An analysis of biodiesel’s potential as an alternative energy source

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Abstract

The purpose of this experiment is to examine the best possible ways to produce biodiesel with different alcohols and oils and whether biodiesel is a practical and feasible solution to the energy crisis. Because of dwindling oil supplies around the world, the utilization of clean alternative energy sources have become paramount. Recently, biodiesel has been explored as a possible alternative to petroleum based fuels.

We conducted three experiments. The first involved the reaction between soybean oil and methanol in a two-liter batch reactor at 60.0°C. After all the products settled, we found the volumetric biodiesel yield relative the initial triglyceride amount to be 99.20%. The second experiment involved the reaction between canola oil and methanol with a volumetric experimental yield of 101.40%. The third experiment involved the reaction between soybean oil and ethanol. However, the substitution of ethanol as the alcohol in the reaction was ineffective due to contaminated materials. There was no phase separation even after we conducted glycerol separation and centrifuging of the mixture of ethanol and soybean oil.

We also obtained numbers from various sources concerning the production of biodiesel on a large scale and whether such production is feasible. By using numbers such as the yearly soybean production and the yearly diesel consumption rates of the United States and performing simple calculations, we find that there simply is not enough soybeans in the U.S. to sustain the fuel economy on biodiesel alone. Biodiesel must be combined with other forms of alternative energy in order to meet the energy requirements of the United States.

Our results establish the reaction between canola oil and methanol as the most efficient in terms of biodiesel production and that biodiesel is viable as an alternative energy source only as a single piece in the puzzle for a cleaner, greener world.

1 Introduction

In 1912, Rudolf Diesel, the inventor of the diesel engine commented, “The use of vegetable oils for engine
fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time.” Because of the abundance and cheapness of petroleum fuels at the time, Diesel’s words were mostly ignored and biodiesel, diesel which originates from vegetable oils, faded into the background. Now, the situation sharply contrasts Diesel’s time as the world is forced to take a non-petroleum-based path. In a study compiled by the International Energy Agency, a report on the world’s largest 800 oil fields revealed that the majority are past their peak productions and that the predicted production decline rates are accelerating at twice the rate predicted in 2007[6]; i.e. fossil fuels will simply run out, especially as usage rates increase. The use of these fuels releases greenhouse gases and other pollutants, causing detrimental effects on the environment. It is also important for countries such as the United States to achieve energy independence, especially because most of U.S. oil originates from the politically unstable Middle East. New forms of renewable energy must be implemented to avoid further problems.

2 The Beginnings of Biodiesel

Currently, there are several different types of biofuels. One of these is first-generation corn-based ethanol and another is biodiesel. Though both are feasible, ethanol production through first-generation technologies such as fermentation in the United States are currently inefficient and impractical because of the large amount of money and carbon dioxide associated with the process. Producing and using ethanol releases almost as much CO₂ as regular petroleum fuels[6]. The production of one gallon of this corn ethanol would require four gallons of water and seven hundred eighty four gallons of irrigation[6]. Science American published that “There is simply not enough available farmland to provide more than about 10 percent of developed countries liquid-fuel needs with first-generation biofuels”[8]. In addition, these lands could instead be more effectively used for agriculture, especially as developing countries face rising food prices and dwindling food supplies, rather than energy.

On the other hand, though diesel engines have been previously criticized for being loud and dirty[1], newer diesel engines are quiet, have lower emissions, and are nearly indistinguishable from gasoline engines in performance[4]. Diesel engines generate more power and have 30 percent higher mileage than gasoline engines[4]. Unlike ethanol which is only two-thirds as efficient as gasoline[6], biodiesel is just as powerful as petroleum diesel[1].

Despite being a viable renewable source of energy, the cost of exchanging biodiesel with petroleum diesel is too high for a complete switch. For one, biodiesel uses a food source for its production, thus detracting from the food supply. Because seventy four million pounds of soybeans requires 28,816 acres, producing biodiesel requires a large space. Currently, only about one percent of soybean oil produced in the US is used for the production of methyl ester. To switch from petroleum diesel to biodiesel would require excessive time and resources and thus should be used in conjunction with other renewable energy sources.

