How Green Is your Fuel? Creation and Comparison of Automotive Biofuels

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Over the past decade, crude oil and fuel prices have fluctuated and spiked to historic highs while use and demand has also grown worldwide. Countries with emerging economies, such as China and India, are increasing consumption of gas and oil at record rates. In addition to a diminishing petroleum supply to meet the growing demand, there is concern that the use of fossil fuels is contributing to global warming and undesirable climate change. Economically, environmentally friendly, and sustainable energy solutions are needed to slow the growth and use of fossil fuels. One such governmental effort, the Energy Independence and Security Act of 2007, specifically directs the Environmental Protection Agency to promulgate regulations to ensure that fuel sold or introduced into commerce in the United States, on an annual average basis, contains specified percentages of alternative fuel (1). Biodiesel and ethanol are two alternative fuels approved by the EPA. Both of these are commercially available as a percent component in the petroleum base. For example, E85 is 85% ethanol in petroleum gasoline and B20 is 20% biodiesel in petroleum diesel.

Other alternative fuels, such as straight or waste vegetable oil (SVO or WVO), have been investigated for use in diesel engines (2–4). However, their use requires a heated fuel-supply system to lower the viscosity to allow proper flow through the fuel system, fuel injector-spray patterns, and atomization of the fuel. An alternate approach to solving the viscosity issue is to blend vegetable oil with petroleum fuels (5). There have been a number of reports and evidence indicating good engine power and acceptable emissions with diesel engines operating on SVO blended with petroleum diesel (6–11). It should be noted that biodiesel is also blended with petroleum diesel to lower viscosity and gel point.

Although there are many standards that a fuel must adhere to in order to become an EPA-certified commercial fuel, viscosity and energy content are two of the most important attributes. Viscosity is critical because the fuel needs to flow easily through the fuel lines and into the engine cylinders to allow proper injector-spray patterns and complete combustion of the fuel. Viscosity is a temperature-dependent physical property and is thus greatly affected by engine-temperature and ambient-weather conditions. Energy content is important because it correlates to engine performance and gas mileage. A fuel with low energy content (heat of combustion in this lab) will have diminished horsepower, torque, and gas mileage.

Previous publications in this Journal have focused on laboratory experiments for the synthesis of biodiesel and measuring its viscosity and energy content (12–15). The experiment presented here intends to educate students about three biofuels developed for automotive applications and the advantages and disadvantages of each. Students replicate commercially available alternative fuels, E85 and Biodiesel, as well as create an experimental fuel blend of waste vegetable oil and petroleum products referred to as “VeggieDiesel”. The goal is to evaluate the viscosity, energy content, production energy requirements, and environmental impact (sustainability) of each alternative fuel. In addition, students evaluate theoretical viscosity models for blended fuels as well as theoretical calculations for predicting heat of combustion. On the basis of laboratory results and literature findings, students draw conclusions on which fuel is the best “alternative”. This lab experiment was developed for the first-semester physical chemistry undergraduate course. However, the experimental procedure is adaptable for other undergraduate laboratory courses, such as general or analytical chemistry.

Materials

Required equipment not commonly found in a teaching laboratory are a bomb calorimeter (we used a Parr 1431 adiabatic calorimeter), gelatin capsules for volatile samples (E85) in bomb calorimetry, viscometers (we used Cannon-Fenske, although other types of kinematic viscometer can be used), and a 1 mg or better precision balance. Synthesis of biodiesel should be performed in a ventilation hood. The required chemicals are soybean oil (if WVO, be sure to filter before use), petroleum diesel, gasoline, kerosene, ethanol (anhydrous), and sodium hydroxide.

General Procedure

The experiment spans two, 4-h physical chemistry lab periods. A general order to perform the individual experiments is shown in Table 1. The time allotments are based on advanced-level students working in pairs. Note that it is important to obtain viscosity data for the WVO in the first lab period, which is needed to theorize a VeggieDiesel blend before the second lab meeting.

