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Transesterification of Waste Oil to Produce Biodiesel and Cost Efficient
Removal of Residues

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Preface and Acknowledgements

At the beginning of this venture I was admittedly daunted by the task. With time however, I have come to love the subject of my study and understand the meaning behind such a seemingly arduous task. During the lab work with my fellow “biodiesel team” members and wonderful advisor I have grown to fully appreciate the relevance of chemistry outside of the lecture classroom. I had always assumed I would pursue a project within my preferred biology major and biodiesel was not something I was at all familiar with before this project. I thought it might be interesting, but I had no idea I would find myself reading and reading seemingly unable to learn enough about biodiesel.

This experience wouldn’t have been nearly as enjoyable if it had not been for my teammates: Melvin Woodland and Shannon Moynihan who were simply fun to be around. Melvin and I spent so many Wednesday afternoons staring at thermometer readings for hours and melting down the fat for our next valiant attempt to make the real thing. Shannon was responsible for all of our analysis and her contributions numerous.

Anyone who has crossed paths with my major advisor, Dr. Mandjiny, knows that his energy and enthusiasm is contagious. He is a professor that possesses the rare ability to provoke higher thinking and still make you laugh. He challenged us in the lab and made us think for ourselves. Why didn’t it work this time? What are you going to try next? He inspires so many and made me want to do the best job possible.

I would also like to thank Dr. Paul Flowers, the Chemistry and Physics Department Chair, for his support of this project and Carolyn Parsons UNCP’s chemistry lab manager for all of her help in finding the necessary chemicals and equipment.

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Abstract

The energy crisis presents a great need for alternative energy sources. Therefore, at this juncture it is planned to produce biodiesel from waste animal fat. In this project the waste animal fat is collected from a local restaurant located in Lumberton. The quality of the oil has been checked for moisture content before the transesterification because it influences the production of soap. The transesterification has been done with methanol. The parameters such as temperature, the quantity of potassium hydroxide (KOH) were optimized. Also, the number of washing has been optimized for better quality of the biodiesel.

A titration procedure was utilized to determine how much catalyst was needed to react with the free fatty acids in the waste animal fat feedstock. Using a thumbrule formula: $[6/0.875 + \# \text{ of mL KOH solution}] / 2$, the amount of catalyst needed to make soap with the free fatty acids is incorporated to determine to total amount of catalyst needed to conduct a complete reaction. The total amount of KOH calculated was 3.83g.

The 3.83g of KOH was utilized in the transesterification of the waste animal fat. The catalyst was combined with 120 mL of methanol and combined with 500 mL of the melted animal fat. The reaction was allowed to proceed for 90 minutes at a constant 65° C. The yield of unwashed and undried biodiesel was 475 mL. The sample was washed and dried.

The sample was analyzed using a Gas Chromatography-Mass Spectrometry instrument. The retention time was 7.891 seconds, indicating the presence of methyl palmitate, or biodiesel.

Introduction

Biofuels are making a comeback. It is a comeback because Rudolf Diesel's compression ignition engine, the first developed, was fueled by peanut oil. Biodiesel, the star of the biofuels, is leading the pack. It is the only alternative fuel that has undergone the health effects testing requirements of the Clean Air Act. The Environmental Protection Agency, California Air Resources Board, Department of Energy, and the U.S. Department of Energy all recognize biodiesel as a legitimate fuel and fuel additive. This might bring to mind the question: What exactly is biodiesel? Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animals fats, designated B100, and meeting the requirements of the American Society for testing and Materials.¹ Transesterification is the chemical reaction that the oils undergo with an alcohol and catalyst to produce biodiesel. B100 is the rating of 100 hundred percent biodiesel, also referred to as "neat." This means that the fuel has been filtered and processed and has no contaminants. The use of biodiesel can have a positive impact on vehicles, fossil fuel conservation, and the quality of the environment as a whole.

Transesterification is the breaking of a triglyceride (oil) with an alcohol and replacing the glycerol component of the starting triglyceride with the alkyl group on the alcohol. Many types of oils can perform this function and some perform better than others. Some of the most used oils are: palm kernel, soybean, canola, and corn. Cost is often a deciding factor is which oils and alcohols are used to produce biodiesel. For instance, in most places methanol is the least expensive alcohol so methyl esters are the

primary type of biodiesel, however, in Brazil ethanol is less expensive (due to their prolific sugar cane industry) so ethyl esters are more common.

Store-bought vegetable oil and waste animal fat (solid steak grease) derived from a local restaurant were used to synthesize biodiesel at a microscale level in UNC-Pembroke's biochemistry laboratory. The fundamental goal was to learn how to make biodiesel from waste vegetable oil and optimize the conditions for an appreciable yield. Making biodiesel from waste oil presents unique challenges. Waste oil has free fatty acids which are a biodiesel maker's worst enemy. They react with the cation in the catalyst forming soap. These soap residues can cause plugging of an engine and extensive damage over time. Thus, knowing the free fatty acid content of one's starting oil is vital. Additionally, excess catalyst can result in saponification. Even adding too much alcohol can have adverse effects. Remaining alcohol must eventually be removed from the finished biodiesel product. Knowing these potential complications it is essential to optimize the amount of catalyst (in our experiment KOH) and alcohol added to the reaction. The focus of the lab work: to determine the ideal amount of potassium hydroxide and methanol for the transesterification reaction using waste animal fat. The purpose of a literature review is to help understand the relevance of biodiesel research and to facilitate lab work.

