An Integrated Approach To Introducing Biofuels, Flash Point, and Vapor Pressure Concepts into an Introductory College Chemistry Lab

Adam R. Hoffman*
Department of Chemistry, Madison Area Technical College, Madison, Wisconsin 53704, and
Present address: Department of Natural and Applied Sciences, University of Dubuque, Dubuque, Iowa 52001, United States
**AHoffman@dbq.edu*

Stephanie L. Britton, Katie D. Cadwell, and Kenneth A. Walz
Department of Chemistry, Madison Area Technical College, Madison, Wisconsin 53704, United States

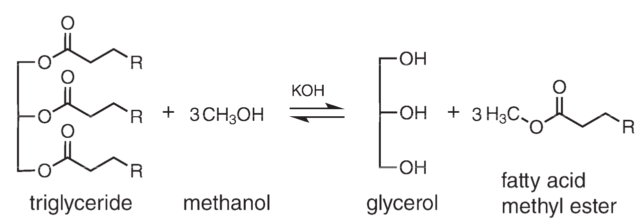
Biodiesel has been touted in recent years as a renewable alternative to petroleum-based fuel because of its economic, energy, and environmental benefits. The environmental advantages of biodiesel compared to conventional petrodiesel include reduced emissions of CO_2, particulate matter, carbon monoxide, and sulfur dioxide *(1)*. Biodiesel's chemical properties also offer safety benefits over conventional petroleum diesel as it is a safer fuel to handle and store because its flash point (lowest temperature at which the application of the ignition source causes the vapors above a liquid to ignite) is nearly double that of petrodiesel *(2)* and higher than many other fuels (Table 1).

Table 1. Flash Points of Common Fuels

Fuel	Flash Point/°C
Gasoline	−43
Methanol	11
Petrodiesel	55
Biodiesel	125

Despite its inherent safety advantage, biodiesel's flash point can be significantly reduced if excessive methanol is present. Methyl ester biodiesel fuel is produced by reacting triglyceride vegetable oil or animal fat feedstocks with an excess of methanol (Scheme 1). If the excess methanol is not properly separated after the reaction is complete, the biodiesel product often will not meet ASTM flash point minimum specifications of 130 °C *(3)*. Aside from being a safety concern, off-spec biodiesel fuel may have adverse effects on engine wear and performance.

Scheme 1. Biodiesel Production Reaction. The Fat or Oil Is Reacted with an Alcohol (Typically Methanol) Using a Basic Catalyst To Form Alkyl Esters (Biodiesel) and Glycerol



Biodiesel lab experiments have been used to explore the chemistry of biofuels in educational settings since 2000 *(4)*, and several lab experiments have been developed exploring the synthesis and properties of the fuel. Donaghy et al. *(5)* used an inquiry-based lesson, in which the students accessed primary literature to develop their own procedure to synthesize biodiesel from a variety of vegetable oils. Various biodiesel studies have focused on the synthesis of biodiesel and measurements of fuel characteristics such as viscosity *(5)*, heat of combustion, density, cloud point *(6)*, and the percentage of glycerol in the final biodiesel product *(7)*. To our knowledge, no educational studies have been published that determine whether the neat or mixed biodiesel product meet flash point ASTM specifications for marketable biodiesel.

We created activities for an introductory chemistry course using a Pensky−Martens closed-cup instrument to measure the flash point of student-manufactured biodiesel and commercially available reference fuels meeting ASTM specifications. Three reasons dictated our decision to create this laboratory experience for undergraduate students: (i) To our knowledge, no other published biofuels lab procedures have measured flash point; we saw this as an opportunity to tie a chemical concept to a practical application. (ii) Homebrew and small-scale commercial biodiesel can be hazards that are often overlooked. (iii) Many misconceptions exist concerning biofuels and their environmental and automotive implications. The goal of this lab is to increase understanding of the fundamental chemical concepts of vapor pressure and flash point in a real-world technical context, while gaining insight into the properties of biofuels, a contemporary societal issue.

