Biodiesel Production and Analysis

Introduction

A key current focus in science and engineering is the development of technologies for generating and utilizing new sources of energy. Climate change, geopolitics, national security, and diminishing resources are driving a significant portion of this work toward renewable sources of energy. The energy obtained is sometimes referred to as “green,” though the environmental impact of different energy sources is a complex topic beyond the scope of this course. Among the renewable energy approaches are a number of strategies for generating fuels from plants. These are particularly relevant to Kansas given the importance of agriculture in the state economy. They include ethanol (C$_2$H$_6$O), which in the U.S. is derived primarily from corn and mixed with gasoline, and biodiesel, i.e., diesel fuel from a biological source, which is a mixture of different organic molecules (involving C, H, and O) obtained from plants such as soybeans. In this experiment, you will generate biodiesel fuel from common vegetable oil and analyze its properties.

While there are many variations of biodiesel synthesis, all follow the same basic premise. In this laboratory experiment, you will react methanol (CH$_3$OH) with sodium hydroxide (NaOH) to form sodium methoxide (NaOCH$_3$) and water. The chemical equation for this reaction is given below in Reaction 1. This is a reversible process, so you will drive the reaction forward by heating the mixture up to 60°C.

You will then take vegetable oil and mix it with sodium methoxide to form 3 equivalents of biodiesel and 1 equivalent of glycerin (Reaction 2). This is called a transesterification reaction.

NOTE: The mixture of carbon chain lengths and the locations of carbon-carbon single/double bonds vary with the type of oil. The following reaction scheme is a simplified representation.

\[
\text{CH}_3\text{OH} + \text{NaOH} \rightleftharpoons \text{NaOCH}_3 + \text{H}_2\text{O}
\]

\[
\text{biodiesel} + 3\text{NaOCH}_3 \rightleftharpoons 3\text{glycerin} + \text{vegetable oil}
\]
Viscosity is simply a measure of a fluid’s thickness, *i.e.*, its resistance to flow. Rigorous measurement of absolute viscosity, expressed traditionally in the unit of centipoise (cP), is beyond the scope of this lab. We will use an ordinary Pasteur pipet to measure relative viscosities; this approach is derived from the Ford viscosity cup method. At right is a table giving results of viscosity measurements obtained with the pipet method for water, ethanol (C\(_2\)H\(_6\)O), and octane. You will likely recognize the latter as a component of gasoline. When referred to in gasoline, it actually involves a number of different molecules with the general formula C\(_8\)H\(_x\), and the octane rating measures the quantity of such molecules in the gasoline blend.

When a change in the energy of a system results in a temperature difference, we say that energy has been transferred as heat. In this laboratory you will determine the energy content in the biodiesel fuel you synthesize by measuring the heat generated by burning it. An equation that expresses heat in the internationally accepted energy unit of Joules (J) is:

\[
q = ms\Delta T
\]

where \(q\) is heat released or absorbed (usually expressed in J), \(m\) is mass (usually in g), \(s\) is specific heat (usually in J/(g°C)), and \(\Delta T = T_{\text{final}} - T_{\text{initial}}\) is the change in temperature (usually in °C). The above equation describes the heat transferred to a calorimeter containing water that is heated as the biodiesel burns. The convention, however, is to focus attention on the “system” from which the heat is being obtained, here the biodiesel fuel, rather than the water in the calorimeter which is receiving the heat. Accordingly, the experimental quantity of interest is numerically equal in magnitude but opposite in sign:

\[
q_{\text{system}} = -q_{\text{water}} = -ms\Delta T_{\text{water}}
\]

This is the heat transfer from the perspective of the system (*i.e.*, if \(q_{\text{system}}\) is negative, energy has been transferred from the system to its surroundings, if \(q_{\text{system}}\) is positive, energy has been transferred to the system from its surroundings). In this experiment you measure the heat transferred by monitoring the temperature of the water. Thus, the specific heat above, \(s\), refers to the water and is the amount of heat gained or lost when one gram of that substance changes temperature by one degree Celsius (°C). Every substance has a particular specific heat that depends on the molecular structure. The specific heat of water is 4.184 J/(g°C). Thus, 4.184 J of energy is required to raise the temperature of exactly 1 g of water by exactly 1 °C.

Given a value for \(s\), what experimental data do we need to calculate the heat transferred, \(q\), for a process? We must know \(m\), the total mass of water inside the calorimeter undergoing warming or cooling. We must also measure the net temperature change of the water, \(\Delta T_{\text{water}}\). Performed as described here, the experimentally calculated quantity \(q\) corresponds to the net heat change, also
known as the *enthalpy* change, $\Delta H$. The enthalpy change is actually defined as the heat transferred under constant pressure conditions. Since the atmospheric pressure in the laboratory does not change much during the course of your experiments, the heat you measure is therefore an enthalpy change.

### Pre-lab

**Safety:** Goggles *must* be worn at all times. This lab involves a number of substances which must be handled with care: 1) Methanol will cause blindness if ingested and is highly flammable. 2) NaOH (sodium hydroxide) is highly caustic - if you get it on you immediately wash the affected area with soap and water. 3) Biodiesel is highly flammable. You will also have excess NaOH in the biodiesel. Remove all potentially flammable items from the area before igniting the biodiesel.

Biodiesel, organic solvent (methanol), and sodium hydroxide should be collected in the appropriate waste container. *Do not discard magnetic stir bars in the waste container. Check with your TA if you have questions about proper disposal. Be sure to return the methanol to the hood immediately after use.*

**Pre-lab Assignment:** Please write out the following in your lab notebook. This assignment must be completed before the beginning of lab. You will not be allowed to start the experiment until this assignment has been completed and accepted by your TA.