Biodiesel fuels originate from natural triglycerides such as vegetable oils and animal fats. It is produced through the process of transesterification, the exchange of a variable hydrocarbon chain R between a triglyceride and an alcohol. In this case, R is a fatty acid. Figure 1 on the next page shows the basic reaction of biodiesel production.
Triglyceride, also called triacylglycerol or TAG, is an ester composed of three fatty acids and a backbone of glycerol. During the reaction, the fatty acids $R$ detach from the central backbone and reattach to the methane component of methanol.

2.1 The Different Varieties

There are many different kinds of plant sources from which biodiesel can be produced - including soybean, rapeseed (canola), coconut, peanut, palm, sunflower, and algae. Though algae and palm plants produce the highest gallons per acre yield, both cannot be grown in America at a large scale. For the time being, we are analyzing soybean oil and canola oil because they are the most readily produced in the United States.

Though canola seeds have a much higher gallons per acre ratio than soybean seeds (122:46), both have the same theoretical output to input ratio (milliliters of biodiesel produced to milliliters of oil used), because the same reaction is occurring regardless of fatty acid composition.

Looking at the molecular formulas of the various oils, canola oil is primarily composed of oleic acid, which has one less double bond than linoleic acid, the primary component of soybean oil. Furthermore, palm oil’s main component is palmitic acid, a completely saturated (no double bonds) fatty acid. The amount of double bonds relates to the temperature at which biodiesel congeals into a gel, with more double bonds corresponding to a higher gelling point. Because a biodiesel with a lower gelling point is more desirable (it is less likely gel in the fuel line of vehicles), we can predict that canola-based biodiesel is superior to soybean-based biodiesel, but because of time constraints on our project, we cannot test this hypothesis.

We also hypothesize that the oil yield per plant and the density of plants per acre may also play a factor in the efficiency of a certain biodiesel’s production process.

As for the alcohol in the reaction, ethanol has the advantage of being able to be produced from plant sources while methanol originates from fossil fuels and thus is less environmentally-friendly. Nevertheless, methanol is less expensive than ethanol and thus we use it in two of our three experiments in biodiesel production.

2.2 Precautions

Though transesterification is a simple reaction, it must be run under carefully controlled conditions. Otherwise, there are several factors which may interfere with the results. For example, it is critical that the reaction is run with a high pH because a basic solution accelerates the reaction as a catalyst. For this experiment, a metal hydroxide such as potassium hydroxide is used. Also, because the production process of biodiesel is chemically reversible, the alcohol is added in excess to shift the equilibrium to the right. The temperature under which the reaction takes place is another factor that needs to be controlled. The optimal temperature for running the reaction around 60.0 °C, right below the vaporization point of the alcohol[7].

Contaminants must also be tightly monitored, especially water. Any excess water results in the production of soap, an unwanted by-product that is created when glycerol reacts with a base in the
presence of water. The production of soap consumes a large amount of basic catalyst and triglyceride, which, in turn, detracts from biodiesel production. Even outside the production process, water contamination presents a multitude of problems, especially when found in the biodiesel. First, water lowers the heat of combustion, which corresponds to more smoke and less power from the engine. Second, if water should freeze into ice crystals, the biodiesel is provided additional areas of nucleation which accelerate the gelling process[2]. Most importantly, water promotes the growth of microbe colonies, many of which happily consume biodiesel and thus exponentially reproduce, potentially causing blockages.

2.3 Biodiesel vs. Petroleum Diesel

Biodiesel shows promise in displacing the petroleum diesel that dominates the fuel market today.

Diesel fuel has differences from traditional gasoline fuel. When using either fuel, combustion of the fuel takes place within the piston assembly, where fuel is drawn into the combustion chamber, compressed, ignited, and exhausted. The difference lies in the method of ignition: gasoline is ignited by a spark plug while diesel fuel ignites spontaneously when it is compressed by the piston. Because the gasoline ignition must be carefully controlled for optimal performance, any spontaneous ignition of the gasoline, called knocking, is not desirable. However, because of diesel’s process of combustion, its ability to knock is very desirable and is measured in the diesel’s cetane number. The higher the cetane number, the less time it takes for the diesel to ignite upon introduction into the piston and the more powerful the stroke. Biodiesel from various sources such as soybeans, sunflowers, peanuts, and rapeseed prove to have a cetane number comparable to that of traditional diesel[5].

