

OPTIMIZATION OF BIODIESEL PRODUCTION PROCESS USING RECYCLED VEGETABLE OIL

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
in
CHEMISTRY

UNIVERSITY OF PUERTO RICO
MAYAGÜEZ CAMPUS
2010

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ABSTRACT

Petro diesel toxic emissions and its limited resources have created an interest for the development of new energy resources, such as biodiesel. Biodiesel is traditionally produced by a transesterification reaction between vegetable oil and an alcohol in the presence of a catalyst. However, this process is slow and expensive due to the high cost of raw materials. Low costs feedstock oils such as recycled and animal fats are available but they cannot be transesterified with alkaline catalysts due to high content of free fatty acids, which can lead to undesirable reactions such as saponification. In this study, we reduce free fatty acids content by using an acid pre-treatment. We compare sulfuric acid, hydrochloric acid and p-toluenesulfonic acid (PTSA) to pre-treat recycled vegetable oil. PTSA removes water after 60 minutes of treatment at room temperature or within 15 minutes at 50 °C. The pre-treatment was followed by a transesterification reaction using alkaline catalyst. To minimize costs and accelerate reaction, the pre-treatment and transesterification reaction of recycle vegetable oil was conducted at atmospheric pressure in a microwave oven. Biodiesel was characterized using a GC-MS method.

RESUMEN

Las emisiones tóxicas del petrodiesel así como lo limitado de este recurso han incrementado el interés de desarrollar fuentes alternativas de energía, como el biodiesel. El biodiesel es tradicionalmente producido mediante una reacción de transesterificación entre aceite vegetal y un alcohol en presencia de un catalítico. Este es un proceso lento y costoso debido a los altos costos de la materia prima. Existe materia prima de bajo costo como lo son las grasas animales o el aceite de cocinar reciclado pero estos no pueden ser utilizados con catalíticos alcalinos debido a su alto contenido de ácidos grasos. El alto contenido de ácidos grasos conlleva a otras reacciones no favorables para la obtención de biodiesel como lo es la saponificación. En este estudio, redujimos la cantidad de ácidos grasos presentes en el aceite reciclado por medio de un pre-tratamiento con ácido. Comparamos ácido sulfúrico, ácido clorhídrico y ácido p-toluenosulfónico (PTSA). PTSA remueve agua del aceite luego de 60 minutos de tratamiento o luego de 15 minutos a 50°C. El pre-tratamiento fue seguido de una reacción de transesterificación utilizando un catalítico alcalino. Para minimizar costos y acelerar la reacción, el pre-tratamiento y la reacción de transesterificación fueron llevados a cabo a presión atmosférica y utilizando un horno de microondas. El biodiesel fue caracterizado utilizando un método de GC-MS.

To God, my family and friends. . .

ACKNOWLEDGEMENTS

During the development of my graduate studies in the University of Puerto Rico at Mayagüez many stood by my side and made this thesis possible.

I especially want to thank my advisor, Dr. Félix R. Román, for his guidance during my research and study. He was always accessible and willing to help me with this research. As a result, it became smooth and rewarding. I would like to acknowledge all the support received by Kevin Casey, for his ideas, his biodiesel reactor and microwave systems setups, and for proving the used oils for the synthesis biodiesel. Without his technical assistance and the systems setups this work would not have been possible. I also like to express my gratitude to Dr. Luis A. Morell who shared with me a lot of his expertise and research insights. Dr. Rodolfo Romañach also deserves special thanks as my thesis committee member and advisor. Special thanks to Dr. José Colucci, Dr. Marcos de Jesús and Miriam Fontalvo who helped me during biodiesel characterization.

It is difficult to overstate my appreciation to Héctor Areizaga and whose thoughtful advice often served to give me a sense of direction during my studies. Not only a great colleague, he has also been a cornerstone in my professional development.

Thanks to all my friends, who were by my side when I needed them the most specially those at the Environmental Nanotechnology and Remediation Research Laboratory who made it a convivial place to work. You had helped me in research through our interactions during the long hours in the lab. Thank you all.

My deepest gratitude goes to my family for their love and support throughout my life; this work would have been impossible without their support. To my mom and dad, my brothers who kept telling me to go on. Special thanks to my husband for all his support and to my son who with his beautiful smiles inspired me to go on.

Last but not least, thanks to God. You have made my life more bountiful. May your name be exalted, honored, and glorified.

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INTRODUCTION

Diesel fuels have become indispensable for our industrial, commercial and individual consumption. From July 2007 to July 2008 the cost of petroleum-based diesel fuel increased 190 cents per gallon as reported by the Energy Information Administration of the US government [1]. This increase in the cost of diesel was related to the high demand of the product versus reduction in the petroleum reserves. The United States consumes approximately 7.5 million barrels of petroleum per year [1].

Economy is not the only factor concerning diesel that affects our society. Environmental and health issues have been related with diesel manufacturing and consumption. Diesel fuel combustion result in high emissions of carbon monoxide, unburned hydrocarbons, particulate matter, nitrogen oxides and carbon dioxide. Greenhouse gases such as carbon dioxide, nitrous oxides and methane trap heat in the higher atmosphere transferring it downward and increasing Earth's temperature.

The particulate matter from diesel includes carbon particles or soot. In 1998, the state of California identified diesel exhaust as a toxic air contaminant based on its potential to cause cancer, respiratory problems and premature death [2]. Children, whose lungs are in development and elderly with serious health problems, are the most vulnerable.

Particles about 10 μm or less can be inhaled and deposited in the lungs. Diesel exhaust particulate matter is less than 1 μm . The chemicals absorbed on the particles can dissolve in the fluid lining and reach the airways and absorbed in the body. Several studies in animals determined that exposure to diesel exhaust is related to pulmonary inflammation [3].

Benzene is listed by the state of California as the principal toxic air contaminant present in diesel and a known cancer causing agent. It has been reported to be present in the gaseous phase of diesel exhaust and in the particulate matter. Other cancer causing compounds present in diesel exhaust are formaldehyde, acetaldehyde, acrolein and 1,3-butadiene.

In 2005 Mills and colleagues exposed 30 healthy men to diluted diesel exhaust in exposure chambers to determine the effects of inhalation of diesel exhaust at levels found in urban environments. They found that exposure to diesel exhaust impaired the regulation of vascular tone and caused endogenous fibrinolysis leading to myocardial arrest [4].

A possible solution to reduce the environmental and health effects caused by diesel exhaust is the use of alternative fuels. Alternative fuels are non-conventional fuels made from renewable sources. Some of the alternative fuels are bioalcohols such as butanol and ethanol, fuel cells, hydrogen, non-fossil methane and vegetable oil.

Rudolf Christian Karl Diesel, an engineer who invented the diesel engine, was the first to develop an engine that ran on peanut oil, which was presented in 1900 at the World Exhibition in Paris. Vegetable oil as a direct fuel can bring several problems to the diesel engine due to its high viscosity. Some of these problems are associated with lubrication, carbon deposits and thickening of the lubricating oil. To overcome these problems the vegetable oil needs a chemical modification.

To convert the vegetable oil into biodiesel, the oil is mixed with an alcohol, in the presence of a catalyst and is passed through a transesterification process that converts the triglycerides of the oil into esters that can be used as the fuel. The reaction between the alcohol and the vegetable oil is slow or does not proceed at all, making necessary the use of a catalyst. The most commonly used catalysts are acidic or alkaline. Acid catalysts give high yields of methyl esters but the reaction is slower than the reaction with the alkali catalyst [5]. The cost of biodiesel production is high: over \$1.10 per liter. This is due to the high cost of the raw materials such as virgin vegetable oils. Low-cost feedstock oils such as recycled oils and animal fats are available but they cannot be transesterified with alkaline catalysts due to the high content of free fatty acids, which can lead to undesirable reactions such as saponification. Free-fatty acid content can be reduced via an acid pre-treatment. The

optimization of biodiesel production processes will guarantee lower biodiesel costs and the possibility of an environmentally friendly and accessible fuel.

The rise in crude oil prices, the limited resources of fossil oil, and the environmental concerns, such as the high emissions profile and the global warming, should renew the focus in the production of alternative fuels, such as biodiesel and ways to make it affordable.

OBJECTIVES

It was our objective to change various parameters to reduce operational costs, reagents quantities and processing time using recycled vegetable oils. These changes in parameters could then be applied to the benefit of industrial processes.

The innovative features of this project consist of the following:

- Reduction of reaction time using microwave heating.
- Reduction of free fatty acids content with acid pre-treatment.
- Reduction of the quantity of catalyst required.

LITERATURE REVIEW

Recycled Vegetable oil

Merve Cüetinkaya, *et. al.* [6] performed transesterification reactions with used cooking oil using methanol as the alcohol and NaOH as the catalyst. Used cooking oil was heated on a temperature-controlled magnetic heater and stirred to 50 °C, followed by the addition of methanol. The catalyst was added to the mixture at 55 °C, which was considered to be the reaction temperature. Reaction temperatures were controlled within a range of ± 2 °C. Throughout the laboratory-scale studies, the following conditions were kept constant: temperature, 55 ± 2 °C; mixing speed, 40 rpm; and test reaction time, 4.5 h. Effects of varying the oil/alcohol ratios (1:3, 1:4, 1:5, and 1:6) and catalyst amounts (1% and 2%) on the transesterification reaction were investigated. After the completion of the reaction, the resulting mixture was quenched in a container full of cold distilled water to stop the reaction and the product mixture was cooled to room temperature and transferred to a separatory funnel by decantation to separate ester and glycerin phases. The catalyst and the excess alcohol stayed in the bottom phase (the glycerin phase). The crude ester phase was washed with hot distilled water, at 50 °C, at a ratio of 1:1, in the following order: two times without stirring and three times with stirring. As mentioned previously, the oil/alcohol molar ratio is an important parameter for transesterification reaction kinetics. From the results obtained, it can be evaluated that the oil/alcohol molar ratios of 1:3 and 1:4 were insufficient to reach 100% ester yield. Also, for a catalyst amount of 1%, as the ester product percentage increased, the reverse reactions became faster and resulted in decreases in ester yield. For an oil/alcohol molar ratio of 1:3, the decrease was 2%, whereas for an oil/alcohol molar ratio of 1:4, this decrease happened to be 16%. Therefore, these ratios were not chosen as alternative reaction sets.

As a result of the experimental studies, three alternative reaction conditions for an alkaline-catalyzed transesterification reaction were obtained for pilot-scale and industrial scale biodiesel production purposes with the following standard conditions:

1. 40 rpm stirring speed
2. Atmospheric pressure
3. 55 ± 1 °C of reaction temperature

The variables are described below:

Table 1. Variable conditions for the three alternative reaction conditions

Option Number	Oil:alcohol ratio	NaOH amount used (% w/w)	Reaction time (minutes)
1	1:6	1.0	60
2	1:5	2.0	120
3	1:6	2.0	30

Reactions with an oil/alcohol molar ratio of 1:6 are preferred if the unit has an alcohol recovery unit to minimize the reaction time. According to Cüentinkaya experimental study on the biodiesel refining process, it was understood that washing with hot water (50 °C) was effective in regard to reducing the glycerin content. The number of washing steps was determined to be seven. Although further washing had a diminishing effect on the glycerin percentage, the difference in glycerin percentage between each step decreased as the number of washing stages increased.

In Cüentikaya's study conventional heat was used. Transesterification reactions using recycled oils with high content of free fatty acids cannot be performed by the above method. High free fatty acids can lead to formation of soap instead of the esters. An acid pre-

treatment should be implemented to reduce free fatty acids and make possible a faster transesterification reaction without adding additional alkaline catalyst. The temperature parameter was not changed on the experiments of this study. Hot water was used for the raw biodiesel wash and water treatment increases the production costs. Acidified water can be used for a less contaminating process.

Catalyst comparison

In the publication by G. Vicente, *et. al.* [7] the researchers used refined sunflower oil and methanol as reactants for the transesterification experiments. The catalysts compared were: sodium hydroxide, tin chloride, magnesium oxide, a titanium chelate (TILCOM STC), a Y-zeolite (USY-292), ionic exchange catalysts (Amberlyst A26, Amberlyst A27 and Amberlyst 15), zirconium-based catalysts (MELCat XZO682:01 and MELCat XZO645:01), titanium-based catalyst (TIS), and an immobilized *Candida antarctica* lipase (Novozym 435). The activity of the catalysts was compared under identical operating conditions at atmospheric pressure. The maximum operating temperature was 60 °C to avoid exceeding the boiling point of methanol. The reaction time for all the experiments was 8 hours, since longer times would be impractical from an industrial point of view. The activity of sodium hydroxide was found to be much larger than that measured for all the other catalysts. After the determination of the best catalyst they proceeded to optimize operating conditions changing temperature and catalyst concentration. The upper temperature level, 65 °C, was determined by the boiling point of methanol. The lower level was 25 °C, room temperature. Maximum ester conversions are therefore obtained for large catalyst concentrations within the lower temperature range. This is due to the fact that the most significant factor is catalyst concentration. Figure 1 shows how biodiesel conversion is affected by temperature and catalyst concentration [7]. At higher temperatures, however, a different behavior is observed. Conversion increases initially, reaching a maximum at intermediate catalyst concentrations, and then decreases at high catalyst concentrations. This is the result of a negative

temperature-concentration interaction and a negative concentration quadratic coefficient, probably caused by side reactions.

