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Characterization of the Esterification Reaction in High Free Fatty Acid Oils

Lucas Eli Porter Altic
University of South Florida

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by

Lucas Eli Porter Altic

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Major Professors: Daniel Hess, Ph.D.
Muhammad Rahman, Ph.D.
Stuart Wilkinson, Ph.D.

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DEDICATION

To my beautiful wife Lara who gave me the courage to carry on and to my new son

Jackson who gave me the will to finish.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Characterization of the Esterification Reaction in High Free Fatty Acid Oils

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ABSTRACT

Energy and vegetable oil prices have caused many biodiesel producers to turn to waste cooking oils as feedstocks. These oils contain high levels of free fatty acids (FFAs) which make them difficult or impossible to convert to biodiesel by conventional production methods. Esterification is required for ultra-high FFA feedstocks such as Brown Grease. In addition, ultrasonic irradiation has the potential to improve the kinetics of the esterification reaction. 2-level, multi-factor DOE experiments were conducted to characterize the esterification reaction in ultra-high FFA oils as well as determine whether ultrasonic irradiation gives any benefit besides energy input. The study determined that sulfuric acid content had the greatest effect followed by temperature and water content (inhibited reaction). Methanol content had no effect in the range studied. A small interaction term existed between sulfuric acid and temperature. The study also concluded that sonication did not give any additional benefit over energy input.

1.0 INTRODUCTION

As an emerging industry, Biodiesel has blossomed from a little-known, speculative, and exotic alternative energy source into a quasi-mainstream fuel for generally accepted use in diesel vehicles and machinery. Mounting political instability in the middle-east, growing environmental concerns, and recent associated hikes in fuel prices have spawned a great deal of public, scientific, and capital interest both for the fuel and the industry in recent years. Between the years 2001 and 2008, Biodiesel production in the United States increased from 9 million to 678 million gallons per year (U.S. Energy Information Administration, 2010). This indicates a major boom in a quickly maturing industry.

Despite this recent economic, technical, and social progress for biodiesel, overwhelming market forces combined with unreliable government support for the industry has resulted in a dramatic decline in biodiesel production and the near extinction of viable biodiesel companies within the United States over the last two years. Upward pressure within the commodities and energy markets has forced unbridled increases in the price of conventional feedstocks for biodiesel such as soy and rape seed oils. Between the years 2005 and 2008, soybean prices rose from $5 per bushel to nearly $11 per bushel on the low side (Wordpress, 2008). Energy prices also increased in relative proportion. This rapid inflation in biodiesel production costs caused the margins for biodiesel sales within the US to shrink. With many companies at breakeven or underwater, the future of biodiesel production hung on the tattered tapestry known as governmental energy policy.

On December 31, 2009, the government subsidy of $1 per gallon of biodiesel production was allowed to lapse. Hope of the program's renewal gradually dwindled though 2010 and many biodiesel plants simply closed their doors (Daily Times Herald, 2010). By this time, even with regulatory support, biodiesel production from conventional feedstocks was, at best, a marginal business and, at worst, economic suicide. As a result, U.S. domestic biodiesel production for the first half of 2010 dropped to levels not seen since 2007 (U.S. Energy Information Administration, 2010).

The solution for many was a fundamental shift in the underpinnings of the industry itself: the use of cheaper recycled or second-use oils for biodiesel production such as yellow grease and brown grease. With the cost of the lipid stock being nearly 80% of the cost of biodiesel production, any amount saved in this category represented huge potential for economic survival if not prosperity (Wordpress, 2010). As of October 2010, yellow grease prices were around 28 cents per pound while soybean oil prices were approaching 48 cents per pound. Brown grease was lowest at 10 cents per pound (The Jacobsen, 2010). In addition to being cheap, second-use oils are also plentiful. A U.S. EPA study recently found that 1 to 3 billion gallons of waste greases are produced annually (Greer, 2010). This is nearly two to six times the national annual peak production of biodiesel for 2008, so it is evident that recycled greases have the ability to completely replace conventional feedstocks in volume. As an added benefit, the use of waste greases to make biodiesel is also more environmentally friendly. The EPA concluded that the total lifecycle greenhouse gas emissions from the production and combustion of biodiesel made from waste greases resulted in an 86 percent reduction over petroleum-derived

diesel. This is in contrast to soy-based biodiesel yielding only 54% fewer greenhouse gas emissions than petrodiesel (Greer, 2010). These figures suggest that biodiesel made from waste greases offers a 59% improvement in greenhouse gas emissions over soy-based biodiesel.

