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Enhancing biodiesel production from soybean oil using ultrasonics

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Enhancing biodiesel production from soybean oil using ultrasonics

by

Priyanka Chand

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Agricultural Engineering

Program of Study Committee:
David Grewell, Major Professor
Larson Dunn, Jr.
John G. Verkade

Iowa State University

Ames, Iowa

2008

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DEDICATION

This work is dedicated to my family

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ABSTRACT

Biodiesel, or fatty acid alkyl ester, is a non-toxic, biodegradable and renewable source of energy. It is mostly produced from vegetable oils. Other sources include animal fat, oils obtained from algae, fungi, bacteria, etc. Esterification of oil with alcohol in the presence of moderate temperature (60°C) and a catalyst to produce fatty acid alkyl esters is known as transesterification. The transesterification process, facilitated by mechanical mixing, is commercially used to produce biodiesel.

In industry, biodiesel is characterized using proton nuclear magnetic resonance spectroscopy (^1H NMR spectroscopy). In the first section of this study, thermogravimetric analysis (TGA) is demonstrated as a potential method for monitoring biodiesel production by transesterification of soybean oil with methanol. Soybean oil and commercially available biodiesel were mixed in varying proportions by weight as standards. In addition, mixtures of different biodiesel/soybean oil ratios were also created by periodically interrupting base-catalyzed transesterification of soybean oil with methanol. The mixtures produced by both approaches were analyzed with TGA and the results were then compared with analytical data obtained by NMR spectroscopy. It was found that results from both analytical methods were in good agreement ($\pm 5\%$). Thus TGA is a simple, convenient, and economical method for monitoring biodiesel production for screening characterization.

In the second section of this study, the effect of ultrasonics on biodiesel production is studied by applying ultrasonics during transesterification reaction to the

reactants, i.e., soybean oil and methanol, in the presence of sodium hydroxide as a catalyst. Ultrasonics are sound waves of a high frequency above the audible range of humans. Ultrasonic energy was applied in two different modes: pulse and continuous sonication. Soybean oil was mixed with methanol and sodium hydroxide and was sonicated at three amplitudes ($60 \mu\text{m}_{\text{pp}}$, $120 \mu\text{m}_{\text{pp}}$ and $180 \mu\text{m}_{\text{pp}}$) in pulse mode (5 s on/ 25 s off). In the continuous mode, the same reaction mixture was sonicated at $120 \mu\text{m}_{\text{pp}}$ for 15 s. The reaction was monitored for biodiesel yield by stopping the reaction at selected time intervals and analyzing the biodiesel content by TGA. The results were compared to a control group where the same reactant composition was allowed to react by mechanical stirring at $60 \text{ }^\circ\text{C}$ without ultrasonic treatment. It was observed that ultrasonic treatment resulted in a 96 % yield (percent conversion to biodiesel) in less than 90 s using the pulse mode; compared to 30 to 45 minutes for the control sample. In continuous sonication, the highest biodiesel conversion of 86 % was obtained at 15 s. It was also found that significantly less energy was used to produce biodiesel with ultrasonics compared to conventional heating and stirring.

Thus biodiesel can be produced at a faster rate and the high efficiency of commercial methods can be maintained by using ultrasonics.

CHAPTER 1: INTRODUCTION

1.1 Introduction

Over the last few decades, the world has experienced an alarming increase in consumption of fossil fuels such as coal, oil, natural gas, etc. Fossil fuels are hydrocarbon deposits formed inside the earth's crust by the decay of plant and animal matter over long periods of time extending up to millions of years. They are non-renewable sources of energy. Today's majority of industrial as well as household activities are accomplished by using energy derived from these fossil fuels. Due to the increasing world population and industrialization, the demand of fossil fuels is also increasing proportionally. The growth in world energy consumption in 2007 was 2 % per year and a growth rate of 1.1 % per year is expected in the future [1]. There is a finite reserve of these depleting fuel sources. Therefore, there have been continuous efforts to explore new renewable sources of energy so that the demand on fossil fuels is reduced.

Another concern regarding the use of fossil fuels is their detrimental effects on the environment. Large amounts of particulate matter, sulfur, and green house gases, such as carbon dioxide and carbon monoxide, are constantly released into the atmosphere by burning fossil fuels. These gases pollute the atmosphere and cause green house effects that ultimately lead to global warming.

A solution to this problem is renewable energy resources also known as alternate fuels or non-conventional sources of energy. Alternate fuels refer to substances that have

characteristics similar to fossil fuels and can efficiently replace fossil fuels. Examples of renewable fuels include biodiesel produced from vegetable oils and ethanol produced from plant biomass. According to the Energy Policy Act of 1992, pure biodiesel (B100) is considered to be an alternative fuel in the United States [2]. Alternate fuels are mostly produced from plant/ animal feedstock; therefore, they are renewable and biodegradable in nature. Combustion of B100 reduces carbon dioxide content in atmosphere. Combustion of biodiesel produces 8.7 % less carbon dioxide per kilogram than diesel [3]. B100 also reduces atmospheric carbon monoxide content by 35 %, sulfur oxides by 8 % and particulate matter by 32 % [4]. Carbon dioxide released from the combustion of these fuels is absorbed by the plants and these same plants are used for additional biodiesel production. Thus carbon dioxide is recycled in the atmosphere, forming a closed system.

Biodiesel is produced primarily from vegetable oil, but there are various other sources currently being used or studied for biodiesel production, such as animal fats, algae, fungi and bacteria. Pure biodiesel sold as B100 can be directly used in standard diesel engines. The disadvantage of using pure biodiesel is its high viscosity, which leads to poor engine performance. To overcome this problem, biodiesel is typically blended with standard diesel fuel. In more detail, B20 contains 80 % diesel and 20 % biodiesel. B5 blend contains 5 % biodiesel and 95 % diesel. Both of these blends are acceptable for use in most diesel engines. It is important that, when using these blends in any diesel engine, the biodiesel should be pure and meet the quality standard D 6751 specified by ASTM International (American Society of Testing and Materials).

The acceptability of biodiesel blends has increased the demand of biodiesel in recent years, as is evident from Figure 1. There has been a sudden increase in biodiesel

production in 2005 and this trend is continuing. According to the National Biodiesel Board, there are 105 plants in operation as of early 2007 with an annual production capacity of 864 million gallons.

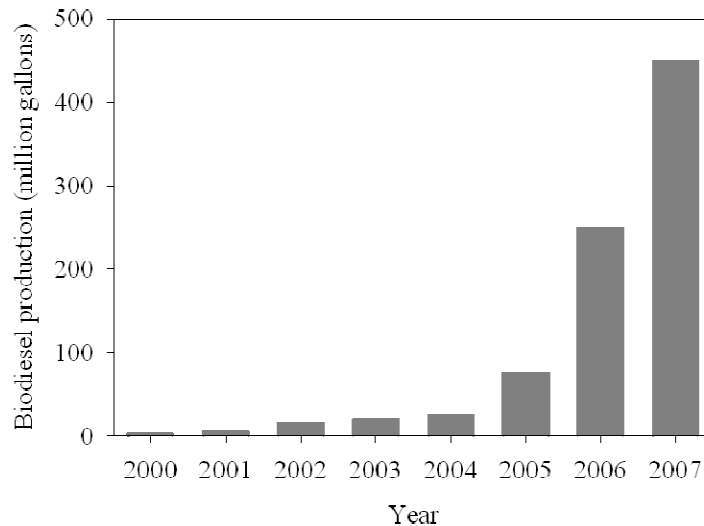


Figure 1. Trend of biodiesel production in United States in recent years [5]

With the increase in the demand for biodiesel, new methods of increasing and enhancing biodiesel production are being researched. The commercial method of biodiesel production is time consuming and energy intensive. It is a batch process that requires maintaining the reactants at a temperature of 60 °C for 1–2 h. In some protocols, the process is repeated 2–3 times. With optimized conditions, a theoretical yield as high as 97–98 % can be achieved.

1.2 Biodiesel

Biodiesel is a term given to fatty acid alkyl esters produced as a result of transesterification reaction between a triglyceride and any alkyl alcohol. It is an alternative fuel and can be used in diesel engines. It is processed mainly from vegetable oils, is non-toxic and free of sulfur and aromatic compounds. Biodiesel has properties similar to diesel fuel, but has many advantages compared to diesel fuel:

- **Reduction of carbon dioxide emissions:** Carbon dioxide is a greenhouse gas and a major contributor of global warming. Combustion of pure biodiesel B100, when use in engines, produces less carbon dioxide emissions [3].
- **High oxygen content:** Oxygen content in biodiesel fuel facilitates its complete combustion. Biodiesel contains 10–11 % more oxygen by wt. as compared to diesel.
- **Reduction of carbon monoxide emissions:** Carbon monoxide is also an important greenhouse gas and causes serious health hazards by blocking oxygen intake in humans and animals. B100 reduces carbon monoxide emissions by 35 % [4].
- **Reduction of particulate matter emissions:** Particulate matter is a mixture of complex organic and inorganic compounds, such as carbon residues, unburnt fuel, lubricating oil components, metal ash, etc., some of which are carcinogenic in nature. B100 reduces particulate matter emission by 32 % [4].
- **Reduction of sulfur oxides emissions:** sulfur dioxide causes respiratory tract irritation. Biodiesel fuel is sulfur-free, as long as sulfuric acid is not used in the biodiesel production process. B100 reduces net sulfur oxide emissions by 8 % [4].

- **Higher flash point:** Flash point is the temperature at which a fuel becomes flammable. Biodiesel has higher flash point (≥ 120 °C) than diesel fuel (≥ 55 °C), which makes it less hazardous during fuel transport and storage.

The density and energy value of biodiesel is comparable to diesel as shown in Table 1.

Table 1. Average density and heating value of diesel, biodiesel and blends [4]

Fuel	Density (g/cu. cm)	Net heating value Avg. (MJ/l)
No. 2 Diesel	0.850	36.09
Biodiesel (B100)	0.880	32.97
B 20 Blend (B20)	0.856	35.47
B 2 Blend (B2)	0.851	36.03

The energy content of biodiesel is 37.2 MJ/kg, which is slightly lower than the energy content of diesel (42.6 MJ/kg). Biodiesel combustion does not produce any NO_x emissions. NO_x emissions are mainly produced by aromatic hydrocarbons, which represent 25–35 % by wt. of diesel fuel. Table 2 shows a comparison of the properties of No. 2 diesel and biodiesel fuels [6].

