

# Biodiesel Synthesis and Evaluation: An Organic Chemistry Experiment

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Recent environmental regulations regarding diesel fuel standards and the role the Midwest may play in future fuel production provides an opportunity to relate principles of organic chemistry to everyday life. Since October 2006, the Environmental Protection Agency regulations have required that all diesel fuel sold in the United States be limited to 15 ppm sulfur compared to the previous 500 ppm standard (1). However, as sulfur and organosulfur compound levels decrease, the fuel lubricity decreases dramatically resulting in increased engine and fuel injector wear. Fuel lubricity can be improved by adding a 2% blend of biodiesel in diesel fuel (2). Biodiesel is the transesterification product of triglycerides of vegetable oils with methanol to form fatty acid methyl esters (FAMEs, Scheme 1) (3). In addition to being an adjunct to low sulfur diesel fuel, biodiesel is also a candidate as a renewable alternative fuel. It has fuel properties similar to petroleum-based diesel (4) and can be used directly in a diesel engine. Fuel usage, though, would tend to increase as biodiesel contains less energy per unit volume than petroleum diesel. For example, biodiesel from soybeans has 8% less energy than No. 2 diesel fuel (118,170 Btu/gal versus 129,050 Btu/gal) (5).

Biodiesel synthesis is accomplished industrially by base-catalyzed transesterification of vegetable oil obtained from soybeans in the United States or low-erucic acid rapeseed (canola) in Europe. In countries with tropical climates palm oil is used (3). Other triglyceride feedstocks such as waste vegetable oil (WVO) obtained from fast food restaurants have also been used. Conversion of WVO as a fuel alternative has been outlined many times in the popular press. Most prominent has been the Veggie Van that traveled across the country using biodiesel fuel made by converting WVO to FAMEs (6).

The conversion of WVO for fuels, however, presents some practical problems. As the oil is used to fry food, the moisture content of the food tends to hydrolyze triglycerides to free fatty acids (FFAs) (7). These FFAs cannot be converted to esters via base-catalyzed esterification and must be esterified by acid-catalyzed mechanisms. Therefore, the conversion of WVO to biodiesel provides practical application of material commonly presented in the second semester of introductory organic chemistry.

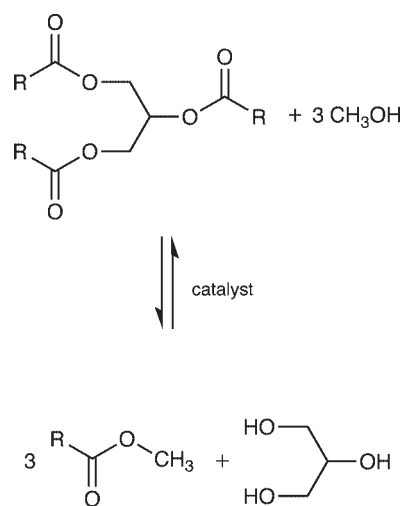
Although many esterification reactions have been presented in this *Journal* (8–12), including one based on biodiesel preparation and viscosity (13), this new lab provides a novel experience as students model a current industrial process by performing acid- and base-catalyzed esterifications and explore oxidation of vicinal alcohols by periodic acid. While

iodometric titration was presented years ago in the context of the organic chemistry lab (14), this new experiment eliminates the necessity of sodium arsenite and presents the titration as a method of determination of completeness of a reaction.

Students synthesize and evaluate fatty acid methyl esters from simulated WVO (oil spiked with oleic acid). To maximize product, students determine weight percent of FFA in the sample and convert the FFAs to FAMEs via acid-catalyzed Fischer esterification. After conversion of the FFAs, the remaining mono-, di-, and triglycerides in the WVO are converted to FAMEs by base-catalyzed transesterification. Finally, the completeness of the conversion is determined indirectly by analysis of total (bound and free) and free glycerol in the final product by stoichiometric oxidation of vicinal alcohols by periodic acid. The ASTM International standard for commercial biodiesel states that total glycerol in the final product must be less than 0.25% and the free glycerol be less than 0.02% (15). From the weight percent of glycerol in the final biodiesel sample, the student determines whether the product meets ASTM total glycerol specifications for marketable biodiesel.

## Experimental

This experiment is typically completed in two, three-hour laboratory periods during the last few weeks of the second semester of introductory organic chemistry. The determination of percent FFA, acid-catalyzed Fischer esterification



Scheme 1. Transesterification reaction of triglycerides to FAMEs.

