in 2 class periods. The first step of the synthesis involves the transesterification and will require a class period to allow the reaction to occur. The prepared biodiesel can be stored for a week between class periods. The washing step is essential to purify the biodiesel and to ensure it will function properly in Activity 2-3. Alternatively, the instructor can perform the washing and extraction steps outside of class to save class time.

Helpful tips:

- While heating the reaction, the reaction will turn clear. The reaction will be done when it turns cloudy and it will begin to turn opaque. The cloudy look will be due to two layers being formed (the top, biodiesel layer and the bottom glycerol layer).
- If you do not have a centrifuge, then the separation can be performed by allowing the biodiesel and glycerol layers to settle (let them sit overnight). The two layers will separate easily and the top layer can be poured off. A separatory funnel can be used to help separate the two layers and this will help when washing with water.
- Ethanol or methanol can be used in this reaction. Ethanol will require more time to react, where methanol will be a quicker reaction (both you will be able to see when they are done by the cloudiness). Both alcohols should be handled carefully. However, methanol poses more of a risk in terms of the hazard and should be used carefully with supervision of the students.
- Be sure to use 200 proof Ethanol, which is dry and water-free. Water in the ethanol can interrupt the reaction. Ethanol is flammable and hazardous by ingestion. Please be sure to take the appropriate safety precautions before using the alcohol. Keep careful watch over students using the alcohol and if needed, dispense the alcohol into the reaction vessel for the students.

Required class time: Two class periods
Time saver: The extraction and wash steps could be done outside of class by the teacher to save a class period and to allow for the next class period to be spent analyzing the biodiesel.

Supplies needed:	***Fisher Catalog Number:***
• Erlenmeyer flask, 25 mL (2)	S63268
• WVO, 10mL/student	

• Stir bar	14-513-58
• Ethanol, 200 proof	AC61510-1000
• KOH* (10 N)	62529032
• Stir/hot plate	S50445HP
• Centrifuge tubes w/ caps	
• Centrifuge	S49018Q
• Pipets	13-674-46K
• Acetic acid, 0.1 M	14532
• Distilled water	S80239
• Balance	

**KOH is corrosive and can cause burns on the skin. If contact with skin is made, wash with copious amounts of water immediately. Be sure to read safety information regarding this chemical and to take the appropriate safety precautions before using in the classroom.*

Activity 2-3: Analysis of biodiesel.

. **Learning Standards:** Acids and Bases and Oxidation-Reduction Reactions.
This activity consists of three tests the students can perform on the biodiesel they have prepared in order to test the properties. They will test the pH of the biodiesel, allowing for a discussion of acids and bases and pH. They can also test the combustion of the product they made, allowing for a discussion of combustion reactions.

Helpful Tips:

- The combustion test should be performed by the teacher and performed in a well-ventilated area such as a fume hood or outside. The biodiesel prepared should combust easily, while the starting material (canola oil) should not burn.
- The melting point test can be done by placing the sample in a freezer or by using ice to cool the sample.

Required class time: One class period

Supplies needed:	***Fisher Catalog Number:***
• Distilled water	S80239
• pH paper	
• test tubes (small)	14-958A
• glass spatula	S63450
• wad of cotton	07-886
• test tube rack	S90342
• sample vial, 3 mL	S31649D
• thermometer	14-997

Student Module

Introduction:

A major source of energy for our society is the burning of fossil fuels such as coal, petroleum and natural gas. These sources of energy have been found to have limited amounts available, and therefore are said to be depleting resources. Scientists are continuously looking to find alternatives to fossil fuels. One such alternative is using vegetable oils to make fuel. Vegetable oils, such as those from corn, soy beans and canola have been found to be suitable alternatives to diesel fuel, which has traditionally come from petroleum.

