Preparation and Viscosity of Biodiesel from New and Used Vegetable Oil. An Inquiry-Based Environmental Chemistry Laboratory

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · JANUARY 2006

Impact Factor: 1.11 · DOI: 10.1021/ed083p257

Kelley Donaghy
State University of New York College of En…

Preparation and Viscosity of Biodiesel from New and Used Vegetable Oil

W

An Inquiry-Based Environmental Chemistry Laboratory

Nathan R. Clarke, John Patrick Casey, Earlene D. Brown, Ezenwa Oneyma, and Kelley J. Donaghy*
Department of Chemistry, American University, Washington, DC 20016-8014; **kdonaghy@dol.net*

Over the last several years it has become apparent that the economic and environmental impact of relying on fossil fuels is reaching a critical level. Research is currently being carried out in many laboratories to find alternatives to these nonrenewable fuels and one area of interest is in biomass fuels. One such fuel is biodiesel, which is produced by the transesterification of vegetable oil. In fact, at least 17 states have passed bills either directly supporting the use of biodiesel or at least encouraging the use of alternative fuels based on biomass *(1)*. These fuels contain no sulfur or nitrogen compounds and hence they do not contribute to acid rain or smog. Furthermore, they would not require the complete overhaul of the typical combustion engine. However, despite promising data from civilian users, there have been many developmental issues related to these fuels; in particular, they solidify at low temperatures and break down at higher temperatures *(2)*.

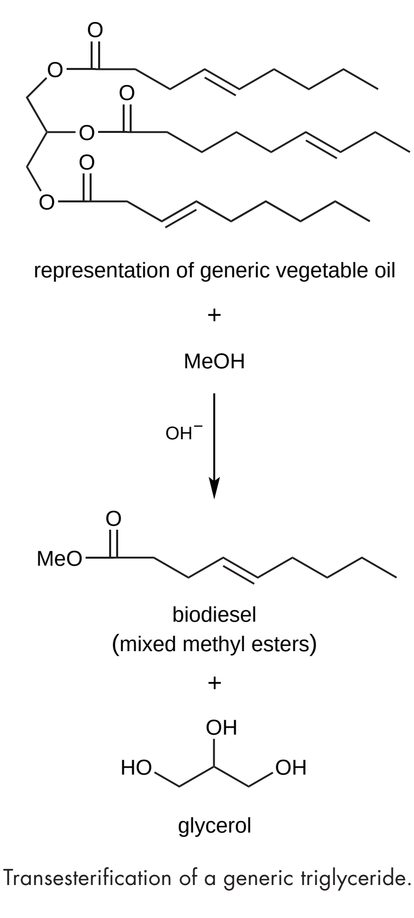
In this laboratory exercise, the students develop a synthesis to make biodiesel from vegetable oils such as soybean, sunflower, and corn oil. In addition to experimenting with organic synthesis, students use viscosity measurements to gain an understanding of an intermolecular property of the biodiesel. There are many experiments in the literature *(3)* that involve the use of viscosity but few *(3c, i)* focus on the use of viscosity to answer real-world questions. In this laboratory students use viscosity to understand an important factor that has limited the implementation of biodiesel on a wide scale basis, solidification at low temperature *(4)*. Students are not given a cookbook recipe to synthesize the biofuel, but instead are expected to use the primary literature to develop a synthetic path. This inquiry-based lab enhances student learning by fostering critical and creative thinking. The following laboratory is suitable for second-semester general chemistry students and is particularly timely during the discussion of intermolecular forces as they relate to the properties of liquids in the general chemistry lecture.

Overview

In this lab, the students receive a mock memo from the National Park Service (NPS) that asks them to develop a synthesis for biodiesel using vegetable oils. The letter requests the students to develop a simple high-yield synthesis and address the feasibility of using the resultant fuel in a variety of temperature conditions. To lead the students, the letter suggests doing viscosity measurements at varying temperatures. In addition, students are instructed to write a memo to the NPS that discusses the laboratory details, reaction mechanism, and viscosity results; expresses their opinion about the real-world feasibility of the fuel; and make suggestions for future improvements. In performing this laboratory, the students learn a number of skills and concepts, such as (i) the ability to research and develop a synthetic protocol, (ii) an understanding of transesterification, (iii) critical analysis of Internet sources, (iv) fundamentals of viscosity, (v) analysis of data in the problem context, and (v) how to write a scientific report that includes a memo to an outside source.

