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Potential Biofuel Additives to Reduce Emissions and Improve Air Quality

CALICIA J. DAHNA¹, CATHERINE JALOMO¹ AND KEN CHEUNG²

Studies have shown that a strong supportive learning community, problem-based and team-based learning that facilitates multiple learning-styles, and healthy functional mentoring, will build healthy self-efficacy, higher academic achievement, increase graduation rates and entry into graduate studies among under-represented minorities in science, technology, engineering and mathematics (STEM).³ Over 53% of the population in the Central Valley is Hispanic but only 8.9% of the Hispanic population attains a bachelor's degree.

Problem-based learning projects that hit close to regional issues may provide under-represented STEM students high-impact learning experiences that facilitate higher order thinking and meaningful learning relating to real-world situations by connecting new multidisciplinary knowledge to their existing knowledge, and higher interests in STEM and self-confidence.⁴ Fresno, Bakersfield, Visalia, Porterville, and Modesto are cities in the Central Valley that are mentioned in the ten most air-polluted cities in the U.S. by *Time Magazine*, and more than 75,000 of Fresno's 900,000 inhabitants suffer from asthma, and another 25,000 suffer from chronic bronchitis.⁵ Particulate pollution is worse in the Central Valley than other air-polluted regions, such as Riverside-San Bernardino, because particulates are often trapped by stagnant air conditions due to the valley's unique topographical and meteorological patterns. Blending petroleum diesel with 20% biodiesel in heavy-duty engines can reduce particulate matter (PM) emissions 10%, carbon dioxide 15% and unburned hydrocarbons 21%, and with negligible increase in nitrogen oxides (NO_x), a PM_{2.5} precursor.⁶

Students in my first semester organic chemistry lab course CHEM-312L use base-catalyzed transesterification to react vegetable oil with methanol to form fatty acid methyl ester (biodiesel).⁷ Acid-catalyzed methanolysis of poly-3-hydroxy-alkanoate (PHA) bioplastics was used in the CHEM-496 research course to form 3-methoxy-alkanoate methyl ester (3MAME) and/or 3-hydroxy-alkanoate methyl ester (3HAME), which may be a potential oxygenated additive to improve petroleum-based diesel fuel quality and

exhaust emissions.⁸

Petrodiesel fuel is becoming a less attractive source of energy due to its negative impact on the environment. Instead, current alternatives are being looked at to replace petrodiesel fuel. One alternative is biodiesel which can be made from a variety of sources, such as vegetable oil. Biodiesel is the only alternative fuel type to pass the Tier I and Tier II Health Effects from the Clean Air Act Amendments of 1990 put in place by the U.S. Environmental Protection Agency.⁹

Biofuels are a broad class of combustible hydrocarbons derived from biomass. Central California is reputed for high PM_{2.5} emissions, which include exhausts from burning fossil fuels, which are consistently above national ambient air quality standards set by the U.S. Environmental Protection Agency.¹⁰ By acting as oxygenated biofuel additives methyl esters derived from PHA will probably improve the combustion efficiency of petrodiesel, thereby reducing PM emissions. One study reported that a 30/70% 3HAME/petrodiesel blend had a combustion heat of 49 kJ/g, comparable to 100% petrodiesel of 50 kJ/g. 3HAME improved the combustion heat of ethanol, and may function as a standalone biofuel, reducing the risk of incomplete burning posed by longer hydrocarbons.¹¹ In addition, possible spills pose less of a hazard to the environment and wildlife because PHA and 3HAME are biodegradable by microbes in various land and marine soils.¹² However, the major downside to using PHA based biofuel is the cost of production, upwards of US\$1200 per ton, which is significantly higher in comparison to petrodiesel production of about US\$200 per ton.¹³ Therefore, it is best to use 3MAME or 3HAME as an additive, rather than as a stand-alone biofuel.¹⁴