The problem with the strategy of using waste greases to produce biodiesel is that recycled oils such as yellow grease or brown grease require extra processing steps to produce ASTM quality fuel. The oils themselves are heavily degraded and contain high levels of free fatty acids (FFA) which are the products of thermal degradation and hydrolization during their use in cooking and residence in grease traps. Dealing with these free fatty acids has become the primary technological dilemma for the few biodiesel plants still in operation. Esterification of the FFA component was widely adopted as a pre-treatment step to reduce the FFA concentration in the oil prior to conversion into biodiesel by conventional means (Tyson, 2002).

While several entities have successfully and consistently produced biodiesel from UCO or Yellow Grease (the commodity term for commercially-collected and rendered used cooking oil) the dynamics of this process has remained a mystery for many. It is not widely known, for instance, whether catalyst concentration, moisture content, or methanol quantity has a greater influence on conversion time or reaction completeness. A formal evaluation of the various factors influencing the esterification reaction is needed as a foundation for optimization. Furthermore, far fewer operations have had success converting even cheaper, but more heavily degraded, feedstocks such as brown grease

3

into quality biodiesel. Brown grease (the commodity name for commercially collected and rendered trap grease) and similar oils such as fatty acid distillates contain FFA concentrations in excess of 50% which has resulted in reluctance for many companies to consider them as viable feedstocks (Tyson, 2002). These latter feedstocks are referred to herein as ultra-high-FFA oils. Some have recently proposed that reaction acceleration techniques such as ultrasonic irradiation can greatly increase the efficiency of conversion of the ultra-high-FFA oils (Hahn, 2009).

It is the dual intent of this thesis to both characterize the esterification of ultra-high-FFA oils by examining the influence of the primary process factors on the reduction of FFA at high concentrations in the oil as well as to evaluate the use of reaction acceleration techniques for applicability to the conversion of low-cost feedstocks into biodiesel.

1.1 OBJECTIVES

1.1.1 REACTION CHARACTERIZATION

As mentioned, the primary objective of this project was to characterize the esterification reaction of free fatty acids in ultra-high-FFA oils such as brown grease. Several major factors are thought to influence this reaction:

1. Relative quantity of methanol
2. Relative quantity of sulfuric acid catalyst
3. Relative quantity of water

4

4. Temperature of the reaction system

5. Agitation speed.

Four of these were selected for evaluation: relative methanol content, relative sulfuric acid content, relative water content, and temperature. Agitation speed was excluded because its effect was thought to be minor within the range of standard low-speed mixers and difficult to alter in many industrial setups. The primary intent of this study was to determine the relative magnitudes of the effects for each of the four chosen factors. Future researchers and process engineers can use this groundwork to determine on which of the factors to focus optimization efforts and which associated cost categories to dedicate resources.

1.1.2   ENHANCED REACTION KINETICS EVALUATION

Biodiesel production from ultra-high-FFA oils is neither a well understood process nor an efficient one. Conventional production techniques require catalyst and alcohol quantities far greater than the theoretical stoichiometric ratio. This results in increased production cost, unnecessary waste streams, impure byproducts, and inconsistent product quality. These glaring process issues have incited many researchers to investigate alternative production methods. Most arising technologies are still in developmental stages, with only a fraction having sufficient merit to pass into the implementation phase (Bournay, 2005). This fraction represents the beginning of second-generation biodiesel production. It is one of the objectives of this project to investigate one of these technologies in

particular as it applies to throughput, quality, and catalysis and several in general as part of a literature review.

