A Simple, Safe Method for Preparation of Biodiesel

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Supporting Information

ABSTRACT: An experiment suitable for organic chemistry students is described. Biodiesel, a “green” fuel, consists of methyl or ethyl esters of long-chain fatty acids called FAMES (fatty acid methyl esters) or FAEEs (fatty acid ethyl esters). A quick way to make FAMES is by a base-catalyzed transesterification of oils or fats derived from plants or from animal sources. This experiment utilizes a safe, convenient basic catalyst, K₂CO₃, anhydrous methanol, and any of several sources of oil to make biodiesel in 20–25 min. Only simple apparatus is required and the product floats on the top of the byproducts. IR spectroscopy, thin-layer chromatography, or relative viscosity are used to evaluate the product.


Great interest worldwide has developed in the production of methyl esters of fatty acids (FAMES) as a fuel for diesel engines or oil heaters and as a means for reducing the use of petroleum, which is entirely a fossil fuel. The bulk of the fatty acids occur as triglycerides derived from plants, which utilize CO₂ in the atmosphere to make triglycerides. Thus, converting triglycerides to FAMES reduces CO₂ emissions compared to the emissions from fossil fuel alone. Methanol is commonly made from natural gas, methane, a fossil fuel. However, methane is also obtainable from biogas coming from closed landfills that are piped to recover some of the biogas that landfills generate.¹ Utilization of the methane released by landfills to make biodiesel for biodiesel would help mitigate the emission of greenhouse gases (GHG) in two ways: (i) lessening release of GHG to the atmosphere; and (ii) producing a fuel component that would not emit oxides of nitrogen (NOₓ) and other pollutants.²

Triglycerides have high molar masses (∼800–935 g/mol) resulting in low volatility and high viscosity, making it necessary to preheat the fuel to enable its use as diesel fuel for RPM (revolution per minute) engines. For use in vehicles, it is necessary to convert the triglycerides into esters of inexpensive, low molar mass alcohols such as methanol or ethanol. These esters, called biodiesel, have about one-third the molar mass of a triglyceride and are more volatile and less viscous than triglycerides. A quick way to make biodiesel is by an acid-catalyzed method and requires a large excess of the alcohol. ⁵

The quickest and easiest method for making biodiesel is base-catalyzed transesterification of triglycerides. Biodiesel can currently be blended volumetrically with petroleum diesel up to 20% FAMES and 80% petroleum diesel. Higher ratios of FAMES can be used as fuel but makers of diesel engines are proceeding cautiously and do not, as yet, guarantee the engines if blended fuels containing more than 20% biodiesel are used. Commercial biodiesel is identified as, for example, B2 (2% FAMES), B5 (5% FAMES), B20 (20% FAMES), and so on. Biodiesel is an excellent fuel and it diminishes air pollution by the engine exhaust except for oxides of nitrogen (NOₓ). It has been found to decrease wear of parts of the diesel fuel injection system and helps to keep the fuel system clean. Fuel consumption is only slightly increased and the fuel may solidify in very cold weather.

Base-catalyzed transesterification was explored long ago³ and later found use as a method for converting animal fats into methyl esters in >99% yield,⁴ Scheme 1. In this reaction, the CH₃O⁻ moieties replace almost all of the bonds from the carbonyl groups to the three oxygen atoms of what will become glycerol. The reaction proceeds because methoxide (CH₃O⁻) is more basic than the anions of glycerol. The pKₐ of methanol is 15.5 and glycerol 14.15.

A second method of making FAMES is by an acid-catalyzed transesterification, Scheme 2. This reaction is slower than the base-catalyzed method and requires a large excess of the alcohol.⁵ In this case, the acid protons attach to the carbonyl oxygens of the fatty acid esters, which facilitates the attachment of methanol to the carbonyl carbons. Also the reaction is an equilibrium and the large excess of methanol is needed to drive the reaction to the right. The reaction mixture can then be separated from a solid acid catalyst so that the reaction will not appreciably reverse and the excess methanol can be distilled off. A useful review reports many aspects of making biodiesel.⁶

There have been several excellent experiments for students published in recent years⁷–⁹ that included new and used oil and determination of properties. Another was a cautionary comment about emulsions that occur when used oils contain free fatty acids.¹⁰ A multistep esterification of free fatty acids was also reported,¹¹ but it would probably not be economical.