Experimental Procedure

Biodiesel Synthesis

In this lab, the students combine methanol with restaurant fryer waste oil to synthesize biodiesel. Existing methods for biofuels production work well for this lab *(6, 7)*, or the method in the supporting information can be followed. To synthesize biodiesel, the students need a ring stand, heating−stir plate, 100 and 125 mL Erlenmeyer flasks, water bath, stir bars, thermometer, 10 and 100 mL graduated cylinder, beral pipets, and KOH/methanol solution (35 g KOH per L methanol).

10.1021/ed100004x Published on Web ■■■

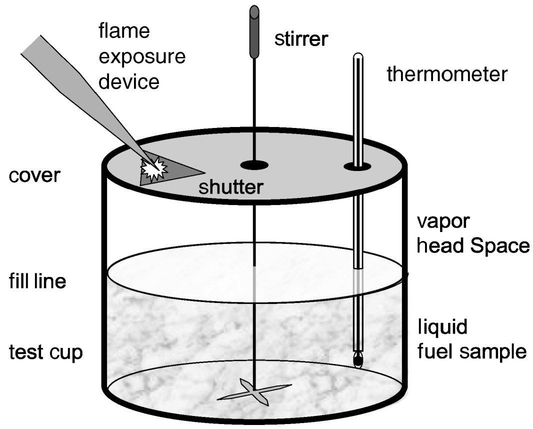


Figure 1. Schematic diagram of a closed-cup flash point test apparatus.

Figure 2. Madison College instructor Ramsey Kropp demonstrates how to use the Pensky−Martens closed-cup apparatus to measure the flash point of a biodiesel sample. (Photo by K. Walz).

Biodiesel Quality Tests

Density Test: Students weigh an empty disposable 15 mL graduated plastic beaker. The beaker is filled to the 15 mL line with their biodiesel product, and the mass of the beaker and fuel together is recorded. Using this information, students determine the density of their biodiesel fuel. This procedure is then repeated with a sample of the commercial biodiesel (ASTM spec) reference fuel for comparison purposes.

Flash Point Test: Each lab group is assigned one or more fuel samples (commercial biodiesel or student-made biodiesel) to measure the flash point using a closed-cup flash point tester (Figures 1 and 2). The flash point tester is inspected to ensure sample test cup is clean. The test cup is filled to the appropriate level, the cover replaced, and the digital thermometer inserted. The propane supply for the flame exposure device is turned on and the test flame is lit. The sample is stirred to ensure equilibrium between the liquid fuel and the vapor phase in the headspace. The flash point is tested by opening the shutter and introducing the test flame into sample cup, following instrument and ASTM standard methods. If no flash is observed, the temperature is increased gradually, and testing is repeated at 5° intervals until a positive flash point response is recorded. The sample is deemed to have flashed when "a large flame appears and instantaneously propagates itself over the entire surface of the test specimen". Accompanying the flash is often an audible "whoosh" sound or gentle popping noise.

Table 2. Flash Point and Density Measures for Biodiesel Fuel Produced by Chemistry Students Compared with Fuel Obtained From a Commercial Source

Biodiesel Fuel Source	Flash Point/°C	Density/(g/mL)
Student (n = 24)	36.0 ± 5.6	0.80 ± 0.09
Commercial (n = 48)	184.1 ± 13.5	0.80 ± 0.14

Hazards

The potassium hydroxide/methanol solution is caustic. Gloves and safety goggles should be worn for the entire procedure. Students should inform the instructor of any spills and wash exposed skin immediately with water. The flash point instrument used in this experiment employed an open flame generated from a cylinder of propane gas. For classes where fire safety may be of concern, alternative models are available that instead utilize a high voltage electric spark ignition source.