1. *Briefly* describe the objectives of this experiment.
2. Write out the experimental procedure in your lab notebook according to the “*Guidelines for Keeping a Laboratory Notebook*” handout.

In addition to these pre-lab requirements, *a short quiz will be given at the beginning of lab* based on the material in this lab write-up.

### Procedure

**Part 1 - Producing Biodiesel from Vegetable Oil**

In this part of the laboratory, you will generate biodiesel from vegetable oil. This will be accomplished through a simple chemical reaction in which the longer-chain hydrocarbons making up the vegetable oil are broken up into shorter-chain molecules (biodiesel) and reaction side products (glycerol). This biodiesel production procedure is based on the published work of S. A. Meyer and M. A. Morgenstern (see *The Chemical Educator* 2005, 10, 130-132).

1. Create a warm water bath (~60 °C) using a large beaker (at least 400-mL-size) on a hot plate.
2. Place a small beaker containing 60.0 mL of vegetable oil on the hot plate.
3. Place 14 mL of methanol in a large test tube. Use a ring stand and clamp to support the test tube in the water bath.

4. Grind 0.5 g of NaOH and add it to the methanol.

5. When the NaOH is dissolved and both the oil and methanol are warm, place the oil beaker on a stir plate and add the methanol solution to it.

6. Use a stir bar to stir the mixture for 30 min.

7. Pour the product mixture into 2 small test tubes (each about two-thirds full) and centrifuge for 3 min.

8. The layer on top is biodiesel. The bottom layer is methanol and glycerol. Use a disposable pipet to decant the biodiesel; collect it in a beaker. Be sure to properly dispose of the waste in the proper container and return the methanol to the hood.

Before using biodiesel in engines, the biodiesel is washed with water to remove sodium hydroxide. Why?

**Part 2 - Analysis of Biodiesel**

In this part of the experiment, several tools will be used to assess the quality of the fuel produced in Part 1. Specifically, the density, viscosity, and energy content will be measured.

**Measure the density:**
1. Weigh a sample of the biodiesel produced in Part 1. Be sure to account for the weight of the container.

2. Measure the volume of the biodiesel in the container.

3. Calculate the density of the biodiesel in g/cm³.

**Measure the viscosity:**
1. Take a disposable pipet (shown at right) and stand it straight up in a beaker, ensuring that the tip is flat against the bottom.

2. Fill the pipet to the brim with biodiesel (some oil will fall out of the pipet, but continue filling it until the oil level reaches the top).

3. Use a stopwatch to determine the time it takes for all of the biodiesel to pour out of the pipet only using gravity (there may be some oil left in the very tip, but stop timing at the moment the oil stops pouring from the pipet).

Considering the viscosities given in the Introduction, what are the implications for your biodiesel in an engine?
Measure the energy content:

1. Mount an iron ring on a ring stand. Take a tin can with two holes cut in the top and insert a glass rod. Hang the can on the iron ring.

2. Weigh the empty tin can. Add approximately 100 mL of water to the can and reweigh. Calculate the mass of water in the can. Return the can to the apparatus and place a thermometer in it. You may gently clamp the thermometer to ensure that it is submerged in the water--but it should be suspended slightly above the can bottom.

3. Place ~1 g of biodiesel on a watch glass. Bend a metal wire to form a small "matchstick stand" and place it on the watch glass. Place the watch glass assembly underneath the tin can. The arrangement is pictured at right (check with your TA if you have questions about the proper setup).

4. Record the initial temperature, \( T_{\text{initial}} \).

5. Remove all potentially flammable items from the area. Light a match and carefully place it on the matchstick stand to ignite the biodiesel.

6. Wait until the biodiesel has been consumed by combustion. The water temperature may continue to increase for a short time after burning has ceased. The highest temperature reached should serve as \( T_{\text{final}} \) in your calculations.

7. Determine the energy content of your fuel, that is, the enthalpy change involved in combustion of the biodiesel, according to the equations given in the Introduction.

When selecting a fuel for your car, would you want a high or low energy content? Why?
**Glossary**

*calorimeter*

an experimental apparatus used for measuring the heat evolved in a chemical process

*climate change*

systemic changes to the earth’s climate that persist for a significant time; often used as a synonym of *global warming,* the rise observed in global average temperature over the past ~50 years, though “climate change” indicates additional changes beyond temperature alone; see the Intergovernmental Panel on Climate Change reports: [http://www.ipcc.ch/](http://www.ipcc.ch/)

*diesel fuel*

petroleum product obtained by refining crude oil consisting of a mix of hydrocarbons with between 10-15 carbon atoms per molecule

*enthalpy*

a measure of the total thermodynamic energy of a system, represented as $H$; the enthalpy is the sum of the *internal energy* and the work involved in changing the system volume; changes in enthalpy, $\Delta H$, are the same as the heat transferred in a constant pressure process (a fact used in this laboratory experiment)

*gasoline*

petroleum product obtained by refining crude oil consisting of a mix of hydrocarbons with between 4-12 carbon atoms per molecule

*octanes*

a saturated (only single-bonded) hydrocarbon with eight carbon atoms, typically C$_8$H$_{18}$

*specific heat*

the energy required to raise the temperature of a 1 g substance by 1 °C; depends on the substance; has units of J/(g⋅°C); also called the *specific heat capacity*

*vegetable oil*

oils extracted from plant material, particularly seeds; the chemical composition typically involves triglycerides (the reactants in Reaction 2 of this write-up)

*viscosity*

a measure of the resistance of a liquid to an applied force; the resistance of a liquid to flow