The majority of the pollutants in traditional diesel fuel come from residual sulfur compounds - of which biodiesel has none[12]. Hence, exhaust from biodiesel-burning engines contain less particulate matter (e.g. less soot) than those of traditional diesel engine. Even from a safety perspective, biodiesel presents an advantage over petroleum diesel. The flash point of a fuel determines its flammability - the lower the flash point, the lower the temperature at which it can ignite, and the higher the flammability. Biodiesel has a higher flash point than traditional diesel - thus, it is safer to store and transport than traditional diesel. Also, unlike ethanol, which is only two-thirds as efficient as gasoline[6], biodiesel is just as powerful as petroleum diesel[1] while retaining its environmental advantages.

3 Producing Biodiesel

3.1 Percent Composition Calculations

Prior to any experimentation, it is crucial to calculate the amount of oil that is required for each reaction since the experiments were limited by a 2 liter batch reactor. Because various vegetable oils are not homogenous but rather a mix of various fatty acids, the compositions of these fatty acids are varied and are not exactly the same in their molecular weight and structure. By averaging the molecular masses of these fatty acids, we found the general molecular mass of all the fatty acids of the specific oil. Because each oil molecule had three fatty acids in a triglyceride, we multiplied that number by three and added the molecular weight of glycerol. Thus, we found the molecular weight of one molecule of oil. Otherwise, we would not be able to calculate the correct theoretical yield from an assumed molecular mass.

3.2 Transesterification of Vegetable Oils

We tested two different oils and alcohols. These two reactions were carried out in a clean batch reactor involving soybean oil; one reacting with methanol and one reacting with ethanol. A third reaction utilized canola oil and methanol.
After carefully measuring both the mass and volume of the reactants, we added them into the batch reactor. In order to accelerate the reaction, all of the reactions were carried out at 60.0 °C, close to the boiling point of the methanol. To achieve a 60.0 °C temperature, we used a heated water jacket that enveloped the reactor to heat it. Because the oil was in a higher volume than the methanol, we preheated the oil in the reactor before adding the methanol to accelerate the reaction, as shown in Figure 2.

Figure 2: A batch reactor in the midst of heating oil to 60.0 °C. A beaker of methanol and KOH can be seen on the countertop with a paper towel covering the top to prevent atmospheric water absorption.

In addition, an automated plastic stirrer in the batch reactor agitated the reaction, allowing us to mix the reactants homogeneously and keep the whole system at a uniform temperature. The stirrer ran at 150 RPM.

Afterwards, we discovered that potassium hydroxide had a higher solubility in methanol than sodium hydroxide did and dissolved it in the alcohol before adding the entire solution into the batch reactor to run for 24 hours.

3.3 Collection of Pure Biodiesel

The reaction produced glycerol and methyl esters when it completed running. These, being completely insoluble with one another, separated into two distinct phases: the orange-colored glycerol on the bottom, and the yellowish methyl esters on the top. The impure glycerol settled on the bottom of the reactor and can thus be drained out by a valve on the bottom of the batch reactor. In addition, a thin line of soap on the interface from slight water contamination must also be drained. Finally, the yellowish methyl esters, the topmost layer, were extracted into an Erlenmeyer flask and were washed and dried.

The purification of the crude biodiesel involves washing and drying. The washing step involves showering acidified water through the biodiesel - because water is immiscible with biodiesel, it separated in bubbles which slowly sank to the bottom, carrying any contaminants with it. This process can be seen in Figure 3.

We used acidified water to lower the pH of the
biodiesel, preventing the production process from running in reverse.

Once the water that collected on the bottom was removed, the biodiesel was put through a wiped film evaporator, which further removed trace amounts of water by using a strong vacuum chamber and wipers to spread out the biodiesel along the walls of the chamber. Through the processes of washing and drying, the crude biodiesel can be purified of contaminants and was then pure enough to be run in diesel engines.

