**Bomb Calorimetry and Viscometry: Which feedstock produces the best biodiesel fuel?**

Animal fats and vegetable oils consist of triglycerides. An example is shown below.

![Triglyceride structure](image)

Biodiesel is a renewable fuel created by transesterifying triglycerides into fatty acid methyl esters. Biodiesel, as well as other fuels derived from biomass, has gained widespread popularity as a viable choice to offset the use of fossil fuels in the transportation industry.

**Theory**

A bomb calorimeter is a sealed container capable of holding several atmospheres of gas pressure. A weighed sample of substance is placed in contact with an ignition wire inside the bomb. The bomb is filled to about 20 atm of pressure with O₂, sealed, and placed in a known amount of water. An electric current is passed through a wire to ignite the mixture. As the combustion takes place, the heat evolved raises the temperature of the calorimeter and its surrounding water, as measured by a thermometer. In order to prevent heat loss from the calorimeter system, some calorimeters are surrounded by a second water bath, whose temperature is continuously adjusted (by the experimenter) to match that of the calorimeter. Thus, the heat transfer between the system (calorimeter and contents) and the surroundings (the water jacket, primarily) is zero, making the process adiabatic: \( q = 0 \). Our calorimeters use good thermal insulation instead of a second water bath to prevent loss of heat to the surroundings.

Since the combustion takes place in a sealed container with constant volume, the work done on or by the system is also zero, so that \( \Delta U = q + w = 0 \) for the overall process shown below.

![Diagram of calorimetry process](image)

**Figure 1:** Since internal energy is a state function, we can break the overall process into two steps.

The initial temperature of the system is \( T_1 \) and the final temperature is \( T_2 \) after combustion of reactants to products and heating of the calorimeter. Since \( U \) is a state function, the pathway...
from initial to final state does not affect the value of $\Delta U$. This allows us to separate the two processes (combustion and heating), although, in reality, they occur simultaneously.

With this in mind, it is true that

$$\Delta U_{\text{overall}} = \Delta U_a + \Delta U_b = 0$$  \hspace{1cm} [1]

or,

$$-\Delta U_a = \Delta U_b$$  \hspace{1cm} [2]

But, since **Step b** simply involves heating up the calorimeter and contents from $T_1$ to $T_2$,

$$\Delta U_b = C_V \Delta T = C_V (T_2 - T_1)$$  \hspace{1cm} [3]

Note that $C_V$ is the heat capacity of the bomb calorimeter and its contents. From equations [2] and [3], the change in internal energy of combustion can be readily found from the change in internal energy of heating.

The **molar enthalpy of combustion $\Delta H_m$** is given by the equation:

$$\Delta H_{\text{comb},m} = \Delta U_{\text{comb},m} + RT_{\text{comb}} \Delta n_{\text{gas}}$$  \hspace{1cm} [4]

where $T_{\text{comb}}$ is the temperature at which combustion occurs, $\Delta n_{\text{gas}}$ is the change in the number of moles of gas (in the balanced reaction representing the combustion of one mole of compound). To ensure that units match, $\Delta n_{\text{gas}}$ should be treated as unitless.

Determining the heat evolved during the combustion from Equation 3 requires knowledge of the heat capacity of the calorimeter often called the calorimeter constant. By combusting a sample with a known molar heat of combustion, we can use the measured temperature change and Equation 3 to calculate the calorimeter constant.

**Pre-Experiment Questions—Part 1**

1. List some properties that could be helpful to consider when choosing a fuel.
2. Define the word “feedstock.”
3. Look up the chemical reaction for the synthesis of biodiesel from fats or oils and write it in your notebook. Show the whole chemical structure for all components.
4. What is a fatty acid methyl ester (FAME), and how is it different from a fatty acid and a fat? Again, use complete chemical structures in your answer.
5. What is a saturated fat? Give an example in your answer. What is an unsaturated fat? Provide an example in your answer.
6. Go to the web (http://www.chempro.in/fattyacid.htm) and look up the fatty acid composition of olive, corn, soybean, coconut, palm, and flaxseed (linseed) oil. Discuss some of the differences that you notice.
7. What is a bomb calorimeter? What information can you gain about a sample by making bomb calorimetry measurements?

8. Fatty acids are often described using lipid number (C:D) notation. For instance, oleic acid is 18:1. Explain this notation.

9. Look up and make a table containing formula, molecular weight, and lipid number for the following FAMEs: methyl laurate, methyl palmitate, methyl oleate, methyl stearate, methyl linoleate, methyl linolenate, methyl caprylate, methyl caprate, and methyl myristate.

10. Based on the structural information that you collected, which of the FAMEs would you predict to have the highest heat of combustion? Rank the FAMEs by increasing heat of combustion. Justify your ranking. Discuss these predictions as a class.

11. Biodiesel can be prepared from different starting oils (i.e., feedstocks). Would you expect a difference in the heat of combustion of the biodiesel fuel if a different feedstock were used (for instance, soybean oil versus olive oil)? Explain.