Literature Review

Oil

Many argue whether the world is in fact in the midst of an energy crisis, but for the purposes of this research that is not the real issue. The principal issue that should be considered is the lack of consumer power in the energy market and the possibility of alternative forms of fuel. Big oil companies are one of the largest barriers for a considerable integration of the use of biofuels. The oil market is extremely tight and it became glaringly apparent after Hurricane Katrina. When the oil rigs and refineries in the Gulf, the largest domestic source of oil, were hit gas prices skyrocketed. One single incident can lead to a crisis. Oil companies do not invest enough of their considerable profits on new refineries and finding new reserves. When a catastrophe strikes, they [oil companies] simply increase prices. Columnist Derrick Jackson contends that oil companies may gain more by not being prepared. He also stated: “stay fixated if you wish, on the thieves and desperate families who are looting stores in New Orleans... but ExxonMobil and big oil are looting the nation and no one is declaring martial law on them.”² Big companies are big playing games and it is the consumers who are left to pay. It is time for fuel consumers to take matters into their own hands.

This is not the first time the world has been posed with the daunting proposition of a fuel revolution. The transition from coal to oil was opposed by many, but with time it became undeniable that oil was cheaper and much more energy dense.³ With more research and development in the field of biofuel production this discovery can be made

again. The key is to make biofuels more accessible and car-friendly. In order for biofuels to take the role they must, as equal alternative fuels in comparison to petroleum based fuels, they need to be made just as, if not more appealing to consumers than fossil fuels. Currently, according to the Clean Cities Alternative Fuel Price Report (Figure 1) biodiesel is 68 cents more expensive per gallon than regular petroleum based diesel.⁴ However, there is hope. While gasoline and diesel prices have increased up to 29 cents per gallon, the price of ethanol and biodiesel has gone down up to 15 cents in some instances. Ethanol, according to the report released in March 2007, is 20 cents less expensive per gallon than gasoline.⁴

Those who disagree on whether there is presently an energy crisis or even an impending crisis agree on one thing: there needs to be alternative technologies available.

History

There is a lot of discrepancy in the history of biodiesel, especially in respect to the inventor of the diesel engine. It is often suggested that the inventor designed the diesel engine with the intent to run on biofuels. Diesel is frequently quoted: "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as the petroleum and coal tar products of the present time."⁵ In papers written by Rudolf Diesel, it is said that his intention was only to build an efficient engine.⁶ A biography of Diesel written by his son states that at the Paris Exposition five diesel engines were shown and that only one was run on peanut oil. While Diesels interest in the use of biofuels is widely known, his push for the use of

biofuels is often exaggerated. Another paper discovered details that Diesel ran one of his show engines on peanut oil at the request of the French government who were interested in utilizing peanuts for energy because peanuts were abundantly found in their African colonies.⁶ The first suggestion in the direction of today's biodiesel was made by J. Walton, who thought that to gain the most energy from vegetable oils was to split the triglycerides and use the residual fatty acids.⁶ A project in Belgium and its then colony the Belgian Congo developed this theory and resulted in a Belgian patent. The Belgian patent 422,877 was granted on August 31, 1937 to G. Chavanne (University of Brussels Belgium). This is the first report of the current model of biodiesel. It details the synthesis of ethyl esters from palm oil to use as diesel fuel (other oils and methyl esters where also mentioned). The reactions were acid-catalyzed.⁶

What is Biodiesel and what is different about waste fat?

Biodiesel can be considered the conversion of the energy stored by plants from the sun into a fuel usable by today's vehicles. Vegetable oil inherently contains all of the energy needed to fuel a vehicle (think back to Diesel's first engine run on peanut oil), but the glycerol portion of the triglycerides makes the liquid much too viscous for use in a modern unmodified diesel engine. The viscosity must be lowered and this is achieved through the replacement of the glycerol component with the alkyl group of an alcohol via a reaction called transesterification.⁷ In order to optimize the conservative quotient, waste oil should be used to make biodiesel. This saves energy and alleviates the pressure of finding a disposal method for waste cooking oil. Using waste oil is the most beneficial

for the environment, but it brings additional complexity to the synthesis of biodiesel. When oil is heated, the triglyceride bonds can break releasing free fatty acid (FFA) chains into the oil. With repetitive use, more and more are FFAs broken off and released into the oil. Excess FFAs have adverse health affects and aren't good news for biodiesel making either. Free fatty acids can react with the cation portion of the catalyst forming soap. Soap in an engine isn't a good thing. These soap residues must be then removed from the alkyl ester product in order to isolate usable fuel.

How is it made?