Materials and Procedures

The first step in this laboratory is to develop an approach to the synthesis of biodiesel: the transesterification of triglycerides to long chain methyl esters (Scheme I). The letter from the National Park Service is handed out in a previous laboratory period and the students are allowed to use the Internet, but encouraged to use the primary literature, to find



Scheme I. Transesterification of a generic triglyceride.

synthetic strategies *(2a, b).* Students are encouraged to bring fryer oil from their dining halls or favorite eating establishment, used (may require filtering) or fresh oil is acceptable. Methanol, ethanol, acetic acid, anhydrous magnesium sulfate, and sodium hydroxide (in pellet form) are made available to the students from laboratory stock and other chemicals can be provided at the instructor's prerogative.

The generalized synthetic strategy involves titrating a sample of the oil to determine the amount of free acid that needs to be neutralized and then a general formula is applied to ascertain the necessary amount of catalytic sodium hydroxide needed. This can also be ascertained via trial and error if time permits, however, several Web sites publish a generalized synthetic method *(2a, c)* and a large scale synthesis has also been reported in the literature *(5).* The students should be encouraged to conduct several reactions side-by-side with varying amounts of catalyst to find the best ratio of catalyst to oil that minimizes soap production even if the general formula is used. The other side product, glycerol, settles to the bottom and the biodiesel may be decanted, dried, and analyzed. If time and instrumentation allow, further characterization may be undertaken. The IR, (neat, NaCl plates) and ^{1}H NMR (TMS, $CDCl_3$) are included in the Supplementary Material$^{\mathrm{W}}$ primarily for comparison; briefly, the ^{1}H NMR for the fryer oil clearly shows that the protons from the glycerol (a complicated set of doublets at δ 4.2 ppm (J_{HH} $\approx$ 8 Hz) disappear after the reaction to be replaced by the methyl protons (singlet δ 3.75 ppm). Furthermore, the NMR indicates that there is some unsaturation (multiplet δ 5.35 ppm) and the IR confirms that there is a carbonyl group (strong peak at 1750 cm^{-1}) but not a free carboxylic acid. Typically, 60 mL of fresh oil will yield approximately 30–40 mL of biodiesel.

One of the problems associated with biodiesel becomes clear when its viscosity is studied. At reduced temperatures (< 5 °C) the biodiesel begins to solidify and at higher temperatures (> 80 °C) it approaches the viscosity of water. Using a viscometer, the first step is to find the viscometer constant. Either a commercially available or student-made viscometers *(3g)* can be used in this experiment. Olive oil is used as the standard liquid since its viscosity is available in a chemistry handbook *(6).* Using the following formula,

$$\eta_{\mathrm{app}} = t\rho C_0 \qquad (1)$$

where η_{app} is the recorded viscosity of olive oil, t is the flow time, and ρ is the density of the oil, the viscometer constant, C_0, is found. This should be done at all temperatures examined. The constant is then used with flow times and a measured density to find the experimental viscosity for the synthesized biodiesel. The viscosity of the resulting biodiesel is then studied at varying temperatures by immersing the functional part of the viscometer in chilled or heated water baths.

Viscosity follows an Arrhenius dependency on temperature as shown in the following equation,

$$\eta_{\mathrm{app}} \propto A e^{\frac{E_{\mathrm{vis}}}{RT}} \qquad (2)$$

where A is the frequency factor, E_{vis} is the activation energy, R is gas constant, and T is the temperature. To get a linear fit for the data so that extrapolation to colder and hotter temperatures can be easily interpreted, the data should be plotted as $\ln(\eta_{\mathrm{app}})$ versus $1/T$. This will allow the students to comment on the feasibility of using biodiesel in an arctic environment or a desert environment.

Hazards

Sodium hydroxide is caustic and ethanol, ethyl acetate, acetone, acetic acid, and methanol are flammable. All substances should be handled with care, and gloves and safety glasses should be worn at all times. Also, the addition of the sodium methoxide (or sodium ethoxide) to the warm oil (be sure not to heat this above the boiling point of the alcohol used) should be done slowly and with extreme caution.