Table 2. Properties of B100 biodiesel and No. 2 diesel fuel [6]

Fuel property	No. 2 Diesel	Biodiesel (B100)
Fuel standard	ASTM D975	ASTM D6751
Lower heating value Btu/gal	129,050	118,170
Kinematic viscosity cSt @ 40 °C	1.3-4.1	4.0-6.0
Specific gravity kg/l @ 60 °F	0.85	0.88
Density, lb/gal @ 15 °C	7.079	7.328
Water and sediment, vol %	0.05 max	0.05 max
Carbon, wt. %	87	77
Hydrogen, wt. %	13	12

Oxygen, by dif. wt. %	0	11
Sulfur, wt. %	0.05 max	0.0 to 0.0024
Boiling point, °C	180 to 340	315 to 350
Flash point, °C	60 to 80	100 to 170
Cloud point, °C	-15 to 5	-3 to 12
Pour point, °C	-35 to -15	-15 to 10

1.3 Transesterification

Transesterification is the process of modifying esters. In more detail, triglycerides such as oils from vegetables can be transesterified into long chain alkyl esters known as biodiesel. The reaction between a triglyceride (present in vegetable oil) and alkyl alcohol produces alkyl esters and glycerol. Examples of triglycerides are vegetable oil, fatty tissues, or tallow obtained from animals. The alkyl alcohols generally used are methanol and ethanol. Figure 1 details the transesterification reaction between a vegetable oil, such as soy oil, corn oil, etc., and methanol.

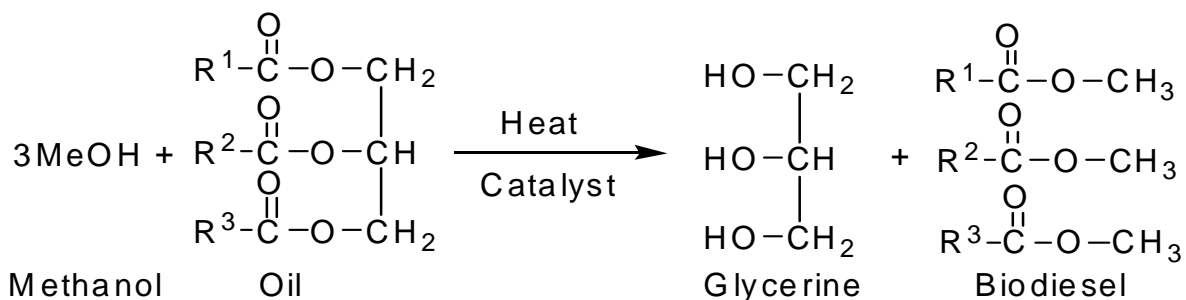


Figure 2. Transesterification reaction

Transesterification reactions were first described in 1852 [7]. They were used in industry mainly for high quality soap and water free glycerol production. It was not until

the 1980's that production of vegetable oil methyl esters for use in diesel engines was industrialized.

1.3.1 Mechanism of transesterification reaction

Figure 3 details the mechanism of an alkali catalyzed transesterification reaction. This reaction takes place in three steps. Triglyceride is converted into a diglyceride in the first step, monoglyceride in the second step, and glycerol in the third step. All the steps of this reaction are reversible, therefore an excess of alcohol is typically provided to promote the reaction in a forward direction. The final products of the reaction are fatty acid methyl esters (or biodiesel) and glycerol, which form two separate immiscible layers, biodiesel forming the top layer and glycerol forming the bottom layer.

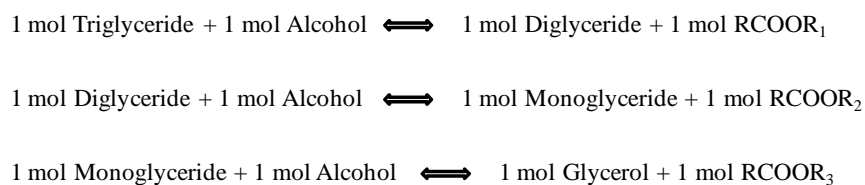


Figure 3. Step by step transesterification reaction [8]

1.3.2 Requirements of the transesterification reaction

In order to successfully promote transesterification of oils, there are three requirements:

- **High temperature:** This reaction occurs efficiently at a temperature between 50-70 °C. The reaction will occur at room temperature, but it will take longer for completion.
- **Catalyst:** A catalyst is required to increase the reaction rate. Various catalysts have been studied. Examples of common catalysts for the reaction include homogeneous strong base catalysts, such as alkali metal hydroxides and alkoxides, metal oxides, and acid catalysts such as HCl and H₂SO₄. Alkali metal alkoxides and hydroxides are considerably more effective catalysts than acid catalysts and in addition, they operate at lower temperatures.
- **Mechanical mixing:** Because oil and methyl alcohol have different densities, they tend to separate and form two different layers due to gravity. For this reason they have to be continuously stirred/ mixed to facilitate the reaction.

1.3.3 Factors affecting transesterification

Assuming the requirements of transesterification are met, process optimization is affected by a range of factors, which are detailed in Sections 1.3.3.1 to 1.3.3.4.

1.3.3.1 Molar ratio of vegetable oil to alcohol

Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature [9]. The stoichiometric ratio required for transesterification is 1:3 moles of vegetable oil to alcohol. However, it has been found that the molar ratio of vegetable oil to alcohol depends on the type of catalyst used for the reaction. For example, the molar ratio of 1:6 moles of soybean oil to methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an excess of alcohol is required to drive the reaction [10]. For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used [11].

1.3.3.2 Moisture content

Water content promotes the formation of soap during the reaction and reduces catalyst efficiency. The presence of water in acid catalyzed transesterification reduces the percentage of biodiesel produced to a greater extent compared to an alkaline catalyst. For example, in a reaction mixture of soybean oil, methanol and sulfuric acid, 0.5% water content reduces the resultant biodiesel conversion from 95% to 90% [12].

1.3.3.3 Free fatty acids

For an alkali catalyzed transesterification reaction, vegetable oil should not contain any free fatty acids. If any free fatty acids are present in the vegetable oil, an alkaline catalyst (e.g. NaOH) is utilized in neutralizing these free fatty acids which only

consumes the catalyst and slows down the reaction. The acid value of glycerides should be less than 1 for a NaOH-catalyzed transesterification reaction [13]. Acid value is the milligrams of potassium hydroxide (KOH) required for neutralizing the free fatty acids present in 1 g of vegetable oil.

1.3.3.4 Catalyst

Transesterification reactions can occur in the absence of catalysts, [14] however, it requires high temperature, pressure and long reaction times. If all these requirements are met, the process cost is relatively high. This method produces relatively high purity esters and soap-free glycerol, but because it is un-economical, it is typically not considered for industrial production of biodiesel.

Three types of catalysts are generally used for biodiesel production: alkaline catalysts, acidic catalysts, and enzymes.

Alkaline catalysts: Alkaline catalysis is the most commonly used process for biodiesel production. Its main advantage is that a high ester yield is obtained in short reaction times under mild reaction conditions [12]. However, alkaline catalysts are highly sensitive to free fatty acids in vegetable oils. Therefore only low acidic vegetable oils produce high ester yields after transesterification. However, de-acidification of vegetable oil prior to transesterification reduces this issue. Examples of alkali catalysts are: sodium hydroxide, potassium hydroxide, alkali metals (such as sodium), alkali metal carbonates (such as sodium carbonate, and potassium carbonate).

Acidic catalysts: Acid-catalyzed transesterification requires a relatively high temperature (~100 °C), pressure (~5 bars) and large amounts of alcohol. It is also slower in comparison to alkaline catalysis. The only advantage of this type of catalytic conversion is that it can efficiently esterify free fatty acids in vegetable oils and is therefore used to transesterify high free-acid-containing feedstock, such as waste edible oil [15].

Enzymes: Enzymes or lipases extracted from microorganisms can also be used as catalysts for the transesterification reaction [16].

The advantages of these biocatalysts are:

- Biodiesel conversion under mild temperature, pressure, and pH conditions.
- No catalyst residues or soap in the final product.
- High quality glycerol is produced.
- These catalysts efficiently esterify free fatty acids and thus can be used for transesterification of oils or fats containing high free fatty acid contents.

The disadvantages of these catalysts include:

- Long reaction times and higher catalyst concentrations are required.
- These catalysts are expensive and not economical for commercial use.
- Enzymes are typically difficult to remove from the final products (i.e., biodiesel and glycerol) after the reaction is complete.

1.3.4 Feedstock for biodiesel production

The various feedstocks for biodiesel production include:

- Vegetable oils, including soybean oil, sunflower oil, rapeseed oil, corn oil, oil palms, peanut oil, cottonseed oil, coconut oil, olive oil and jatropha oil.
- Waste vegetable oil.
- Animal fats and fish oil: These are by-products of meat and fishery industries and are available at relatively low prices. These include beef tallow, lard, and fish oil.
- Oil extracted from algae, bacteria, and fungi [17].

In the United States, soybean oil is the main feedstock for vegetable oil production, followed by canola and corn oils. This is due to their availability and high oil content. Approximately 90 % of biodiesel produced in the US is processed from soybean oil. The average soybean yield in Iowa in 2007 was 50 bu/ac [18].

1.3.4.1 Soybean oil

Soybean seeds contain an average of 20% oil by wt. Typical fatty acid composition of soybean oil is detailed in Table 3 [15]. Mechanical extraction of soybean oil has historically been the extraction method typically used. In this process, a hydraulic press squeezes the oil from the beans. Although the soybean oil obtained by this method is free of impurities, the yield is low and a significant amount of oil remains in the soy meal. Hexane extraction is a more efficient method of oil extraction and is used widely in newer soybean oil extraction plants. For hexane extraction, soybeans are first dehulled by cracking and separating hulls by mechanical separation. Cracked soybeans are then heated to a temperature of 75 °C. These cracked beans are then cut into flakes and put in counter-flow hexane percolation extractors. Hexane dissolves soybean oil from flakes

and is collected separately. Soybean oil is separated from hexane in evaporators and recovered hexane is recycled into the process.

Table 3. Fatty acid composition of soybean oil

	16:1 [wt%]	18:0 [wt%]	18:1 [wt%]	18:2 [wt%]	18:3 [wt%]
Soybean oil	11-12	3-5	23-25	52-56	6-8

1.4 Characterization of biodiesel produced from vegetable oil using thermogravimetric analysis

Thermogravimetric analysis is a method of measuring changes in composition of a substance (element or compound) relative to the change in weight of the substance as a function of temperature [19]. It can be used to measure the amount of biodiesel and soybean oil present in a mixture of soybean oil and biodiesel.