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fication, and base-catalyzed transesterification are completed in the first lab period. Glycerol content by periodic titration is determined in the second lab period. Students are given a sample of olive oil to which up to 6% oleic acid is added. The %FFA is determined by titration of sample dissolved in 70% isopropyl alcohol with standardized 0.1 M KOH. Fisher esterification of FFAs is performed with a 40:1 mole ratio of methanol to FFA and 5.0% concentrated sulfuric acid as weight percent of free oleic acid and stirred at reflux for 1 hour. The samples are centrifuged and the oil/FAME layer is removed for base-catalyzed transesterification. Sodium methoxide (0.5% weight of oil/FAME) in methanol is added to the oil/FAME and stirred at reflux for 20 minutes. The resultant mixture is centrifuged to obtain a hydrophilic glycerol phase and a hydrophobic biodiesel phase. The less dense biodiesel is separated and stored until the following week for analysis of total and free glycerol. Glycerol in the final biodiesel sample is determined by oxidation with periodic acid and subsequent iodometric titration. In this method, glycerol reduces periodate to iodate; the iodate in turn, and any remaining periodate, is determined by reaction with thiosulfate. Thus, the decrease in the quantity of thiosulfate required, when compared to a blank containing the same initial quantity of periodate, gives a measure of the quantity of glycerol present. (The detailed procedure is in the Supplemental Material.<sup>u</sup>)

## Hazards

Students should wear goggles and gloves when performing this experiment. For all the reagents used in this experiment, students should avoid contact with eyes and skin: they may be harmful if swallowed or inhaled so care should be used when handling. Sodium methoxide is caustic, highly flammable, and reacts violently with water. Periodic acid is a strong oxidizer and can react violently if put in contact with rubber. Methanol is toxic and flammable. The sulfuric acid catalyst is toxic and corrosive.

## Results and Discussion

This experiment has been completed using olive or partially hydrogenated soybean oil, as well as oleic or stearic acid added to simulate WVO conditions. To facilitate the handling of starting materials for this reaction, the use of olive oil and oleic acid, which are both liquids at room temperature, is recommended. Partially hydrogenated soybean oil with stearic acid presents problems in that it requires heating to decrease viscosity enough for the magnetic stirring used in most student organic chemistry labs. The use of actual WVO presents the same stirring problems as it usually contains hydrogenated oils and FFA contents of up to 15% causing the starting material to be a solid at room temperature (16).

The use of olive oil in the lab also simplifies factors in FFA analysis. The triglycerides in olive oil contains up to 85% oleic acid naturally, so any FFA before spiking is predominantly oleic acid. Analysis on the purchased oil before spiking indicated a 0.22% FFA as oleic acid. Communications with the olive oil manufacturer confirmed these findings as their lot analysis on the oil purchased was also 0.22% free

oleic acid. Students' determination of %FFA on the spiked sample results in a range of 4–8% error of the known spiked %FFA. This seems to be an acceptable level of error in that this value is used to determine a catalytic quantity of acid required for acid-catalyzed esterification. In this lab activity, the initial spiked 6% FFA is reduced to less than 0.5% FFA, which is the accepted upper limit of %FFA in a base-catalyzed reaction (16).

Total and free glycerol (1.0–3.0% and 0.25–0.50%, respectively) obtained in student reactions are generally higher than the ASTM accepted values (0.25% and 0.02%, respectively). The relatively high quantity of total glycerol is a result of the 20 minute time allotted for transesterification. Using sodium methoxide, complete conversion is usually attained in 1–2 hours (16). The excess free glycerol can be attributed primarily to not washing the biodiesel produced with water to remove excess glycerol. Attempts to wash the biodiesel by extraction results in an emulsion that may not separate by the following week's glycerol determination lab. As these are equilibrium reactions, the increased level of total glycerol provides an opportunity to discuss Le Châtelier's principle and other modifications to improve yield.

Variations on the lab can also allow for guided-inquiry type studies. Students can explore transesterification reactions by monitoring the percent conversion versus reaction time and the effect of alcohol structure or catalyst (sodium methoxide or sodium hydroxide) on percent conversion.

## Conclusion

This new esterification experiment and periodate analysis of glycerol for the introductory organic chemistry laboratory provides an opportunity to relate topics of organic chemistry to renewable fuel sources and food chemistry while performing a lab that directly correlates to a current industrial process.

## <sup>u</sup>Supplemental Material

Student handout and notes for the instructor are available in this issue of *JCE Online*.

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