Biodiesel is a fuel made from renewable resources such as vegetable oils that is used in diesel engines. Rudolf Diesel developed the diesel engine in 1893. He developed the engine to first run on peanut oil and he demonstrated this at the World Fair in Paris, France in 1900. Later on, the Diesel engine was modified to use a fraction of petroleum, obtained from fossil fuels. Today, many vehicles use the diesel engine, including many large vehicles such as trucks and buses. And, today more and more diesel engines are being modified to use biodiesel, which was the original intent of Ruldof Diesel when he developed the engine.

Biodiesel can be used directly in unmodified diesel engines, or blended with regular diesel fuel. When burned, biodiesel smells like french fries or popcorn.

Part 1
Properties of Vegetable Oils

Which vegetable oils are the best for use as biodiesel? What properties do you think a vegetable oil should have in order to operate properly in a diesel engine? To think about this, we will first take a closer look at vegetable oils that we find in the kitchen. These oils are similar to those that are used as biodiesel. Please note that the oils, although similar in properties, are not the same oils that are used as biodiesel fuel. The oils can be converted quite easily to biodiesel fuel as you will find in a later lesson when we perform a chemical reaction.

. ***Activity 1-1:*** Determining the physical properties of vegetable oils.

In this experiment, you will be given 4 different kinds of vegetable oils to evaluate. The four vegetable oils have different melting points, which are listed in the table below. If you have been given the following information, determine which is which:

Type of Oil	Melting Point (°F)
Peanut Oil	37.4
Soybean Oil	3.2
Coconut Oil	77
Canola Oil	14

Inquiry: Develop an experiment (test) to determine the relative melting points of the four unknown oils. Record your results and verify your answers with your teacher.

Test (please describe):

Unknown Oil #	Observations
1	
2	
3	
4	

Notice how you are able to determine the differences in the oils just by studying the physical changes of the oils. The physical change does not change the actual structure of the oil molecules, it simply changes the state of the matter. A physical change is when a substance undergoes a change while the chemical properties of the substance remain constant. In this example, the oil is still oil, but it is just in a different form (liquid versus solid). This is similar to ice and water: water will freeze below 32°F and turn into a solid. The chemical structure of water is still the same (H_2O), but the state of the substances changes.

A chemical change is different from a physical change in that the substance will undergo a chemical change and change the chemical makeup of the substance. Thinking about the purpose of the oils we are testing, our hope it to use them in a diesel engine. A diesel engine is an internal combustion engine where the fuel (diesel fuel) is burned in order to produce energy. This example is a chemical change where the chemical makeup of the biodiesel fuel is changed by being converted to carbon dioxide and water. We will observe this chemical change later on when we are able to test the biodiesel we make.

***Inquiry*:** Questions

1. What other properties might help you determine which oil is which?

2. Describe a physical change that you observed while testing the different vegetable oils.

3. If you are investigating the use of these four vegetable oils for the use in a biodiesel engine, which one(s) would you recommend? Why?

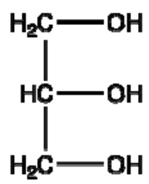
4. What benefits do you think using biodiesel has compared to using traditional diesel fuel?

5. What are some examples of chemical changes? How are they different from physical changes?

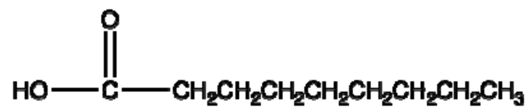
Part 2
Preparing Biodiesel

Once we understand the physical properties of the various oils that can be used for biodiesel, we can then learn how the oils and fats from vegetables can be converted into useful biodiesel fuel.

Plant vegetable oils are made of what are called triglycerides; which are composed of three fatty acids that are linked to a glycerol molecule by an *ester* bond. **Fatty acids** are long, straight chains of carbon atoms with hydrogen atoms attached **(hydrocarbon**s) with a carboxylic acid group (COOH) at one end and a methyl group (CH_3) at the other end. These long, straight chains combine with the **glycerol** molecule to form a triglyceride (oil).