Initial investigation established sonochemistry as a reaction technology with a high degree of industrial potential. Its application possessed many characteristics that tailor it to an ideal reaction technology for biodiesel: it decreases the surface to volume ratio of the associated reactants, it shortens reaction times sometimes by orders of magnitude, it increases catalytic efficiency, and it is readily suitable for continuous production (Mason 1999).

The literature review yielded several specific areas of biodiesel research which might be improved by the application of sonochemistry. The first is catalysis. As mentioned previously, sonochemistry can increase catalytic action during a reaction (Mason, 1999). A second area for potential improvement is reaction length: sonication has been shown to reduce reaction time in transesterification reactions as well as esterification reactions (Stavarache, 2003). Further investigation of the literature, however, left the author with a lack of confidence that sonochemistry had any additional advantages over other reaction enhancement technologies. All technologies reviewed seemed to have one primary advantage: they had the ability to add far more mechanical energy to the reaction system than conventional stirring techniques. A simple experiment was designed to test, on a fundamental level, whether sonication afforded any benefit over conventional stirring when the input of thermal and mechanical energy using either technique was made the same. With energy input held constant, sonication as an agitation method should show a

demonstrable improvement over conventional stirring if the former offered any additional

benefit beyond the amount of energy it is capable of delivering to the reaction system. If

no improvement is observed, it can be implicitly concluded that energy input is the sole

benefit of sonochemistry over conventional stirring. Catalyst content was varied along

with the agitation method to evaluate whether sonication had an improvement on

catalysis at high and low levels of catalyst.

1.1.3   IMPLEMENTATION

Implementation of this project was conducted in four parts: First a literature review was

done to evaluate the state of the art and current level of understanding of the esterification

reaction in ultra-high-FFA oils as it applies to biodiesel production as well as to identify

viable reaction acceleration technologies with suitable merit for experimental evaluation.

Next appropriate experimental designs were chosen using DOE methods for both the

esterification reaction characterization and the enhanced reaction kinetics evaluation.

Both experiments were considered to be screening experiments because the objective was

to determine the relative magnitude of factor effects. For this reason 2-level factorial

designs were chosen and are outlined in sections concerning their design and

implementation.

The experiments were then performed and measurements were taken according to the

experimental design. Stirred reactions were performed with a Fisher Scientific Isotemp

magnetic stirrer with maximum rotational output of 1400 RPM. The Isotemp provided

temperature control as well. Sonication reactions were performed with a probe-type

sonicator (Mason, 1990). The sonicator model used was a Misonix XL-2020 with a

frequency of 20 kHz and maximum power output of 600 W. Final FFA was the response

variable in all experiments and FFA measurements were made by wet titration with an

automatic titrator.

Finally, statistical methods were applied to the data to identify the significant effects and

to draw conclusions about their statistical significance and practical applicability to

modern biodiesel production. ANOVA and regression analysis were applied to the data

using the Minitab 16 statistical software suite.

2.0 LITERATURE REVIEW

2.1 SCOPE OF SURVEY

The scope of the literature review of the various studies was limited to their application to esterification reactions in ultra-high-FFA or high-FFA oils. Where necessary, non-esterification related works, such as those applying to transesterification, are discussed in order to furnish rudimentary background of the process itself and to familiarize the researcher and the reader with its basic application and manifestation.

2.2 INTRODUCTORY

In order to fully understand the importance of adopting new technologies for the enhanced production of biodiesel fuel, it is first necessary for one to know the background of the fuel itself, the hurdles it has overcome during its journey into mainstream acceptance, and the technologies available currently or in the near future for use in its production. This chapter serves to bring the reader up to speed on the state of biodiesel production within the United States and abroad. It aims to address the technical problems with the fuel and to hint at possible methods for correcting them. After an introduction to biodiesel production and its many technical features, the reader will then be exposed to an array of cutting edge processing technologies which may or may not have been developed to the point of industrial implementation. Finally, a description of the field of sonochemistry will be presented as a means for providing background on the

prevailing technology of this study. With this review, an understanding of the importance of technical improvement of the biodiesel process will be gained and the reader will be better prepared to grasp the significance of the use of sonication in industrial biodiesel production.