The fundamental reaction used to make biodiesel is called transesterification. In this reaction a triglyceride (fat) is combined with an alcohol/catalyst mixture. The catalyst can be either alkaline or acidic. Basic catalysts are generally faster acting and sodium or potassium hydroxide are the most commonly used catalysts.⁸ The alkyl group of the alcohol then replaces the glycerol chain of the oil. The glycerol portion breaks off and will eventually settle out of the solution due to its higher density than the formed alkyl ester. In order to gain than maximum yield of biodiesel (alkyl ester) from the reaction the alcohol should be free of water and the (FFA) content should be less than 7%.⁸ A lack of moisture is important because water in the solution can result in the cutting of the formed alkyl esters into free fatty acids via hydrolysis, this means additional possibility of soap formation. Additionally, the triglycerides could be hydrolyzed to produce FFAs.⁷

Transesterification By-Products

As mentioned above, transesterification involves the removal of glycerol from triglycerides. The glycerol then separates out of the solution. There are two major types of glycerol, bound and free. Free glycerol is the kind that sinks to the bottom of the container as it is generally insoluble in biodiesel. This glycerol is easily removed from the container, but a small amount may remain in solution with the biodiesel. If there is excess free glycerol in solution, this can cause settling of glycerin and plugging problems in the engine later on.⁹

Alcohol is usually added in excess to ensure full conversion. This results in alcohol often left in the biodiesel product. Biodiesel usually contains 2-4% methanol after separation from glycerol. This is about 40% of the alcohol in the initial reaction. Excessive alcohol levels can lead to decreased flashpoints as much as from 170° C to less than 40° C. Because of this direct effect, the regulatory specifications for residual alcohol levels are actually covered by the specifications for flashpoint. Most often, however, residual alcohol will not have a negative effect because it is usually in a negligible amount.⁹

Washing

Washing is essential when using waste oil to make biodiesel. It is necessary to remove any soap residues formed from any FFA's in the oil, any residual methanol, and any free glycerol still in solution. There is a very wide range of washing techniques currently used. Some form of water washing is almost always used as it is the easiest and

most economical. Water is added to the biodiesel product and agitated in some fashion whether it is by a stirring mechanism or aeration (bubble washing).⁸ By any method, the goal is to have soap, methanol, and glycerol dissolve in the highly compatible solvent and separate from the biodiesel for easy removal. This process is usually repeated several times to ensure the purest biodiesel possible as contaminants can lead to serious engine problems.

Drying

Biodiesel can retain up to 150 ppm of dissolved water. Regular diesel can usually only absorb around 50 ppm.⁹ This is why special attention must be made to the removal of water after the washing step. Excess residual water can lead to corrosion of closely fitting parts in the fuel injection system and also microbial growth.⁹

Fuel Properties

Almost All fuel properties have standards specified by the American Society for Testing and Materials (ASTM)-see Figure 3.

Flashpoint

Biodiesel has a very high flashpoint which makes it safer to handle than diesel. Flashpoint is the temperature in which a fuel vaporizes and a spark can ignite. The flashpoint of gasoline is very low, less than 40° C. Diesel has a flashpoint of 52-66° C and when compared to biodiesel's flashpoint of greater than 150° C, it is much more volatile.¹⁰

Cetane Numbers (Biodiesel handbook)

Cetane numbers (CN) indicate the ignition quality of diesel fuel. Ignition quality is directly correlated with the length of a hydrocarbon chain and its branching. Fuels with high ignition quality tend to be long chains with little branching. Fuels with oppositely low ignition capability are shorter and highly branched. The cetane number of a sample of biodiesel or any diesel is determined by a comparative test.¹¹ The diesel in question is compared to a high quality standard and low quality standard and the number designated based upon where the fuel falls in the scale. The standards are primary reference fuels or commonly referred to as PRFs. The test is typically executed with the high quality standard being a compound named hexadecane ($C_{16}H_{34}$). Its trivial name is cetane and it is the essentially perfect hydrocarbon (in terms of ignition capability). It is a long and straight hydrocarbon (no branching). Its CN is 100. The low quality standard is very short and highly branched. Its name is 2, 2, 4, 4, 6, 8-heptamethylnonane (HMN, $C_{16}H_{34}$ also) and its CN is 15.¹¹

Cetane numbers are important because if the CN is too high the fuel will ignite before the air and fuel are combined in proper proportions, causing incomplete combustion and smoke. If the CN is too low incomplete combustion will also occur with other side effects including: roughness, misfiring, higher air temperature, and slower engine warm-up.¹¹

The international standards for cetane number are designated by the International Organization for Standardization (ISO), ISO 5165. In the United States the standard for

CN determination is ASTM D613. For the ASTM standard the PRFs are hexadecane and HMN. When using the ASTM standard the minimum CN required is 40 for petrodiesel and 47 for biodiesel. The CN range recommended by most engine manufacturers is normally 40-50.¹¹

Cetane number has been found to be correlated with NO_x emissions. Higher CN numbers in petrodiesel usually saw a decrease in NO_x emissions. Because of this, measures have been taken to increase the CN in biodiesel fuels. Additives called cetane improvers were implemented. According to *How to Make Biodiesel* cetane improvers are not needed for biodiesel because of its naturally higher CN numbers. Even with high CN, when biodiesel is used in a diesel engine there is an increase in NO_x emissions. This effect has many factors including the structure of the alkyl esters (biodiesel). It was found that the shorter and more unsaturated the chains the more NO_x emissions. The correlation between cetane number and NO_x emissions is especially evident in older diesel engines. This can be attributed to discrepancy of injection times. More modern engines have a mechanized control of injection rate.¹¹

Lubricity

The high lubricity of biodiesel is a widely recognized advantage. When sulfur restrictions were placed on diesel fuels, the lubricity of the fuels decreased as well. Low-sulfur diesel is in fact associated with low lubricity, however studies reveal that it is not the lack of sulfur that contributes to the low lubricity but the loss of oxygen and nitrogen during the sulfur removing process.¹³ Biodiesel has even been added to the diesel in

France simply for this function.¹² Biodiesel's advantage as a fuel additive is that is not only aids in lubrication, it does not hinder the fuel economy, as it itself is a fuel.