Biodiesel from vegetable oil is known to have a kinematic viscosity ranging from 1.9 to 6.0 mm²/s, while petrodiesel has a range of 1.9 to 4.1 mm²/s at 40 °C using ASTM D445.¹⁵ Viscosity is resistance to flow, and often is thought as how thick or thin a liquid is, and this is usually measured by the efflux time for it to flow through the capillary of a viscometer, such as Ubbelohde or Ostwald. Even though biodiesel has a relatively higher viscosity than petrodiesel, there is research that shows with different additives this viscosity can be reduced when it is mixed with less viscous substances.¹⁶ This is considered more optimal because the more viscous the

biodiesel is, the more difficult it will be to use during cold weathers. During an engine's warm-up, the biodiesel can have a negative effect on the engine if the surrounding temperature is cold; this can result in excessive fuel injection pressures.¹⁷ This issue is not seen as much of a problem for using traditional petrodiesel fuel. Therefore, harsh cold weather is a disadvantage for biodiesel, but with the use of additives it is possible to make its viscosity like that of petrodiesel, making it more competitive as an alternative.

Methods and Materials

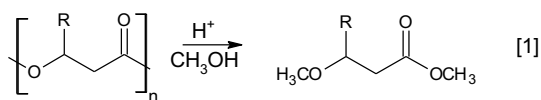
Biodiesel was synthesized using base-catalyzed transesterification of 40 mL of soybean oil with 10 mL of 0.4 M sodium hydroxide in methanol solution between 40°C and 50°C for 45 minutes. The mixture was cooled and settled into an upper biodiesel phase and a lower glycerol phase for a week. Three solutions of biodiesel mixed with 3MAME were prepared: 1 mL of 3MAME additive was added to 19 mL of biodiesel to prepare 5% solution, 2 mL of additive was added to 18 mL of biodiesel to prepare 10% solution, and 3 mL of additive was added to 17 mL of biodiesel to prepare 15% solution. The solutions were then placed in Erlenmeyer flasks, covered with parafilm, and stored at room temperature. Some separation of the solution was observed, where there was a gel-like substance settled to the bottom of the flask. The gel was most likely remains of unreacted 3HAME rather than the non-polar 3MAME. Only the miscible liquid phase of 3MAME/biodiesel solutions were used for kinematic viscosity measurements.

Ostwald viscometers were used for this experiment. The temperatures the solutions were tested at for this experiment were 0°, 20°, and 48°. The temperatures were achieved using a constant water bath, and each solution was in the bath for at least 10 minutes to reach thermal equilibrium before testing begun. When testing the viscosity at different temperatures the Ostwald viscometer of Size 1, with a constant of 0.01005, was used to test the solutions at 20° and 48°. The Ostwald viscometer of Size 1C, with a constant of 0.03036, was used to test the solutions at 0°. These sizes were chosen based on their viscosity range to attain the most accurate reading. The efflux times in seconds required to reach the distance labeled in the viscometer were recorded and then multiplied by the respective constant to achieve the kinematic viscosity. A total of five trials were conducted for each

solution at each temperature. The average kinematic viscosity was then determined from the five trials for each solution at each of the three temperatures. The viscometer constant was not re-calibrated at each temperature, but for the present relative comparison of the effect of 3MAME as a biofuel additive on the kinematic viscosity of biodiesel, this procedure is adequate.

