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Brandon Ackley

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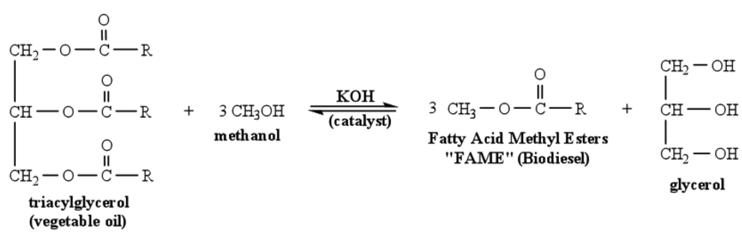
Brandon Ackley is a junior Chemistry major with a concentration in professional chemistry. Brandon began doing research in the summer of 2011 as part of the STREAMS (STudent REtention Across Mathematics and Science) Summer Bridge program. STREAMS invites 16 incoming freshman in the STEM field to participate in 3 weeks of intensive class and research work. Brandon conducted this research under the mentorship of Dr. Edward Brush (Chemistry) with funding from a 2013 Adrian Tinsley Program summer research grant. Brandon presented this research at the 247th American Chemical Society National Convention in Dallas, TX.

In 2011, the U.S. consumed over 18 million barrels per day *of refined petroleum products and biofuels; almost 22% of global petroleum consumption.[1] This includes oil used for transportation, electricity, and production of consumer products. More than half of this oil was imported from foreign countries, and in his 2006 State of the Union Address President Bush warned that, "We have a serious problem, America is addicted to oil, which is often imported from unstable parts of the world".[2] With the need for new energy sources more apparent than ever, serious research is needed to further the advancement of alternative fuels, so that they may become a more practical source of energy. Biodiesel is an alternative fuel to petroleum diesel, and is produced from renewable and/or recycled resources. Biodiesel's benefits include reduced emissions of unburned hydrocarbons, carbon monoxide, particulate matter and nitrogen oxides, plus reduction of greenhouse gas emissions.[3] The process of making biodiesel involves transesterification of triacyl-glycerides in Waste Vegetable Oil (WVO) with methanol, using potassium hydroxide (KOH) as a catalyst, Figure 1.[4,5,6]*

Figure 1. Traditional Transesterification Reaction of Vegetable Oil into Biodiesel.



Research in Dr. Brush's group has focused on developing an efficient and cost-effective process for converting 50 liter (13 gallon) batches of Waste Vegetable Oil (WVO) from BSU cafeterias into biodiesel fuel for campus use. However, in a detailed analysis of our efficiency in producing biodiesel by this traditional process, we found that this "simple" transesterification reaction is only one small part of a complex, interrelated, and inefficient overall production process.

Trans-esterification is an equilibrium chemical reaction, and at some point a "balance" is reached and reactants are no longer converted into products. In order to "force" this balance in favor of biodiesel formation we use an excess of methanol to ensure that all of the WVO reacts to form biodiesel. The excess methanol must be removed as it is flammable and can cause pre-ignition problems in a diesel engine. Furthermore, the KOH catalyst is strongly basic, corrosive and an irritant, and is essentially hazardous waste. The most significant obstacle involves washing the crude biodiesel with water to remove excess methanol, KOH catalyst, and glycerol byproduct. Failure to remove these chemicals results in engine corrosion, making the biodiesel useless. The washing process is time-consuming and water-intensive, requiring two volumes of water for each volume of biodiesel produced.

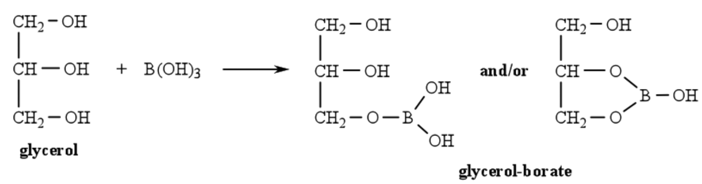
Green chemistry is the science of making smart, sustainable decisions in how we design, make, use and dispose of chemicals. Green chemistry is incredibly important today: the production of chemical products generates hazardous waste that damages the environment, resulting in unintended exposure to humans. Table I summarizes the 12 Principles of Green Chemistry, which provide a general framework for a sustainable future in the design of more efficient technologies to produce consumer products that are better, safer and cheaper.[7] Our research was focused on applying appropriate Principles to develop an efficient and cost-effective process for converting WVO into biodiesel. For this research project we determined that Principles 1, 2, 3, 6, 9 and 12 were most relevant towards improving the efficiency of the biodiesel process.