Cold Weather Performance

Biodiesel has a higher gelling temperature than diesel making it tricky to use to in cold climates. There must be special care taken when using this fuel in cold seasons or perpetually cold geographical areas. The properties associated with the performance of a fuel in cold temperatures are cloud point and pour point. Cloud point (CP) is the temperature at which waxes inherent in the fuel begin to visibly form crystals. Pour point (PP) is the Temperature at which gelling prevents free pouring of the liquid. Some distributors treat their biodiesel with cold point and pour point depressors during the cold months.¹⁴ Several types of depressors include: petrodiesel (blended with biodiesel can lower the CP and PP), and other commercial additives that inhibit wax crystal growth.

Environmental Implications

Overview of Emission Pollutants from Diesel

When discussing the environmental effects of changing from diesel to biodiesel it is necessary to identify the compounds that are present in regular diesel emissions.

Nitrogen oxides (NO_x) are the most frequently discussed emitted compound in the battle of diesel vs. biodiesel, only because there is actually an increase of these compounds when biodiesel is used in regular diesel engines. The most prominent

nitrogen oxides emissions are Nitric oxide (NO) and nitrogen dioxide (NO₂). In exhaust, nitric oxide gases are the most abundant and they react with the atmosphere to form nitrogen dioxide. The nitrogen dioxide products then react with hydrocarbons and in the presence of sunlight create ozone. The nitrogen dioxide remains in the atmosphere for approximately one day, after which it converts back to nitric oxide and returns to ground level as acid rain. Individually nitrogen oxides are harmful to plants, ecosystems, and humans. They are proven respiratory irritants. Their roles as ozone producers and acid rain are the most detrimental to the environment.¹²

Sulfur dioxides (SO₂) are well-known pollutants that have previously been abundant in diesel engine emissions. However, presently low-sulfur diesel has been introduced causing a proportional decrease in Sulfur dioxide emissions. Sulfur dioxides are formed by the oxidation of sulfur residues in fuels during combustion. SO₂ is an acidic gas that produces acid rain when it mixes with atmospheric water. The problems caused by SO₂ are: as previously mentioned, acid rain (however it can descend dry), damage to plants and buildings, and degradation of soils and waterways. It has also been linked to asthma and chronic bronchitis.¹²

Carbon Monoxide (CO) is a toxic gas that is a product of combustion. Another source of CO is the oxidation of hydrocarbons and other organic compounds. In urban areas of developed countries vehicle emissions are the primary source of CO (90%). In addition, the slower the vehicle move the larger the amount of CO. It is inferred that the, slowness of traffic and elevated density of vehicles, accounts for the incredibly high

amount of CO in highly populated areas. CO is extremely compatible with hemoglobin and so is readily absorbed into the bloodstream through the lungs. The binding of CO to hemoglobin prevents the binding of oxygen, essentially starving blood of oxygen. Heart disease and damage to the nervous system have been associated with chronic exposure to CO. Death can also result from long-term, high concentration, exposure. CO can also pose a threat to unborn fetuses potentially causing low birth rate and an increase in fetal mortality. It takes around one month for CO to leave the atmosphere at which time it is oxidized to form CO₂ which is still harmful by aiding in the greenhouse effect and global warming.¹²

Hydrocarbons are pollutants and they are the very structures that make up the fuels in question, both diesel and biodiesel. When using petrodiesel, hydrocarbons can evaporate from the fuel and be released into the atmosphere. They can also be emitted from the incomplete combustion of diesel. These hydrocarbons are the foremost contributing factor in the production of smog and harmful ground-level ozone.¹²

Physical particles, normally composed of carbon, a regular product of fuel combustion can pose serious environmental harm and health risks. Size is the determinant of whether particles are harmful. If they are larger than ten microns they usually settle fairly quickly and are not as easily inhaled. Those that are less than 10 microns, however, stay in the air much longer and can be easily inhaled. Particles have been released into the atmosphere since the beginning of time. Volcanoes and forest fires are some of the natural sources. Humans have been contributing particles into the air

since they discovered fire. Currently, vehicle emissions are the major source of this form of pollution. These particles have the potential to cause asthma, bronchitis, emphysema, other lung diseases, and death. The fact that extremely small particles can carry harmful compounds, including carcinogens, and be inhaled very deep into the lungs makes them a formidable threat.¹²

Volatile Organic Compounds (VOCs) are compounds comprised of carbon that evaporate easily. This covers a wide range of compounds including the previously mentioned hydrocarbons. The VOCs of large concern with respect to vehicle fuels are benzene, and 1,3-butadiene. Benzene is only present in gasoline emissions while 1,3-butadiene is present in both gasoline and diesel emissions. 1,3-butadiene pollution is often just the result of evaporation of fuel. It can also be released from incomplete combustion. 1,3-butadiene is a known carcinogen that can also pose harm to: the central nervous system, liver and kidneys, reproductive systems, and unborn fetuses.¹²

The category of toxic organic micropollutants (TOMPs) is very large and highly varied. The kinds that can be found in vehicle emissions are polycyclic aromatic hydrocarbons, (PAHs), dioxins, and furans. These compounds are formed by the incomplete combustion of fuels. TOMPs are emitted in very low amounts but they are carcinogenic and very toxic to wildlife.¹²