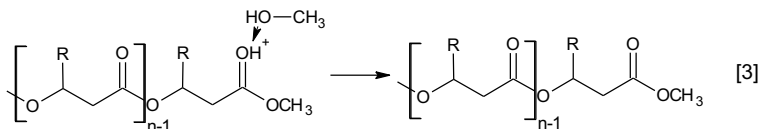
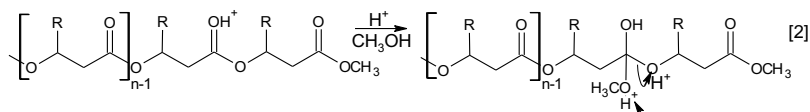
Commercially produced poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB-3HV) was dissolved in a round-bottom flask to make a solution of 7.5g PHA/250 mL chloroform. The first acid-catalyzed reaction used pure chloroform, but all subsequent trials used chloroform distilled from the reaction mixture. The acid catalyst was sulfuric acid in a 10% (v/v) solution with methanol. Acid-catalyzed reactions were refluxed at 60°C for 50 and 72 hours. After the solution mixture was cooled to room temperature, it was washed and stirred with 20 mL of saturated sodium chloride solution for 10 min. The solids were separated from the liquid by settling, and then both the liquid organic and water phases were separated with a separatory funnel. The organic phase was dried with anhydrous sodium sulfate, and then distilled under vacuum to remove most of the solvent to obtain a brownish yellow liquid, which might be a sign of larger PHA fragments not totally methanolized or possibly methyl esters of the sulfuric acid formed. All liquid samples were analyzed using gas chromatography coupled with mass spectrometry (GC-MS), ^1H nuclear magnetic resonance (NMR) and infra-red (IR) spectroscopy.

PHA underwent sulfuric acid-catalyzed methanolysis so that $-\text{OCH}_3$ nucleophilic substitutions occurred at the carbonyl carbon and at the β -carbon:

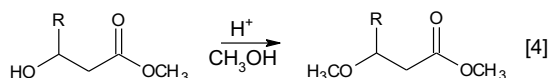


The first step in the mechanism is protonation of the carbonyl oxygen. The second step is nucleophilic addition of methanol at the carbonyl carbon, followed by loss of a proton from the attached methanol, to yield a tetrahedral addition intermediate. The next steps are the elimination of a

hydroxy-alkanoate segment, as the leaving group, and the deprotonation of the carbonyl oxygen to regenerate the acidic methanol.



Acid-catalyzed alcohol condensation reaction between the excess CH_3OH and the $-\text{OH}$ group at the β -carbon of methyl-3-hydroxy-alkanoate will form the methoxy $\text{H}_3\text{CO}-$ group:



Results & Discussion

^1H NMR (Thermo Scientific™ picoSpin™ 45 spectrometer) was used to analyze the acid-catalyzed biofuel products. ^1H NMR of the acid-catalyzed product showed methylation of PHA (Figure 1). Peak #6 is the methyl ether, and Peak #9 is the methyl ester in the 3MAME product. Peaks at 1.07-1.37 ppm are the alkyl sidechains in 3MAME, namely methyl and ethyl groups. The chloroform peak is at 7.26 ppm. No differences appeared in the ^1H NMR spectra for acid-catalyzed biofuel refluxed for 50 and 72 hours. The $-\text{OH}$ groups from methanol or 3HAME might be the down-shifted peak at 7.0 ppm in Figure 1 due to acidity in the solution. However, ^1H NMR was taken after separating the polar aqueous phase, drying with anhydrous sodium sulfate and vacuum distillation to remove the volatile components in the solution, and so the 7.0 ppm is most likely be the $-\text{OH}$ group of 3HAME because of incomplete acid-catalyzed alcohol condensation to 3MAME. The IR spectrum of the pure additive in Figure 2 confirms the assignment with a

broad peak at $\sim 3200\text{-}3600\text{ cm}^{-1}$ because of hydrogen bonding, representing the O-H stretching mode. There is also a weak IR peak at $\sim 2980\text{ cm}^{-1}$, which is a C-H stretching functional group. There is a strong peak at $\sim 1718\text{ cm}^{-1}$ that shows a C=O functional group. There are moderate IR peaks at 1439 and 1379 cm^{-1} , representing O-H bending of a carboxylic group, and O-H bending of an alcohol, respectively.