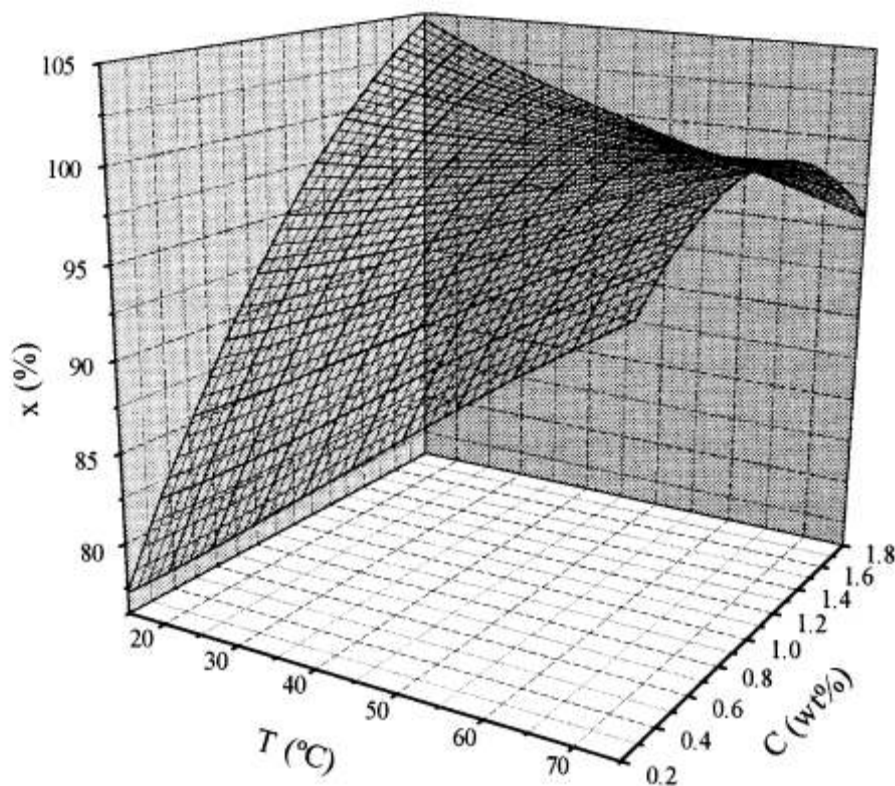


Figure 1. Catalyst amount and temperature effect on biodiesel formation

At low catalyst concentrations there is a moderate increase in conversion with temperature, since the temperature effect is positive and smaller than that of concentration. For larger catalyst concentrations the increase of conversion with temperature becomes smaller and finally, conversion becomes almost constant with temperature at high catalyst concentrations.

Large amounts of catalysts make the process costly and inefficient because there are higher quantities of catalyst to remove, making the washing process more difficult. The only reagent used in this work was ethanol but methanol is the most used reagent in the transesterification process in the production of biodiesel because of its low cost. Vicente

and coworkers also used refined sunflower vegetable oil. Waste vegetable oil has higher free fatty acids and may need an acid pretreatment of the oil.

Low Catalyst Concentration

A.Y. Tremblay et al. [8] used a membrane reactor which consisted of a permeate system with a pressure valve, a circulation pump, a mass flow rate meter, a heat exchange system and a safety and relief valve. Figure 2 shows the schematic of Tremblay equipment setup.

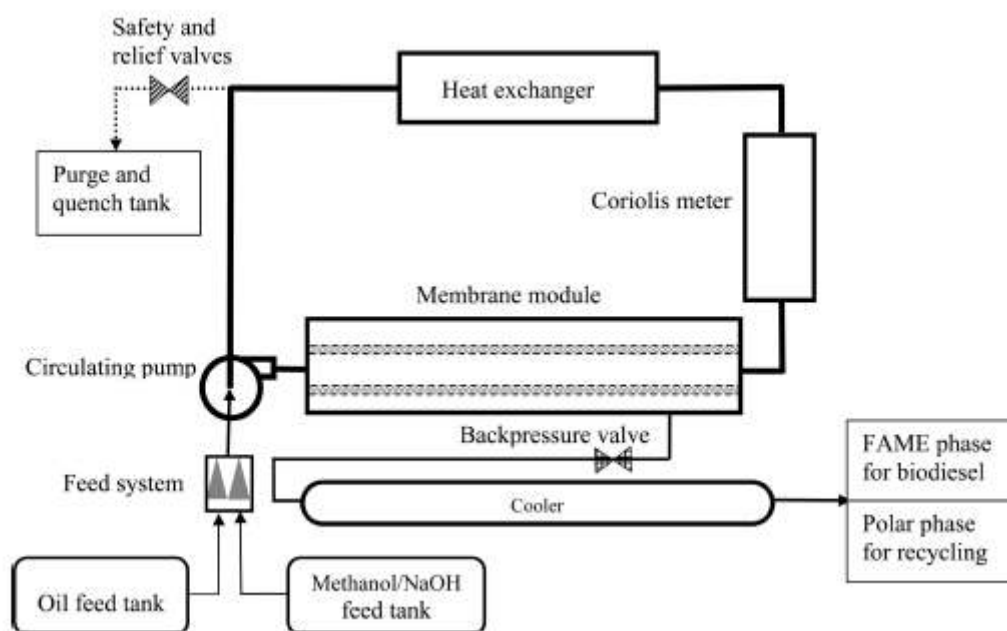


Figure 2. Schematic of Tremblay equipment setup

New canola oil was used and the methanol / NaOH solution was pumped into the pressurized loop on a 1:1 volume ratio. Retention time of the mixture in the reactor varied from one to two hours. Catalyst quantities varied from 0% catalyst to 0.05%. All runs were performed at 65 °C and 1.7 atm. The amount of base required to neutralize free fatty acids (FFA) in the oil

was 0.02% NaOH. This was determined by titration with phenolphthalein. The reaction took approximately 1 hour to reach 65 °C. After the temperature was reached, the oil and the methanol/catalyst solution were continuously fed to the pressurized loop and then to the reactor, where the mixture was retained for the residence time determined. The continuous flow permitted the removal of fatty acids methyl esters (FAME) and glycerol from the reactor through the pores of the membrane. At catalyst concentrations of 0.03% at a retention time of 1 hour and catalyst concentration of 0.01% at a retention time of 2 hours not a good conversion was obtained. When concentrations of catalyst reached 0.05% at a retention time of 1 hour or 0.03% catalyst concentration at a retention time of 2 hours, the continuous reaction of the oil fed to the reactor was allowed and the oils were fully converted into methyl esters. The results showed the use of higher catalyst concentration favored faster conversions. The results obtained indicated that reaction time used in this methodology can be reduced when increasing catalyst concentration. When FAME were produced in the membrane reactor, they entered the continuous methanol- rich phase circulating in the reactor. Under the reaction conditions, FAME, methanol and glycerol are mutually soluble in this phase because the membrane retains the oil droplets in the reactor and allows the permeation of the methanol-rich continuous phase.

Microwave Heating

T. Michael Barnard, et al. [9] used a commercially available microwave to accelerate the rate of transesterification reaction. Biodiesel was prepared under atmospheric conditions, with the reaction being completed in a few minutes when using new soybean oil. The microwave consisted on a continuous power delivery system with an operator- selectable power output from 0 to 1600 W. Reactions were performed in a reaction vessel with an overhead paddle stirrer. Figure 3 shows a picture of Barnard's equipment setup. The vegetable oil, the potassium hydroxide and the methanol were added using a 1:6 ratio of vegetable oil/methanol and 1% wt catalyst. A portion of the feedstock was pumped into the reactor

until full. Microwave power of 1600 W was used to heat the contents of the vessel from room temperature to 50 °C, this took 3 minutes. Temperature was held for 1 minute, the feedstock was restarted and the material passed through the reactor at a rate of 7.2 mL / min for 6 minutes.



Figure 3. Barnard equipment setup

After the removal of glycerin, the biodiesel was washed with water. The biodiesel conversion was 97%. A power meter was installed to measure energy consumption. With the microwave running with a continuous output of 1600 W, 960 W power was being drawn. This indicates the magnetron is 60% efficient. Energy consumption was calculated to be 92.3 kJ/L of biodiesel prepared. Rudimentary energy consumption calculations suggest that the continuous-flow microwave methodology for the transesterification reaction is more energy efficient than using a conventional heated apparatus.

Acid Pre-Treatment

M. Canacki and J. Van Gerpen [10] used a two step pre-treatment process to reduce 20% FFA to 1%. The objective of their project was to investigate the use of low-cost, high FFA

feedstock to produce fuel-quality biodiesel. Increasing the amount of acid catalyst is very effective in decreasing the acid value of the mixture. In the first pre-treatment step using a 10:1 molar ratio and 30 min of reaction time, the acid value was reduced from 41.33 mg KOH / g to 1.37 mg KOH / g using 15% acid catalyst. To use KOH as the alkaline catalyst, it was found that the acid value must be reduced to 0.5%. The two-step acid-catalysis pre-treatment process was successful in decreasing the acid value of yellow and brown grease to less than 1%. The reaction time was one hour using 10% catalyst and using a 20:1 methanol/oil molar ratio for the first step and a 40:1 methanol/oil molar ratio in the second step.

Large quantities of catalyst and long reaction times are needed to obtain a successful decrease in acid number. This makes the process costly and inefficient. It required two steps of 30 minutes each using 15 % w/w of sulfuric acid to achieve a significant acid number reduction, which means the need to use more energy and more reagents. This will increase reaction process costs. Conventional heating was used during this experiment, which requires heating from the surface to the internal side of the sample. Conventional heating is responsible for localized heating effect provoking sample degradation. To reduce reaction time we applied microwave heating. Microwave heating irradiates sample directly, making the heating uniform on the sample. Strong acids will be used during experimentation, which is favorable during microwave heating due to its polarity.

THEORETICAL BACKGROUND

In this chapter the theory of the most relevant topics to this research are discussed including reaction mechanisms, GC-MS, Microwave Heating and acid pre-treatment.

Acid Number

When the oil is heated in presence of oxygen and water, oxidative and thermolytic reactions occur that end up in oil degradation and the formation of free fatty acids (FFA).

Through the action of oxygen, new functional groups are produced on oils are triglycerides with three long chains of carboxylic acids called fatty acids. The presence of these free fatty acids gives the molecule polarity. Oil at high temperature can be oxidized, polymerized and hydrolyzed. Oxygen produces new functional groups on the triglyceride hydrocarbon chain and hydrolyzes it, producing new FFA, monoglycerides and triglycerides, which make the polarity of oil higher. The fatty acids separate from the glycerol due to differences in polarity. If they are unsaturated they can deteriorate even more by oxidation. The unsaturated oils react with oxygen by free radicals producing aldehydes.

To measure the increase in the polarity of the oil due to FFA, the standard test method for acid number is used. Acid Number is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample required to titrate a sample to a specified end point. The test method ASTM D-974 can be used to indicate relative changes in oil during these oxidizing conditions.

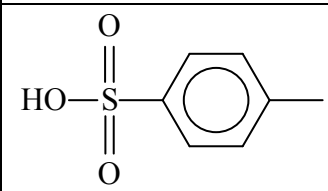
To determine the acid number, the sample is dissolved in a mixture of toluene and isopropyl alcohol, and the resulting single phase solution is titrated at room temperature with standard base solution to the end point indicated by color change using phenolphthalein as indicator.

Acid Pre-Treatment

Waste oils and fats are currently collected from large food processing and service facilities where they are rendered and used primarily in animal feed. Rendered animal fats and restaurant waste oils with free fatty acid levels of less than 15% are known as yellow grease. If the FFA level exceeds 15%, it may be sold at a discount as brown grease, or blended with low FFA material to meet the yellow-grease specifications. Yellow and brown grease are attractive feedstocks for biodiesel production because they are inexpensive compared with food-grade vegetable oil. Alkaline catalysts have been used and the FFAs were removed from the process stream as soap and considered waste. As FFA levels increase this becomes undesirable because of the loss of feedstock as well as the deleterious effect of soap on glycerin separation. Soaps promote the formation of stable emulsions that prevent separation of the biodiesel from the glycerin during processing. Waste greases typically contain from 10% to 25% FFA's. This is far beyond the level that can be converted to biodiesel using an alkaline catalyst. An alternative process is to use acid catalysts that some researchers have claimed are more tolerant of free fatty acids.

Sulfuric acid, hydrochloride acid and p-toluenesulfonic acid (PTSA) were compared as catalyst in the pre-treatment esterification reaction. Acids used were strong acids. All three acids are soluble in water. Hydrochloric acid and sulfuric acid are highly corrosive clear liquids acids and PTSA is non-oxidizing crystal-white solid.

Table 2. Comparison between acids used for pre-treatment

Acid	Sulfuric Acid	Hydrochloric Acid	p-toluenesulfonic acid (PTSA)
Structure	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{S}-\text{OH} \\ \parallel \\ \text{O} \end{array}$	H—Cl	
Type of acid	Strong Inorganic acid	Strong Inorganic acid	Strong organic acid
Appearance	Clear, colorless, liquid	Clear, colorless, liquid	White solid
pka	-3	-8	-2.8

Pre-Treatment Mechanism

First step

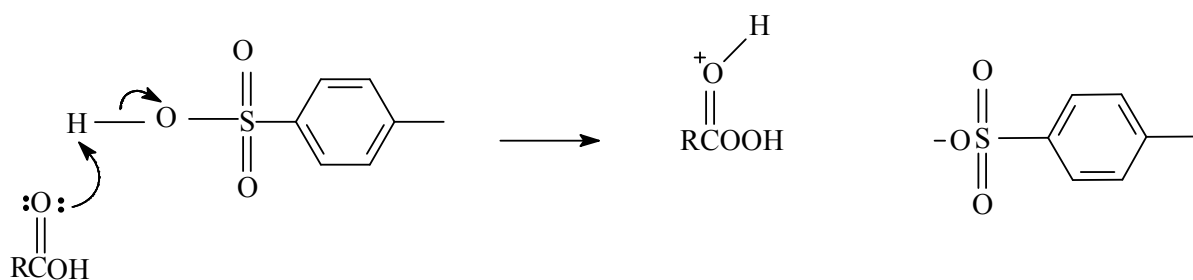


Figure 4. First step in cooking oil pre-treatment.

In the first step, the carboxylic acid is protonated by the strong acid, in this case, PTSA. The proton becomes attached to one of the lone pairs on the oxygen which is double-bonded to the carbon.

The transfer of the proton to the oxygen gives it a positive charge. The positive charge is delocalized over the whole of the right-hand end of the ion, with a fair amount of positive charge on the carbon atom (an electron pair shifting).

Second Step

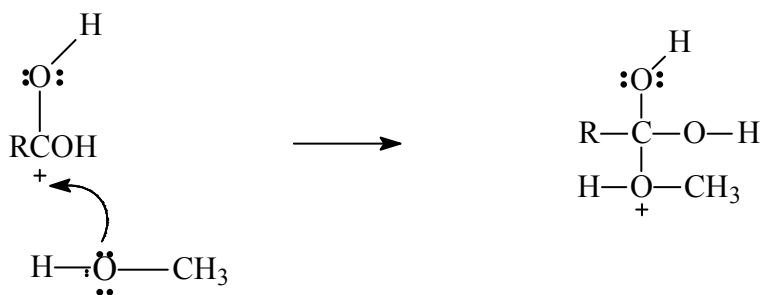


Figure 5. Second step in cooking oil pre-treatment

The positive charge on the carbon atom is attacked by one of the lone pairs on the oxygen of the methanol molecule.