The formation of ozone has been previously mentioned as a harmful secondary result of vehicle emissions. Ozone is made of O₃ molecules instead of normally

encountered O₂ molecules of oxygen. High in the stratosphere ozone is a helpful shield against UV radiation from the sun. Ozone is only considered harmful at the ground-level. This ozone can be dangerous for plants and cause irritation of their eyes, breathing difficulty, and even lung damage. Because of the reactive nature of ground-level ozone it can damage fabrics, rubber, and other materials.¹²

Emissions From Biodiesel Compared to Diesel

Overall, emissions are reduced when using biodiesel. There is however one type of emission that is increased by the use of biodiesel and that is of nitrogen oxides. Nitrogen oxide emissions can increase by up to 10% (See Figure 4).¹⁵ This increase has been associated with older model vehicles. In addition, there have not been many studies performed on the emissions of light-duty diesel vehicles in the U.S. This is due to the small market for light-duty diesel vehicles in the U.S. Most studies of emissions have been performed on heavy-duty vehicles.

In *Biodiesel Basics and Beyond* the author, William Kemp, cites a study conducted by the EPA saying: compared emissions from No. 2-D diesel fuel (the type of diesel regularly used in heavy-duty engines) and biodiesel in a highway truck, urban bus, and full-size pickup truck. The results of this study indicated 20% reduction in total hydrocarbons, 12% reduction in Carbon Monoxide, and up to 12% reduction of total particulate matter. The study did reflect the characteristic increase in nitrogen oxide emissions, but only an increase of about 3%.⁸

According to the EPA's released report, "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions," findings were a 10.1% decrease in particulate matter, a 21.1% decrease in hydrocarbons, and a 11.0% decrease in carbon monoxide emissions when using a 20% biodiesel and 80% diesel blend fuel (in comparison to regular diesel fuel) (See figures 4 and 5).¹⁶ Sulfur dioxide emissions are practically eliminated with the use of biodiesel.¹²

Methodology

To address the complications of working with waste oil, a plan was devised to determine the optimal amounts of Potassium hydroxide (KOH) and Methanol. This is imperative to ensure a complete conversion and to minimize the amount of saponification and excess methanol.

The method to determine the exact amount of catalyst needed to complete the transesterification reaction was to complete a titration procedure. The titration procedure would determine how many milliliters (mL) of Potassium hydroxide (KOH) solution is needed to react with a given sample of the fat in question. This is conducted by first melting 1ml of the solid fat and combining it with 10mL isopropanol in a beaker. The addition of 2 drops phenolphthalein indicator follows. The purpose of the indicator is to provide a color response when the reaction has taken place. The fat and alcohol mixture is then titrated against 0.018M KOH. This is achieved by placing 50 mL of the 0.018M KOH solution into a buret and allowing it to fall dropwise into the beaker with the oil and isopropanol solution. The flow of KOH is stopped when the solution in the beaker reaches an intense fuchsia color. The titration is repeated six times and the average number of mL is noted. The average number of mL of KOH is equivalent to the number of grams of KOH needed for saponification of 500 mL of fat with 120 mL of methanol. This amount of KOH will react with the inherent amount of free fatty acids in the fat. Thus, the remainder of the catalyst will be free to react with the usable triglycerides.

The total amount of KOH is calculated using an industry thumb rule:
 $[6/0.875 + \text{number of mL of KOH}] / 2$. The 6 indicates the number of grams of KOH needed to react with one liter of oil. The 0.875 corresponds to the purity of the KOH obtained from the university's chemistry store room. Using the formula one can then determine the total number of grams needed to react with 500 ml of melted fat.

After determining the necessary grams of KOH one can begin the transesterification reaction. One must dissolve the calculated quantity of KOH in methanol (methoxide). The waste vegetable oil, originally in solid form, is heated until it melted. A quantity of 500mL is taken for the experiment. The temperature is then adjusted to 65° C for the transesterification process by placing the oil in a beaker, with a magnetic stirring bar, and utilizing a water bath on a hot plate. A solution is prepared by dissolving the necessary amount of potassium hydroxide (KOH) in 120mL of methanol. Once the oil reaches a constant temp of 65° C, the methoxide solution is introduced slowly to the heated oil. After all the methoxide solution is added, the reaction is allowed to proceed for 90 minutes with constant supervision to monitor the temperature. Once the waiting period expires, the mixture is placed into a separatory funnel and left to settle into two distinct layers consisting of glycerol and biodiesel; the top phase being the biodiesel layer. The biodiesel layer is removed and reserved for washing and drying.

Washing of the raw biodiesel will be conducted by spraying water onto the surface of the raw biodiesel and allowing the water to fall thru the solution. Water is added in a 1:1 ratio. Hence, for 50mL of raw product 50mL of water is used. Via this process, the water will dissolve methanol, soap residues, and some free floating glycerol.

The water soluble contaminants will settle to the bottom of the container (because of water's higher density than biodiesel). The water and its solutes can then be easily removed. Two immiscible layers form: a top layer consisting of washed biodiesel and a bottom layer composed of the water mixed with excess methanol and soap. The top layer is then set aside for further washing. The washing is repeated four consecutive times to ensure thorough cleansing. An immersion test will indicate whether the product has any remaining soap or glycerol. This is conducted by adding water to a sample of the washed biodiesel. If there are any visible contaminants at the interface or in the water layer, washing must be repeated.

Drying is performed by pumping the washed biodiesel out of a beaker and spraying into a funnel. The spraying mechanism and the funnel will allow a greater surface area of the biodiesel to gain air exposure. This will in turn expedite the evaporation of water without heat.