Thinking About the Data—Part 1 (complete while calibrating the calorimeter, below)
In addition to the data that your research team will be collecting in the lab, your collaborators have shared data they collected for the combustion of multiple FAME samples. You should treat this data as your own when carrying out the Thinking About the Data questions.

12. What units should be used for the heat of combustion? When thinking about a fuel, what units might be of greatest importance to us?

13. Construct a graph with the carbon chain length (of the FAMEs) on the x-axis and heat of combustion on the y-axis; is there a discernible trend? Are there points on your graph that appear to be outliers?

14. Is there a relationship between degree of unsaturation and heat of combustion among the FAMEs? If so, represent it graphically.

15. Does your graphed data correlate with your rankings from PEQ#10? As a class devise a statement that describes the relationship between degree of unsaturation and heat of combustion and chain length and heat of combustion. Write your statement on the board.

Calibrating the Calorimeter

1. Watch the video posted on the web site.

2. Turn on the calorimeter.

3. Use a top-loading balance to weigh out approximately 0.9 g of special grade benzoic acid not exceeding 1 gram. Use this to make a pellet in the pellet pressure. Make three of these pellets.

4. Tare an analytical balance with the metal combustion cup, and then place a pellet into the cup and obtain its mass to ± 0.01 mg.
5. Attach one strand of cotton string to the wire connecting the electrodes. Make sure that the string touches the pellet, and that the ignition wire is attached firmly to the electrodes. Gently wiggle the electrodes; they should not be loose.

6. When closing bomb, tighten down the cap by HAND only. Fill the bomb with oxygen, allowing the pressure to build up slowly to 25 atm. Purge the bomb with pure oxygen twice. Fill a third time, and then connect the ignition head to the top of the bomb.

7. Put the bomb in the calorimeter. Make sure that it is centered on the three pins at the bottom of the water bath.

8. Fill the reserve tank to the line with tap water.

9. Close the lid, and hit the button under “prepare an experiment”.

10. When the calorimeter has finished filling with water, take temperature readings every 30 seconds for two minutes before igniting the bomb.

11. Hit the button under “ignite”.

12. After a delay of 10 or 15 seconds, the temperature should begin to rise. Read the temperature of the calorimeter every 15 seconds for 3 minutes after igniting the bomb.

13. The temperature will begin to level off. Take temperature readings every 30 seconds for two more minutes.

14. Open the lid, wait for the water to drain, and then remove the bomb. Release the pressure in the bomb. Open the bomb, and check to make sure that no sample is left. Wash and dry the bomb vessel and head.

Pre-Experiment Questions—Part 2

16. Outline the procedure you will need to follow and the measurements that you will need to take to measure the heat of combustion for your biodiesel sample.

Experimental Interlude 2: Heat of Combustion
The heat of combustion of each biodiesel sample must be determined. Each sample must be measured at least twice.

Calculations

For each combustion, determine $\Delta T$.

During ignition, the cotton string combusts, thereby adding heat to the system. The extra heat must therefore be subtracted from the total. The amount of heat liberated (50 J) is stated on the bag of string.

$$\Delta U = -C_v \Delta T + q_{\text{string}}$$  \[5\]
Heat Capacity of the Calorimeter

The balanced equation for the combustion of one mole of benzoic acid [122.1 g mol\(^{-1}\)] is:

\[
\text{C}_6\text{H}_5\text{CO}_2\text{H}(s) + \frac{15}{2}\text{O}_2(g) \rightarrow 7 \text{ CO}_2(g) + 3\text{H}_2\text{O}(\ell) \tag{6}
\]

The standard molar enthalpy of combustion for benzoic acid is \(\Delta H_{\text{comb},m} = -3227 \text{ kJ mol}^{-1}\). The standard molar energy of combustion for benzoic acid can thus be calculated.

\[
\Delta U_{\text{comb},m}^o = \Delta H_{\text{comb},m}^o - RT\Delta n_{\text{gas}}
\]
\[
= -3227 \text{ kJ mol}^{-1} - (8.314 \times 3 \text{ kJ mol}^{-1}\text{K}^{-1})(298\text{K})(7 - 15/2)
\]
\[
= -3227 \text{ kJ mol}^{-1} + 1.24 \text{ kJ mol}^{-1}
\]
\[
= -3226 \text{ kJ mol}^{-1}
\tag{7}
\]

Using \(\Delta U_{\text{comb},m}^o\) the heat capacity for the calorimeter, \(C_{\text{cal}}\) can be calculated using equation 5.

Protocol
1. Following the instructions for the bomb calorimeter, calibrate the instrument to determine its heat capacity using a standard.
2. Take the mass of the combustion crucible using and analytical balance. Pipette 500 \(\mu\text{L}\) of biodiesel sample into the combustion crucible, and then record the mass again.
3. Using the information collected from the bomb calorimeter, calculate the heat of combustion for each sample.