Biodiesel is created through transesterification of the vegetable oil with methanol in a base-catalyzed environment. Because the biodiesel is used only for viscosity and bomb calorimetry analysis, the students do not wash the biodiesel to remove the leftover catalyst and alcohol. Once the reaction is complete, students use a centrifuge to separate the biodiesel from the viscous glycerol. E85 is created by mixing gasoline and anhydrous ethanol in the appropriate ratio. The complete procedure for VeggieDiesel formulation is given in the student laboratory instructions available in the supporting information. Students are told that the fuel blend must have a viscosity no greater than 15 cSt at 32 °F and can only be made from gasoline, diesel, kerosene, and WVO. The exact ratio of all components is left to the student to determine through the theoretical viscosity-blending equation presented in the laboratory instructions.
Viscosity is a measurement of a fluid's resistance to flow and is temperature dependent according to
\[
\ln v = -BT + A
\]
where \( v \) is the viscosity in centistokes and \( A \) and \( B \) are the intercept and slope, respectively, of the straight line formed when \( \ln v \) is plotted against temperature, \( T \), in Kelvin \( (7) \). Many models have been developed for predicting viscosity of a blend \((16, 17)\). The Arrhenius equation, as discussed by Grunberg and Nissan \((18)\), is the most fundamental and uses mole fractions of each blend component to determine the overall viscosity
\[
\ln v_{\text{blend}} = X_1 \ln v_1 + X_2 \ln v_2
\]
where \( X_1 \) and \( v_1 \) are the mole fraction and viscosity of component 1, \( X_2 \) and \( v_2 \) are the mole fraction and viscosity of component 2 at the same temperature. The equation can be expanded to include multiple components in the blend. In addition, the equation can be used with volume or mass fractions. In this lab, students determine which of the three fraction types most accurately predicts the actual blend viscosity.

Kinematic viscosity measurements are conducted with the viscometer immersed in a water bath to regulate the temperature \((19)\). Data are taken at two different temperatures so that \( A \) and \( B \) can be determined for each sample. This allows prediction of viscosity at a range of temperatures, which is necessary when theorizing a VeggieDiesel blend. Students compare theoretical blend-viscosity predictions with actual results.

Bomb calorimetry experiments are conducted in a typical manner where the heat capacity of the bomb is already known and can be used to determine the heat of combustion for the sample. Although all fuel samples are fairly volatile, the E85 is the only one that requires a gel capsule to minimize evaporation. Theoretical heats of combustion for each fuel can be determined through bond-enthalpy analysis and compared to actual results. Heats of formation data could be used as well, but reliable heat of formation data for biodiesel and vegetable oil are more difficult to obtain through literature. However, these values can be calculated using molecular modeling software, such as Scigress, Gaussian, and Spartan.

### Hazards

Vegetable oil, diesel, gasoline, kerosene, ethanol, and methanol are flammable. Gasoline, kerosene, and ethanol can cause skin and eye irritation. Methanol may be fatal or cause blindness if swallowed. Sodium hydroxide is caustic and should be handled with gloves. The bomb calorimeter requires handling high-pressure oxygen, which is a strong oxidizer. Synthesis of each fuel should be carried out in a ventilation hood. Smaller quantities of each fuel can be kept in capped containers near experimental setups. Disposal of the organic chemical waste should be in accordance with institutional protocols.

### Discussion

Completing the entire lab experiment in two, 4-h periods is possible when pairs of students work together in a coordinated effort. However, students must complete the prelab activities each week to make this a realistic possibility. Before the first lab, students need to determine the quantity of methanol required in the biodiesel synthesis. Before the start of the second lab period, students need to theorize their VeggieDiesel blend and have the quantities of each component calculated. When only one student was conducting the experiment (due to odd enrollment numbers), the procedure was abridged by requiring only one bomb calorimetry run and one viscosity measurement for each sample tested. The results are then presented to the instructor to verify the accuracy and additional experiments on a sample can be completed as needed. Alternatively, the lab procedure can be shortened by eliminating the biodiesel synthesis or completely eliminating the E85 portion of the experiment. However, we have found that students are interested in completing the biodiesel synthesis. Since we have incorporated this experiment in to the physical chemistry laboratory curriculum, we felt it most appropriate to eliminate the multiple runs of an experiment when there are time constraints.

This comprehensive lab challenges students to compare experimental data to theoretical predictions of two important parameters of fuels, viscosity and energy content. Literature searches on this timely topic are robust and add significantly to student understanding of the true environmental impact and sustainability of biofuels. The biodiesel synthesis serves as a good review of fundamental organic lab skills. Student comments indicate that they enjoyed the experiment and that it helped clarify misunderstandings they held about biofuels. The experiment is easily adaptable for upper-level chemistry laboratory courses, such as physical, analytical, and organic, by inclusion or exclusion of the various tasks and topics covered. Its timely relevance is of interest to anyone interested in environmental chemistry or engineering.

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### Literature Cited


**Supporting Information Available**

Student laboratory instructions; instructor notes; suggested student questions and answers. This material is available via the Internet at http://pubs.acs.org.