Figure 4 shows the set-up for thermogravimetric analysis. The sample is placed in a pan in a furnace and is weighed by a sensitive balance. A gas (oxygen or nitrogen) is continuously purged into the furnace. The temperature of the furnace is programmed to increase at a particular rate with time. The highest temperature obtained in most thermogravimetric furnaces is 1500 °C and the rate of temperature change is 1 °C to 50 °C. The weight loss percent of the sample is monitored throughout the process. The weight loss of the sample is relative to the weight percentage of the components of the sample.

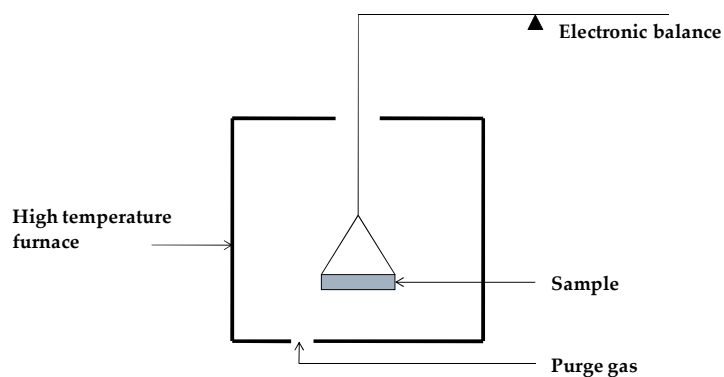


Figure 4. Thermogravimetric analysis furnace

Figure 5 shows the thermogravimetric plots for pure biodiesel and pure soybean oil. The mass of the biodiesel starts to decrease approximately at temperatures higher than 150 °C and it continues its decrease until all the biodiesel present in the sample is vaporized. Similarly, evaporation of soy oil starts at approximately 350 °C. Because these evaporation temperatures vary by a relatively large amount (ca 200 °C), this method is quite effective in distinguishing biodiesel from soybean oil.

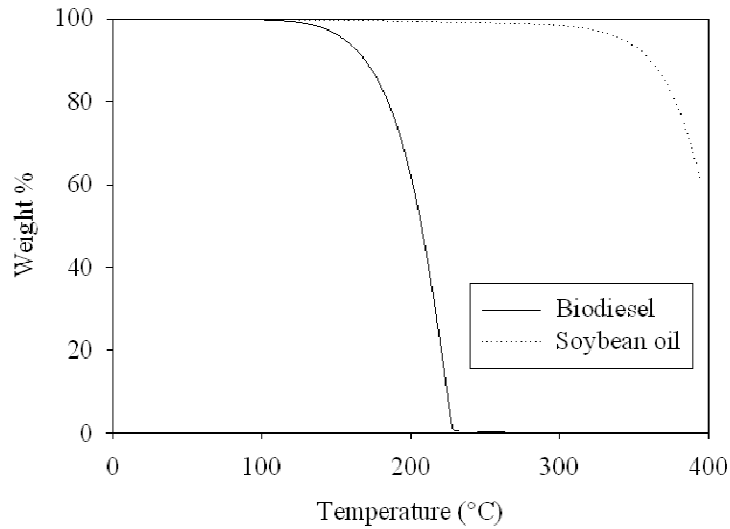


Figure 5. Overlay of thermogravimetric curves for pure biodiesel and soybean oil (mass % versus temperature)

1.5 Ultrasonics

Ultrasonics is the term used for sound waves having frequencies higher than the normal human hearing range (i.e., > 18 kHz) [20]. Ultrasonic waves propagate in a medium as a series of alternate compression and rarefaction regions of pressure as detailed in Figure 6 [21]. The frequency of a sound wave is defined as the number of waves that pass through a single point at unit time (s). Wavelength is the peak to peak distance between two adjacent waves.

Ultrasound can be divided into two categories:

- High power ultrasound: These ultrasonic waves have high power and typically lower frequency. These waves, if applied to liquids, have the potential of producing physical and chemical changes in the liquids. They are used in industry for welding,

cleaning, chemical reactions, etc. They typically have a frequency range of 20 kHz – 100 kHz.

- **Low power ultrasound:** These ultrasound waves typically have high frequency and low power. They do not cause and chemical physical changes. They are used to measure velocity and the absorption coefficient of waves in a medium, and thus are used in medical scanning, imaging, treatments of stains, dentistry, etc. High frequency ultrasonic waves have small wavelengths that enable detection and imaging of small areas with high definition. Frequencies of 1-10 MHz are used for this purpose.

Ultrasonic waves or ultrasound has been used in industry for many years. The first commercial application of ultrasound was in 1917, when it was used for estimating the depth of water through an echo-sounding technique. Ultrasound has found its application in many fields, including:

- **Industry:** Ultrasonic welding and ultrasonic cleaning are the most common applications of high power ultrasonics. It is also used for drilling, cutting, and grinding. Low power applications include non-destructive testing and flaw detection.
- **Medicine:** Ultrasound imaging (2-10 MHz) is used in obstetrics, cleaning, drilling of teeth, and muscle strain treatments (20-50 kHz).
- **Biology and biochemistry:** High power ultrasound is used for cell disruption, filtration (e.g. reducing clogging of filters and by increasing filtration rates), degassing of liquids, crystallization (by producing more uniform and smaller crystals in supersaturated solutions), and dispersion of solids. The use of ultrasonics in chemistry is known as sonochemistry. Research has shown that ultrasonics can

accelerate the rate of reaction in many chemical reactions. This is also true for the experiments in this thesis.

Ultrasonics do not directly react with liquids in a chemical reaction but it induces several physical effects in the liquid that help in increasing the reaction rate; namely cavitation and streaming, which are detailed in the following sections.

1.5.1 Cavitation

Cavitation is the phenomenon of the generation of large numbers of microbubbles (cavities) in a liquid when a negative pressure is applied. When sound waves propagate through a liquid medium, they generate compression and rarefaction regions in the liquid. The intermolecular distances between the liquid molecules also expand and contract along these waves. At very low pressure in the rarefaction region, the intermolecular spaces exceed the critical molecular distance and the liquid tears apart to form void spaces or micro bubbles. These micro bubbles oscillate with the wave motion and grow in size by taking in vapor from the surrounding liquid medium and by aggregating with other micro bubbles [21]. Within a few cycles they grow to an unstable size and collapse violently, releasing large amounts of energy and creating localized temperatures of up to 5000 °K [22]. The growth and subsequent collapse of cavitation bubbles is shown in Figure 6. The bubble collapse produces high shear forces which mix the liquid vigorously and fracture nearby particles.

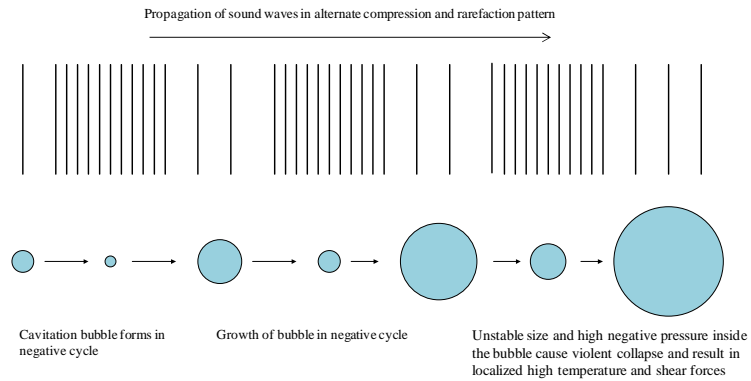


Figure 6. Growth and collapse of cavitation bubble in a liquid medium when ultrasonic waves are applied

1.5.2 Acoustic streaming

When ultrasonic waves are introduced into a liquid, movement of liquid opposite to the direction of ultrasonic waves is observed (Figure 7). The sound energy is converted into kinetic energy and this effect is independent of the cavitation effect. Acoustic streaming helps in heat and mass transfer in the liquid. It facilitates distribution of ultrasonic energy and dissipation of heat [25]. In addition to cavitation and acoustic streaming, heat is produced in the liquid by shearing at interfaces such as the interface between the metal horn and liquid.

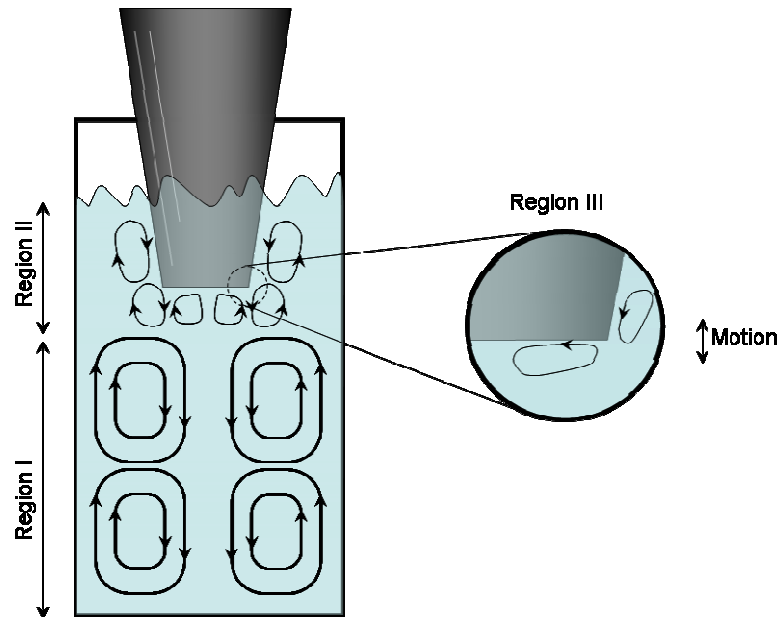


Figure 7. Phenomenon of streaming observed in a liquid on application of ultrasonic waves

1.5.3 Tooling design

An ultrasonic probe is used to produce and transfer ultrasonic waves to the liquid medium. Figure 8 shows a typical set-up of an ultrasonic stack assembly. The stack is connected to a power supply which converts line voltage to DC voltage which is then modulated at the desired high frequency. This stack consists of three components:

1.5.3.1 Converter

The converter (transducer) converts electrical energy to mechanical energy (ultrasonic vibrations). The transducer consists of a piezoelectric element. Thin crystals of piezoceramic are stacked together and voltage is applied to their relative interfaces.

When a charge is applied to the two faces of a piezoelectric material, it expands and contracts depending on the polarity of the applied charge. Thus, if a rapidly alternating voltage is applied to such a material, its dimensions change depending on the frequency of the applied voltage and ultrasonic vibrations. The converter used in this study produces 20-25 μm_{pp} at 20 kHz [24].