4 Results

4.1 Experiment 1: Soybean Oil

For biodiesel production, the main standard of quality is percent yield. By stoichiometry, we found that the theoretical yields of the reaction between soybean oil and methanol should be as follows:

Thus the theoretical yields should be as follows:

<table>
<thead>
<tr>
<th></th>
<th>Moles</th>
<th>Grams</th>
<th>Milliliters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>1.588 mol</td>
<td>146 g</td>
<td>116 mL</td>
</tr>
<tr>
<td>FAME</td>
<td>4.760 mol</td>
<td>1396 g</td>
<td>1586 mL</td>
</tr>
</tbody>
</table>

After we conducted our experiment and collected the products, we found that the actual yields are:

<table>
<thead>
<tr>
<th></th>
<th>Moles</th>
<th>Grams</th>
<th>Milliliters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol + Methanol</td>
<td>n/a</td>
<td>291.3 g</td>
<td>n/a</td>
</tr>
<tr>
<td>FAME</td>
<td>4.49 mol</td>
<td>1314.6 g</td>
<td>1493.87 mL</td>
</tr>
</tbody>
</table>

Thus the percent yields and errors for the FAME are:

\[
\text{Percent Yield: } \frac{1314.6g}{1396g} = 94.2\%
\]

\[
\text{Error: } \left| \frac{1314.6g - 1396g}{1396g} \right| = 5.83\%
\]

4.2 Experiment 2: Canola Oil

Similar to the soybean oil and methanol reaction, the reaction between canola oil and methanol also had a relatively high percent yield. Using stoichiometry, we found that the theoretical should be as follows:

Thus the theoretical yields should be as follows:

<table>
<thead>
<tr>
<th></th>
<th>Moles</th>
<th>Grams</th>
<th>Milliliters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>1.49 mol</td>
<td>136.92 g</td>
<td>116 mL</td>
</tr>
<tr>
<td>FAME</td>
<td>4.46 mol</td>
<td>1319.79 g</td>
<td>1499.8 mL</td>
</tr>
</tbody>
</table>

However, after we collected the products, we found the actual yields are:

<table>
<thead>
<tr>
<th></th>
<th>Moles</th>
<th>Grams</th>
<th>Milliliters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol + Methanol</td>
<td>n/a</td>
<td>314.1 g</td>
<td>n/a</td>
</tr>
<tr>
<td>FAME</td>
<td>4.5 mol</td>
<td>1269 g</td>
<td>1442.84 mL</td>
</tr>
</tbody>
</table>

Thus the percent yields and errors for the FAME are:

\[
\text{Percent Yield: } \frac{1269g}{1308.2g} = 96.2\%
\]
Error: \( \frac{|1269g - 1308.2g|}{1308.2g} = 3.8\% \)

And in all, the product to reactant ratios were:

- Soybean Oil: \( \frac{1493.87 \text{ mL}}{1505 \text{ mL}} = 99.20\% \)
- Canola Oil: \( \frac{1442.84 \text{ mL}}{1423 \text{ mL}} = 101.40\% \)

These numbers include the extra volume contributed by the chemical reaction with the methanol; thus, the product to reactant ratio for canola oil was over 100%.

5 Discussion

A comparison of output-input ratios and percent yields is an essential step in evaluating the yields of various biodiesels. With 1505 mL of soybean oil-based TAG, 1493 mL of FAME (i.e. the methyl esters) were produced. This is a 94.2% yield when compared to the theoretical 1586 mL yield and a 0.992 to 1 output to input ratio (the volume of the product compared to the volume of the reactant TAG). For 1423 mL of TAG from canola oil, 1442.8 mL of FAME were produced which resulted in 1.014 to 1 output to input ratio. The calculated yield was 1499.8 mL for canola oil, thus canola oil had a 96.2% percent yield, higher than the soybean oil. Theoretically, both Experiment 1 and Experiment 2 should have had output-input ratios of 1.05 to 1, even though canola plants yield 122 gallons of oil per acre and soybean plants only yield 46 gallons of oil per acre. Despite the small difference in the yields between the two successful experiments, which we believe to be due to a larger amount of unreactive free fatty acids in the soybean oil, these numbers were close to the theoretical yields and validated that diesel production efficiency is based off of the efficiency of the plant-oil conversion process rather than the efficiency of the oil-biodiesel process.