2.3   THE BACKGROUND AND HISTORY OF BIODIESEL

It was first suggested to use vegetable oil-derived fuels as a means for motive power by the inventor of the diesel engine himself, Rudolf Diesel. On April 13, 1912, Diesel proclaimed that, through vegetable oils "…Motive power can still be produced from the heat of the sun, always available, even when the natural stores of solid and liquid fuels are completely exhausted" (Pahl, 2005). These prophetic words indicated that Diesel was a visionary, carefully considering the instability of the petroleum supply chain well before the common consumer had even imagined that they were finite. Indeed, early models of the diesel engine were designed to run on vegetable oils and other alternative fuels, not the low grade petroleum distillate known today as diesel fuel. In the course of time, economics favored the use of petrodiesel (then a waste by-product) over higher cost virgin oils such as peanut and hemp (Pahl, 2005). The diesel engine was optimized for the use of petrodiesel and the vision of the engine's inventor to use clean, renewable fuels was all but forgotten.

It was not until nearly 60 years after Diesel's death that the diesel engine's ability to utilize vegetable oil-based fuels was rediscovered during the oil embargo of 1973. Previous to that however, early work was conducted at the University of Brussels by G.

Chavanne on the use of ethyl esters of palm oil in a diesel engine. This preliminary

research resulted in Belgian patent #422877 (Peterson, 2006). That patent deals little

with the production of methyl ester and focuses primarily on its use as a transportation

fuel (Iowa State University, 2006). Wartime experiments also commenced in these early

years of Biofuels research, however interest was suppressed with the reemergence of

cheap petroleum-based fuels in peacetime (Mittelbach, 2004).

With the Oil Embargo in full effect during the Fall of 1973, oil prices and supplies were

severely limited (Pahl, 2005). By 1974, the price for a barrel of oil had risen from $3 to

over $12 (Pahl, 2005). Renewable energy once again moved into the public eye and

agriculturally derived fuels were among the many sources investigated. Early

experiments suggested that the diesel engine had been highly optimized for the use of

petrodiesel over the years and that the use of straight vegetable oil held the potential for

severe engine damage (Pahl, 2005). The two viable options were to either modify the

engine, or to modify the fuel in order to attain compatibility (Mittelbach, 2004). The first

would require a mechanical alteration, the second a chemical one. Modifying the diesel

engine for straight vegetable oil use, though possible, is somewhat impractical due to the

existence of incumbent technology. The entire world had adopted petroleum-fueled

diesel engines and an alteration to the technology would result in vast infrastructure

change accompanied by an extreme resistance to adoption of the fuel for use. A more

sensible approach was to modify the fuel to suit the engine. This was the source of a

great deal of research and trials in years to come.

Early patents relating to the use of alkyl esters after the oil embargo began to appear in 1980 (Mittelbach, 2004). In 1981 and 1982, researchers in South African, Germany, and New Zealand were studying the use of vegetable oil esters in diesel engines (Mittelbach, 2004). By 1982, a young chemist and researcher by the name of Martin Mittelbach had begun development of a simplified process for producing fatty acid methyl esters under mild conditions and received a patent on the process soon thereafter. Mittelbach in collaboration with Wörgetter began feasibility testing of rapeseed methyl ester as diesel fuel at Graz University in 1983 (Mittelbach, 2004). Mittelbach himself even used the early fuel in his own diesel powered vehicle. Most feasibility testing between 1982 and 1987 were conducted on diesel tractors. It was felt that, being an agricultural fuel, the fuel should primarily benefit agricultural producers, namely farmers. Ironically, this vision has yet to come to pass as the major users of biodiesel currently are city and governmental fleets (Pahl, 2005).

Mittelbach continued his research throughout the 1980s and produced a vast body of work which resulted in the foundation for the biodiesel industry. The initial process which he developed remains the primary method by which biodiesel is produced on an industrial scale.