Conclusions

The development of laboratories based on realistic problems increases student interest and excitement about the laboratory discovery. The organic synthesis is straightforward and suitable for general chemistry students. The lab is usually scheduled at the end of the first semester after organic chemistry is introduced or at the beginning of the second semester once intermolecular forces, with respect to the properties of liquids, are covered in lecture. Further, the lab is safe enough that it can reasonably be done in an inquiry-based, discovery setting. Finally, the viscosity study introduces a technique not commonly covered in the chemistry curriculum until physical chemistry but is simplified for a general chemistry course. It is reasonable that the two pieces of the experiment can be separated to fit individual program time constraints and student level.

The students write a comprehensive report at the end of the laboratory experience in the form of a memo to the NPS about (i) mass producing biodiesel, (ii) using it in a variety of temperature applications, and (iii) suggesting alternatives to enhance the properties of the biodiesel. This report encourages critical and creative thinking since the students are asked to report on what they did, interpret their own data in realistic terms, and suggest ways to improve what they have discovered.

Acknowledgments

KJD thanks the American University's Schwartz Undergraduate Fellowship Fund and American University Chemistry Department for funding. Pamela Proulx-Curry is acknowledged for trying the laboratory in her course and for her valuable discussions and support.

$^{\mathrm{W}}$Supplemental Material

Notes to the instructor, handouts for the students, sample National Park Service memo, details about the use and calculations associated with viscometers, sample synthesis, viscosity data, and spectral data are available in this issue of the *JCE Online*.

Literature Cited

1. National Biodiesel Board Home Page. *http://www.biodiesel.org* (accessed Nov 2005).
2. See for example: (a) Mike Pelly's Biodiesel Method *http://journeytoforever.org/biodiesel_mike.html* (accessed Nov 2005). (b) Hemp Car Transamerica Home Page. *http://www.hempcar.org* (accessed Nov 2005). (c) Grassroots Biodiesel Home Page. *http://www.dancingrabbit.org/biodiesel* (accessed Nov 2005). (d) University of Idaho Biodiesel Research Home Page. *http://www.uidaho.edu/bae/biodiesel* (accessed Nov 2005). (e) Biodiesel-Clean, Green Diesel Fuel. *http://www.ott.doe.gov/biofuels/pdfs/biodeisel_clean-green.pdf* (accessed Nov 2005).
3. See for example: (a) Papadopoulos, N.; Pitta, A. T.; Limniou, M; Lemos, M. A. N. D. A.; Lemos, F. M.; Freire, F. G. *J. Chem. Educ*. **1999**, *76,* 1600. (b) Urian, R. Craig; Kundkar, Lutfur R. *J. Chem Educ*. **1998**, *75,* 1135–1136. (c) Fountain, C. Wes; Jennings, Jeanne; McKie, Cheryl K.; Oakman, Patrice; Fetterolf, Monty L. *J. Chem. Educ*. **1997**, *74,* 224–227. (d) Richards, John L. *J. Chem. Educ*. **1993**, *70,* 685–689. (e) Hemmerlin, William M.; Abel, Kenton B. *J. Chem. Educ*. **1991**, *68,* 417. (f) Rosenthal, Lois C. *J. Chem. Educ*. **1990**, *68,* 78–80. (g) Diagnault, L. G.; Jackman, D. C.; Rillema, D. P. *J. Chem. Educ*. **1990**, *67,* 81–82. (h) Mathias, Lon J. *J. Chem. Educ*. **1983**, *60,* 422–423. (i) Perrin, J. E.; Martin, G. C. *J. Chem. Educ*. **1983**, *60,* 516–518. (j) Belliveau, James F.; O'Leary, Gerard P., Jr.; Hajian, Harry. *J. Chem. Educ.* **1981**, *58,* 442–444. (k) Miller, Don Paul. *J. Chem. Educ*. **1980**, *57,* 200. (l) Sorrell, Charles A. *J. Chem. Educ*. **1971**, *48,* 252–254. (m) Malinauskas, A. P.; Whisenhunt, S. J., Jr.: Searcy, J. Q. *J. Chem. Educ*. **1969**, *46,* 781–783. (n) Moynihan, C. T. *J. Chem. Educ*. **1967**, *44,* 531–535.
4. McGraw, Linda Cooke. *Agricultural Research* **1998**, *46,* 21.
5. Wenzel, Gaby; Lammers, Peter Schulze. *J. Agric. Food Chem.* **1997**, *45,* 4748–4752.
6. *CRC Handbook of Chemistry and Physics;* 67th ed.; Weast, Robert C., Astle, Melvin J., Beyer, William H., Eds.; CRC Press, Inc: Boca Raton, FL, 1986.