Nevertheless, there is belief that the higher yield and ratio numbers for the canola oil do suggest that the properties from the gallons/acre values do transcend to the oil/biodiesel production stage.

Overall, both of these experiments involving methanol had a high percent yield. In terms of the results, the numbers proved our biodiesel production process to be very successful, having expected/actual yields above 94%. However, there are several modifications that can be done to improve our results. First of all, we could have conducted more trials under different temperatures or with different bases to analyze the varying reaction rates as well as the percent yields. Secondly, we could have run the experiment on a shorter time interval rather than over twenty four hours. According to the literature, this reaction requires approximately five hours. The longer we left the experiment alone after the reaction completed, the more time it had to succumb to other environmental factors. Furthermore, if time permitted, we could have analyzed the differences in using vegetable oil and canola oil by taking samples from each reaction and chilling them to compare the gelling points - the temperature at which biodiesel congeals. High-quality biodiesel would gel at a lower temperature.

On the other hand, the third experiment, run with soybean oil and ethanol, produced a 0% yield when 1505 mL of oil was used. At first, we believed this was due to the fact that the reaction was running at too high a temperature, but when we lowered the temperature of the experiment to 50.0°C from the normal 60.0°C, there wasn’t much change. Even after we turned off the batch reactor’s agitator, there still wasn’t any separation.

From here we ran the reaction through the wiped film evaporator to try and remove any excess ethanol that may have interfered within the phase separation. After the evaporation, the mixture still failed to separate. The mixture was still homogenous even after being chilled for twenty four hours.

We later discovered that another research group from Beijing had discovered an interesting phenomenon: phase separation in transesterification experiments
involving ethanol was dependent on component concentrations and overall temperature. Their results are summarized in the phase diagram in Figure 5. After analyzing our own data and comparing it to theirs, we found out that our glycerol numbers were slightly below the tie line and that perhaps a little more could tip balance in favor of phase separation. This, too, was to no avail. Even with a minor experiment in which we added 100% (volumetrically) more glycerol to a sample of the mixture and put it in a centrifuge to attempt to shift the concentrations to separate into phases, there was minimal separation.

This was the best explanation for the no results in our third experiment. A soap is as miscible in glycerol as it is in water. Ultimately, this could only mean that some way or another, water was introduced into the reaction. We used the same soybean oil as in the first reaction so this could only mean that there was water in the supposedly ‘anhydrated’ ethanol or dessicated from the air from the pellets of potassium hydroxide.

6 Conclusions

The goal of our experiment was to determine the most efficient oil and alcohol combination for biodiesel production. An efficient process is needed for biodiesel to assist in the alleviation of the global energy crisis and global warming from the excessive use of petroleum-based fuels. We solved this by testing two different alcohols, ethanol and methanol, and two different oils, soybean and canola, in the transesterification process using a batch reactor.

We found that the combination of canola oil and methanol was the most efficient, producing both the highest percent yield of 96.2% and the highest output to input ratio of 1 to 1.014. The high percent yield suggested that canola oil had less free fatty acids (which do not react in the transesterification reaction) and thus could produce more biodiesel. The high output to input ratio meant that the canola reaction produced a larger volume of biodiesel than the volume of oil used as a reactant.

The issues of scaling up biodiesel to levels where it could support the fuel economy were limiting factors, however. Soybeans are the primary biodiesel source in the United States, but the amount of soybeans needed to support the current fuel economy is larger than the maximum amount of soybeans that can be supported by the land[3] - thus, using biodiesel alone is not a viable solution. However, when combined with other alternative energies, biodiesel is indeed a viable solution for an alternative source of energy.

Because our experiments were limited by a four-week

Figure 4: Phase diagram of FAEE(1) + ethanol (2) + glycerol (3); the lines are at constant temperatures of (from top to bottom) 27.15°C, 50.15°C, and 70.15°C. [11]
program, many additional experiments could have been conducted to further analyze biodiesel’s effectiveness as an alternative energy source. The three experiments outlined in this paper could be repeated several times to ensure consistent results and the experiment using ethanol and soybean oil could be repeated and modified to gain adequate results. We can also experiment with a wider range of oils to see if there are any more efficient combinations of oils and alcohols.

7 Acknowledgements

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