Results and Discussion

Because of the lack of postsynthesis treatment, significant differences were obtained in the flash point values between the student-produced and commercially available biodiesel (Table 2). Upon completion of the reaction, the excess methanol partitions between the polar glycerol and the nonpolar methyl ester phases, with roughly 10−20% remaining in the methyl ester layer depending on the molar ratios of reactants and the temperature of the system. For reactions employing a six-to-one molar ratio of methanol-to-triglyceride reactants (the most common production method), the distribution coefficient for methanol in the product phases has been reported to be 10.9 at room temperature *(8)*. Thus, although most of the methanol is captured in the glycerol, some unfortunately ends up in the desired methyl esters, resulting in a methanol content of 3.4 wt % in the crude biodiesel product. To address this, commercial biodiesel manufacturers typically employ an aqueous wash, a distillation, or an adsorbent polishing step after the transesterfication reaction is completed *(3)*. This postsynthesis treatment removes the residual excess methanol from the biodiesel product, thereby increasing the flash point of the finished fuel.

Despite the significant difference in flash points between the student and commercial biodiesel, the densities of the fuels were similar (Table 2). This can be explained by the realization that methanol and biodiesel have similar densities, but their flash points differ. The difference in the parameters of flash point and density also effectively illustrates the reason why multiple quality assurance and quality control (QA−QC) tests are necessary for fuels: no single test is a good measure of quality on its own.

Upon introducing this lab in our chemistry courses, we learned that some of the students were already engaged in biodiesel production in their homes or workplaces, whereas several others

Table 3. Selected Flash Point Data for Other Samples Tested

Fuel Source − Process Method	Feedstock	Post-Processing	Flash Point/°C (n = 1)
Homebrew −2 L batch	Waste Vegetable Oil	None	35
Restaurant processor − 25 gallon reactor	Waste Vegetable Oil	None	40
Farm processor − 50 gallon reactor	Sunflower Oil[a]	None	65
Co-Op processor − 30 gallon reactor	Waste Vegetable Oil	Absorbent	180
Farm processor − 50 gallon reactor	Soy Vegetable Oil[b]	Aqueous wash	190

[a] Fresh pressed. [b] Mixed sources.

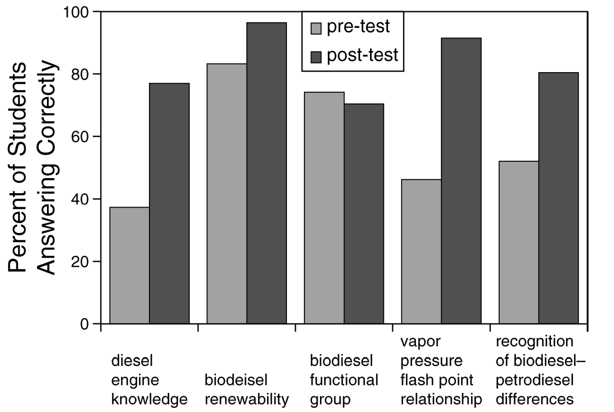


Figure 3. Percent of students correctly identifying biofuel content on pre- and post-lab assessments.

were purchasing biodiesel fuel for use in their own vehicles or equipment. Thus, our students had a keen interest in assessing the fuel quality of some local biodiesel supplies. Additional biodiesel sources, including samples from farm processors and local biofuel co-operatives that varied in terms of preparation methods, feedstocks, and postprocessing, were tested. Samples with no form of postprocessing had flash points similar to the biodiesel made by the chemistry students, whereas samples treated with either an aqueous wash or dry adsorbent had flash points above 180 °C (Table 3). The students found it interesting to realize that some small-scale fuel producers were using biodiesel in farm equipment that was well below ASTM standards. Such fuel quality issues have also been observed in the marketplace, as documented by a 2005 study by the Minnesota Department of Commerce *(9)* and a 2006 study conducted by the National Renewable Energy Lab in which over 30% of the retail B100 samples failed to meet flash point specifications *(10)*.

Assessments were done with pre- and post-tests to determine content knowledge and retention of the material in the laboratory, and a student assessment of learning gains (SALG) survey was completed to gauge the students' feelings about how much this newly implemented laboratory exercise helped them learn the material. Pre- and post-test surveys showed that the students demonstrated an increase in their understanding of many biodiesel characteristics (Figure 3). Furthermore, after the lab, 96% of all students recognized that biodiesel is a renewable fuel whereas conventional diesel is not, and 76% of students responded that measurement of flash point helped them better understand the concept of vapor pressure.