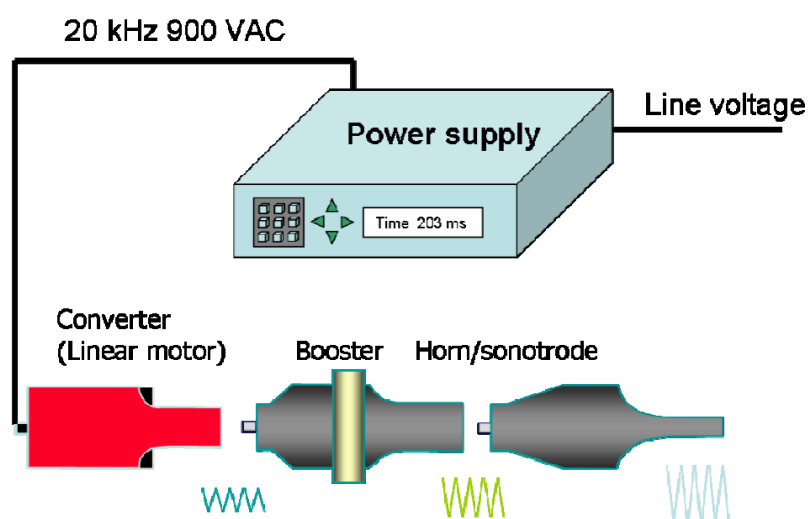


Figure 8. Ultrasonic probe used for sonochemical reactions (Picture by David Grewell)

1.5.3.2 Booster

The booster, as well as other stack components, is generally made of titanium or aluminum alloy. The function of the booster is to transfer the ultrasonic vibrations from the converter to the horn. It can also be used to amplify or decrease the amplitude of ultrasonic waves, depending on the design of booster.

1.5.3.3 Horn

The horn is generally made of titanium or aluminum alloy. Its function is to pass the ultrasonic waves into the liquid medium. For this reason, the horn should be chemically inert, resistant to deterioration from cavitation, and should have maximum efficiency in transferring ultrasonic waves. The horn can also amplify the amplitude of ultrasonic waves. Horns will have different ultrasonic amplitude gains, depending on their design (or mass).

1.5.3.4 Relation between frequency of ultrasonic waves and power

The frequency of ultrasonic wave propagation is inversely proportional to available power. In more detail high power is typically generated at lower frequencies of 20 kHz to 100 kHz. As the frequency increases, the size of the converter decreases and power density (power per unit volume) of the converter increases. Because converters are 95-96% efficient, a small amount of energy is dissipated as heat from the converter surface. At high frequencies, the smaller converter results in higher energy densities and promotes heating of the converter, which causes internal stresses in the transducers. To maintain proper balance, high frequency transducers are designed for lower power dissipation applications.

High frequency waves cannot effectively be used for producing cavitation effects. At higher frequency, the rarefaction or low pressure phase is very short in duration. It does not allow micro bubble formation and therefore cavitation does not effectively

occur. Therefore, higher amplitude (or power) is required to produce the same cavitation effects as produced at lower frequencies. Because high power at high frequency cannot be obtained owing to the limitations discussed in last paragraph, cavitation cannot be produced at high frequencies.

1.6 Enhancing transesterification reaction using ultrasonics

Transesterification reactions involve reactions between oil and alcohol in the presence of a catalyst. Oil and methyl alcohol are immiscible liquids and form separate layers when mixed together in a vessel. Traditional transesterification reaction requires mixing continuously for long periods of time to facilitate the reaction between oil and alcohol, because the reaction can take place only in the interfacial region between the two liquids. When this mixture is sonicated, ultrasonic waves produce cavitation at these interfacial areas. As a result, an emulsion of oil and alcohol forms, providing large surface areas for reaction. It is observed that reaction time is reduced significantly.

1.7 Literature review

Vegetable oils (and fats) are made up of water-insoluble molecules which are called triglycerides. The first evidence of use of vegetable oil as fuel was by Rudolf Diesel [25]. In 1900, during the Paris Exposition, a prototype of his engine used peanut oil instead of petroleum (for which the engine was originally designed). Vegetable oils were used as fuel for diesel engines in some countries until the 1930's and 1940's when petroleum-

derived fuels became less expensive. The interest in vegetable oil as fuel diminished in the following years because of the relatively lower prices and availability of fossil fuels. Vegetable oils have a high heat content (80% of heat content of biodiesel), and are renewable, they have several issues associated with their direct use in diesel engines. They have a viscosity 10-20 times higher than that of diesel fuels [15]. In addition, they have low volatility, which results in poor atomization of the fuel in the engine, incomplete combustion, and engine deposits upon prolonged use. Although vegetable fuels have extremely high flash points, they undergo thermal oxidation and oxidative polymerization at elevated temperature, forming higher molecular weight compounds which increase the viscosity of oil. The high flash point of vegetable oil implies low volatility and hence low fire hazard, this property causes ignition delay and difficulty in starting the engine in cold weather. Oxidative polymerization leads to deposit formation on injector nozzles, degradation of lubrication oil, and sticking of piston rings [26]. Blends of vegetable oil and diesel were also tested for their performance in diesel engines but the problems of acid composition, high density, free fatty acid content, oxidation, polymerization, carbon deposits, and thickening of lubricating oil still existed [27]. Three possible solutions [28] to this problem were considered as discussed below:

Pyrolysis is the process of thermally decomposing vegetable oils in the presence of catalysts and in absence of oxygen to produce short- and long-chained alkanes, alkenes, alkadienes, aromatics, and carboxylic acids. The catalysts used are mainly SiO_2 and Al_2O_3 . The resultant composition is similar to the hydrocarbons in fossil fuels. The properties of pyrolysis synthesized fuel, such as sulfur, water and sediments

concentration are within acceptable limits. But its high viscosity, ash and carbon content make it an inefficient fuel for long time use [27].

Micro emulsifications are thermodynamically stable colloidal dispersions of vegetable oil with alcohols, such as methanol and ethanol [26]. Organic solvents are used as surfactants for this purpose. Droplet diameters of microemulsions typically range between 100 and 1000 Å. These microemulsions are also not suitable for long term use in engines as they also have high viscosity, undergo incomplete combustion, and form carbon deposits. Also, they have a low heating value owing to the high alcohol content of their compositions.

Transesterification is the conversion of vegetable oil and an alkyl alcohol into biodiesel in the presence of high temperature and a catalyst, as discussed in previous sections.

Transesterification is the most common method used for the production of biodiesel on a commercial scale. It has been shown by various studies that ultrasonics can be used to increase the rate of biodiesel production. Ultrasonic treatment of soybean oil and methanol resulted in almost 100% biodiesel yield in 10-20 min [29]. Ultrasonics can also be used to increase the rate of transesterification in corn oil, grapeseed oil, canola oil, palm oil, etc. [30].

Thermogravimetric analysis has been used in the past to measure the boiling point and vapor pressure of short chain hydrocarbons present in biodiesel made from rapeseed oil and tallow [31]. The volatilities and boiling points of methyl and ethyl esters made up of various vegetable oils, such as canola oil, soybean oil, etc. have been measured using thermogravimetric analysis [32].

1.8 Thesis organization

This thesis is divided into four chapters:

1. Chapter 1 includes the introduction, literature review and objectives.
2. Chapter 2 is a journal paper to be submitted to Energy & Fuels and is titled “Thermogravimetric quantification of biodiesel produced via alkali catalyzed transesterification of soybean oil”.
3. Chapter 3 is also a journal paper to be submitted to Energy & Fuels and is titled “Enhancing biodiesel production from soybean oil using ultrasonics”.
4. Chapter 4 includes general conclusions from chapter 2 and chapter 3.

1.9 Objectives

The objectives of this study are:

1. To find a suitable method for shortening the time of the biodiesel production process, while maintaining the efficiency of biodiesel conversion and, if possible, reducing the energy consumption.
2. To experiment with the effect of ultrasonics on the transesterification reaction and biodiesel production and estimate its efficiency with respect to biodiesel conversion, and
3. To establish thermogravimetric analysis as a possible viable method of characterizing biodiesel. For this purpose, thermogravimetric analysis is compared with NMR spectroscopy.

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**CHAPTER 2: THERMOGRAVIMETRIC QUANTIFICATION OF BIODIESEL
PRODUCED VIA ALKALI CATALYZED TRANSESTERIFICATION OF
SOYBEAN OIL**

A paper submitted to Energy & Fuels

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2.1 Abstract

The aim of this study was to demonstrate the use of thermogravimetric analysis (TGA) as a potential method for monitoring biodiesel production by transesterification of soybean oil with methanol. Soybean oil and commercially available biodiesel were mixed in varying proportions by weight as standards. In addition, mixtures of different biodiesel/soybean oil ratios were also created by periodically interrupting base-catalyzed transesterification of soybean oil with methanol. The mixtures produced by both approaches were analyzed with TGA over a temperature range of 25-500 °C. The results were then compared with analytical data obtained by proton nuclear magnetic resonance spectroscopy (¹H NMR spectroscopy), an industry standard for biodiesel quantification. It was found in the TGA experiments that a significant weight loss at ca 150 °C correlated to the volatilization of biodiesel. The relative weight losses in both sets of mixtures

correlated well to the proportion of biodiesel present in the transesterification samples and the results from both analytical methods were in good agreement ($\pm 5\%$). Thus, TGA is a simple, convenient and economical method for monitoring biodiesel production.

2.2 Introduction

Burgeoning demand for biodiesel derived from plant oils has grown significantly over the last decade¹⁻⁹. As is commonly known, the conversion of vegetable oil to biodiesel occurs during a transesterification process in the presence of a catalyst and heat (Fig. 9).

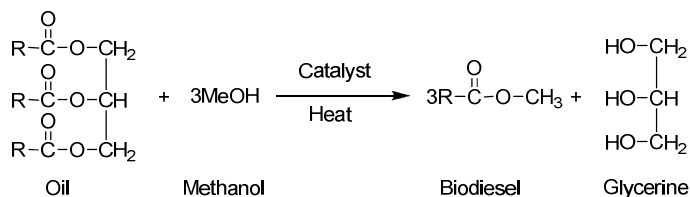


Figure 9. Transesterification reaction of soybean oil with methanol in presence of sodium hydroxide as catalyst.