Mass spectrometry, ^1H NMR, and IR were cross-referenced to determine the possible molecular structures of 3MAME and/or 3HAME synthesized from P(3HB-3HV) bioplastics (Figure 3). The higher 87.1 , 103.1 , 117.1 and 131.1 m/z peaks representing the larger fragments and were more useful for molecular structure determination. The most likely methyl esters synthesized were 3-methoxy-butyrate methyl ester (3MBME), 3-hydroxy-butyrate methyl ester (3HBME), 3-hydroxy-valerate methyl ester (3HVME) and possibly 3-methoxy-valerate methyl ester (3MVME).

Little difference was observed between ^1H NMR spectra of samples using recycled chloroform and samples using pure chloroform. Using pure chloroform each time, while more effective for dissolving PHA, is not cost-effective green chemistry. Recycling the chloroform distillate for later synthesis reduced the overall quantity of pure chloroform but increased the volume handled per cycle by 1.5 times the volume of pure chloroform needed to dissolve PHA.

Conclusions

CHEM-496 students involved in bioplastics and biofuels research had presented their findings in national conferences,¹⁸ which helped to open doors to top research universities and careers in STEM. Undergraduate research develops the process skills (self-efficacy, information processing, critical thinking, problem solving, teamwork, interpersonal communication, and metacognition) required for a modern innovative STEM workforce. A higher education at Fresno Pacific University will empower underrepresented minorities to overcome generational poverty and to advance diversity, equity, and inclusivity in the STEM workforce.

Acknowledgements

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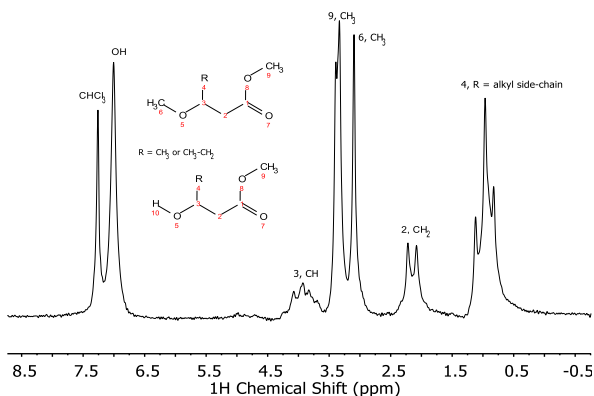


Figure 1. ^1H NMR of 3MAME synthesized by reacting PHA dissolved in chloroform with acidic methanol (10% v/v H_2SO_4 in methanol). The chloroform residue served as the reference at 7.26 ppm. Both the β -CH peak of PHA at 5.2 ppm and the OH peak of methanol at 4.7 ppm are completely disappeared, indicative of methyl esterification of methanolized PHA. The peak at 3.1 ppm is assigned to the methoxy OCH_3 (6) next to the carbon-3 in the backbone. The OH group (10) due to incomplete acid-catalyzed alcohol condensation to 3MAME is assigned to 7.0 ppm. The multiplet at around 3.8 ppm is assigned to the β -CH (3), and the peak at 3.3 ppm is assigned to the methyl CH_3 ester group (9). The alkyl sidechain (4) and α - CH_2 (2) spectral lines are more shielded in the upfield (right side).

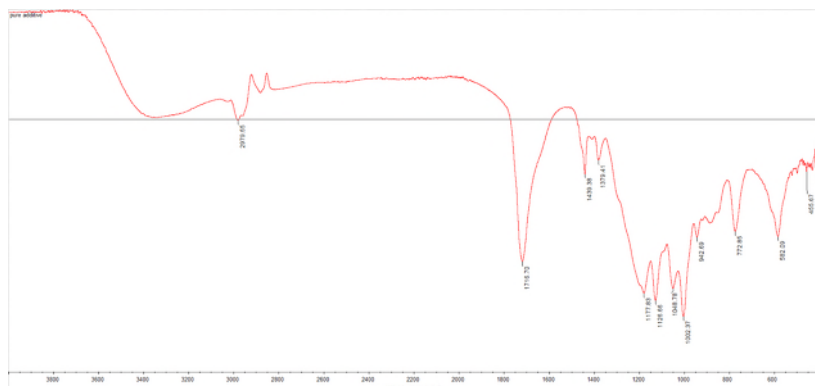


Figure 2. The signature broad IR peak at $\sim 3200\text{-}3600\text{ cm}^{-1}$ represents the O-H functional group of methyl-3-hydroxy-alkanoate. The peak at $\sim 2980\text{ cm}^{-1}$ is C-H stretching typical for an alkane. The strong peak at $\sim 1718\text{ cm}^{-1}$ shows the C=O functional group.