Table 1. The 12 Principles of Green Chemistry.
(Principles in bold were applied to this research)

#1.	Preventing hazardous waste.
#2.	Maximizing the Atom Economy.
#3.	Decreasing or eliminating all hazards in the chemical synthesis.
#4.	Design functional chemical products with minimal toxicity.
#5.	Minimize the use of solvents and auxiliary substances, and employ safe
#6.	More efficient use of water and electricity.
#7.	Use renewable raw materials for feedstock.
#8.	Minimize or avoid derivatization and additional reagents.
#9.	The use of safer, more benign catalysts.
#10.	Design chemical products that break down in the environment.
#11.	Develop analytical methods for real-time monitoring of hazardous substances.
#12.	Preventing accidents through inherently safer chemistry.

In this preliminary study, our initial focus was on Principles #6 and #9, and we selected and evaluated boric acid and sodium borate as catalysts for transesterification.[8] These compounds are less hazardous than KOH, and if found to be effective catalysts they would reduce the energy required for heating our reactions. Furthermore, we believed that Principle #2 was relevant as boric acid and sodium borate may react with and remove the glycerol byproduct, essentially forcing the equilibrium to completion, and avoiding the need for excess methanol (Figure 2). Finally, by removing the glycerol byproduct during the reaction we would use less water during the washing and extraction step (Principle #6).

Figure 2. Proposed Reaction of Boric Acid with Glycerol to Form Gylcerol-Borate.



Preliminary Results and Discussion:

We carried out a number of small-scale room temperature reactions to evaluate the effect of boric acid and so-

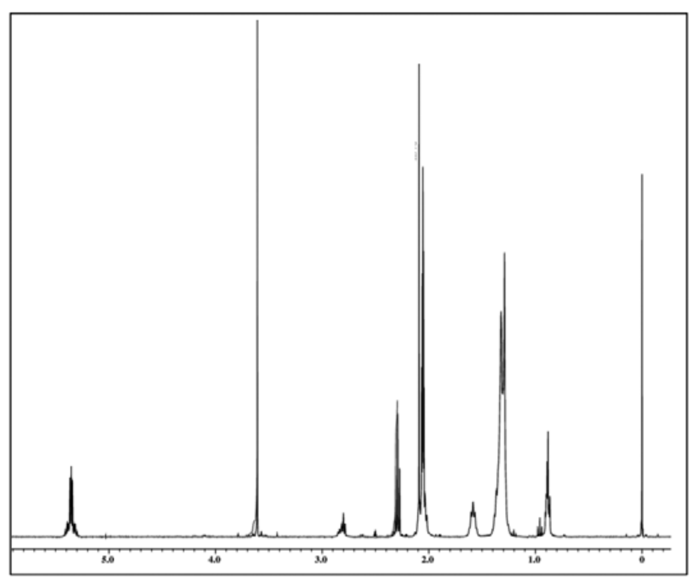


Figure 3. NMR spectrum of biodiesel product obtained from the standard transesterification reaction. General reaction conditions: 50g WVO, 4.96g methanol, and 0.175 g of KOH catalyst were mixed together and stirred for 60 minutes at room temperature (about 25°C). Reactions were extracted with 3 x 20 mL of water, and 0.002 g (1 drop) of the product mixture was dissolved in 1.0 mL of deuterated acetone, and the NMR spectrum was recorded. For test catalysts we used 1%, 5%, and 10% by mole amount (catalyst/theoretical glycerol amount).

dium borate as transesterification catalysts, and analyzed these reactions using Nuclear Magnetic Resonance spectrometry (NMR). Figure 3 illustrates the NMR from our traditional synthesis and purification of biodiesel (Figure 1), and our general reaction conditions are given in the legend.

Although NMR analysis of our small sale reactions using either boric acid or sodium borate did show the biodiesel signals seen in Figure 3, we also observed a substantial amount of unreacted WVO, suggesting that neither of these compounds were effective catalysts for transesterification with methanol, either on their own or when added in combination with KOH catalyst. Sodium borate gave the most encouraging results as NMR analysis suggested a very slow, continuous formation of biodiesel product; however, the reaction did not go to completion. Our conclusion from this preliminary work is that neither boric acid or sodium borate would be suitable catalysts for WVO transesterification.

We did notice that the NMR spectra from these experiments indicated very little contaminating glycerol, implying that boric acid and sodium borate might have potential for purifying biodiesel. Boric acid in particular may improve the efficiency of the water wash by: (1) KOH neutralization, and (2) glycerol extraction. We are following up on this idea by evaluating the effect of KOH-borate additives on the reaction equilibrium, and the effectiveness of acidic washing using aqueous boric acid.

Future Work:

In order to complete our evaluation of the effects of boron compounds on biodiesel production efficiency, we are conducting a more detailed assessment of sodium borate as a chemical additive (with KOH) to help push the equilibrium reaction to completion by removing the glycerol byproduct. We will also follow up on our preliminary results suggesting that boric acid increases the efficiency of the water wash of crude biodiesel by both neutralizing the KOH catalyst and binding the glycerol byproduct.

Acknowledgements:

I would like to thank Dr. Edward Brush for helping me through every step of this project, and the Adrian Tinsley Program and Center for Sustainability for funding this research.

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