Biodiesel production has increased from 500,000 gallons in 1999 to 450 million gallons from October 1, 2006 to September 30, 2007 in the United States alone and it is expected that this growth will continue to increase at a high rate¹⁰. It is anticipated that with this growth in production there will be an accompanying need for convenient and rapid analytical means for monitoring biodiesel production. Currently, there are a variety of standard methods for analyzing biodiesel contents in mixtures, including gas chromatography (GC)¹¹, high performance liquid chromatography (HPLC)¹², gel permeation chromatography (GPC)^{13, 14}, proton nuclear magnetic resonance

spectroscopy (^1H NMR)^{7, 14}, near infrared (NIR)¹⁵ spectroscopy, and Fourier transform infrared spectroscopy (FTIR)¹⁴. Among these, ^1H NMR spectroscopy has been used extensively and is often considered a standard characterization method of biodiesel^{7, 15, 17}.

Thermogravimetric analysis (TGA) is a technique for characterizing a material (element, compound or mixture) by measuring changes in its physico-chemical properties expressed as weight change as a function of increasing temperature¹⁸. Therefore, the change in mass of a substance is measured as a function of increasing temperature and it is correlated to the thermal stability of a material that is directly related to the material's volatility or thermal degradation to gaseous products.

The TGA instrument consists of a precision mass balance which records the initial and instantaneous mass of a sample and a furnace which is heated in a linear relationship as a function of time (the range of temperatures obtained typically being between 20°C and 1000 °C). Mass measurements are performed in air or in an inert gas such as nitrogen or argon. The advantages and limitations of TGA as a method of quantitating biodiesel production in comparison to other methods are tabulated in Table 4.

Table 4. Comparison of TGA with other methods known for the quantitation of biodiesel.

Quantification method	Advantages	Disadvantages
TGA	No reagent or solvent required Differentiates easily between biodiesel and plant oil due to large differences in boiling points Relatively inexpensive compared with ^1H NMR Gives acceptable results (as detailed in this paper)	Does not differentiate among different fatty acid methyl esters in biodiesel

^1H NMR	Simple, accurate and precise in determining the biodiesel content	Deuterated solvents required (CDCl_3 in the present case) Instrumentation relatively more expensive
GC	Can differentiate mono-, di- and tri-glycerides, methyl esters and glycerol	Standard solutions of components prepared for addition to biodiesel samples for dilution with heptanes Cumbersome to calculate direct conversion
NIR	No solvent required Can differentiate soybean oil, biodiesel and glycerol	Can not quantify low levels of contaminants
HPLC	Differentiates mono-, di- and tri-glycerides, methyl esters and glycerol	External solvents and standards such as triolein, trilinolein, trilinolenin, etc. are required to determine particular components of the mixture Cumbersome to calculate direct conversion

This paper examines the agreement of TGA and ^1H NMR spectroscopy in determining biodiesel content in soybean oil with the aim of evaluating TGA as a viable alternative analytical method for monitoring biodiesel production in research as well as industrial settings.

2.3 Experimental procedures

Mixtures of laboratory grade biodiesel and soybean oil were prepared and analyzed by TGA and ^1H NMR spectroscopy. TGA results were then compared to ^1H NMR results in order to determine the accuracy and precision of the TGA analysis of biodiesel. In addition, sample mixtures were taken during the conversion of soybean oil to biodiesel catalyzed by sodium hydroxide, a commonly used catalyst in the industry.

2.3.1 Materials

The materials used in this study were commercially refined soybean oil obtained from Watkins E. Inc. Sodium hydroxide, methanol, anhydrous magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and hexane were all obtained from Fisher Scientific and used as received. The biodiesel used as the external standard for TGA was prepared using our previous protocol¹⁷.

2.3.2 Preparation of standard mixtures of biodiesel and soybean oil

Mixtures of commercial soybean oil and biodiesel from the aforementioned sources were prepared. In more detail, the biodiesel was prepared at ambient temperature from soybean oil and methanol using nanocrystalline calcium oxide as the catalyst¹⁷. This biodiesel was found to be $\geq 99\%$ pure by ^1H NMR spectroscopy. The soybean oil was also analyzed by ^1H NMR spectroscopy and was also found to be virtually free of contaminants.

The oil and biodiesel were mixed in different proportions by weight. For preparing a 50:50 mixture of biodiesel and soybean oil, 10.00 g of soybean oil was first added to a glass vial using an analytical balance. Biodiesel was then added to complete the total weight of the mixture to 20.00 g. The mixture was then mixed thoroughly for 1 minute using a vortex mixer. The remaining standard mixtures were prepared similarly. The weight proportions of soybean oil to biodiesel used for the analyses were: 25.00:75.00, 30.00:70.00, 50.00:50.00, 75.00:25.00 and 80.00:20.00, respectively. These samples were then analyzed by TGA and ^1H NMR spectroscopy.

2.3.3 Preparation of biodiesel/soybean oil mixtures during transesterification

Biodiesel/oil mixtures were also prepared by partially transesterifying soybean oil. Using a syringe, 5.00 mL of methanol was added to 0.20 g of sodium hydroxide to generate a 0.74M solution of sodium hydroxide. This mixture was continuously stirred magnetically at a temperature of 40 °C for 5 min to form a sodium methoxide/sodium hydroxide equilibrium mixture which was then added to 20.00 mL of soybean oil. It should be noted that for this amount of oil, the theoretical amount of methanol required is approximately 3.00 mL for 100% conversion to biodiesel (i.e., a 1:3 molar ratio). However, an excess of 2.00 mL of methanol was supplied to drive the reaction equilibrium nearer to completion and to accelerate the reaction. The mixture was allowed to react at 60 °C in a shaker water bath with continuous stirring of the reactants via swirling of the flask. The reaction was quenched at a predetermined time by adding water (50.00 mL) and hexane (50.00 mL) to the reaction mixture. Additional hexane (200.00 mL) was then added to extract the biodiesel and residual soybean oil and the mixture was allowed to settle for ten minutes in a separatory funnel for separation of the two layers. The top layer containing the biodiesel, soybean oil and hexane was then isolated and anhydrous magnesium sulfate was added to remove trace amounts of water. This mixture was then passed through filter paper to remove the magnesium sulfate and then the filter paper was washed with hexane (3×20 mL) to obtain residual biodiesel and soybean oil. The filtrate was subjected to rotary evaporation to remove the solvent and then the remaining sample was analyzed by TGA and ^1H NMR spectroscopy for the degree of conversion to biodiesel. It is critical that the all the glycerin (the bottom layer in the

separatory funnel) is removed from the sample prior to TGA analysis as this method does not accurately distinguish between biodiesel and glycerin.

2.4 Analytical methods

^1H NMR spectra were recorded at ambient temperature on a Varian VXR-400 MHz spectrometer using standard procedures. The chemical shifts were referenced to the residual peaks of CHCl_3 in the CDCl_3 (7.26 ppm). The relevant signals chosen for integration were those of methoxy groups in the FAMES (3.66 ppm, singlet) and those of the α -methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil. The conversion was calculated directly from the integrated areas of the aforementioned signals¹⁸. ^1H NMR integrations on five separately created standard samples of 25/75 wt% biodiesel/soybean oil biodiesel mixtures, and on five separately made standard samples of 75/25 wt% biodiesel/soybean oil mixtures indicated that the experimental error was within $\pm 3\%$ in all cases.

TGA analyses of the biodiesel and oil contents were completed with 10.00 μL samples of biodiesel and oil mixtures heated at a constant heating rate of 10 $^\circ\text{C}/\text{min}$ in an atmosphere of nitrogen. The temperature range employed was 25 - 500 $^\circ\text{C}$. As further detailed in the following paragraph, the mass loss recorded for biodiesel at ca 150 $^\circ\text{C}$ correlates to the mass percentage of biodiesel present in the sample. Similarly, the mass loss associated with soybean oil (ca 350 $^\circ\text{C}$) correlates to the mass percentage of soybean oil in the sample. Because these temperatures vary by a relatively large amount (ca 200 $^\circ\text{C}$) this method should be quite effective in distinguishing biodiesel from soybean oil.

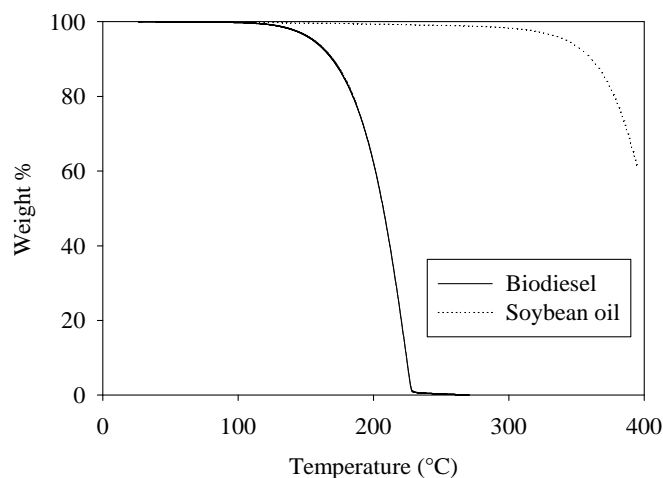


Figure 10. Overlay of thermogravimetric curves for pure biodiesel and soybean oil (mass % versus temperature).

Figure 10 shows the thermogravimetric plots for pure biodiesel and pure soybean oil. The mass of the biodiesel starts to decrease at approximately after 150 °C and it continues its decrease until all the biodiesel present in the sample is vaporized. Similarly, evaporation of soy oil starts at approximately 350 °C. The percentage of biodiesel and soybean oil in a sample could be calculated from the TGA plot of the sample taking into account the first derivative of the weight change of the sample mixture.

As shown in Figure 11, when the mixture is analyzed by TGA, we first used the rate of weight loss (“derivative weight percentage”) to determine the relevant temperatures. Here it was assumed that inflection points at the lowest rate of weight change values correlated to the temperatures of interest. In order to better indentify the inflection point, the second derivative of the mass change was calculated in EXCEL ® and an absolute value greater than 3% wt/s² (approximately 0.02 mg/s²) was assumed to indicate a significant rate change. Using this procedure instead of the conventional approach of

evaluating the weight loss resulted in a significant increase in the accuracy of the measurement. Our approach resulted in only a maximum of a 5% difference between the measurements and the actual values, while the conventional approach resulted in differences as high as 10%. Thus, for example, as seen in Figure 3, the initial inflection point is at 100.44°C and the second inflection point is at 260.85°C. Thus, the relative weights were 99.79% and 23.15, respectively, indicating 76.64% bio-diesel content, which is in good agreement with the actual value of 75.00%. The initial loss of 0.21% weight of the sample is attributed to the presence of volatile impurities. The accuracy of the approach is further discussed in the Results and discussion section. This approach, while non-standard, takes into account the relatively wide range of molecular weights of the biodiesel esters to be included in the measurements.