Third Step

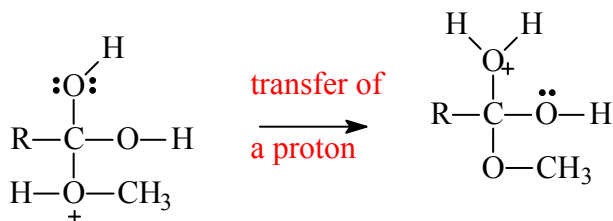


Figure 6. Third step in cooking oil pre-treatment

A proton (a hydrogen ion) gets transferred from one of the oxygen atoms to another. It gets picked off by one of the other substances in the mixture (for example, by attaching to a lone pair on an unreacted methanol molecule), and then dumped back onto one of the oxygens more or less at random.

Fourth Step

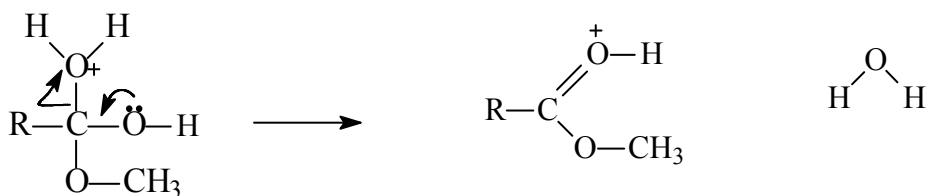


Figure 7. Fourth step in cooking oil pre-treatment

A water molecule is lost from the ion.

Fifth Step

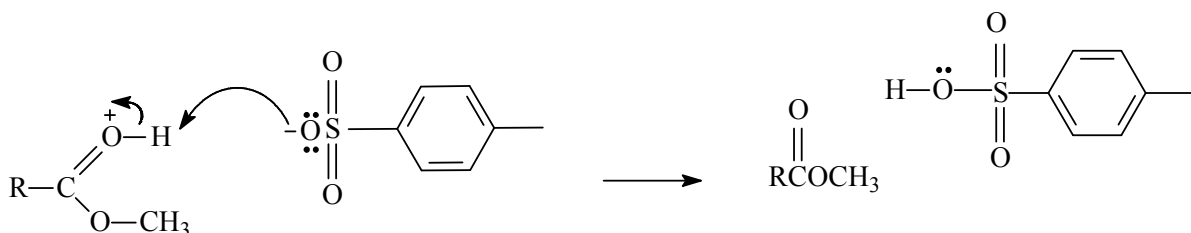


Figure 8. Fifth step in cooking oil pre-treatment

The hydrogen is removed from the oxygen by reaction with the p-toluenesulfonate ion which was formed in the first step.

Transesterification Mechanism

First Step

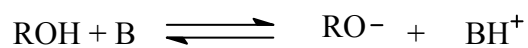


Figure 9. First step in alkaline transesterification reaction

The alcohol is deprotonated by the strong base.

Second Step

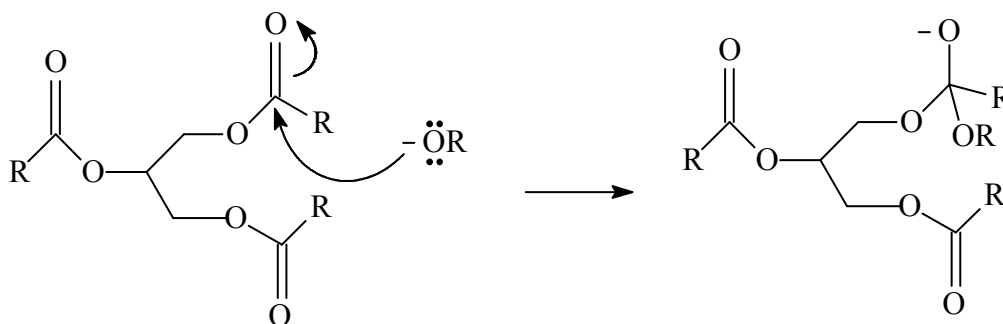


Figure 10. Second step in alkaline transesterification reaction

The nucleophilic hydroxide attacks the electrophilic C of the ester C=O, breaking the pi bond and creating the tetrahedral intermediate.

Third Step

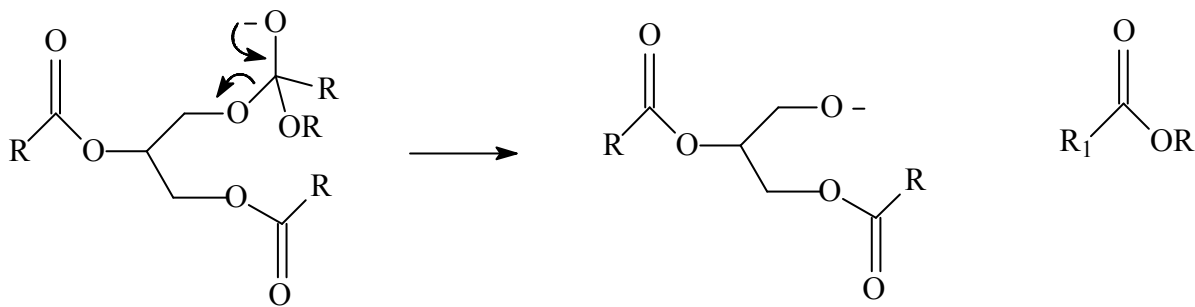


Figure 11. Third step in alkaline transesterification reaction

The intermediate collapses, reforming the C=O results in the loss of the leaving group, the alkoxide, leading to the carboxylic acid.

Fourth Step

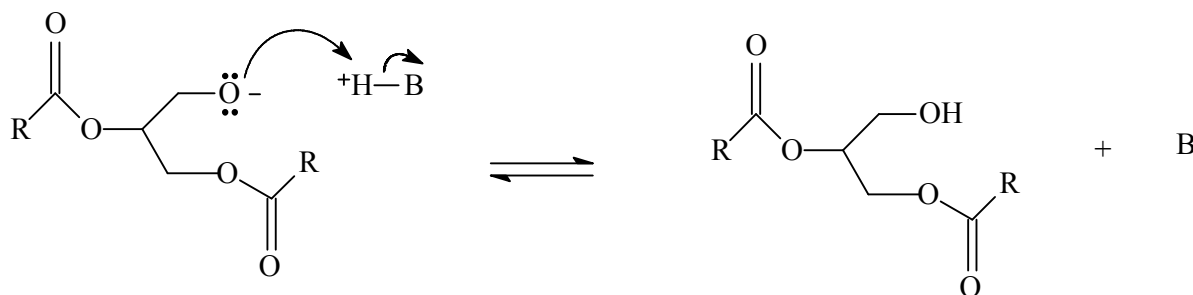


Figure 12. Fourth step in alkaline transesterification reaction

An acid / base reaction occurs. A rapid equilibrium is established where the alkoxide functions as a base deprotonating the carboxylic acid. The final product is a diglyceride. These four steps occur 2 more times to produce the glycerol and three methyl esters (biodiesel).

Microwave Heating

In 1950, microwave energy was applied in various chemical and related industries. These applications can include food processing drying, analytical chemistry, polymer science, biochemistry, pathology and medical treatments. It was implemented in organic chemistry since mid 1980. Early studies were carried on glass containers in domestic household microwaves without temperature or pressure measurements. The results were often violent explosions due to rapid uncontrolled heating of organic solvents under a closed vessel conditions[11].

Microwaves are electromagnetic waves with wavelengths between infrared light and radio waves. Its electromagnetic irradiation has frequency ranges between ultra-high frequency

(UHF; 0.3 to 3GHz), super high frequency (SHF; 3 to 30 GHz) and extremely high frequency (EHF; 30 to 300 GHz) signals.

Microwave-assisted chemistry is based on the efficient heating of materials by microwave dielectric heating effects, which are dependent on the ability of a specific material to absorb microwave energy and convert it into heat. The electromagnetic waves of a microwave are composed of an electric and a magnetic component, of which the former is important for interaction with materials. Heating by the electric component of the microwave electromagnetic field occurs through two major mechanisms: dipolar polarization and ionic conduction. When exposed to microwave frequencies, the dipoles of a sample align in the applied electric field. As the alternating electrical field oscillates, the dipole or ion attempts to realign itself with the fluctuating field. In this process, energy is lost in the form of heat due to molecular friction and dielectric loss. The amount of heat generated is directly correlated with the ability of the matrix to realign with the phase of the microwave field.

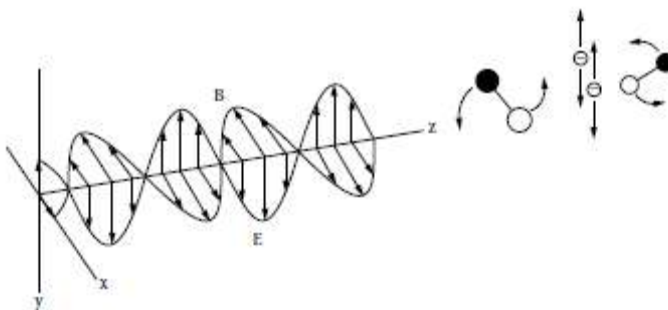


Figure 13. Dipolar molecules trying to align with oscillating electric field

When molecules rotate in a matrix, they generate heat by friction. The amount of heat generated by a given reaction mixture is a complex function of its dielectric property, volume, geometry, concentration, viscosity, and temperature.

Dielectric polarization arises from the rotation of dipoles in an electric field. Compounds that have large permanent dipole moments also have large dielectric constants because the dielectric polarization depends primarily on the ability of their dipoles to re-orient in an

applied electric field. Essentially, the ability of a substance to heat in a microwave field is dependent upon the efficiency of the substance to absorb the microwave energy and the efficiency with which the absorbed energy can be converted to heat. When the dielectric properties of the sample are too poor to allow efficient heating by microwave irradiation, the addition of small amounts of polar or ionic additives, with large loss tangent values, can significantly overcome this problem and enable adequate heating of the entire mixture.

Microwave and Conventional Heating

Microwave dielectric heating has certain advantages over conventional heating for chemical synthesis.

The microwave energy is introduced into the chemical reactor remotely, meaning that there is no direct contact between the energy source and the reacting chemicals. If microwave invisible materials are selected to contain the reactants, the microwaves can pass through the walls of the vessel and only heat the reactants.

Most organic reactions requiring heat have been heated using traditional heat transfer equipment such as oil baths, sand baths or heating mantles. These techniques are rather slow and create a temperature gradient within the sample. Conventional heating of a sample makes a heterogeneous heating of the surface and it depends on the thermal conductivity of the materials. The external surface of the sample has higher temperature and the heat goes inside the sample (see Figure 14). Moreover, the hot surface of the reaction vessel may result in localized overheating leading to product, substrate and reagent decomposition when heated for prolonged periods.

When using microwave dielectric heating the energy is introduced into the chemical reactor remotely and there is no direct contact between the energy source and the reaction mixture.

nuclei,” and the rate at which the temperature of the mixture returns back to the normal boiling point is solvent dependent. Another aspect affecting the sample during microwave radiation is called local hot spot effect or thermal runaway effect. The thermal runaway effect is the microwave heating resulting in a non-uniform increase of the local temperature. The reaction rate increases due to an increase in temperature.

Biodiesel Characterization

GC-MS

Gas chromatography (GC) can separate volatile and semi volatile compounds with great resolution, but it cannot identify them. Mass spectrometry (MS) can provide detailed structural information on most compounds such that they can be exactly identified, but it cannot readily separate them. Therefore, it was not surprising that the combination of the two techniques was suggested shortly after the development of GC in the mid-1950s.

Gas chromatography mass spectrometry is an important tool for the identification and quantization of volatile and semi volatile organic compounds in complex mixtures. It is very useful for the determination of molecular weights and the elemental compositions of unknown organic compounds in complex mixtures. Among other applications, GC-MS is widely used for the quantization of pollutants in drinking and wastewater. It is the basis of several official EPA (Environmental Protection Agency) methods. It is also used for the quantization of drugs and their metabolites in blood and urine. Both pharmacological and forensic applications are significant. GC-MS can be used for the identification of unknown organic compounds both by matching spectra with reference spectra and by *a priori* spectral interpretation. The identification of reaction products by synthetic organic chemists is another routine application, as is the analysis of industrial products for control of their quality

GC-MS has a few limitations. Only compounds with vapor pressures exceeding about 10 torr can be analyzed by GC-MS. Many compounds that have lower pressures can be analyzed if they are chemically derivatized (for example, as trimethylsilyl ethers). Determining positional substitution on aromatic rings is often difficult. Certain isomeric compounds cannot be distinguished by mass spectrometry (for example, naphthalene versus azulene), but they can often be separated chromatographically.

The sample enters the system through the injection port (see Figure 15). The carrier gas moves the sample into the GC column, where the components are separated. It reaches the transfer line, which is the interface between both systems. The jet separator then separates the carrier gas from the component due to their diffusion-coefficients difference. The sample gets into the ion source region which can convert gas phase sample molecules into ions (or, in the case of electrospray ionization, move ions that exist in solution into the gas phase). After ionization the sample goes through the mass analyzer, which sorts the ions by their masses by applying electromagnetic fields; and a detector, which measures the value of an indicator quantity and thus provides data for calculating the abundances of each ion present.

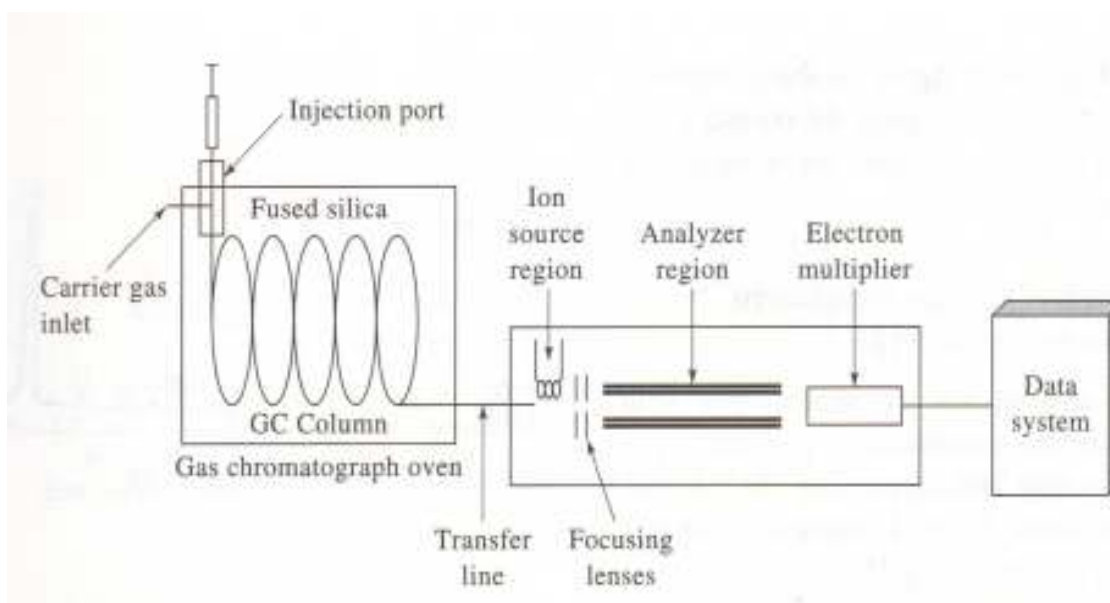


Figure 15. GC/MS equipment

Gas chromatography and mass spectrometry are compatible techniques. In both techniques, the sample is in the vapor phase, and both techniques deal with about the same amount of sample. The major incompatibility between the two techniques is that the compound exiting the gas chromatograph is a trace component in the GC's carrier gas at a pressure of about 760 torr, but the mass spectrometer operates at a vacuum of about 10^{-6} to 10^{-5} torr. This is a difference in pressure of 8 to 9 orders of magnitude, a considerable problem. Quantitative accuracy is controlled by the overall analytical method calibration.