Whether biodiesel was synthesized will be confirmed by using a Gas Chromatography and Mass Spectrometry instrument.

Results

One successful synthesis of biodiesel from waste animal fat was completed from transesterification reaction to drying phase. The GC-Mass Spectrometry analysis confirmed the sample was methyl palmitate. The titration procedure, to determine the needed amount of catalyst, ensured the conversion of the triglycerides to methyl palmitate.

The Potassium hydroxide (KOH) titration was conducted six times (See Figure 6). The average volume of the buret readings was 0.8 mL of 0.018M KOH. This value was used in the formula for catalyst determination: $[6/0.875 + 0.8\text{mL}] / 2$. With the formula it was determined that 3.53 grams of 87.5% KOH would be needed to proceed with the transesterification process.

After allowing the reaction to proceed according to the protocol specified in the methodology section, the two phases in the separatory funnel were separated. The unwashed and undried biodiesel was measured at 475 mL and it appeared transparent and golden champagne in coloration. The texture was slightly viscous. The glycerol was measured to be 55 mL. The glycerol was highly viscous and the coloration was a dark red-orange brown.

An immersion test was conducted by putting 10 mL of biodiesel and 10 mL of distilled deionized water in a test tube, sealing it with parafilm and shaking vigorously. The mixture quickly formed two phases with the water setting at the bottom of the test

tube and the biodiesel floating to the top. The interphase showed the characteristic foaming of soap residues, further confirmation that the intended reaction had taken place.

Washing and drying was conducted. An immersion test directly following washing showed no signs foaming or cloudiness in the water phase. The drying pump setup was allowed to proceed overnight.

A Mass Spectroscopy and Gas Chromatography instrument was used to determine if the desired product was in fact synthesized. For the GC-Mass Spectrometry readings a solution composed of 10 drops of biodiesel produced from waste animal fat and 5mL of hexane was combined in a test tube. A syringe was used to remove 2 μ L of headspace and this was injected into the Agilent Model 5793N with 6890N GC-Mass Spectrometer. The conditions were as follows: Inlet Temp: 250° C and Initial Temp: 150° C. The temperature increased 5°C per minute up until 260°C. The split ratio was 50:1. The Retention time (t_r) was 7.891 seconds. This indicated the presence of methyl palmitate.

Conclusion

The synthesis of biodiesel was attempted several times all unsuccessfully until using the catalyst determining formula. The catalyst formula and titration of KOH are responsible for the transesterification reaction's completion and successful conversion of the restaurant waste animal fat into methyl palmitate or biodiesel.

Store-bought virgin vegetable oil was the first feedstock utilized during the initial efforts. The vegetable oil was used to become familiarized with the reaction and its reagents and to devise a setup that was appropriate for the small biochemistry lab in the Oxendine building. Through trial and error, the struggle to obtain a methyl ester finally resulted in the production of biodiesel.

The purpose of this study was to develop a protocol to make biodiesel in a laboratory setting using the waste steak grease from Outback Steakhouse. This presented many difficulties and the attempts of synthesizing the methyl ester with only the means provided by the facilities at Oxendine, seemed to yield no answers. Dr. Mandjiny helped the research team find answers when he discovered the catalyst thumbrule $[(6/0.875 + \text{avg. mL from titration}] / 2]$ and shared this information. This provided the missing link and allowed the single complete conversion of the animal fat to biodiesel, in this instance methyl palmitate.

The time constraint on the project limited the amount of variation of the research procedure. This preliminary study has a vast amount of potential for further development. Research should be furthered using the known optimal level of catalyst but

varying temperature and mode of agitation. Also bomb calorimetry tests should be conducted on the confirmed biodiesel samples. A continuous mode of biodiesel synthesis could be attempted. A setup involving larger containers and tubing from container to container would be necessary. This would provide more samples for study at a quicker pace and possibly compensate for the length of time it takes for washing and drying.

In addition, the synthesis could be conducted varying the sources and types of waste animal fat. Free fatty acid content in the feedstock should be accurately determined by means of commercial paper indicators or a titration procedure. The relationship between free fatty acid content and biodiesel yield could be plotted in correspondence to calorimetric value.

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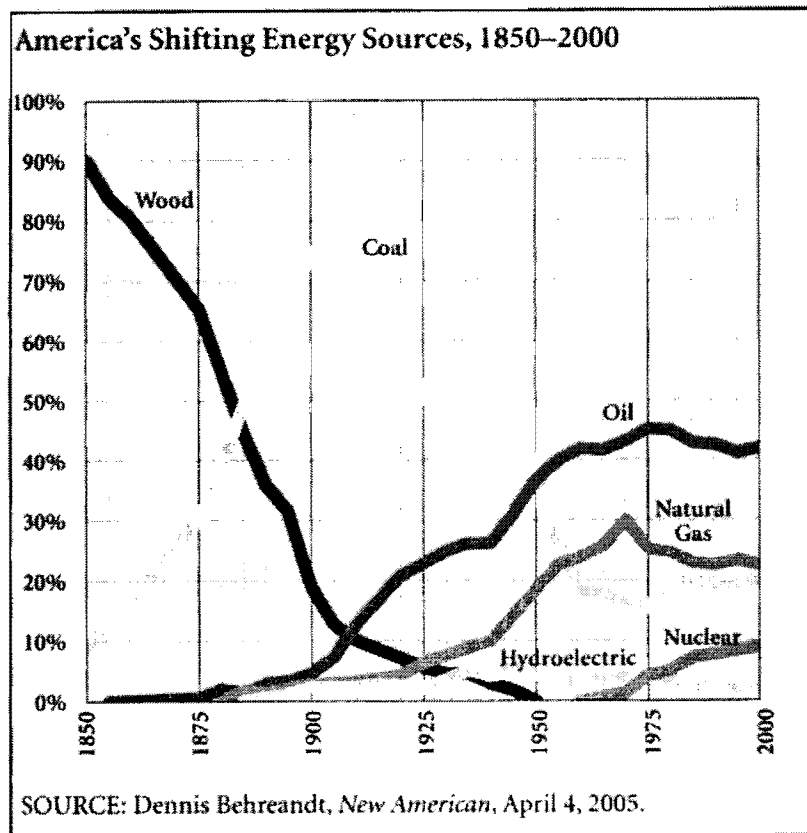
APPENDIX A