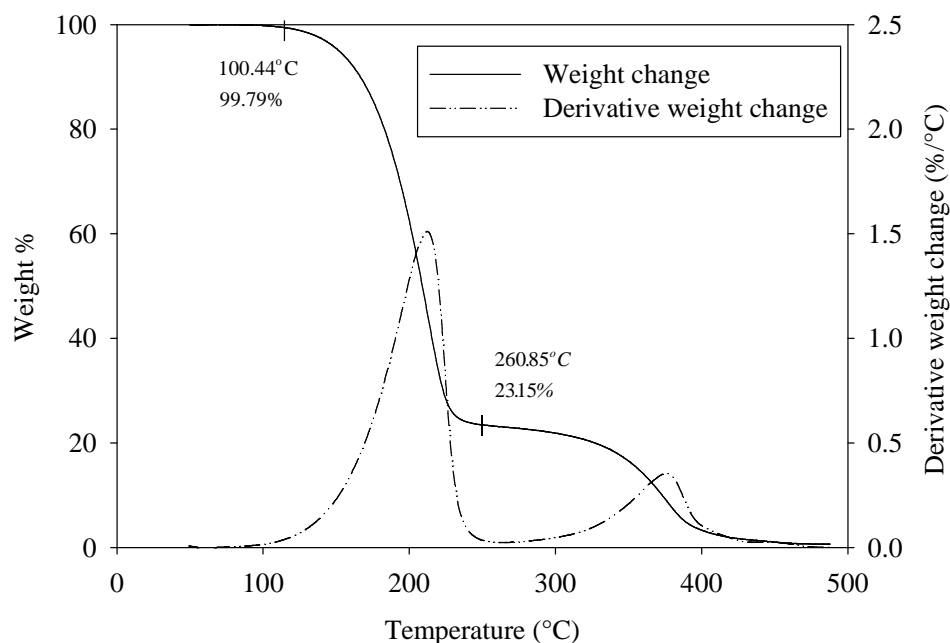


Figure 11. Thermogravimetric curve for a mixture containing 75.00% biodiesel and 25.00% soybean oil.

Typically, and as is consistently assumed in this paper, the amount of biodiesel present in a sample is equal to the mass percentage that lies between the condition where the biodiesel mass drops (at ca. 150 °C) and the condition where all the biodiesel is vaporized and the mass remains constant. The biodiesel/soybean oil TGA plots were compared with plots from known mixtures, thus allowing a determination of the percent by weight of biodiesel in the sample obtained from the transesterification reaction.

2.5 Results and discussion

The biodiesel yields as measured by TGA analysis of the standard biodiesel/soybean oil mixtures were very similar to their actual values based on weight percent in those mixtures (Figure 12). The linear fit between the two data series results in an R^2 value of 0.9981 which confirms this conclusion. The TGA biodiesel analyses were also plotted as a function of the ^1H NMR analyses as seen in Figure 13. The data is typically within $\pm 1.5\%$ of agreement, with the largest difference being $\pm 4.5\%$.

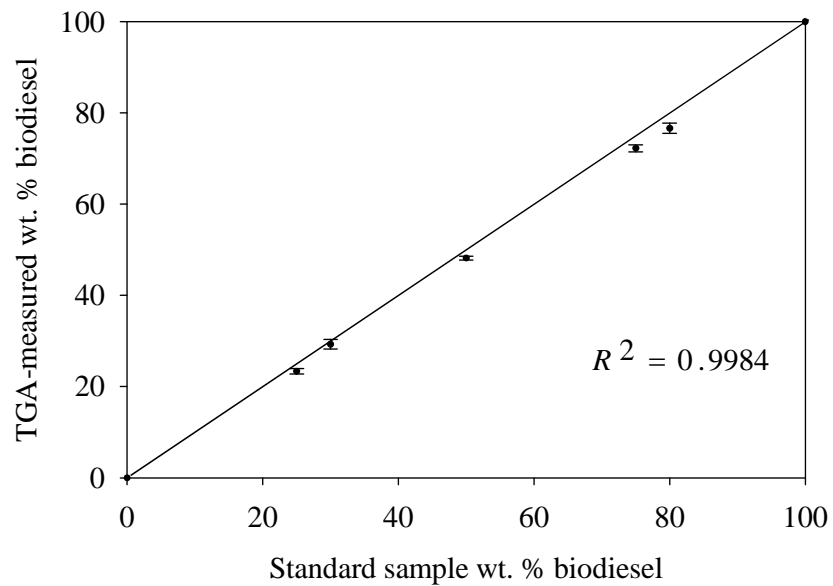


Figure 12. Biodiesel % by weight obtained from TGA analysis plotted against the actual biodiesel weight % in the standard sample.

The linear fit between these two methods showed an R^2 value of 0.9997. Again the linear regression analysis suggests that TGA accurately quantifies the amount of biodiesel present.

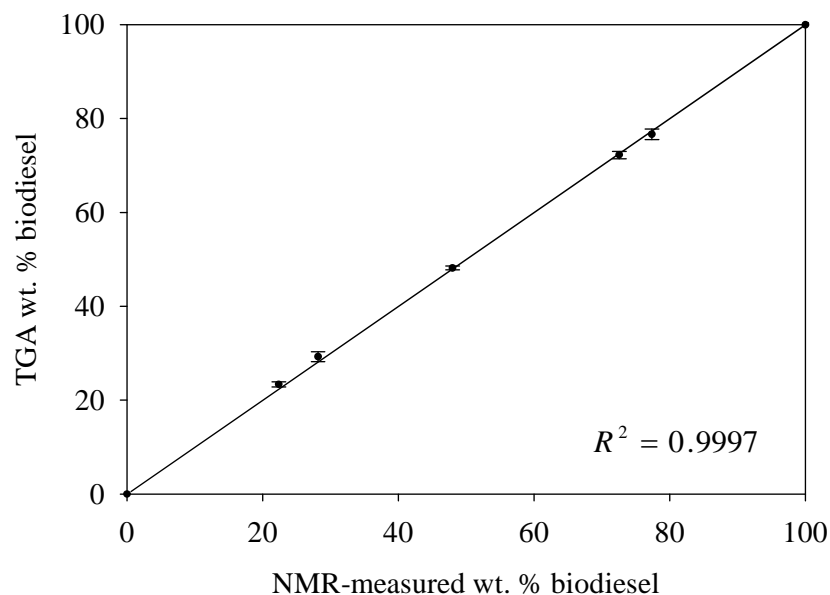


Figure 13. Biodiesel content (weight %) in the standard mixtures obtained by TGA and NMR spectroscopy.

Figure 14 shows biodiesel production as a function of transesterification time as determined by ^1H NMR spectroscopy and by TGA. It is important to note that in these experiments that there are varying amounts of partially transesterified oil, unlike the previously detailed experiments with the standard mixtures that contained pure biodiesel and pure soybean oil with all the glycerin removed. Thus, the data depicted in Figure 14 are more representative of actual laboratory or industrial production conditions. Nonetheless it is again seen that there is good correlation between the two characterization methods. These results suggest that TGA can be efficiently used for analyzing biodiesel contents within $\pm 5\%$ (the average of the differences between TGA and NMR measurements) in vegetable oil transesterification reactions.

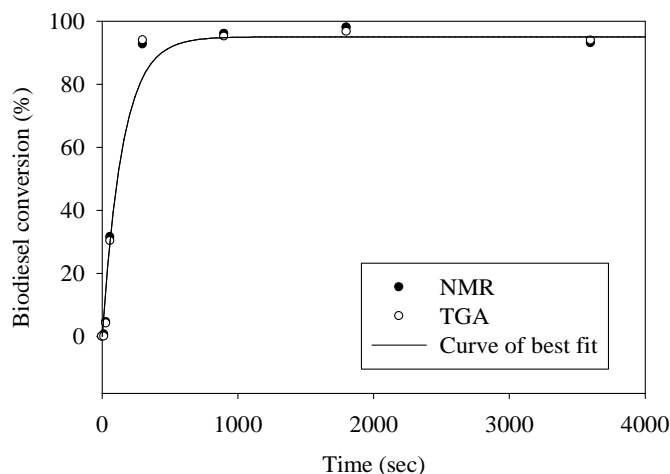


Figure 14. Biodiesel conversion in the transesterification of soybean oil determined by TGA and NMR analysis.

2.6 Conclusions

Our results suggest that thermogravimetric analysis (TGA) is an effective method, typically within $\pm 1.5\%$ relative to the proton NMR method for estimating the percentage of biodiesel in transesterification reaction mixtures. This method was validated with the existing NMR spectroscopic method for this analysis and the two methods produced results that were very comparable. With respect to the time required to perform various methods of biodiesel characterization, TGA is comparable to GC and HPLC, but requires more time than NMR and NIR. However, the TGA method does not require addition of reagents or solvents to the sample prior to analysis, thus reducing the cost and the probability of errors from such sources.

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CHAPTER 3: ENHANCING BIODIESEL PRODUCTION FROM SOYBEAN OIL USING ULTRASONICS

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3.1 Abstract

The objective of the study was to determine the effect of ultrasonics on biodiesel production from soybean oil. In this study, ultrasonic energy was applied in two different modes: pulse and continuous sonication. Soybean oil was mixed with methanol and sodium hydroxide and was sonicated at three amplitudes ($60 \mu\text{m}_{\text{pp}}$, $120 \mu\text{m}_{\text{pp}}$ and $180 \mu\text{m}_{\text{pp}}$) in pulse mode (5 s on/ 25 s off). In the continuous mode, the same reaction mixture was sonicated at $120 \mu\text{m}_{\text{pp}}$ for 15 s. The reaction was monitored for biodiesel yield by stopping the reaction at selected time intervals and analyzing the biodiesel content by TGA. The results were compared to a control group where the same reactant composition was allowed to react at 60°C for intervals ranging from 5 minutes to 1 hour with no ultrasonic treatment. It was observed that ultrasonic treatment resulted in a 96 % yield (percent conversion to biodiesel) in less than 90 s using the pulse mode; compared to 30 to 45 minutes for the control sample. Also in pulse mode, the highest yield was obtained

from sonicating the mixture at 120 μm_{pp} amplitude. In continuous sonication the highest biodiesel conversion obtained at 15 s is 86 %.