The interface

The jet separator takes advantage of the differences in diffusibility between the carrier gas and the organic compound. The carrier gas is commonly a small molecule such as helium or hydrogen with a high diffusion coefficient, whereas the organic molecules have much lower diffusion coefficients. In operation, the GC effluent is sprayed through a small nozzle, into a partially evacuated chamber (see Figure 16). Because of its high diffusion coefficient, the helium is sprayed over a wide angle, whereas the heavier organic molecules are sprayed over a much narrower angle and tend to go straight across the vacuum region. By collecting the middle section of this solid angle with a skimmer and passing it to the mass spectrometer, the higher-molecular-weight organic compounds are separated from the carrier gas, which is removed by the vacuum pump. Most jet separators are made from glass by drawing down a glass capillary, sealing it into a vacuum envelope, and cutting out the middle spacing. It is important that the spray orifice and the skimmer be perfectly aligned.

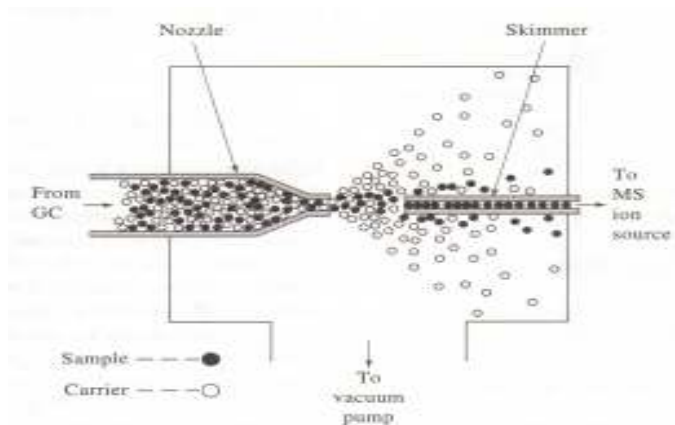


Figure 16. GC/MS jet separator

3/27 test

3/27 test, also called the Jan Warnqvist test, indicates if waste vegetable oil was converted into biodiesel. The triglycerides have a very low solubility, but biodiesel does. Any unreacted oil will fall to the bottom of the methanol. Partially converted biodiesel can fallout as well over time.

The test relies on the fact that biodiesel is quite soluble in methanol, while triglyceride has a very low solubility in methanol. It is believed that diglycerides are partially soluble, but less so than monoglycerides. In essence, if any more than a trace of triglyceride is present, it can be seen with this test. If triglycerides are present, so are diglycerides and monoglycerides. The amount of remaining triglycerides is a direct reflection of the degree to which the oil was converted to biodiesel. The lower the amount of triglycerides, the higher the conversion to biodiesel.

Temperature is important with this test. It should be conducted with both the oil and the methanol at room temperature. If temperature is too high, a false pass can be obtained. If temperature is too cold, you can get a false fail.

PROCEDURE

Materials and Reagents

Samples of waste vegetable oil (WVO) were collected from local restaurants. All the WVO samples used in this study were from recycled cooking oil and animal fats since most local restaurants discard this product after no longer complies with the Department of Health regulations (approximately FFA contents of 20%). Acid number of waste oil was determined using ASTM D-974. Phenolphthalein, potassium acid phthalate, barium hydroxide, anhydrous methanol, p-toluenesulfonic acid, sulfuric acid, hydrochloric acid, toluene and 2-propanol (HPLC grade) were supplied by Fisher Scientific. Potassium hydroxide and sodium hydroxide (A.C.S. pellets) by Aldrich Chemical Company, Inc. Analytical standards were purchased from Aldrich Chemical Company, Inc. The following standards GLC-10, a provisional standard of commercial biodiesel, were supplied by Alltech Associates, Inc. containing: (1) Palmitate (C16); (2) Stearate (C18:0); (3) Oleate (C18:1); (4) Linoleate (C18:2); and (4) Linolenate (C18:3).

Laboratory Equipment Set Up

Analytical instruments used in this study have been separately tested with similar materials to those to be analyzed in this project, and each analysis method was validated using their respective standards and guidelines. A description of the equipment employed in this study is presented below:

GC/MS

A Hewlett Packard 6890 Series Gas Chromatograph coupled with a Hewlett Packard 5973 Mass Selective Detector. Supelco 1909BD-113 capillary column, length of 30 m, a film thickness of 0.25 μm , upper temperature limit of 260 $^{\circ}\text{C}$, and an internal diameter (ID) of 0.32 mm.

The following parameters and experimental conditions were used:

To determine oils compositions, the temperatures of injector and detector were 230 $^{\circ}\text{C}$. Mode injector: Split-less. Oven temperature was held at 60 $^{\circ}\text{C}$ for 3 min. After that, the oven temperature was ramped from 60 to 255 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, and then held at 255 $^{\circ}\text{C}$ for 8 min., for a total run time of 34 min. Helium was used as carrier gas with a flow rate of 1.4 mL / min and a backpressure of 1.8 psi.

MS detector conditions used were as follows: capillary direct interface 280 $^{\circ}\text{C}$; ion source 230 $^{\circ}\text{C}$; mass/charge 50-550 a.m.u.; scan rate 2.94 scan / sec; electron multiplier 1482 V.

All liquid samples were diluted at a concentration of 50 μL in 5 mL of hexane, and filtered through a 0.2 μm PTFE membrane (Whatman Inc., New Jersey). One microliter samples were injected manually with a syringe (Microliter Syringe 1705 RNR 10 μL ; Hamilton Co., Nevada).

Weight and Volume Determinations

Weight determinations were made using calibrated analytical scales. Volume determinations were made using beakers, pipettes, burettes, flasks, and syringes calibrated ranging from 1

micro-liter to 300 ml. Special care was taken when handling acids due to their corrosive properties; glass material is mandatory.

Pre-Treatment and Transesterification Reaction

The pre-treatment and transesterification reaction was performed in a modified commercial microwave oven (see Figure 17). To maintain a continuous flow from the microwave oven to the reaction vessel, the microwave was drilled and twenty five feet Teflon tube was made in a loop inside the oven that can hold near 300 milliliters volume. The tubing gets out the oven and get into the reaction vessel. The mixture was moved using a pump (Figure 17). The tubing outside the microwave was attached to a digital thermometer to monitor and control temperature range from 49 – 51 °C . To monitor pressure a pressure gauge was attached. The mixture was stirred while in the reaction vessel to enhance reaction using a Corning Magnetic Stirrer.

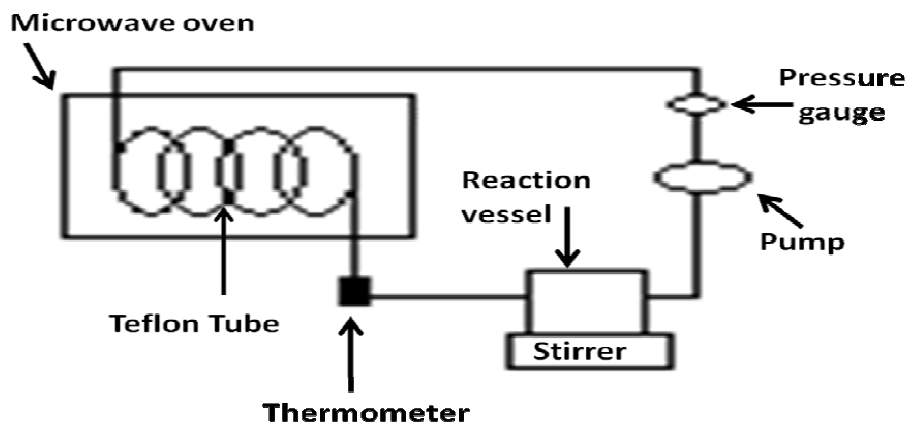


Figure 17. Schematic of reaction equipment assembly.

Microwave oven

A Emerson commercial microwave model MW93225SL was used for pre-treatment and transesterification reactions. The power of microwave was 900 watts. The microwave oven was used at 50% power.



Figure 18. Microwave oven used

Experimental design

Used cooking oil was characterized for the presence of free fatty acids. Biodiesel characterization was performed by GC-MS.

Optimal conditions were determined by statistical screening of different reaction temperatures and reaction times using recycled cooking oil as feedstock. A two step process was determined. First step would be the oil pre-treatment followed by the alkaline transesterification reaction. The optimal selected conditions were replicated three times for fine-tuning considering the following aspects:

The methanol to used oil ratio was 9:1 and initial weight percent of acid (5% w/w) were selected according to the literature review [10]. Three acids used as catalyst were evaluated and compared (sulfuric acid, hydrochloric acid and p-toluenesulfonic acid). Microwave system was used at 50% power (900 Watts). Fifty percent power means that the 900 watts microwave its turning on and off 50% of the time. The experimental conditions are described in the following table:

Table 3. Experimental conditions for acid pre-treatment

Reaction Time (minutes)	Acid	Acid concentration (%w/w)	Temperature
60	H ₂ SO ₄	5	uncontrolled
	HCl	5	
	PTSA	5	
		2.5	
		1	
		0.5	
		0.25	
		5	Room temperature
15	PTSA	5	50°C
		2.5	
		1	
		0.5	

The smallest sample size to perform an analysis of variance calculation is two replicates.

After the analysis of the information provided by the statistical design with used cooking oil, the optimal conditions for reaction time and temperature were established. Optimal conditions are 15 minutes reaction time and 50 °C. These optimum conditions were used to

perform the acid pre-treatment followed by an alkaline transesterification reaction with methanol for ten minutes of reaction using 1.0 % NaOH catalyst as described in literature [9].

Biodiesel Wash

Upon cooling to room temperature, the content of the reaction vessel was decanted into a separatory funnel. After twenty four hours of settling the glycerol phase was decanted and removed. The biodiesel phase was water washed. One liter of water per liter of biodiesel was used in the washing process. Three water washes were needed to remove biodiesel pollutants. Washed biodiesel was filtered through a Whatman Grade 50 filter. Above the filter a thin layer of magnesium sulfate was added to remove excess water and present in the biodiesel.

Sampling and Chemical Analysis

The biodiesel synthesis was divided in two main steps which consisted of a FFA acid pre-treatment and alkaline transesterification of triglycerides. Once the acid pre-treatment was optimized, the alkaline transesterification was performed in the microwave oven according to literature review [9].

Samples were drawn from the middle of the reactor using sterile pipettes and titrated. Samples were taken at 0, 1, 10, 20, 30, 40, 50, 60 minutes and after 24 hours of reaction. Each sample was analyzed by titration using the method mentioned above, to determine the acid number reduction by reaction time. Experimental setup for transesterification of Biodiesel was taken from literature review [9]. Biodiesel was characterized by GC-MS with the experimental conditions mentioned above. Samples were diluted taking an aliquot of 50 micro liters of biodiesel in 5 milliliters of hexane; 0.1 microliter of sample was injected in the GC-MS.

3/27 Test

In a clear vial, 27 mL of methanol and 3 mL of biodiesel at room-temperature were added. The biodiesel and vial were water-free. The mixture was shaken for 5 seconds and allowed to settle. Oily precipitate after 30 minutes indicates that the fuel contains more than trace amounts of triglycerides, and therefore mono and diglycerides as well. If no precipitate was observed, high converted fuel was obtained.

RESULTS

Series of tests were conducted to develop the acid-catalyzed pretreatment process followed with the transesterification reaction and the characterization results.

The initial acid number of the recycled cooking oil used was 35.7 mg KOH / g sample, which is very high when compared with the recommended value of 2 mg KOH / g sample for the biodiesel synthesis. Published literature [12] suggested that the alkaline catalyzed reaction stops at an acid value above 2 mg KOH / g sample. This means that at high free-fatty acids concentrations, if an alkaline catalyst is used, soap formation seriously hinders the production of fuel-grade biodiesel. Soap forms when the metal hydroxide catalyst reacts with FFAs in the feedstock. Soap production gives rise to the formation of gels, increases viscosity, and greatly increases product-separation cost. When using acid catalysts, at the higher FFA levels, the methanol-water mixture removed during pretreatment carries greater amount of methyl ester and unreacted fat. The acid is more soluble in water than in the oil, meaning that the acid will go into the water phase stopping the acid esterification reaction. This is due to the effect of the water produced when the FFA's react with the alcohol to form the esters.

Process Development

In a literature review [10] Canacki used different concentrations (5% w/w, 15 %w/w and 25% w/w) of sulfuric acid and monitored the change of acid number with time. The heating method was conventional heating and the temperature used was 60 °C. They obtained a reduction of free fatty acids from 20% to 2% using 5% of sulfuric acid within sixty minutes of reaction time. In our work, to investigate the influence of time in the acid number reduction and determine a reaction time, experiments were performed with sulfuric acid, hydrochloric acid and p-toluenesulfonic acid using 5% w/w of each with a reaction time of 60 minutes (see Appendix A for data). The heating method used was microwave heating.

Figure 19 shows a graph which compares the acid number change within sixty minutes of reaction time for the three acids evaluated. For HCl, the acid number reduction pattern was observed up until 15 minutes of heating. For the other acids a continuous reduction is observed. The pattern was similar in all three acids. After 24 hours of reaction completion, no phase separation was observed and an increase in the acid number was obtained. Similar behavior was observed for both trials on each acid. Working with high concentration of acids catalysts ether formation could be promoted due to alcohol dehydration.