Gasoline (Regular)	\$2.30	\$2.22	\$0.08	per gallon
Diesel	\$2.63	\$2.62	\$0.01	per gallon
CNG	\$1.94	\$1.77	\$0.17	per GGE
Ethanol (E85)	\$2.10	\$2.11	(\$0.01)	per gallon
Propane	\$2.62	\$2.33	\$0.29	per gallon
Biodiesel (B20)	\$2.53	\$2.66	(\$0.13)	per gallon
Biodiesel (B2-B5)	\$2.60	\$2.75	(\$0.15)	per gallon
Biodiesel (B99-B100)	\$3.31	\$3.31	\$0.00	per gallon

Table 1. Overall Average Fuel Prices

Source: (Clean Cities Alternative Fuel Price Report, March 2007)⁴

FIGURE 1



Source: (Oil: Opposing Viewpoints)³

FIGURE 2

ASTM STANDARDS FOR BIODIESEL

Analysis	Method	Min.	Max
Acid Number, mg KOH/gram	ASTM D664		0.80
Ash, Sulfated, Mass %	ASTM D874		0.020
Total Sulfur, Mass %	ASTM D5453		0.05
Cetane Number	ASTM D613	47	
Cloud Point, °C	ASTM D5773		
Copper Corrosion	ASTM D130		No. 3
Vacuum Distillation End Point	ASTM D1160		360°C at 90%
Flash Point, °C	ASTM D93 Procedure A	130.0	
Method for Determination of Free and Total Glycerin	ASTM D6584		
Free Glycerin, Mass %			0.020
Total Glycerin, Mass %			0.240
Phosphorus (P), Mass %	ASTM D5185		0.001
Carbon Residue, Mass %	ASTM D4530		0.05
Kinematic Viscosity, Centistokes at 40°C	ASTM D445	1.9	6.0
Water and Sediment	ASTM D1796		0.050

