

Determination of the Heat of Combustion of Biodiesel Using Bomb Calorimetry

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A Multidisciplinary Undergraduate Chemistry Experiment

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Bomb calorimetry is a popular component of many thermodynamics laboratory courses and is included in most laboratory manuals (1, 2). In its simplest incarnation, the bomb calorimetry experiment consists of measuring the heat of combustion of compounds, then comparing the results with tabulated values. This type of experiment provides a valuable introduction to thermochemistry, but students typically take thermodynamics courses in their third or fourth years, so they are more challenged by a thermochemistry experiment that combines bomb calorimetry with another technique to solve a richer, more complex problem. One physical chemistry laboratory manual (2) and two articles in this *Journal* (3, 4) successfully combine bomb calorimetry with structural analysis, food science, or computational methods, respectively. This article presents an experiment for the undergraduate laboratory that allows advanced students to apply their organic synthesis skills and their understanding of thermodynamics to an increasingly important green technology—biodiesel.

Biodiesel is a diesel fuel substitute derived from vegetable oil that has several environmental benefits. Biodiesel and petroleum diesel both burn to produce greenhouse gasses like carbon dioxide, but growing peanuts or soybeans to make biodiesel removes carbon dioxide from the atmosphere, so it has less impact on the climate than petroleum diesel. Current EPA regulations (5) require diesel to have a low sulfur content, which necessitates costly sulfur removal from the oil. Biodiesel, on the other hand, is naturally low in sulfur (6, 7). One of the most complex parts of a diesel engine is the fuel pump and injector assembly, which is lubricated only by the fuel itself. Biodiesel has better lubricity than petroleum diesel (6, 7), so it prevents wear in these critical engine components. Finally, engines burning biodiesel have been shown to produce exhaust that is less toxic and reportedly smells like French fries (6, 7).

In the proposed laboratory experiment, students synthesize biodiesel by transesterification of waste vegetable oil using common glassware and reagents, and then characterize it by measuring heat of combustion, cloud point, and density. Measuring the heat of combustion and density together allows the students to calculate the energy density of the fuel on a per-gram and a per-milliliter basis for comparison with petroleum diesel.

When diesel or biodiesel is cooled, wax crystals begin to form (7, 8). The temperature at which this occurs is known as the cloud point and is an indicator of the thermal stability of a fuel. The measurement is usually done with a dedicated instrument that is not commonly found in undergraduate laboratories, but we describe a method of measuring the cloud point of biodiesel using a UV–visible spectrometer with a temperature controlled sample cell.

Experimental

Synthesis of Biodiesel

The synthesis of biodiesel was done in a 500-mL three-neck round-bottomed flask fitted with a thermometer, reflux condenser, and glass stopper on a magnetic stir plate (Figure 1). A thermostatically controlled, recirculating hot water bath (Neslab RTE-220) provided a convenient way to maintain a 65 °C reaction temperature (9, 10). Used peanut cooking oil was obtained from the university food services. Food particles were removed from a sample of oil by vacuum filtration. Sodium hydroxide (NaOH, EM Science) was dried in an oven at 100 °C for 24 hours, then ground using a mortar and pestle to speed its dissolution in methanol. Petroleum diesel was purchased from Watts Petroleum Corporation (11) and was used as delivered.

Filtered peanut oil (260 g), methanol (75 g, 8:1 methanol:oil mole ratio¹; ref 12) and NaOH (2.6 g, 1% wt of oil) were combined in the round-bottomed flask (9, 10). The reaction was allowed to proceed at 65 °C for one hour with continuous stirring. At the end of this time, most of the bottom glycerol layer was removed by pipet. The mixture was then allowed to react for an additional 30 minutes. Upon termination of the reaction, the product mixture was

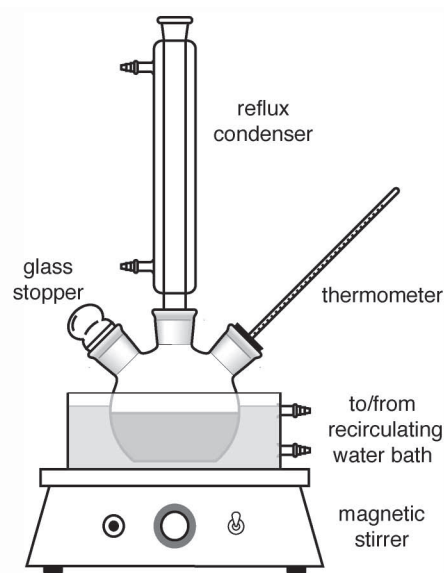


Figure 1. This diagram represents the experimental apparatus used during the synthesis of biodiesel. A recirculating hot water bath is used to maintain a constant reaction temperature.

transferred to a separatory funnel where it was allowed to stand for one day. Afterward, the remaining glycerol layer was removed from the biodiesel product. The biodiesel was transferred to separatory funnels and washed dropwise with water until the wash water became neutral. This ensured that all of the remaining catalyst was removed from the product.