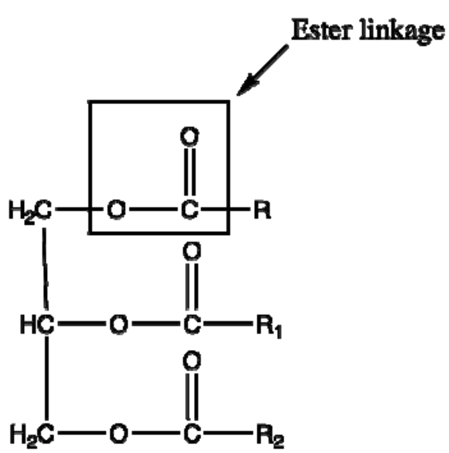


Glycerol



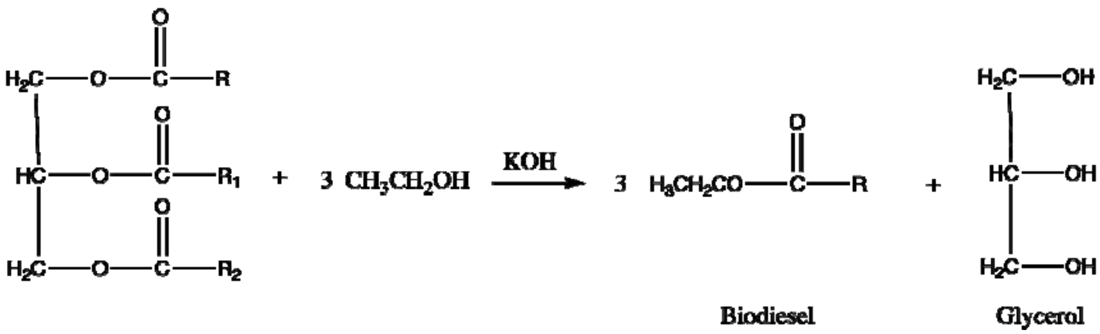
Fatty Acid

Note that three fatty acids are used to form the triglyceride. Depending on the oil or fat, the lengths of the fatty acid chains will vary and the three fatty acids that make up the triglyceride can be three *different* fatty acids. Because they can be three different fatty acids, the term "R" is used to represent the carbon chain. R, R_1 and R_2 all represent different lengths of carbon chains. These oils and fats are commonly found in plants and in our bodies.



Triacylglyceride (oil or fat)

In order to make biodiesel the triglyceride molecules can be converted into a simpler form through what is called a *transesterification* reaction. This reaction converts one type of ester group to another. In the reaction scheme below you can see that the ester groups that are attached to the glycerol portion of the molecule are broken and converted to a different type of ester.



The reaction scheme above shows that we use an alcohol, such as ethanol (CH_3CH_2OH) and a catalyst (potassium hydroxide, KOH) to convert the vegetable oil into biodiesel and glycerol, a by-product of the reaction. You can see that since the starting material on the left side of the equation had three fatty acid hanging off the glycerol that we needed 3 ethanol molecules to produce 3 biodiesel molecules.

Keep in mind that since biodiesel is actually a ***mixture*** of esters, different types of vegetable oils can produce fuels with different properties.

. ***Activity 2-1:*** Titration of WVO.

Your "raw material" for making biodiesel will be the Waste Vegetable Oil (WVO) from the cafeteria. When heated at high temperatures in the presence of water from food, the fatty acid esters in vegetable oil begin to break down by a chemical reaction called hydrolysis, producing free fatty acids and glycerol. The fatty acids can inhibit the transesterification reaction by reacting with the base (KOH) catalyst used in the transesterification. For this reason, it is very important that we determine the exact concentration of free fatty acids by titrating the WVO with a known concentration of sodium hydroxide (NaOH). You can then calculate the amount of additional KOH catalyst you will need in the transesterification reaction.