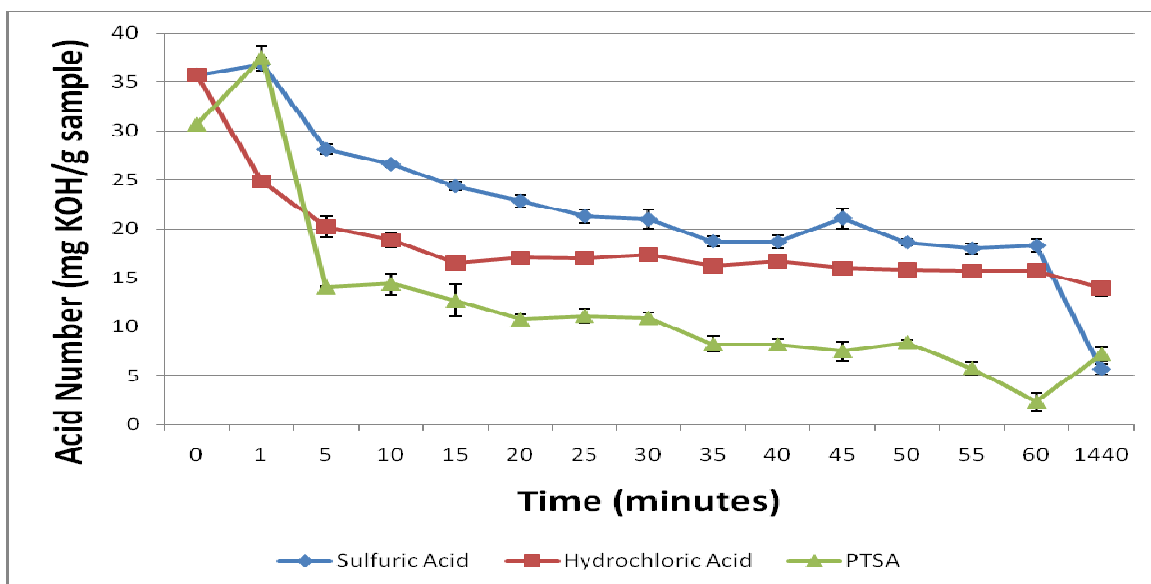


Figure 19. Acid number variation with time for different acid pre-treatments

Due to the erratic behavior observed in the PTSA, the concentration of the acid was reduced. Table 2 in Appendix A shows the acid number change data within 60 minutes reaction time. Figure 20 shows a graph which compares the acid number change within sixty minutes reaction time using lower catalyst concentrations for PTSA acid.

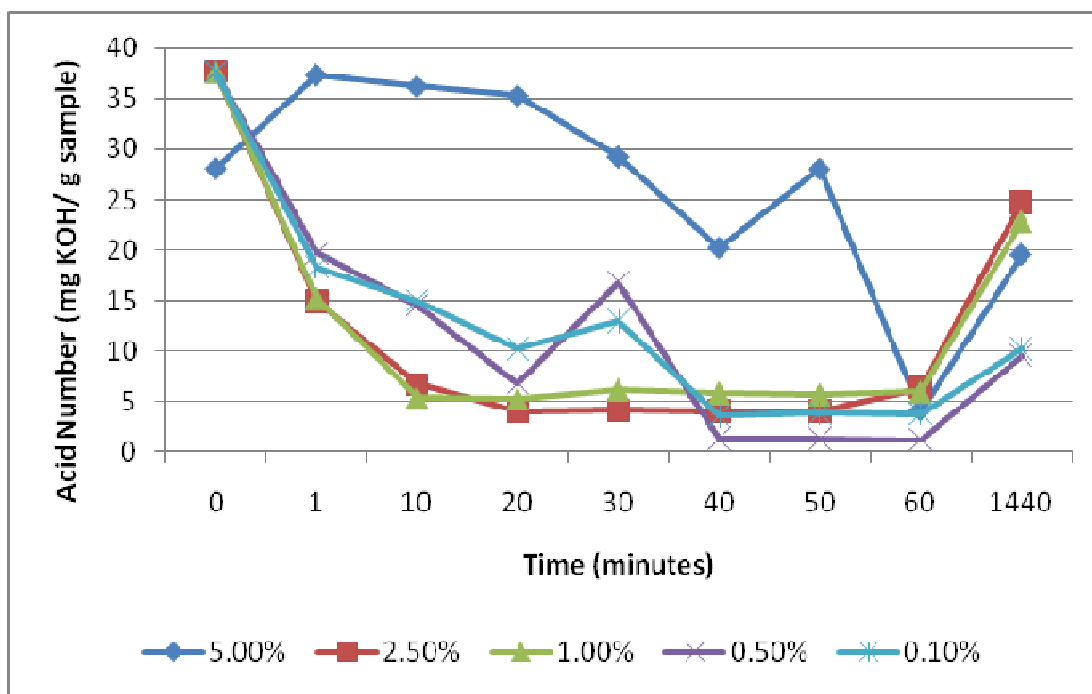


Figure 20. Acid number variation with time for different PTSA concentrations

Similar behavior was observed when using 5% w/w of PTSA during the reaction time. After 24 hour of reaction completion no phase separation was observed. When exposed to high acid concentration and / or high energy inputs for a long period of time, side reactions occur. We used 5% of strong acids, using microwave heating, which reduces reaction time due to its increase in energy for a period of 1 hour. Temperature in all reactions was above the 60 °C. The result was a black solution with a black precipitate. A change in color was observed after 20 minutes of reaction time for the three acids tested. As explained before, microwave heating accelerate reaction rates and reduce reaction times due to superheating effects. Increases in temperature, addition of catalyst and high methanol/oil molar ratio during long reaction times (60 minutes reaction time) can promote ether, alcohol and acid formation instead of the ester wanted. Figure 21 shows a mechanism for those side reactions.

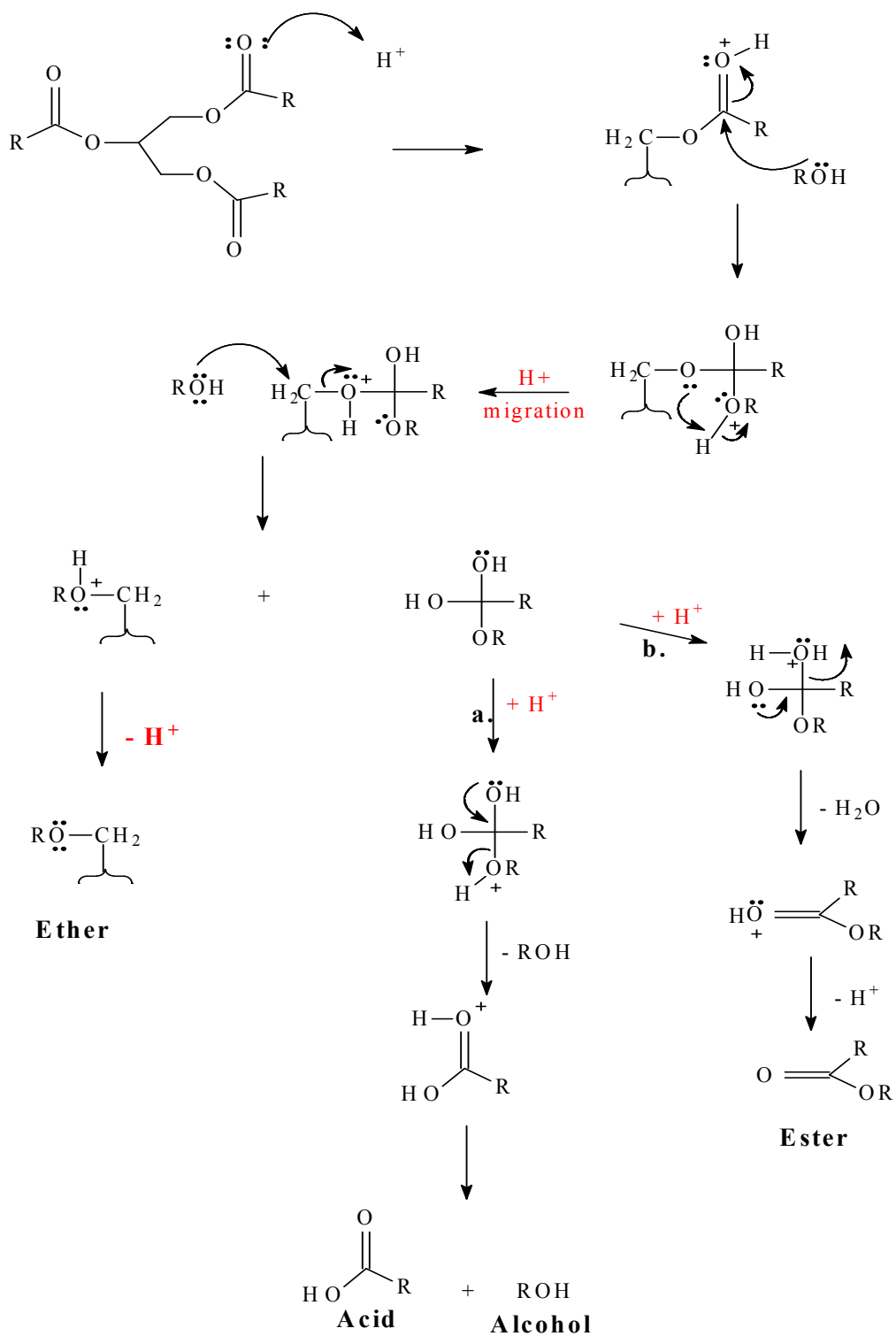


Figure 21. Side reactions mechanism

To remove one of the possible variables affecting the ester formation, the reaction was performed at room temperature using PTSA. Table 3 in Appendix A shows the acid number change data with 1 hour reaction time. Figure 17 shows a graph comparing acid number reduction at room temperature and without controlling temperature.

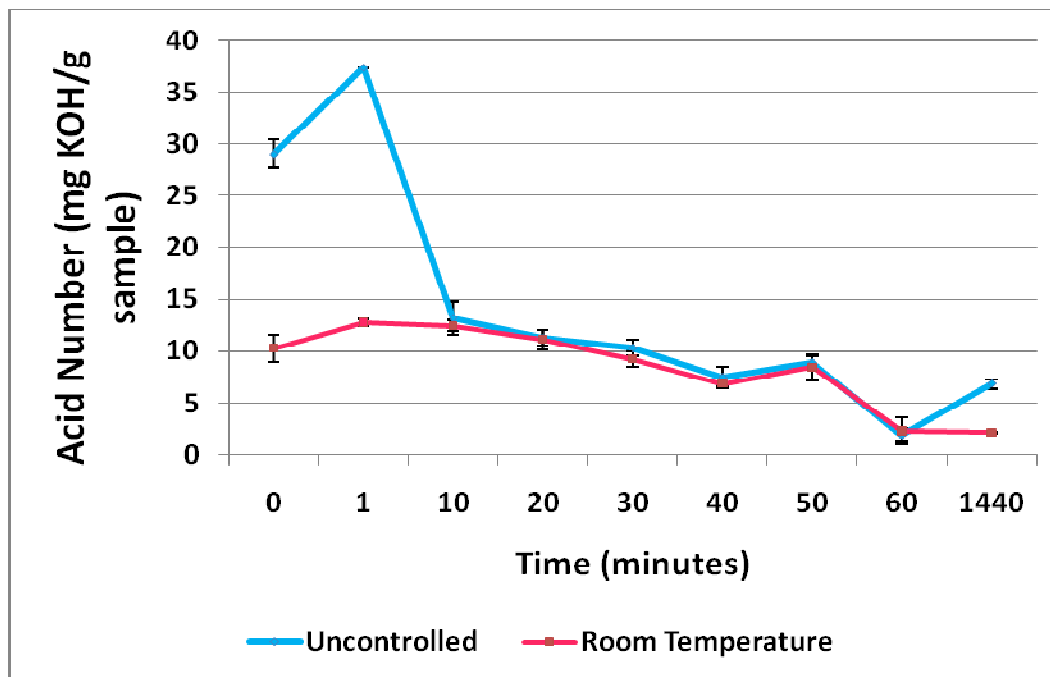


Figure 22. Comparison of acid number variation with time using PTSA catalyst

After 1 hour of reaction, at room temperature a phase separation was observed. The reaction mixture was transferred into a separatory funnel to rest for 24 hours. After 24 hours the water phase was removed and the acid number was measured. A significant reduction in acid number was observed. Literature review establishes [10] that for 1% w/w sulfuric acid at 77 °C using conventional heating takes 20 hours to obtain a phase separation. It is known that an increase in catalyst quantity reduces the reaction time. Figure 22 shows the acid-number behavior within reaction time for room temperature compared to the other PTSA pre-

treatment with uncontrolled temperature. For room temperature a steady acid number reduction was observed. For uncontrolled temperature an erratic behavior was observed.

To reduce reaction time, pre-treatment conditions and procedures were changed. Temperature was controlled at 50 °C through the reaction period, as recommended in the literature review [10] for alkali transesterification reaction using microwave heating. Oil was heated to 50 °C and recirculated through the microwave oven through the reaction vessel as seen in Figure 17. To achieve that temperature, using 50 % microwave power, approximately 5 minutes were required. After obtaining that temperature, a mixture of methanol/acid was added. Reaction was stopped, turning off the microwave oven, after 10 minutes, for a total of 15 minutes reaction time for acid pre-treatment. Sample was decanted into settling vessel for phase separation. After 5 minutes in settling vessel, phase separation was observed. The sample stayed in the settling vessel for 24 hours. Table 4 in Appendix A shows the acid number change with time for all acids.

Figure 23 shows acid number change with 15 minutes reaction time for sulfuric acid, hydrochloric acid and p-toluenesulfonic acid at 5% w/w concentration. Similar behavior was observed between hydrochloric acid and PTSA. PTSA has an acid constant similar to sulfuric acid since both, the sulfonic acid and the oil, are organic in nature, the reduction in acid number was greater.