We found that an emulsion formed very easily during the washing process. We produced emulsions with 100-mL samples of biodiesel and tested two common methods for breaking emulsions: treatment with methanol and treatment with saturated sodium chloride solution. The emulsion was combined with 5 mL of methanol or sodium chloride solution in a separatory funnel, then gently inverted several times. The product was allowed to stand for five days, then the biodiesel fraction was collected and excess methanol was removed by rotary evaporation. When sodium chloride was used to break the emulsion, the samples were rewashed with distilled water until the wash water tested negative for the chloride ion using 0.1 M silver nitrate.

The density of biodiesel was easily measured by pipetting 10.00-mL aliquots into a beaker on an accurate balance.

Determination of Heat of Combustion of Biodiesel

A Parr 1261 bomb calorimeter was used to measure the heat of combustion of biodiesel, petroleum diesel, and two samples of biodiesel recovered from emulsions: one with methanol (biodiesel–MeOH) and one with sodium chloride solution (biodiesel–NaCl). After standardization with benzoic acid, 0.5 g samples of each fuel were burned in the bomb. All measurements were repeated seven times.

Determination of Cloud Point

An HP8453A UV–visible diode array spectrophotometer equipped with a temperature control apparatus was used to measure the cloud point of the biodiesel, biodiesel–MeOH, and biodiesel–NaCl. Transmittance spectra (300–900 nm) for the three biodiesel products are shown in Figure 2. All of the samples absorbed light in the 380 to 400 nm range, which accounts for its faint amber color. Carefully prepared samples

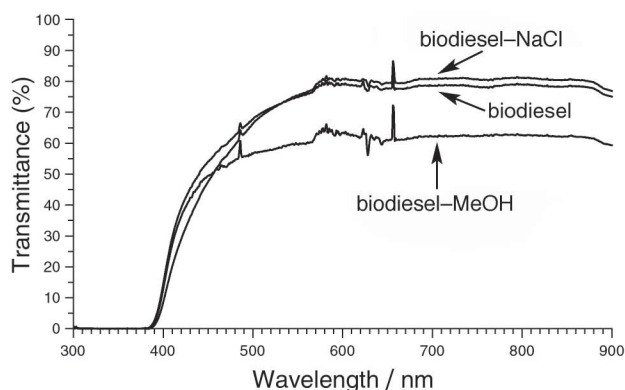


Figure 2. This graph compares the transmittance spectra of the three biodiesel products at room temperature.

were perfectly transparent as long as no emulsion was present. The temperature of the sample in the spectrophotometer was decreased and transmittance measurements were taken over a temperature range of 0–25 °C. In the 25 to 5 °C range there was little change in the transmittance and the sample appeared clear. As the temperature dropped below 5 °C, the samples became cloudy as wax crystals formed. Figure 3 shows the transmittance of biodiesel as a function of sample temperature. Note that the wax crystals in these samples scattered short wavelength light more effectively than long wavelength light. The strong, wavelength dependent scattering in these samples indicated that the crystals were close to the wavelength of visible light, a few hundred nanometers (13).

Hazards

Hot vegetable oil and methanol are both flammable. Sodium hydroxide is caustic and should be handled with gloves. The bomb calorimeter requires handling high pressure oxygen, which is a strong oxidizer.

Results and Discussion

Calculation of Heats of Combustion

The heats of combustion of the samples were calculated using the procedure recommended in the Parr manual. The biodiesel prepared by the conventional method and the biodiesel recovered from the emulsions using two different techniques produced 41.2 ± 0.2 kJ/g with no measurable difference between the three preparations. Petroleum diesel yielded 47.0 ± 0.2 kJ/g. The fuel injectors in a diesel engine deliver a premeasured volume of fuel to each cylinder and the densities of petroleum diesel and biodiesel are the same, so engines running on biodiesel should produce less power. This has, in fact, been observed in laboratory test engines (5). The heats of combustion for the biodiesel products are reported in Table 1 and are compared to the heat of combustion of petroleum diesel.