3.2 Introduction

Vegetable oils such as soybean oil have been considered as fuel for diesel engines.¹ However, such oils cannot be used directly in standard diesel engines because of their high molecular mass, kinematic viscosity, poor atomization, lubrication problems, and carbon deposits due to incomplete combustion.² These issues can be resolved by: dilution, micro emulsification, pyrolysis³ and transesterification with methanol; the latter approach being used most commonly in industry.⁴ As is commonly known, the conversion of vegetable oil to biodiesel occurs during a transesterification process in the presence of a catalyst and heat (Fig. 15).

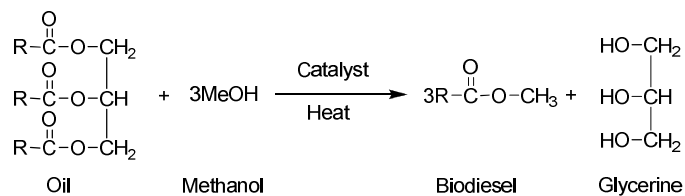


Figure 15. Transesterification reaction of soybean oil with methanol in presence of sodium hydroxide as catalyst.

As mentioned earlier, biodiesel is produced by reacting vegetable oil and an alcohol in the presence of a suitable catalyst. This process requires continuous mixing at 60°C, which represents significant energy consumption.

It has been observed that the transesterification reaction time can be significantly reduced by irradiating the reactants with ultrasonic sound waves at room temperature.⁵ Ultrasonic waves are sound waves that are above normal human hearing range (i.e., above 18-20 kHz).⁶

The effect of ultrasonic waves on liquids has been explained in detail by Suslick.⁷ When ultrasonic waves are passed through a mixture of immiscible liquids, such as vegetable oil and alcohol, extremely fine emulsions can be generated. These emulsions have large interfacial areas, which provide more reaction sites for the catalytic action and thus increase the rate of the reaction. For example, in this work, ultrasonic energy increased the reaction rate several fold, reducing the reaction time from approximately 30 to 45 minutes to less than a minute. In addition, ultrasonic treatment of liquids produces streaming,⁸ which further promotes mixing of reactants.

In this work, Thermogravimetric Analysis (TGA) was used to study the reaction rate of biodiesel production.⁹ TGA is an experimental method for characterizing a system (element, compound or mixture) by measuring the changes in its physico-chemical properties as a function of increasing temperature. A study by Grewell et al. of the thermal degradation of biodiesel and soybean oil mixtures using TGA showed that the weight percentage of biodiesel in a mixture consisting of soybean oil and biodiesel can be easily determined by TGA.⁹

The goal of this work was:

- a) To obtain a high biodiesel conversion percentage in less time from transesterification of soybean oil with the ultrasonic treatment. For this purpose, biodiesel was produced by two methods:

- By mechanical stirring of the reactants, and
- By applying ultrasonics to the reactants.

The biodiesel conversion percentage at various times was recorded for both methods and compared to determine the effect of the ultrasonic energy.

- b) Comparison of energy balance between the processes.

3.3 Experimental Procedures

3.3.1 Materials

The materials used in this study were commercially refined soybean oil obtained from Watkins E. Inc. Sodium hydroxide, methanol, anhydrous magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and hexanes were all obtained from Fisher Scientific. A Branson 2000 Series bench scale ultrasonics unit with a maximum power output of 2.2 kW and a frequency of 20 kHz was used. The ultrasonic horn used was a 20 kHz catinodial titanium horn with a flat 13 mm diameter face and a gain of 1:8. The booster used in this study had a gain of 1:1.5.

3.3.2 Preparation of biodiesel/soybean oil mixtures from transesterification through mechanical stirring:

Mixtures were prepared by collecting samples from a transesterification reaction mixture at specific times. In the experiments that characterized conventional mixing techniques for biodiesel production, 150 mL of methanol was added to 6 g of sodium hydroxide (0.74 M). This mixture was continuously stirred at a temperature of 40 °C for 5 min to form a sodium methoxide solution. This mixture was then added to 600 mL of

soybean oil, which requires approximately 90 ml of methanol to undergo 100% conversion to biodiesel (1:3 molar ratios); however, excess methanol was supplied to drive the reaction equilibrium to completion and to account for losses during the reaction. The mixture was allowed to react at 60 °C in a shaker water bath with continuous stirring. Samples of 5 ml were withdrawn from the reaction mixture at predetermined times. The reaction was stopped by adding water (50 mL) and hexanes (50 mL) to the reaction mixture. Water stops the reaction and the biodiesel and residual soybean oil are extracted with the hexanes. Additional hexanes (200 mL) were added to dissolve biodiesel and soybean oil. This mixture was allowed to separate for ten minutes in a separatory funnel to produce the two distinct layers. The top layer contained biodiesel, soybean oil, and hexanes, while the bottom layer contained glycerol, water, catalyst, and soap. The layers were separated and anhydrous magnesium sulfate was added to the top layer to remove trace amounts of water. This mixture was then passed through filter paper to remove the magnesium sulfate, and the filtrate was subjected to rotary evaporation to remove the solvent. The remaining sample was then analyzed by TGA to determine the degree of conversion to biodiesel. For accuracy of results, all the experiments in this paragraph were replicated five times.

3.3.3 Preparation of biodiesel/soybean mixtures from transesterification through ultrasonics:

For the experiments that evaluated ultrasonic treatment for biodiesel production, 10 ml soybean oil was added to sodium methoxide solution prepared by reacting 2.5 ml methanol and 0.1 gm sodium hydroxide. The same method of preparation of sodium

methoxide as explained in the previous section was used. The sample size was scaled to match the available reaction chamber size for the ultrasonic horn (~30 mL). Ultrasonic energy was applied in two different modes; pulse and continuous sonication. In pulse mode the ultrasonic energy was applied as 5 s on and 25 s off. Thus, samples were collected at the end of every 30, 60, 90, 120 and 150 s time intervals. Three amplitude levels were studied: 60 μm_{pp} , 120 μm_{pp} and 180 μm_{pp} . In continuous sonication mode, the reactants were sonicated continuously for 15 s at 120 μm_{pp} . In this case, samples were collected at every second i.e. 1, 2, 3,...15 s. The reaction was stopped by adding water (50 mL) and hexane (50 mL) immediately after ultrasonic treatment. Mixtures of oil and biodiesel were separated in a similar manner as detailed in the previous section. For accuracy of results, all the experiments in this paragraph were replicated five times. It is important to note that external heating was not used in any of these experiments.

3.4 Analytical methods:

TGA was used to measure the biodiesel and oil contents in the samples. In this experiment, 10 μL samples of biodiesel and oil mixture were heated at a constant heating rate of 10 $^{\circ}\text{C}/\text{min}$ in an atmosphere of nitrogen. The temperature range was maintained at 25 $^{\circ}\text{C}$ to 400-500 $^{\circ}\text{C}$ and the weight loss occurring at approx. 150 $^{\circ}\text{C}$ was assumed to correlate to biodiesel as reported by Grewell et al.⁹ The weight loss provided the weight percentage of biodiesel present in the sample. Similarly, weight loss associated with soybean oil occurred at approx. 350 $^{\circ}\text{C}$ providing the weight percentage of soybean oil in the sample.

3.5 Results and Discussion

Figure 16 shows biodiesel conversion as a function of time for the conventional production method of heating and mixing only. It is seen that the highest conversion to biodiesel was 97% and the reaction time was 60 min (3600 s).

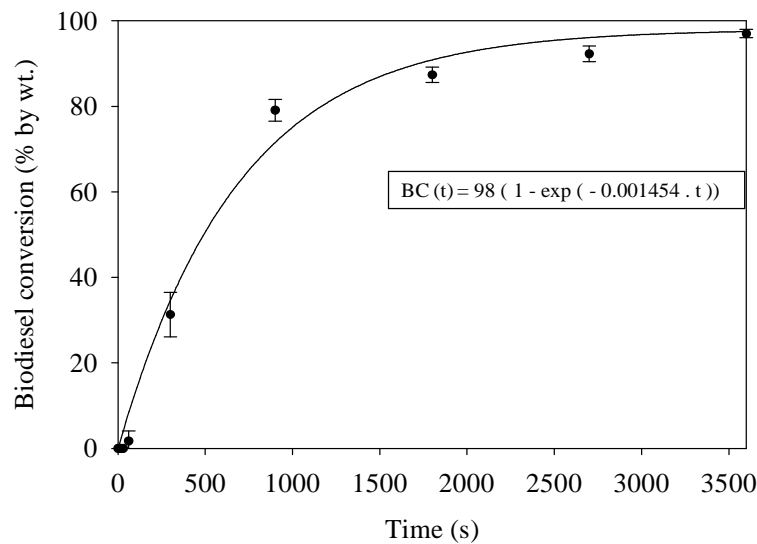


Figure 16. Biodiesel conversion (%) from transesterification of soybean oil through mechanical stirring

Figure 17 shows the biodiesel production as a function of esterification time with the ultrasonic treatment in pulse mode at three different amplitudes. It is seen that relatively high yields (+85%) were achieved within 90 s and yields as high as 96% were produced within 120 s with amplitude of $120\mu\text{m}_{pp}$. Compared to the control group (Figure 16), the time required to achieve a yield above 95% is reduced from 30 min to 1.5 min by using ultrasonic treatment.

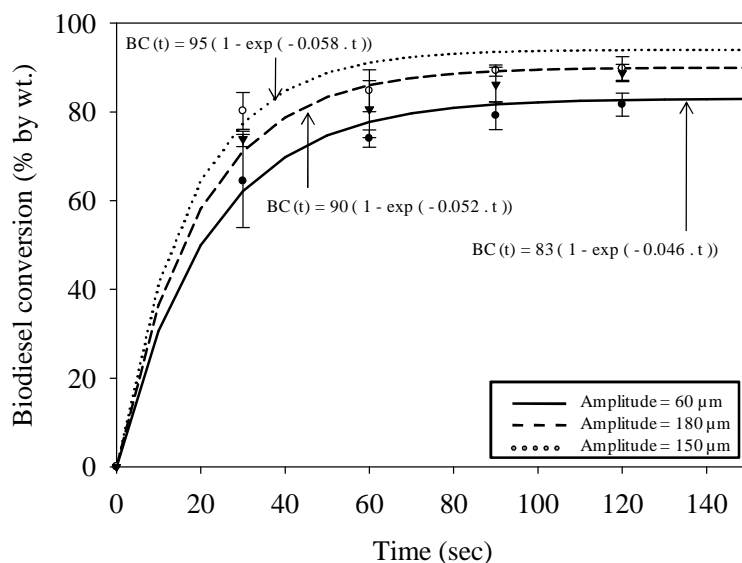


Figure 17. Comparison of biodiesel conversion (% by wt.) obtained at three amplitude levels in pulse mode.