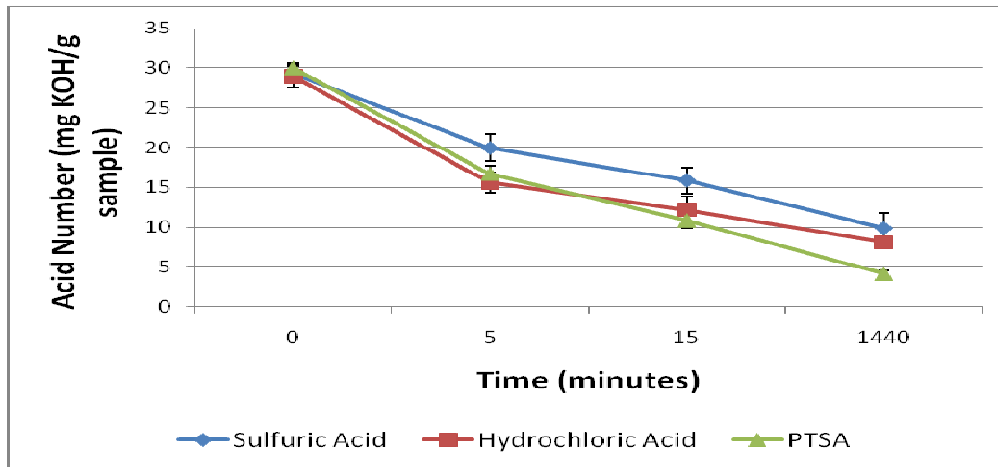


Figure 23. Acid number change with time for different acids at 50 °C and 15 minutes reaction time

PTSA concentrations were reduced to study the effect of acid concentration in the acid number reduction. No significant difference was found with acid reduction (See Table 5 of Appendix A and Figure 24). Similar behavior is observed during the 15 minutes reaction period; but at 24 hour (1440 minutes) after reaction time, a higher reduction in acid number is observed with higher concentrations of acid. Reduction of PTSA tenfold (5 to 0.5%) caused an acid number reduction to half its initial value.

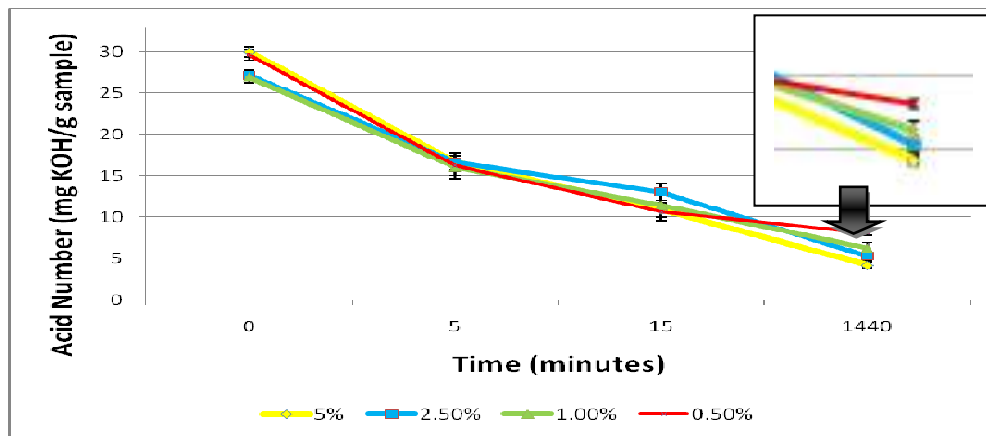


Figure 24. Acid number change with time for different PTSA concentrations at 50 °C and 15 minutes reaction time

After water was decanted, the sample was transferred into reaction vessel. Following literature review [9], reaction mixture was heated to 50 °C. Microwave power was 50%. Lipids took about 4 minutes to achieve that temperature. At 50 °C, methanol/ catalyst mixture was added and refluxed in and out of microwave oven through reaction vessel for 6 minutes; for a total reaction time of 10 minutes. The resulting mixture, biodiesel, was decanted into a separatory funnel for 24 hours. Phase separation was observed within 5 minutes of resting at the separatory funnel. Biodiesel was cleaned and filtered as described above.

Biodiesel Characterization

Biodiesel was characterized using GC-MS. A GLC-10 standard, containing biodiesel common components as palmitate (C16), stearate (C18:0), oleate (C18:1), linoleate (C18:2) and linolenate (C18:3) was injected into the GC/MS. Figure 20 shows GC chromatogram and peak separation. Table 2 shows the retention times for the standard components.

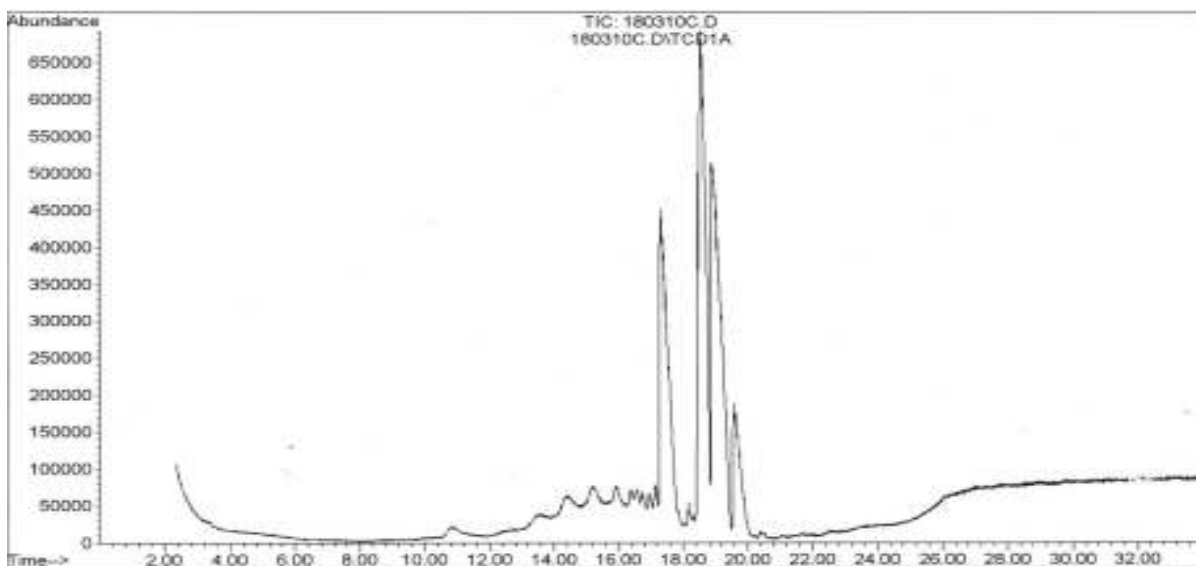


Figure 25. Chromatogram for Standard GLC-10

Table 4. Retention times for biodiesel components

Component	Retention time (minutes)
Palmitate (C16)	17.32
Stearate (C18:0)	18.54
Oleate (C18:1)	18.30
Linoleate (C18:2)	18.97
Linolenate (C18:3)	19.58

The MS spectrum shows the m/z ratio for each component. Table 4 identifies the molecular weight for each component.

Table 5. Molecular weight for biodiesel components

Component	Molecular weight (g/mol)
Palmitate (C16)	270
Stearate (C18:0)	298
Oleate (C18:1)	296
Linoleate (C18:2)	294
Linolenate (C18:3)	292