While Mittelbach and Wörgetter were hard at work defining the biodiesel process in Europe, Jon Van Garpen of Idaho University was bringing the Biodiesel movement to America. Charles Peterson of the Colorado School of Mines was also at the forefront of early biodiesel in the United States (Pahl, 2005).

By 1988, the term "Biodiesel" had made its way into the global alternative fuels vocabulary. The term was coined by Wang in a Chinese article on the subject (1988). The number of articles using the term "Biodiesel" to refer to the alkyl esters of vegetable oil increased almost exponentially between 1988 and 2009. Figure 1 shows this trend visually. Publication frequency seems to have begun to accelerate in 1996 and from 2000 on, the magnitude of academic interest in the topic increased rapidly.
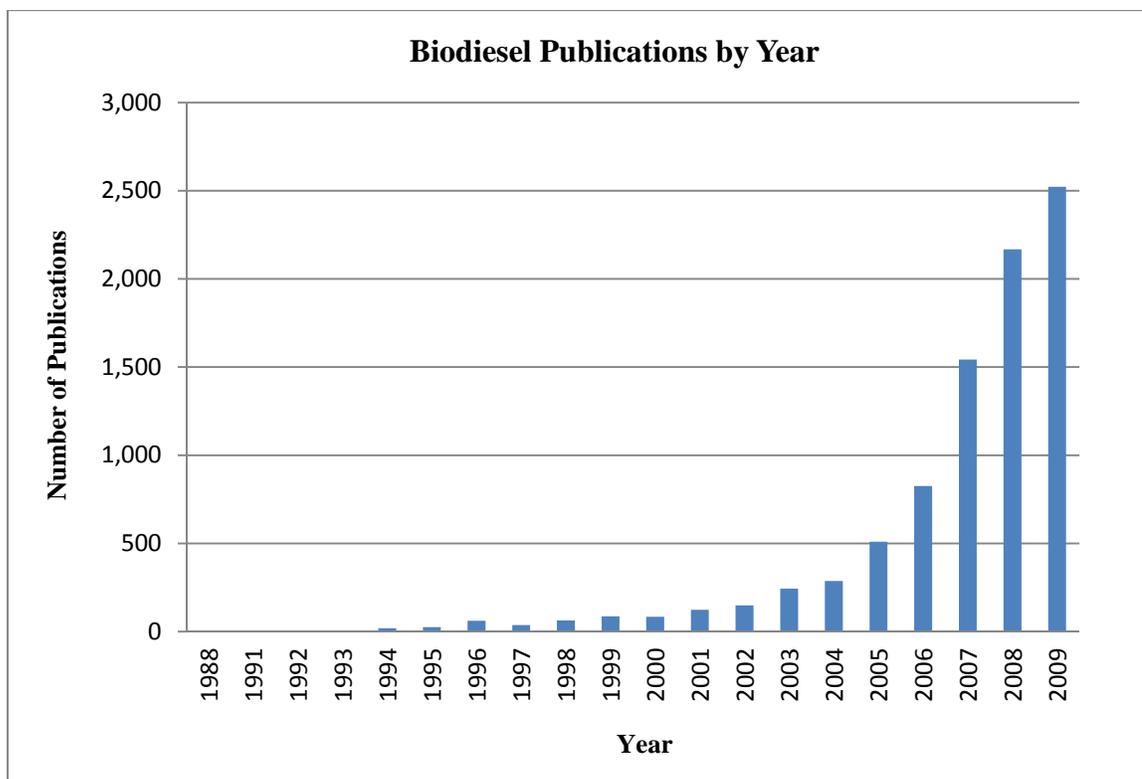
Figure 1: Biodiesel publications by year (SciFinder Scholar, 2010)

A new alternative energy source was born. As of 2009, 8,752 articles on Biodiesel had been referenced in SciFinder alone. This does not account for articles published in databases not searched by SciFinder. It also does not account for articles not using the

phrase "biodiesel" to refer to the fuel. It is evident that much scientific interest exists for Biodiesel and associated technologies and this can only lead to further breakthroughs.