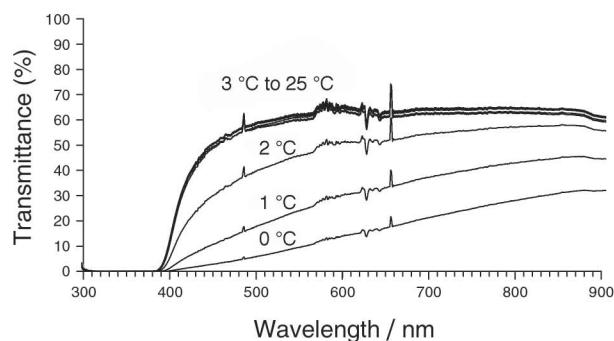


Figure 3. This plot demonstrates the decrease in transmittance as the biodiesel–MeOH is cooled from 25 to 0 °C. From 25 to 3 °C there is little change, but the transmittance drops sharply between 3 and 0 °C as wax crystals form in the fuel and scatter the light.

Calculation of Cloud Points

Cloud points were determined by creating a plot of the percent transmittance of a sample as a function of the sample temperature. Figure 4 shows the transmittance of the three biodiesel products at 540 nm as a function of temperature. The cloud point occurs in the temperature range where the transmittance rapidly decreases toward zero. In methods previously described, the value of the cloud point is defined as the inflection point of a curve that represents the gathered data (14). Each data set in Figure 4 was fitted with a fifth-order polynomial and the inflection point of the polynomial was taken as the cloud point. This procedure can be expected to give a rough approximation of the cloud point, which can only be properly measured by controlling the cooling rate of the sample per the ASTM D 2500 method (8). Notice that the cloud point for biodiesel was much higher than for petroleum diesel, which suggests that biodiesel may cause cold weather performance problems. Wax crystals can clog fuel filters and will increase the fuel viscosity, requiring the use of fuel line heaters. Cloud point data obtained for the biodiesel products are reported in Table 1 and compared to a reported value (11) for petroleum-based diesel.

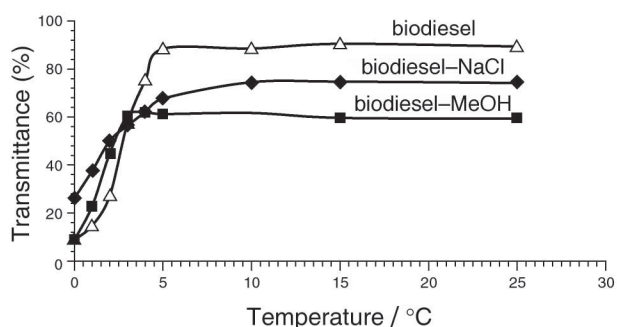


Figure 4. This plot shows the transmittance at 540 nm as a function of temperature for the three biodiesel products.

Table 1. Calculated Heat of Combustions, Densities, and Cloud Points for Three Biodiesel Products and Petroleum Diesel Fuel

Substance	Heat of Combustion/ (kJ g ⁻¹)	Density/ (g mL ⁻¹)	Cloud Point/ °C
Diesel Fuel	47.0 ± 0.2	0.85 ± 0.02	-31.7 ^a
Biodiesel	41.2 ± 0.2	0.87 ± 0.02	2.6
Biodiesel-NaCl	41.1 ± 0.2	0.87 ± 0.02	0.5
Biodiesel-MeOH	41.2 ± 0.2	0.87 ± 0.02	1.6

^aThis value provided by Watts Petroleum Corporation (11).

Summary

Synthesizing and analyzing biodiesel can serve as a challenging and enlightening introduction to thermochemistry, fuel science, and green chemistry for physical chemistry students. In addition to the physical chemistry skills, most students find that this experiment requires fundamental organic chemistry laboratory skills that are both valuable and easily forgotten. It also encourages careful planning, data processing, and critical thinking. Most importantly, though, this experiment teaches basic chemistry skills and knowledge in the context of an important and timely environmental topic.

Supplemental Material

Instructions for the student, a three-week timetable for the experiment, and notes to the instructor are available in this issue of *JCE Online*.

Note

1. Vegetable oil does not have a uniform molecular weight because it is a natural product. Reference 12 has a table of fatty acids found in many common vegetable oils that can be used to calculate an average molecular weight.

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