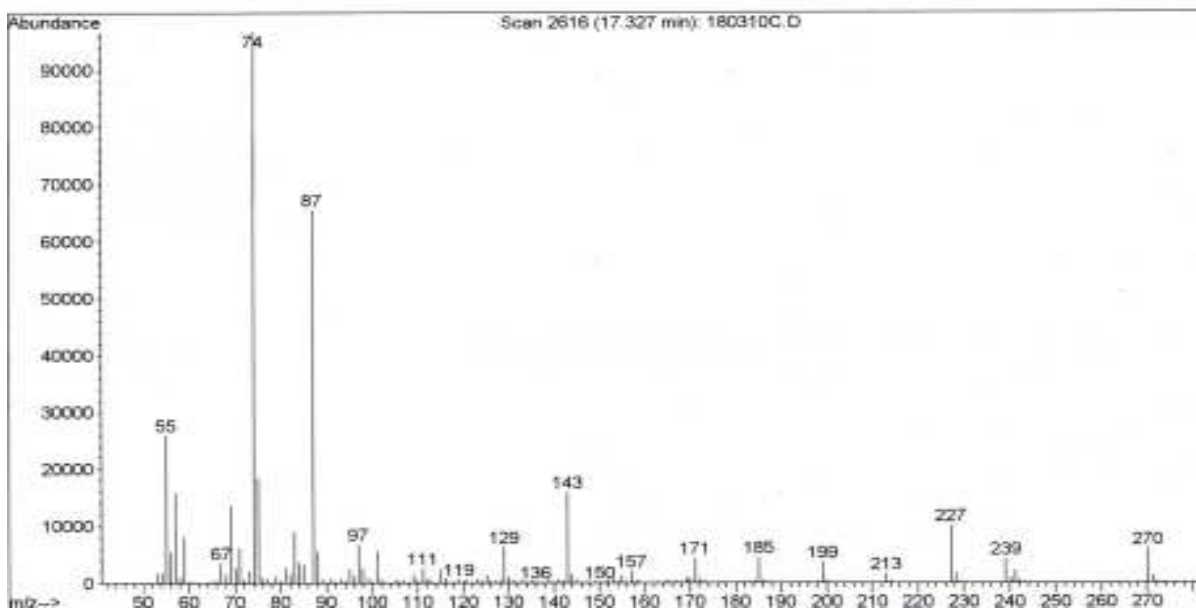


Figure 26. MS spectrum for C16 biodiesel component from standard GLC-10

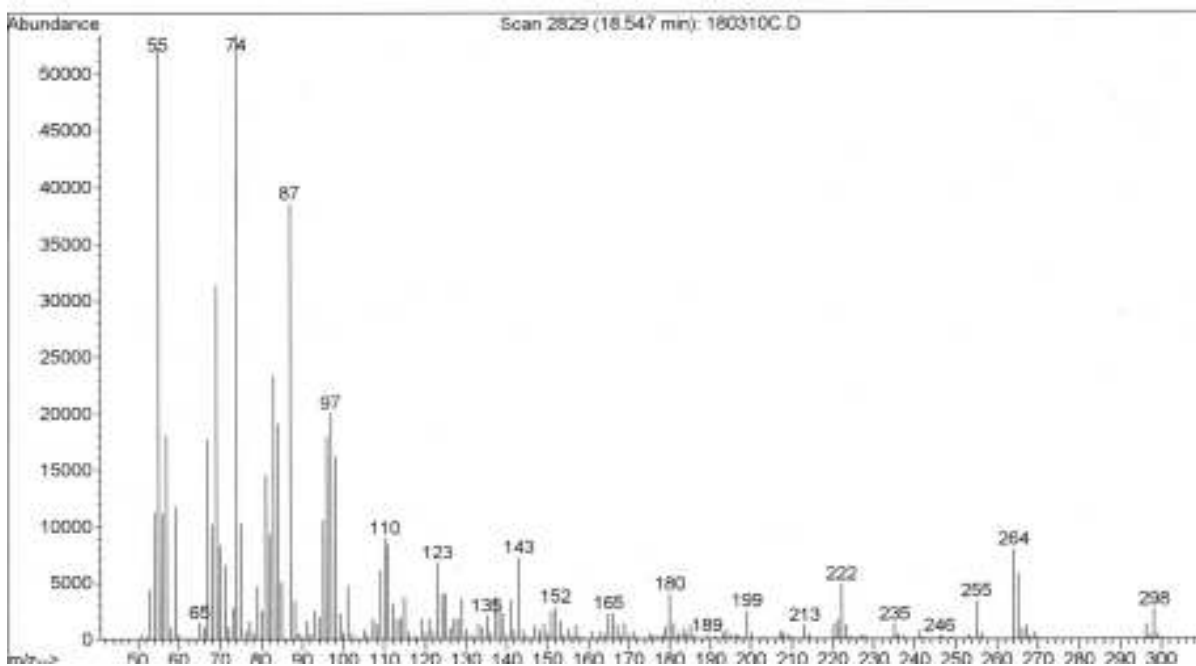


Figure 27. MS spectrum for C18:0 biodiesel component from standard GLC-10

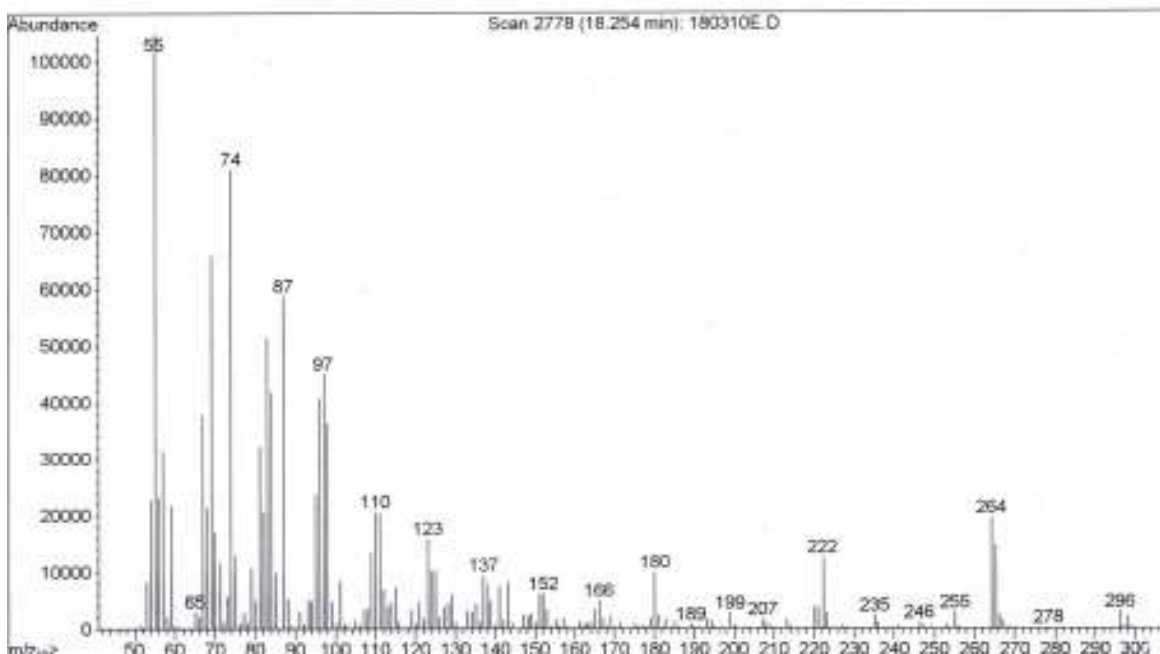


Figure 28. MS spectrum for C18:1 biodiesel component from standard GLC-10

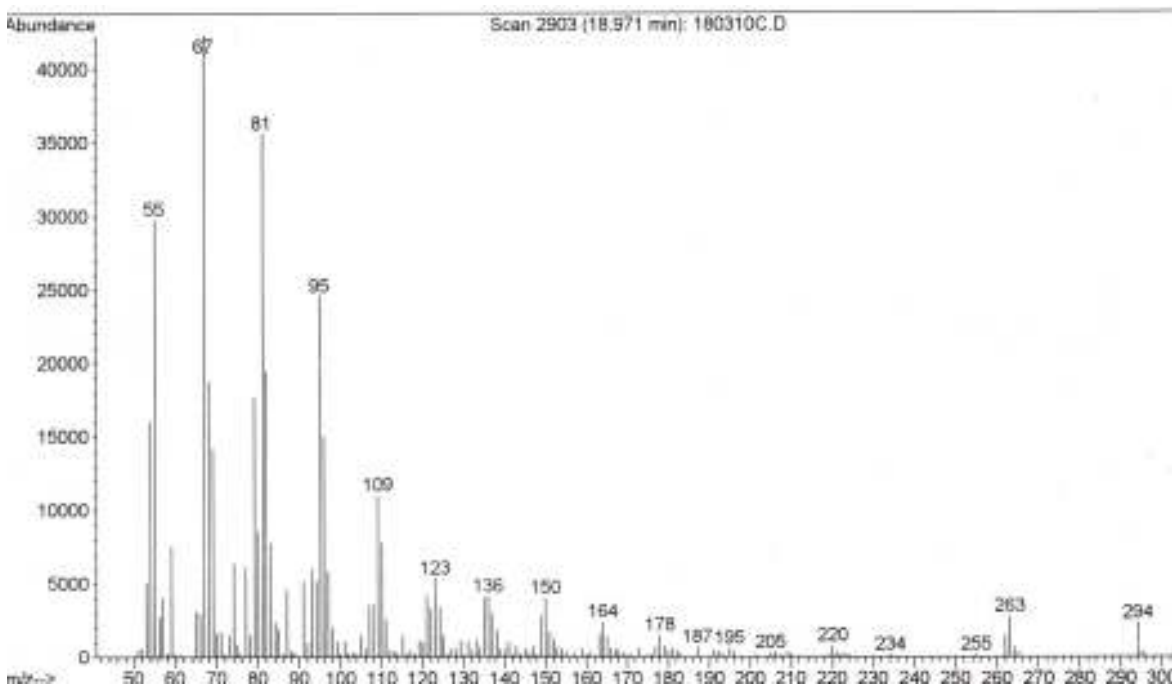


Figure 29. MS spectrum for C18:2 biodiesel component from standard GLC-10

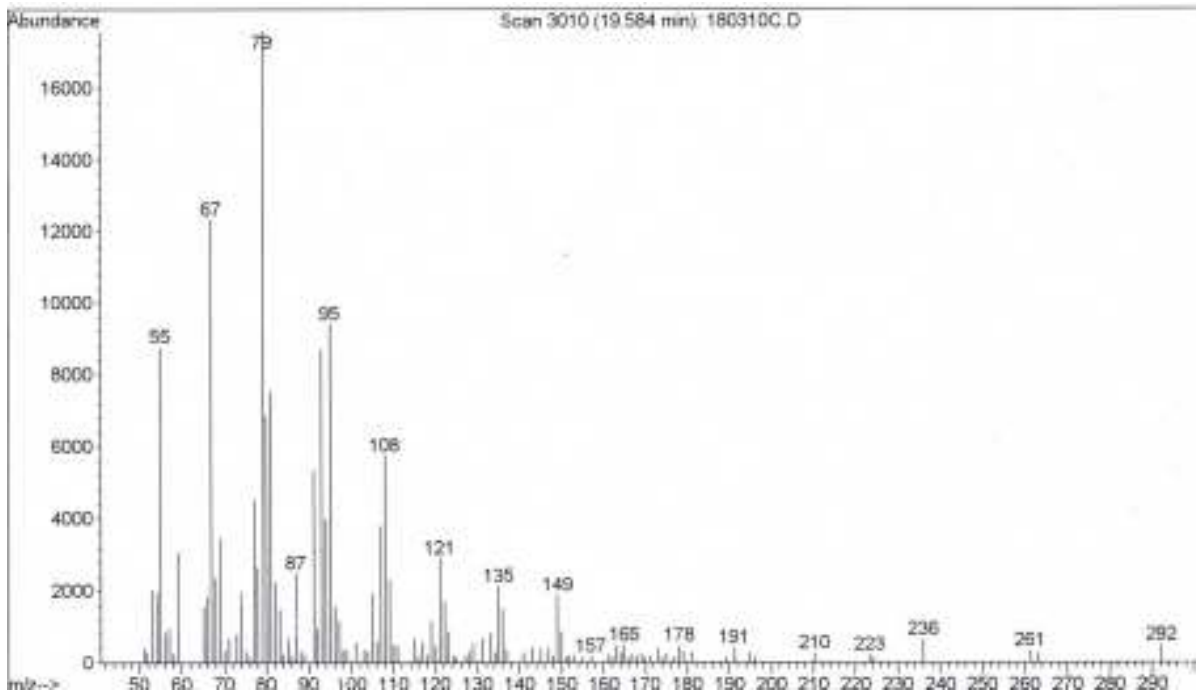


Figure 30. MS spectrum for C18:3 biodiesel component from standard GLC-10

Figure 31 shows the GC chromatogram for biodiesel sample. Biodiesel sample aliquot of 50 microliters using 0.5% PTSA for pre-treatment was diluted in 5 milliliters of hexane. Retention times for palmitate (17.18 min), stearate (18.54), oleate (18.25 min), linoleate (18.48 min) and linolenate (19.77 min) were within experimental error from those obtained for the GLC-10 standard.

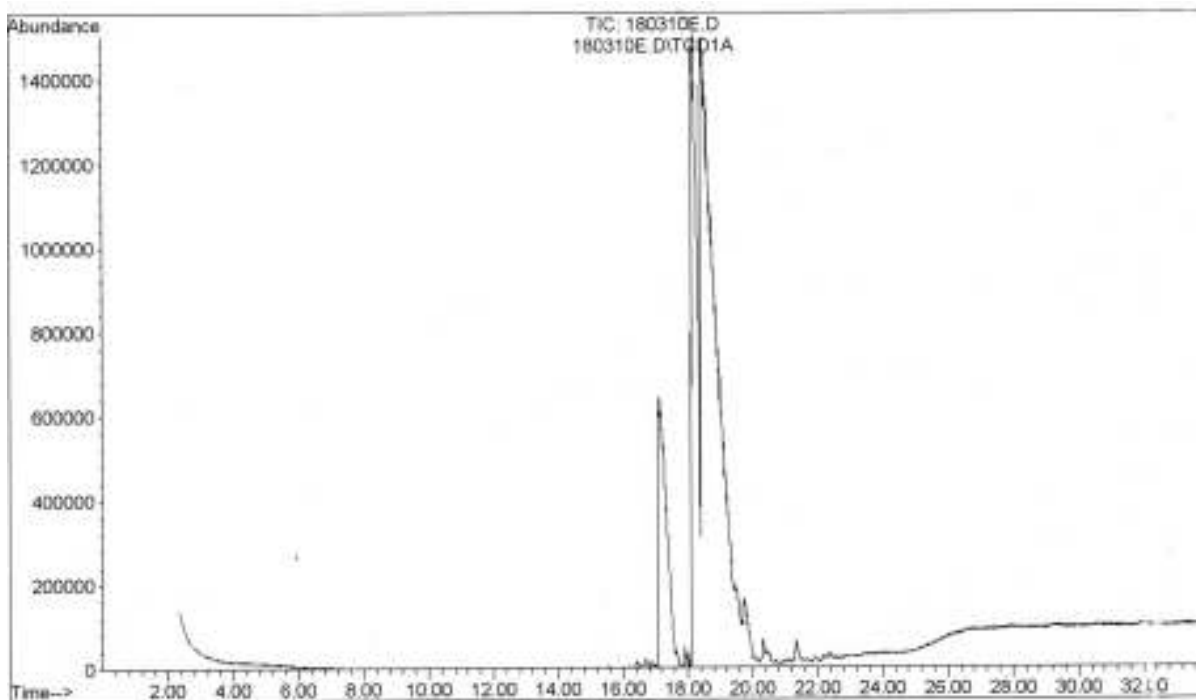


Figure 31. Chromatogram for Biodiesel sample

Usually the first strategy for identifying an unknown compound is to compare its experimental mass spectrum against a library of mass spectra. Standard GLC-10 gives us the guidance for the mass-to-charge ratio for each component. Figure 32 shows a mass-to-charge ratio of 270 which identifies the peak at a retention time of 17.18 min as C16 component. Figure 33 shows a mass-to-charge ratio of 298 which identifies the peak at a retention time of 18.55 min as C18:0 component. Figure 34 shows a mass-to-charge ratio of 296 which identifies the peak at a retention time of 17.18 min as C18:1 component. Figure 35 shows a mass-to-charge ratio of 294 which identifies the peak at a retention time of 17.18 min as C18:2 component. Figure 36 shows a mass-to-charge ratio of 292 which identifies the peak at a retention time of 17.18 min as C18:3 component.