Nearly all the students (57 of 59) indicated that synthesizing biodiesel was easier than they thought it would be. Over a third of all students indicated that they would carry “a lot” or “a great deal” of understanding concerning vapor pressure and biofuels into other classes or aspects of their life as a result of this lab activity. Many students commented on the practical nature of the lab experiment, and a significant number of students included observations related to technical issues involved in the production of commercial fuels:

- It was one of my favorite labs. I liked that the real-world applications were very clear.
- I enjoyed learning about biofuels. They are becoming such a large part of our lives and learning about them has helped me better understand the world around all of us.
- Cool lab. My family uses biodiesel in our farm tractor.

One of the most valuable impacts of this lab exercise was that students came away with a better understanding of chemical testing and standard operating procedures. By exploring a real-world application, students observed firsthand the importance of QA−QC practices. Another important aspect of this research was the realization that, despite extensive media coverage of biofuels by both television and the popular press, the majority of students had only minimal knowledge and casual familiarity with biodiesel fuel prior to the lab experience. Following completion of this lab and associated pre- and post-lab questions, over 80% of the students were able to recognize that biodiesel and petrodiesel differ in feedstock material, flash point, atmospheric environmental impacts, and contribution to climate change.

Conclusions

This biodiesel lab experiment increased the student's understanding of biofuels and associated chemical concepts. The flash point testing proved to be a constructive activity to relate vapor pressure properties of biodiesel and other fuels to their chemical structure. Comparison of student-produced biodiesel with that obtained from a commercial supplier illustrated how fuel properties depend on the production process and the resulting composition and purity of the fuel product. The contrast between density and flash point testing also demonstrated the reason why multiple QA−QC tests are necessary for fuels. The fact that the crude biodiesel produced by students did not conform to ASTM standards was a good lesson in QA−QC and provided students with insight to the rules and processes concerning industrial chemical production and commercial regulation.

Acknowledgment

The authors wish to thank the National Science Foundation Center for Integrating Research Teaching and Learning (NSF Award #0227592) and the UW−Madison Delta program for supporting this study. We also thank the MATC students for their involvement in this lab and for their effort in helping assess this new lab exercise. MATC diesel and heavy equipment instructor, Paul Morschauser, provided additional technical assistance and instructional advice. Partial financial support was provided by the Consortium for Education in Renewable Energy Technology (www.ceret.us) and the National Science Foundation Advanced Technological Education Program (NSF Award # 0501764 and 0903293). This manuscript benefited greatly from the suggestions and comments of three anonymous reviewers.

Literature Cited

1. King, A. G.; Wright, M. W. *J. Chem. Educ.* **2007**, *84*, 202–206.
2. National Biodiesel Board. http://www.biodiesel.org (accessed Nov 2010).
3. Knothe, G.; Van Gerpen, J. H.; Krahl, J. *The Biodiesel Handbook*; AOCS Publishing: Chicago, IL, 2005.
4. Mitchell, R. *Sci. Teach.* **2000**, *67*, 30–33.
5. Clarke, N. R.; Casey, J. P.; Brown, E. D.; Oneyma, E.; Donaghy, K. G. *J. Chem. Educ.* **2006**, *83*, 257–259.
6. Akers, S. M.; Conkle, J. L.; Thomas, S. N.; Rider, K. B. *J. Chem. Educ.* **2006**, *83*, 260–262.
7. Bucholtz, E. C. *J. Chem. Educ.* **2007**, *8*, 296–298.
8. Chiu, C.-W.; Goff, M. J.; Suppes, G. J. *AIChE J.* **2005**, *4*, 1274–1278.
9. Minnesota Department of Commerce. http://www.state.mn.us/portal/mn/jsp/common/content/include/contentitem.jsp?contentid=536908362 (accessed Nov 2010).
10. Alleman, T. L.; McCormick, R. L.; Deutch, S. B100 Quality Survey Results National Renewable Energy Lab Milestone Report. NREL/TP-540-41549. **2007**.

Supporting Information Available

Student handouts, student data tables, and instructor notes are available. This material is available via the Internet at http://pubs.acs.org.