Your WVO was collected from the cafeteria and was filtered to remove food particles.

Experimental Procedure:

1. Clamp a 10.0 mL clean, dry buret to a ring stand. Check that the buret is dry. Using a graduated cylinder obtain about 5-7 mL of 0.0100 M NaOH. Make sure that the stopcock is closed, and pour the NaOH solution into the dry buret.

2. Using a graduated cylinder measure obtain 10 mL of 2-propanol (isopropanol) and pour into a 25 mL Erlenmeyer flask. Using an automatic pipet add exactly 1.00 mL of WVO to the isopropanol and swirl to dissolve. Add 2-3 drops of phenolphthalein.

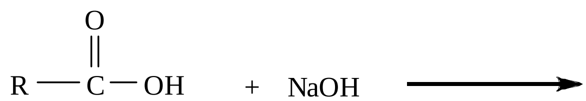
3. Record the exact volume of NaOH in the buret to two decimal places. Place the flask containing the WVO under the buret and begin adding the NaOH dropwise, while swirling the flask. If drops of the NaOH fall on the sides of the flask you will need to rinse them down with a few drops of distilled water. The solution in the flask may turn milky; this is normal. Continue adding the NaOH dropwise to the swirling flask until you get a light pink color that persists at least 15 seconds. If the solution turns bright pink you need to start over. RECORD the final volume of NaOH in the buret to two decimal places.

4. Before continuing to PART II, you and your lab partner must complete the PART I Worksheet on the next page to determine the moles of fatty acids present in the WVO sample, and the total amount of KOH catalyst you will need for the transesterification reaction.

5. Rinse your buret with distilled water and clamp upside down with the stopcock open.

Name:________________________________ ***. Activity 2-1 Worksheet***

1) Complete the following reaction for the titration of a carboxylic acid with NaOH (acid/base reaction):



2) Volume of 0.0100 M NaOH used in the WVO titration ______________________

3) Moles of NaOH needed to neutralize the free fatty acids in 1.00 mL of WVO_____________________

4) Moles of **KOH** you will need to neutralize the free fatty acids in **10.0 mL** of WVO__________________

The amount of base needed as a catalyst for the transesterification reaction is equal to 3.5 grams of **<u>NaOH</u>** per 1000 mL of **<u>PURE</u>** veggie oil.

5) How many grams and moles of NaOH will be needed as catalyst for **<u>10.0 mL</u>** of **<u>PURE</u>** veggie oil?

_________________________grams ________________________moles

6) We are using **KOH** as catalyst. How many moles of **<u>KOH</u>** will be needed for **<u>10.0 mL</u>** of **<u>PURE</u>** veggie oil?

_______________________moles KOH catalyst for 10.0 mL pure veggie oil

7) NOW, how many **TOTAL** moles of KOH will be needed for the transesterification reaction:

moles KOH to neutralize fatty acids + moles KOH as reaction catalyst = ________________total moles

8) The KOH for transesterification is provided as a 10.0 M aqueous solution. How many mL and μL of 10.0 M KOH will be needed?

__________________________mL _________________________μL

. ***Activity 2-2:*** Synthesis of Biodiesel from WVO.

You are now ready to make your own biodiesel fuel from WVO. The process involves a few steps over 2-3 class periods.

Experimental Procedure:

1) Determine the mass of a clean, dry 25 mL Erlenmeyer flask. Add to this flask 10.0 mL of WVO using the bottle dispenser, and record the exact mass of the WVO. Add a stir bar to the WVO, 2.0 mL of ethanol, and the appropriate volume of 10.0 M KOH calculated in PART I. Stir the reaction mixture vigorously (setting of 8-9) at **50^{o}C for 30 minutes**. Record all observed changes during the reaction.

2. Transfer the reaction mixture to two centrifuge tubes, and centrifuge for 5 minutes. You should end up with two layers, with the biodiesel on top. Using a pipet, discard the lower layer which contains glycerol and KOH catalyst into the labeled waste container.