PROCEDURE

A popular method for making FAMES is to use lye¹² as the base but this produces some soap (a salt of a fatty acid). A much simpler and safer method for making FAMES was reported in 2009:¹³ 15 min at 60 °C with the oil of Jatropha curcas seeds using
anhydrous potassium carbonate as the catalyst. Anhydrous potassium methoxide has been shown to form by reaction of methanol with potassium carbonate.\textsuperscript{14} Potassium hydrogen carbonate forms and is only sparingly soluble in methanol. The method used here is to prepare a mixture of the desired oil assumed to have an average molar mass of 880, anhydrous K$_2$CO$_3$ (6% of the mass of oil), and 6 mmol of anhydrous methanol per mmol of oil. The mixture is heated to 60°C and stirred for 25 min. A dilute solution of acetic acid or household vinegar is slowly added with stirring to neutralize the basic compounds and extract the residual methanol and glycerol. The biodiesel floats on top. Measuring the time of passage of biodiesel through a calibrated 6 in. Pasteur pipet followed by the time of passage of the source oil through the same pipet yields the relative viscosity: The “calibration” consists merely of putting a mark on the body of the pipet with a pen followed by a second mark put on the narrow stem, 2 cm up from the tip. With a finger held against the tip, one fills the pipet with the sample slightly above the top calibration. The finger is removed when the meniscus reaches the top mark and the starting time is noted. As the last drop reaches the lower mark, the time is noted, (Relative Viscosity) = (oil time)/(biodiesel time). Laboratory details are available in the Supporting Information.

**SOURCES OF OIL**

Economical sources of oil are readily found. Several kinds of vegetable oils are available in supermarkets: olive oil, canola oil, “vegetable” oil (often soy or cotton seed oils), peanut oil, and so on. To include an extraction component to the experiment, dried, used coffee grounds are a good source of oil,\textsuperscript{15} but soap was also formed due to the presence of free fatty acids. Used cooking oil may sometimes be obtained from fast food restaurants. This oil may have to stand for a period of time to let water settle out.

**BIO DIESEL PRODUCTS**

The biodiesel was made in good yield from olive oil, soy oil, peanut oil, and used cooking oil and was analyzed by gas chromatography—mass spectroscopy (GC—MS). More than 90% of the product comes from saturated and unsaturated C$_{16}$ and C$_{18}$ free fatty acids with small quantities of C$_{20}$ and C$_{22}$.\textsuperscript{16} Unsaturated free fatty acids in the (Z) (cis) configuration usually have lower melting points than those derived from saturated free fatty acids.

IR spectroscopy provides a convenient estimate of the quality of the products. Bands above 3007 cm$^{-1}$ indicate the presence of methanol. The symmetry of the band at 1743 cm$^{-1}$ reveals the conversion of the oils, and bands at 1467 and 1436 cm$^{-1}$ show the presence of methyl esters.\textsuperscript{13} A band at 1164 cm$^{-1}$ in the oil disappears and bands at 1197 and 1171 cm$^{-1}$ appear in the product. As a matter of interest, the band at 3007 cm$^{-1}$ is a H to sp$^2$ C single-bond stretching frequency. The lack of strong bands at 980—960 cm$^{-1}$ and a sharp band at 723 cm$^{-1}$ indicates that the double bonds are mainly in the (Z) configuration.

Thin-layer chromatography (TLC) can also be used to determine the completion of the transesterification reaction. A suitable developing solvent consists of 85 vol of mixed hexanes, 15 vol of ethyl ether, and 1 vol of glacial acetic acid. Visualization is quickly accomplished in a chamber containing iodine vapor.

Two of the students who helped develop the experiment, (J.O.S. and J.A.D.) obtained yields of 90.7% (peanut oil) and 93.2% (vegetable oil), respectively. The relative viscosities were 7.9 and 10.2, respectively. Working in teams of two or three using vegetable (soy) oil, the students in the chemistry class obtained yields averaging 72.5 ± 24.6% (range: 97 to 21.7%) and relative viscosities of 7.3 ± 2.3 (range: 3.7—10.0). The experiment was completed in 3 h.

**HAZARDS**

With the possible exception of used cooking oil, the oils purchased in markets are edible. Methanol is flammable and poisonous so it must be handled with care. Anhydrous potassium carbonate is an irritant and caustic. If the procedure is followed, the product biodiesel is oily and could make floors slippery if spilled and the byproduct will be a water solution of containing potassium acetate and small quantities of methanol, and glycerol.

If evaluation of the product by thin-layer chromatography (TLC) is incorporated, a developing solvent comprising mixed hexanes, diethyl ether, and glacial acetic acid is needed. The double bonds are mainly in the (Z) configuration.

**ASSOCIATED CONTENT**

\section*{Supporting Information}

Student handout; tables of the equipment and chemicals needed. This material is available via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

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\section*{Notes}

\begin{enumerate}
  \item Undergraduate students.
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REFERENCES

(1) USEPA Landfill Methane Outreach Program (LMOP) and links therein http://www.epa.gov/lmop/ (accessed Jun 2011).