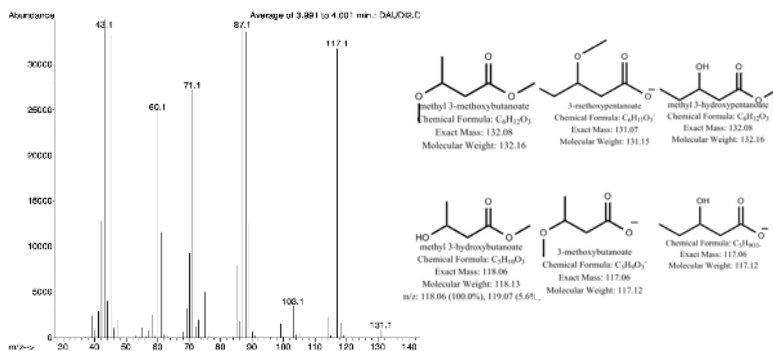


Figure 3. The most probable 3MAME and/or 3HAME molecules synthesized from P(3HB-3HV) were methyl-3-methoxy-butanoate or 3-methoxy-butyrate methyl ester (3MBME) and methyl-3-hydroxy-pentanoate or 3-hydroxy-valerate methyl ester (3HVME) both with exact mass of 132.1, and methyl-3-hydroxy-butanoate or 3-hydroxy-butyrate methyl ester (3HBME) with exact mass of 118.1, and possibly a small

amount methyl-3-methoxy-pentanoate or 3-methoxy-valerate methyl ester (3MVME) with exact mass of 146.1, matching the fragmentation patterns of these parent ions: $M^+ - CH_3$ (or $M^+ - 15$) shown in the MS peaks at 103.1, 117.1 and 131.1 m/z, and $M^+ - OCH_3$ (or $M^+ - 31$) at 87.1 m/z.

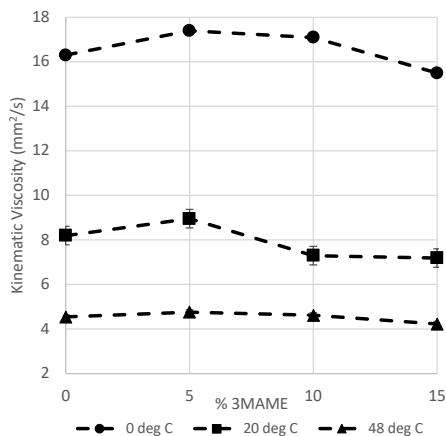


Figure 4. Effect of adding 3MAME on the kinematic viscosity of biodiesel at 0°C, 20°C, and 48°C. The lower temperature, the more resistance to flow is the biofuel. The kinematic viscosity values are acceptable within the specification for biodiesel. One-way ANOVA at $\alpha = 0.001$ shows statistically significant differences in the kinematic viscosity mean values by adding 3MAME: $F(3, 5) = 609.8 > F_{crit}$ and $p = 1.06 \times 10^{-16} < 0.001$ (at 0°C); $F(3, 5) = 1210.6 > F_{crit}$ and $p = 4.56 \times 10^{-19} < 0.001$ (at 20°C); $F(3, 5) = 816.0 > F_{crit}$ and $p = 1.05 \times 10^{-17} < 0.001$ (at 48°C).

NOTES

- Equal contributions by the two students.
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