3. Combine the crude biodiesel into one centrifuge tube. Add 1 mL of 0.1M acetic acid to the biodiesel, cap the tube, invert gently five times (do not shake), then centrifuge for 5 minutes. Discard the bottom, aqueous layer into the labeled waste container. Repeat the extraction step using 1 mL of distilled water.

The extraction or "washing" in step 3 removes flammable ethanol, glycerol byproduct, catalyst, and fatty acid salts ("soaps") from your biodiesel. If the water wash is not done properly, contaminating ethanol could create a fire hazard, and contaminating glycerol, catalyst, and soaps will negatively affect combustion and engine performance. Furthermore, mixtures of biodiesel and water will form an emulsion if shaken. Fuel emulsions with water would be disastrous in a diesel engine. Finally, all traces of water must be removed from the washed biodiesel before use in a diesel engine is possible.

4. Using a pipet transfer the washed biodiesel to a pre-weighed 25 or 50 mL Erlenmeyer flask. Heat this sample at 70-80^{o}C for 10-15 minutes to evaporate residual water. Obtain the mass of your dry biodiesel.

. ***Activity 2-3:*** Analysis of Biodiesel.

You will now test your biodiesel sample to determine the properties of the fuel. You will perform some simple tests to test the properties. Record your results on the worksheet on the following page.

Determining the pH: add 5 drops of your biodiesel to 1 mL of distilled water and mix thoroughly. Using pH paper, estimate the aqueous pH of your biodiesel.

Combustion Test: Obtain a small wad of cotton and roll this tightly onto the end of a glass spatula to form a "torch." Dip this into your biodiesel and stand up in a beaker or test tube rack. Now, take your "torch" to your teacher and and they will try lighting the sample with a match. Time how long your sample burns, the color of the flame, and whether any smoke or soot is observed. Was the torch easy to light? Is there an odor?

Freezing Point: Biodiesel will "gel" at low temperatures. Transfer your biodiesel to a 3 mL reaction vial, and place in the test tube rack in the freezer for 15-20 minutes. Your biodiesel should "gel" in this time. **If your biodiesel does not gel, repeat the drying step.**

Remove the sample from the freezer and immediately add a digital thermometer and record the temperature. Holding the vial near its top, stir the gel with the thermometer and record the temperature when the sample has completely "melted" or clarified. BE SURE TO CLEAN THE THERMOMETER WHEN DONE!

Disposal: When you are done, pipet your biodiesel sample into the labeled collection container.

Name:_______________________________ ***. Activity 2-2 and 2-3 Worksheet***

Actual mass of the 10.0 mL of WVO used ________________________(g)

Mass of dry, purified biodiesel ________________________(g)

%Yield of biodiesel based on mass ________________________

Color of purified biodiesel____

Estimated aqueous pH of your biodiesel_____________________

Time (minutes) that your biodiesel sample burned_____________________________

Temperature at which your gelled biodiesel "melted" or clarified___________________

. ***Activity 2-3:*** *Questions*

1. List four advantages of using biodiesel as a fuel.

2. Explain the difference between renewable and non-renewable resources.

3. Based on the aqueous pH of your biodiesel, comment on its corrosive properties.

4. Explain the purpose of the acid wash in step #3. Write a balanced chemical equation as part of your explanation.

5. At what temperature did your gelled biodiesel "melt" or clarify? Is biodiesel a practical fuel for the northeastern U.S.? What options are possible to improve the freezing point characteristics of biodiesel

6. In the commercial production of biodiesel, 1.20×10^3 kg of vegetable oil produces 1.10×10^3 kg of biodiesel. How does your yield compare to this

7. One argument against biodiesel being a "green" fuel is that combustion produces CO_2, which is a greenhouse gas. Is it possible to counter this argument from the standpoint of using renewable resources?