This enhanced reaction kinetic is believed to be related to the emulsions that are generated by the ultrasonic treatment as well as the streaming effects of the ultrasonics. Figure 18 A and B shows the microscopic image of reaction mixture which was sonicated for 15 sec in continuous mode and conventional mixing respectively. These pictures were taken a few seconds after sonicating/ mixing the mixture. It is seen that the ultrasonic sample has a finer emulsion compared to the conventional mixing. When these samples were allowed to settle for approximately 1 hour, two separate layers were formed. The top layer consists of biodiesel and soybean oil (if any was left in the sample) and bottom layer was glycerol.

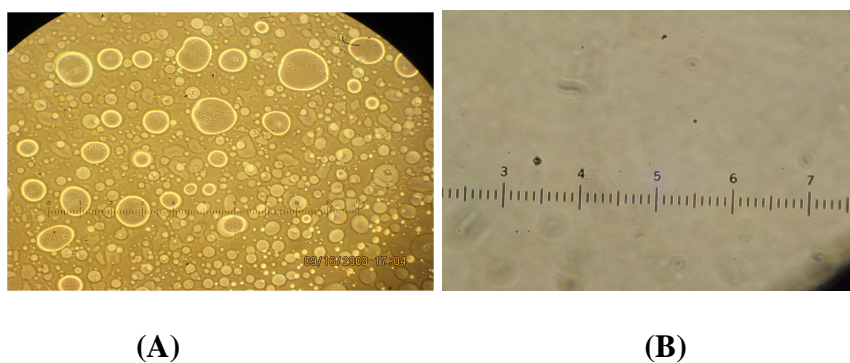


Figure 18. (A) View of reaction mixture under microscope after sonication for 15 sec. (B) View of reaction mixture after transesterification by the commercial method.

The highest biodiesel conversion yield was obtained when the reactants were sonicated for 150 s in the pulse mode as detailed in Table 5. It is seen that the highest yield was generated with the $120 \mu\text{m}_{\text{pp}}$ amplitude. It is believed that the higher amplitude $180 \mu\text{m}_{\text{pp}}$ (109 W, average power during sonication) promoted degradation of the chemistries and the lower amplitude $60 \mu\text{m}_{\text{pp}}$ (44 W) required longer times than those studied to achieve a higher yield.

Therefore $120 \mu\text{m}_{\text{pp}}$ was used for continuous sonication of the reactants. Figure 19 shows the results of continuous sonication. The highest biodiesel yield obtained at 15 s and was 86%. Because the temperature was not regulated the temperature in the reaction chamber reached 60°C at the end of the 15 s.

Table 5. Highest biodiesel production and temperature for various sonication treatments in pulse sonication mode

Amplitude (μm_{pp})	60	120	180
Highest biodiesel content in the product (% by wt.)	87	96	92
Highest temperature ($^\circ\text{C}$)	48	52	60

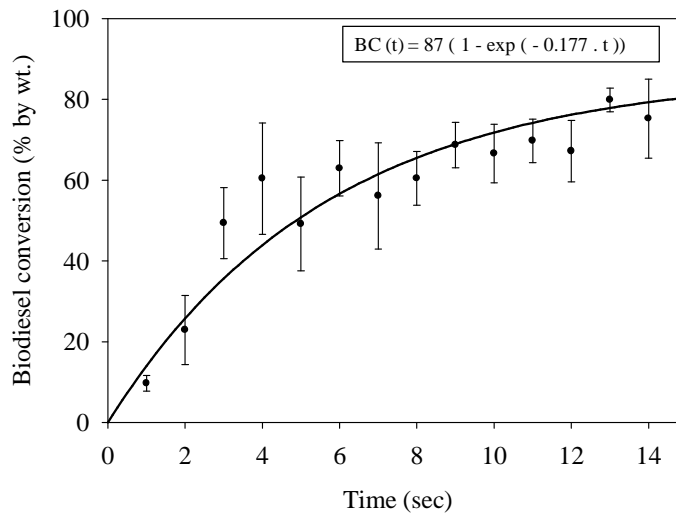


Figure 19. Biodiesel conversion (% by wt.) from transesterification of soybean oil by application of ultrasonics in continuous sonication mode.

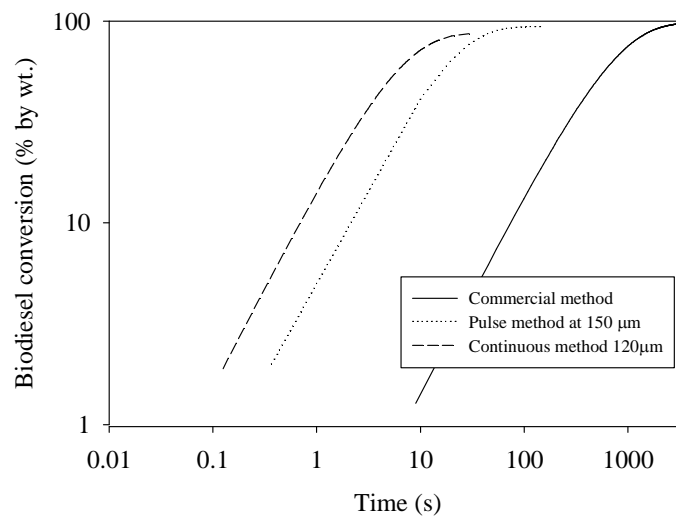


Figure 20. Comparison of biodiesel conversion (% by wt.) obtained by commercial method, pulse sonication mode and continuous sonication mode (log/log plot).

Figure 20 shows the biodiesel conversion % obtained by all three methods discussed in this paper. It is important to note the lines are the plotted functions from the previous models of the experimental data (equations) and not the experimental data. It is also

important to note that in order to differentiate between the treated samples and the control sample, a log/log plot was used. That is to say, without using a log/log plot, the extreme scales of the various plot (0-60 s for the treated samples and 0-3000 s for the control sample) made it difficult to visualize the separate plots. It is seen that the application of ultrasonics reduces the time of reaction while maintaining the biodiesel yield. Reaction time can be lowered to a few seconds by using either pulse mode or continuous sonication mode, as compared to 45-60 min in case of commercial method.

Based on these results it is believed that high yields can be obtained in a continuous sonication mode with ultrasonic chambers designed for continuous flow systems. In continuous flow, oil, methanol and catalyst can be continuously fed into the reactor and sonicated for 15-20 sec and biodiesel along with glycerol will be released at the outlet of the reaction chamber.

As previously mentioned the second objective of this study was to compare the energy utilized in commercial method and sonication method.

The energy consumed during conventional production was estimated assuming adiabatic heating. In more detail the energy required to raise the temperature of reaction mixture from room temperature i.e. 20 °C to 60 °C was estimated based on adiabatic heating and applying following formula:

$$\text{Energy} = C_{p \text{ oil}} * \rho_{\text{ oil}} * \Delta T + C_{p \text{ methanol}} * \rho_{\text{ methanol}} * \Delta T$$

$$^{10}C_{p \text{ oil}} = 2269 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\rho_{\text{ oil}} = 0.918 \text{ g cm}^{-3}$$

$$C_{p \text{ methanol}} = 2470 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\rho_{\text{ methanol}} = 0.791 \text{ g cm}^{-3}$$

$$\Delta T = 40 \text{ K}$$

$$\text{Total Energy} = 162 \text{ kJ L}^{-1}$$

Thus 162 kJ of energy is required to raise the temperature of soybean oil and methanol. The energy required for stirring the reactants was assumed to be insignificant and therefore excluded from this calculation.

The energy consumed by the ultrasonic system was based on integration of the power dissipation as reported by the power supply of the ultrasonic system and is detailed in Table 6 for the various conditions.

Table 6. Amount of energy supplied during transesterification through sonication and commercial method

Reaction mode	Pulse Mode			Continuous Mode	Commercial Method
	60 μm	120 μm	180 μm		
Energy (kJ/L reaction mixture)	82	110	117	112	162
Highest temperature ($^{\circ}\text{C}$)	48	52	60	60	60

In all these four experiments, the energy consumed per litre of reaction mixture is less than the energy consumed in commercial method. Thus, 47% more energy is consumed if the reaction is done by the commercial method instead of the 120 μm pulse mode.

3.6 Conclusion

The time required to achieve a 96% yield was reduced by several fold by ultrasonic treatment in a pulse mode. In more detail, by using standard mixing systems, the time required to achieve 96% biodiesel yield was about 45 minutes, while in contrast, this time was reduced to 1.5 minutes when ultrasonic treatment was used in pulse mode. Also in continuous sonication mode, an 87% biodiesel yield is obtained in 15 s.

The energy required for transesterification through ultrasonics method is less than commercial method, for comparable biodiesel yields.

Further experiments are required to determine the optimum amplitude for highest biodiesel conversion percentage as well as to characterize the quality of the biodiesel in terms of consistency, energy content and gel temperature.

3.7 References

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CHAPTER 4: FINAL CONCLUSION

Thermogravimetric analysis can be used for testing the amount of biodiesel present in a biodiesel and soybean oil mixture for screening purposes. As detailed in Chapter 2, the results from thermogravimetric analysis are comparable to the results from NMR spectroscopy, which is the prevailing method of biodiesel characterization. It can be used in industry as well as in laboratories owing to its inexpensive and convenient set up. It should be noted that TGA is not able to distinguish between glycerin and oil, but with proper washing of the mixture to remove the glycerin is able to measure the level of biodiesel conversion within 5%.

Use of ultrasonics can increase the reaction rate by a factor of 10 as shown in the previous chapter. The time required to achieve a 96 % yield was reduced by several fold by ultrasonic treatment in a pulse mode. In more detail, by using standard mixing systems, the time required to achieve 96 % biodiesel yield was about 45 minutes, while in contrast, this time was reduced to 1.5 minutes when ultrasonic treatment was used in pulse mode. Also in continuous sonication mode, an 87 % biodiesel yield is obtained in 15 s.

The energy required for transesterification through ultrasonic conversion is less than that required for mechanical stirring as calculated in Chapter 3. The increasing demand for biodiesel in present times, it proves to be a very efficient method for biodiesel production using considerable less time. The advantage of this method is that continuous flow ultrasonic chambers of required capacity can be constructed and used in laboratory as well as in industry.

Future work should include testing and optimizing continuous flow ultrasonic chambers for transesterification. Thermogravimetric analysis should be tested for biodiesel and oil mixtures of various oils other than soybean oil. More work is required for finding the optimum amplitude for maximum biodiesel conversion in a minimum amount of time.