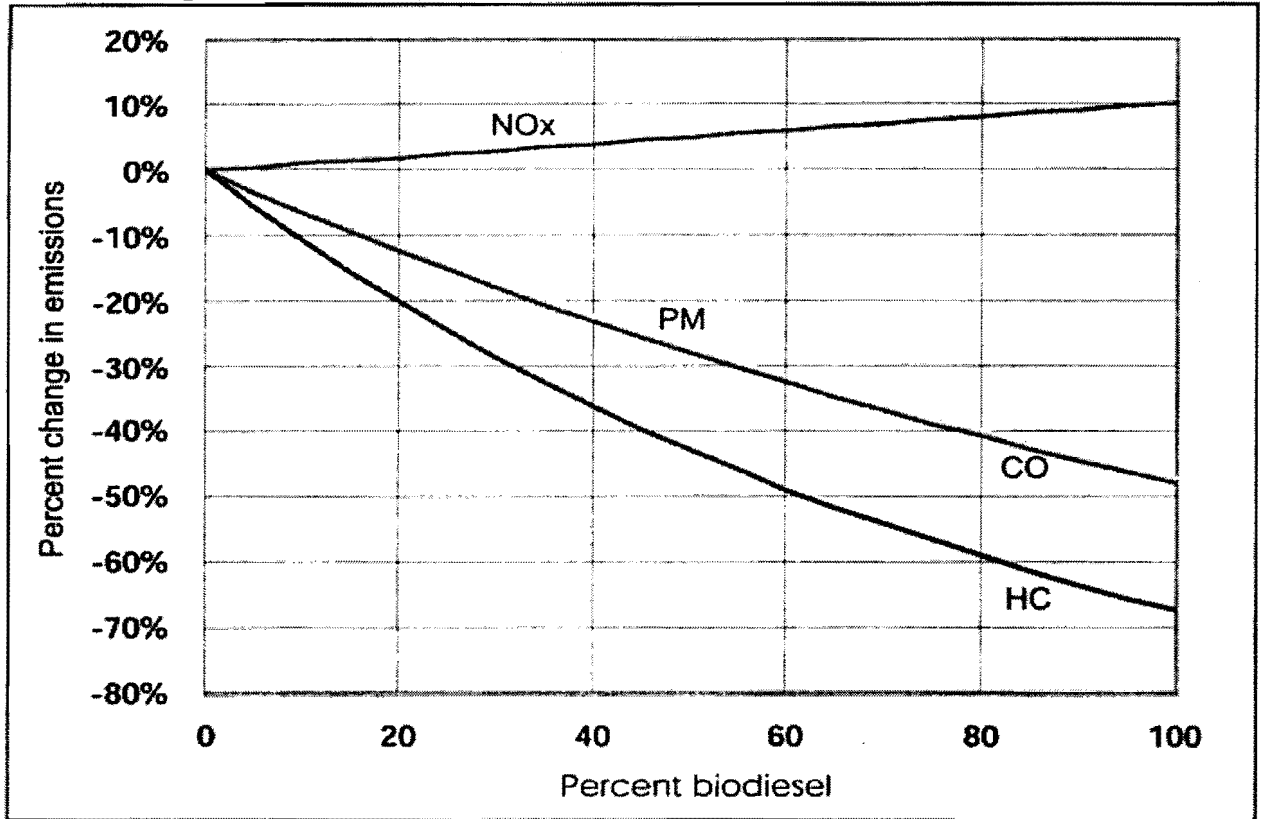
Table 3.3-2 D6751-02 Test Parameters

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Source: (Biodiesel Basics and Beyond)³

FIGURE 3

Figure ES-A
Average emission impacts of biodiesel for heavy-duty highway engines



Source: (EPA: A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions)¹⁶

FIGURE 4

Table ES-A
Emission impacts of 20 vol% biodiesel
for soybean-based biodiesel added to an average base fuel

	Percent change in emissions
NOx	+ 2.0 %
PM	- 10.1 %
HC	- 21.1 %
CO	-11.0 %

Source: (EPA: A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions)¹⁶

FIGURE 5

APPENDIX B

RESULTS OF TITRATION

TRIAL NO.	ML OF KOH ADDED
1	0.80
2	0.85
3	0.70
4	0.90
5	0.85
6	0.70
Avg. volume of KOH added: 0.8 mL	

FIGURE 6

GC-MASS SPECTROMETRY READING

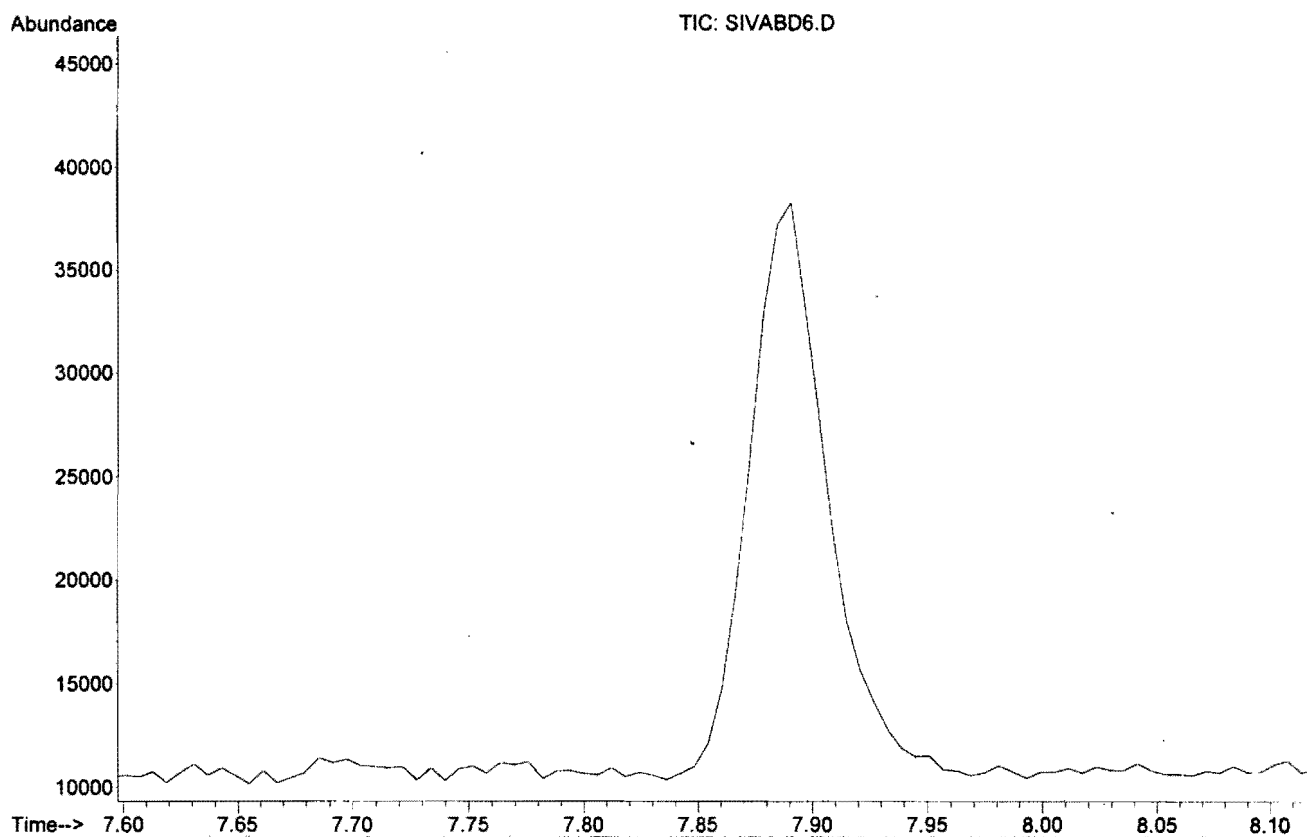


FIGURE 7