Thinking About the Data
17. Share your calorimetry results with the class by recording them in a common spreadsheet. Discuss what units should be used.
18. Does this data seem to confirm the class statement from TATD\#14?
19. Using the heats of combustion that you calculated for the FAMEs in this experiment, calculate the theoretical heat of combustion for biodiesel made from each feedstock. Be sure to write down any assumptions that you used in this calculation. How does this calculated value(s) compare to your experimental value(s)?
20. Considering the different biodiesel samples, how does the feedstock impact the heat of combustion of a biodiesel sample?
21. Considering heat of combustion only, which of the tested feedstocks would produce the best biodiesel fuel?

Pre-Experiment Questions—Part 3
22. What is the definition of viscosity? What factors influence viscosity?
23. There are three main methods for determining viscosity: the Ostwald viscometer, the falling ball viscometer, and the cup viscometer. Briefly describe how each method works.
24. Which of the FAMEs would you predict to have the highest viscosity? Rank the FAMEs by increasing viscosity. Justify your ranking.
25. Look up the viscosity and density of olive oil. Look up the viscosity of diesel fuel.
26. Physical chemistry is a quantitative science in which data is modeled. The model is often (but not always) a known equation based on a definition or concept. One common form of modeling is accomplished by graphing the data and fitting it to a linear equation using least squares analysis. The slope and intercept of the fitted line are related to modeling parameters. The temperature dependence of a sample’s viscosity can be modeled using a version of the Arrhenius equation,

$$\eta = Ae^{E_{vis}/RT}$$  \hspace{1cm} (1)

where $E_{vis}$ is the activation energy of viscosity, $R$ is the gas constant, $T$ is the Kelvin temperature, and $A$ is the Arrhenius constant for the process. Rewrite the Arrhenius equation in a linearized form.

27. What are the independent and dependent variables of the linearized function? What variable in the equation can be evaluated by the slope of this linearized equation? What data must be collected in order to evaluate this function?

28. Look up $E_{vis}$ and define the term. What is it a measure of?
29. How might $E_{vis}$ and viscosity impact a fuel?
30. As a class, determine what data you will need to collect to determine $E_{vis}$ and how you will do this.
31. As a class, read over the brief protocol for the density measurements. Discuss: How will you determine density? What do you physically need to do?

**Experimental Interlude 3: Viscosity and Density**

**Information**
It is necessary to determine the viscometer constant using the following formula:

$$\eta = \rho tC$$

where $\eta$ is the recorded viscosity of the sample, $\rho$ is the density of the sample, $t$ is the flow time, and $C$ is the viscometer constant. Once the viscometer constant is determined from a sample with a known viscosity, the viscosity of other samples can be calculated. For this experiment, we will use water as our known sample.

**Protocol**
Your group will need to make viscosity and density measurements for the biodiesel samples. In addition, you will need to take viscosity measurements for water in order to determine the viscometer constant.

**Viscosity**
1. Mount an Ostwald viscometer vertically in a constant temperature bath so that both fiducial marks can be seen and are under the water level.
2. Pour a 10 mL-aliquot of sample into the viscometer and allow it to thermally equilibrate for about 10 minutes.
3. Use a rubber bulb to pull the sample a little higher than the upper fiducial mark. Remove the bulb and clock the flow time of the liquid between fiducial marks using a stopwatch.

4. Do at least three trials at each temperature for each sample. Clean the viscometer well between liquids using water, then acetone. Shake out all the acetone, and bake in an oven for 10 minutes.

**Density**

For each of the temperatures at which viscosities were measured, determine the density of the biodiesel sample. Density should be determined at each temperature used for the viscosity measurements.

In addition to the data that your research team collected in the lab, your collaborators have shared data they collected for multiple FAME samples. You should treat this data as your own when carrying out the Thinking About the Data questions.

**Thinking About the Data**

32. Share your viscosity and density results with the class by adding them to a common spreadsheet.

33. How do your viscosity values compare to that of diesel fuel (as found in Question 24)?

34. Construct a plot to determine the relationship between chain length of the FAMEs and viscosity (specify the temperature you used).

35. Make a plot using the data collected in order to determine $E_{\text{vis}}$ for each sample. Compare the values of $E_{\text{vis}}$ and propose an explanation at the molecular level for any trends that you observe.

36. Considering the different biodiesel samples, how does the feedstock impact the viscosity and $E_{\text{vis}}$ of a biodiesel sample?

37. Considering the viscosity only, which of the tested feedstocks would produce the best biodiesel fuel?

**Post-Experiment Questions**

38. Would you choose the same feedstock to make biodiesel fuel for use in the Virgin Islands and Alaska? Why or why not?

39. Which feedstock would you choose for a climate that varies in temperature? Justify your answer.

40. Compare the heat of combustion (in kJ/gallon) of the biodiesel sample(s) to that of petroleum diesel fuel and gasoline.