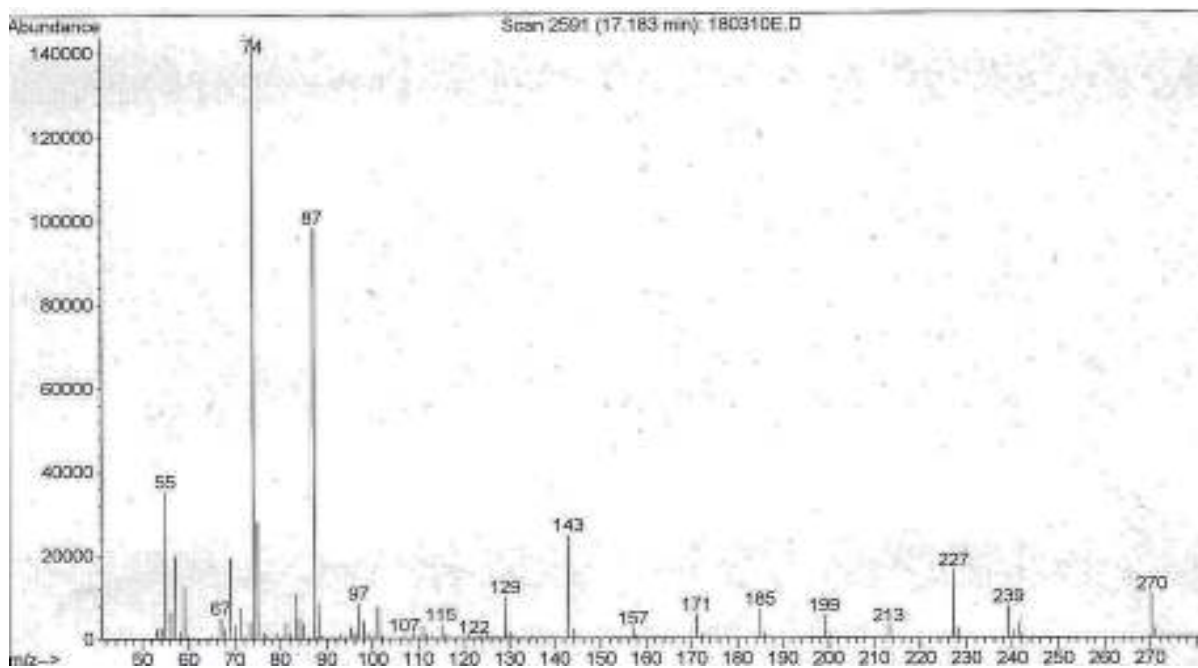


Figure 32. MS spectrum for C16 biodiesel component from biodiesel sample

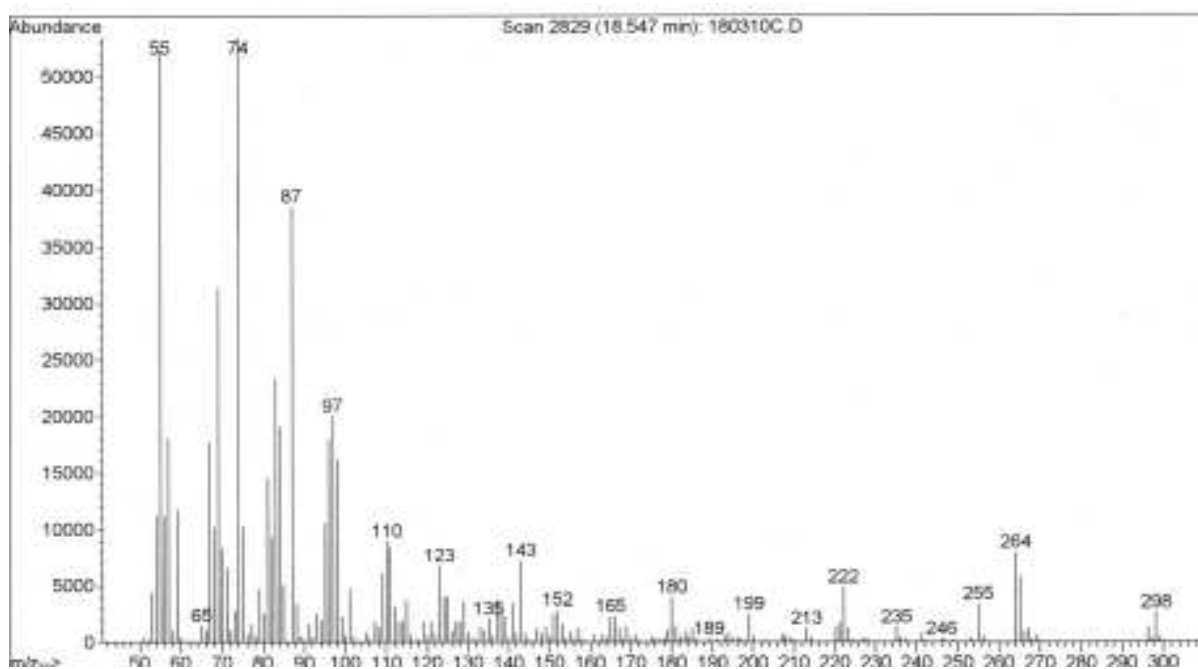


Figure 33. MS spectrum for C18:0 biodiesel component from biodiesel sample

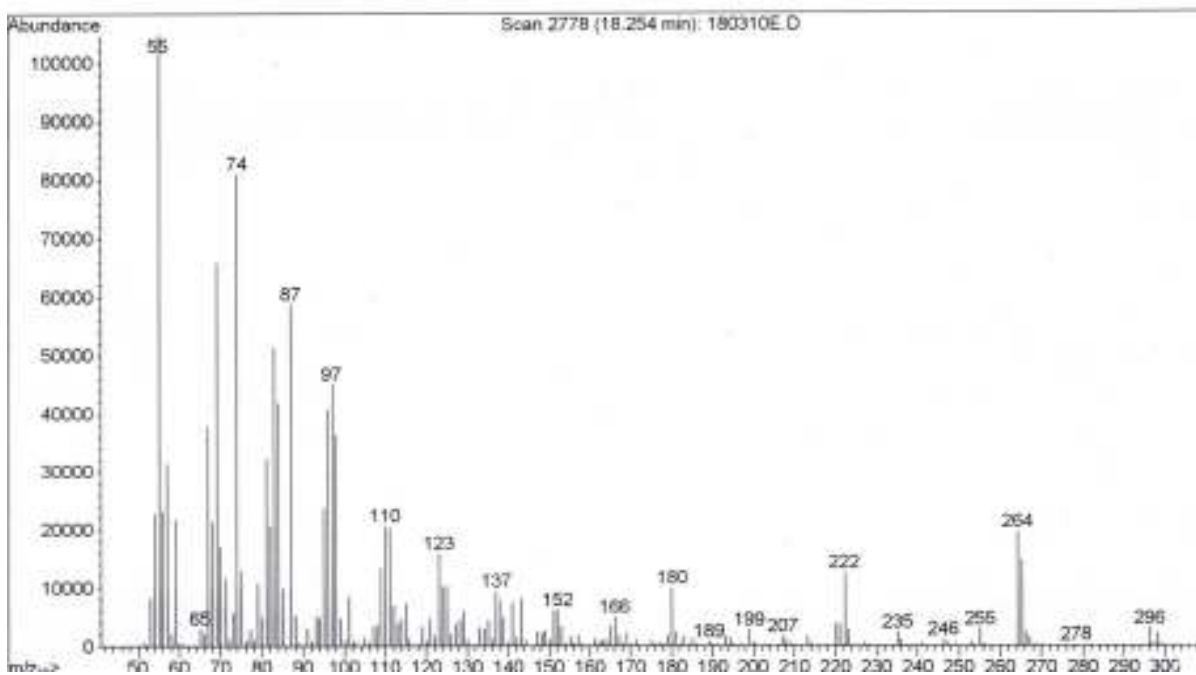


Figure 34. MS spectrum for C18:1 biodiesel component from biodiesel sample

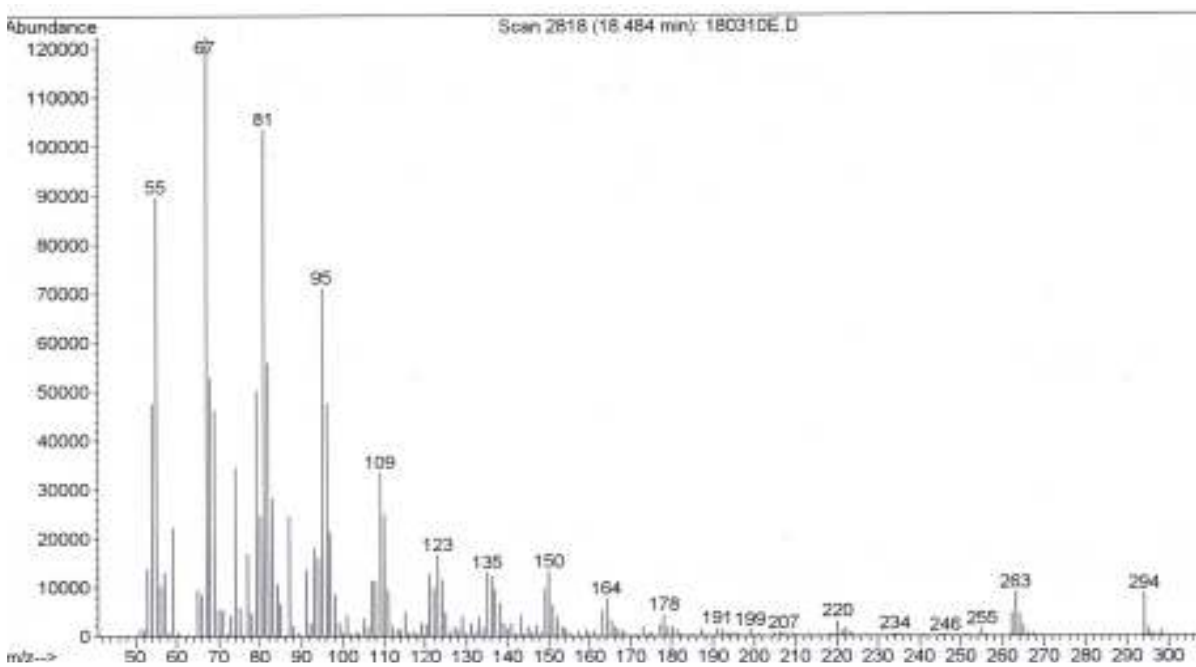


Figure 35. MS spectrum for C18:2 biodiesel component from biodiesel sample

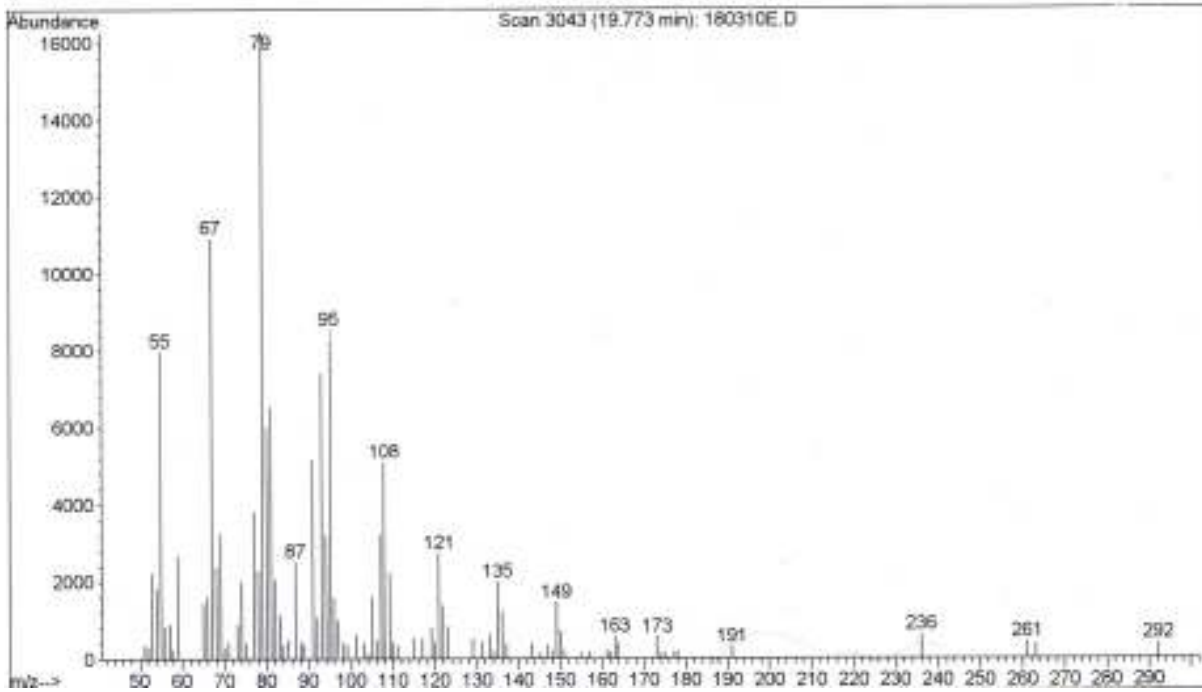


Figure 36. MS spectrum for C18:3 biodiesel component from biodiesel sample

3/27 test

The test was performed twice on every batch produced. No fallout was observed in the biodiesel batches produced. This means that no triglycerides were found in the biodiesel during the test and conversion was completed.

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions, observations and recommendations for this project are the following:

High acid concentrations for acid pre-treatment using microwave heating cannot be used together. High-acid concentrations attached to microwave superheating effects leads to side reactions producing ether, acids and alcohol instead of the ester needed in biodiesel reaction process. Reduction in PTSA concentration using microwave heating did not make a significant change in the reaction; no phase separation was observed.

Pre-treatment of recycled cooking oil with alcohols catalyzed by strong acids within a microwave oven is a complex reaction where the reaction acceleration comes from the oscillating microwave and the constant alignment of the molecule dipole leading to high acid number reduction. Strong acids and highly polar molecules conduct heat by dipolar polarization. Another way to conduct heat is by ionic conduction. Ionic liquids are environmentally friendly and can conduct heat due to ionic conduction. The use of ionic liquids as catalyst for transesterification reaction is recommended as future works.

Graphs of the acid number reduction with time were very helpful to understand the effect of microwave heating in the acid number reduction.

High polarity of the sulfuric acid versus lower polarity of the oil leads to slower reaction rate and less reduction in acid number. PTSA has an acid constant similar to sulfuric acid but due to both, the acid and the oil are of organic nature, reduction in acid number was greater.

Alkali transesterification reaction was performed following literature recommendations [9]. This reaction was completed in 10 minutes.

GC/MS was very helpful in biodiesel characterization. It identified typical biodiesel peaks and m/z and it was compared to GLC-10 standard injected.

The 3/27 test indicated that waste vegetable oil was fully converted into biodiesel. The 3/27 test is an easy to do test to conduct, and is the preferred choice of biodiesel homebrewers. No presence of fallout was observed in all tests. Results of the 3/37 test showed there were no triglycerides present in biodiesel produced.

In order to improve pre-treatment reaction time several steps should be followed:

1. Reaction time should be maintained at 15 minutes because the objective of microwave heating is to reduce reaction time.
2. Reaction temperature, molar to oil ratio or quantity of catalyst could be reduced.
3. Perform a two step acid pre-treatment. In the first step, 75% of the reagents could be mixed, allow the reaction to proceed for 15 minutes; for phase separation allowed 24 hours and after removal of aqueous phase, addition of the rest of the reagents. Pre-treatment should also be tested with oils containing higher free fatty acids.

After pre-treatment optimization, time reduction in alkali transesterification reaction should be made. Reduction in alkali catalyst should be tested, increasing reaction temperature.

Based on the results from our studies seems reasonable to increase the relative amount of PTSA from 5% to 10%. In addition, is it also reasonable to reduce the relative amount of PTSA from 0.5% to 0.05% to test whether PTSA amount is truly catalytic in nature.

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APPENDIX A

EXPERIMENTAL DATA

Table 1. Acid Number with 5% w/w of three different acids with uncontrolled temperature

Time (minutes)	Acid Number (mg KOH/ g sample)					
	Sulfuric Acid		Hydrochloric Acid		PTSA	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
Oil	37.65					
0	35.67	35.67	35.67	35.67	28.0901	35.67
1	36.11	37.41	24.91	24.80	37.3631	37.45
5	27.59	28.55	21.68	20.19	12.45	16.46
10	26.81	26.34	17.75	18.82	12.07	14.35
15	24.78	23.90	16.06	16.50	11.90	12.64
20	23.45	21.22	16.42	17.01	10.32	10.72
25	21.96	20.56	16.23	16.99	11.76	11.10
30	21.87	20.00	16.54	17.32	9.74	10.88
35	19.24	18.20	16.36	16.19	7.44	8.22
40	19.34	17.98	16.43	16.66	6.75	8.18
45	22.12	17.90	16.42	15.97	7.07	7.50
50	18.94	18.29	16.36	15.80	9.35	8.40
55	18.50	17.47	16.28	15.68	4.44	5.75
60	18.98	17.60	16.26	15.71	1.38	2.34
After 24 hours	5.18	6.24	14.91	13.89	6.51	7.19

Table 2. Acid Number variation using different PTSA concentrations with uncontrolled temperature

Time (minutes)	Acid number using PTSA Acid (mg KOH/ g sample)			
	2.5 % w/w	1.0 % w/w	0.5 % w/w	0.1 % w/w
Oil	37.65			
0	14.92	15.24	19.71	18.33
1	14.64	14.77	12.38	15.76
10	6.72	5.42	14.56	15.01
20	4.01	5.28	6.84	10.24
30	4.17	6.21	16.81	12.97
40	4.10	5.90	1.36	3.66
50	4.11	5.75	1.35	3.90
60	6.41	6.00	1.28	3.82
After 24 hours	24.75	22.87	9.58	10.24

Table 3. Acid number variation for PTSA pre-treatment at room temperature

Time (minutes)	Acid Number using PTSA acid (mg KOH/g sample)	
	Trial 1	Trial 2
Oil	37.65	
0	9.36	11.20
1	12.46	13.04
10	12.07	12.79
20	11.76	10.44
30	9.74	8.69
40	6.75	6.93
50	9.34	7.54
60	1.38	3.22
After 24 hours	4.51	3.89

Table 4. Acid number variation with time for the three acids at 5% w/w concentration with 15 minutes reaction time

Time (minutes)	Acid Number (mg KOH/g sample)								
	Sulfuric Acid			Hydrochloric Acid			PTSA		
Oil	35.67								
0	29.63	32.32	28.28	28.54	30.47	27.77	30.23	29.33	30.37
5	21.01	16.75	20.87	14.42	18.07	15.38	15.68	17.65	16.85
15	20.80	12.46	16.65	10.46	13.96	12.07	11.73	10.93	9.92
After 24 hours	10.69	7.76	11.21	8.13	8.29	7.86	3.97	4.01	4.54

Table 5. Acid Number change with 15 minutes reaction times for different PTSA concentrations

Time (minutes)	Acid Number (mg KOH/g sample)								
	PTSA 2.5% w/w			PTSA 1.0 % w/w			PTSA 0.5 % w/w		
Oil	35.67								
0	27.61	26.50	27.49	29.50	26.34	26.71	30.05	28.92	32.82
5	15.36	17.43	17.15	17.57	13.97	15.56	16.87	14.93	17.93
15	11.16	13.11	14.00	11.83	9.81	12.58	10.04	9.98	13.36
After 24 hours	4.69	5.26	5.88	6.15	5.53	6.95	7.88	8.03	8.38