2.4   THE BIODIESEL PROCESS

2.4.1   TRANSESTERIFICATION

The chemical reaction by which a lower alcohol reacts with a tri-glyceride (oil) to yield a fatty acid alkyl ester is known as transesterification. The process was first described by Duffy in 1852 and was referenced by Mittelbach (2004). Transesterification is also more broadly referred to as alcoholysis. When the process refers to a specific alcohol, the -ysis suffix is appended to the name of the reacting alcohol – for instance, transesterification with methanol is referred to as methanolysis. A slightly different reaction (described later), by which glycerol reacts with a fatty acid is known as glycerolysis. This is not explicitly considered as a transesterification reaction because glycerol is not a lower alcohol and the reactant is not a triglyceride, however it yields di- and monoglycerides and even some methyl esters (Tyson, 2002).

Transesterification occurs easily with the lower alcohols such as methanol or ethanol. The process is slow under normal conditions without the presence of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures. The catalytic reaction is complicated, however the necessity for a catalyst arises from the relative

insolubility of alcohol in oils. Catalysts provide a phase-transfer as well as an ion-exchange effect which reduces reaction times by many orders of magnitude (Mittelbach, 2004).

Transesterification will occur within a reasonable time period without the presence of a catalyst in a process known as supercritical methanolysis. Conditions are typically extreme with temperatures as high as 235 C and pressures in the range of 62 bars (Mittelbach, 2004). If temperatures and pressures are high enough, methanol becomes fully soluble in oil and the reaction occurs readily. These conditions are typically not practical for industrial purposes, however investigations by Han (2005) using gas-phase co-solvents have been made which have resulted in much milder reaction conditions.

Following is a basic schematic of a methanolysis reaction. By definition, the catalyst does not participate in the reaction so is not shown in the schematic.
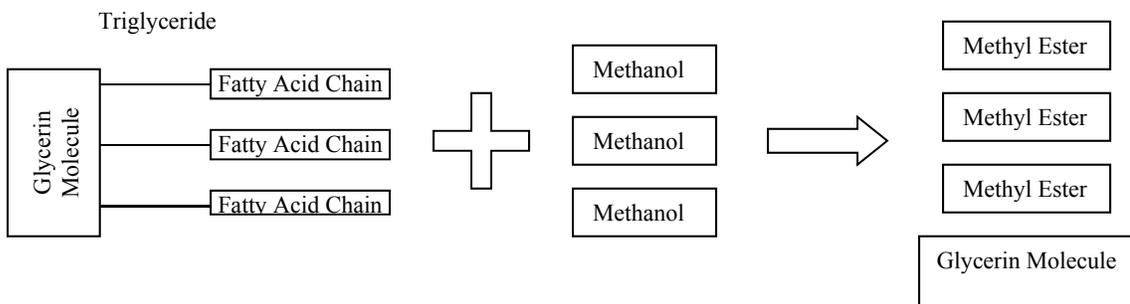
Figure 2: Basic methanolysis reaction schematic

Figure 2 is a highly simplified representation of transesterification with methanol. In actuality, the reaction occurs in 3 steps. The triglyceride is first converted into a

diglyceride, then to a monoglyceride, and finally into a free glycerin or glycerol

molecule. In each step, a methyl ester molecule is created. The total result is three

methyl ester molecules and a glycerol molecule. The following equations show the

reaction in more detail on a step-by-step basis.

$$
\begin{array}{c}
CH_2{}^-O{}^-COR^1 \\
| \\
CH{}^-O{}^-COR^2 \\
| \\
CH_2{}^-O{}^-COR^3
\end{array}
+\; CH_3OH \quad \Longleftrightarrow \quad
\begin{array}{c}
CH_2{}^-O{}^-COR^1 \\
| \\
CH_2{}^-O{}^-COR^2 \\
| \\
CH_2{}^-OH
\end{array}
+\quad R^3{}^-COOCH_3 \qquad (1)
$$

$$
\begin{array}{c}
CH_2{}^-O{}^-COR^1 \\
| \\
CH{}^-O{}^-COR^2 \\
| \\
CH_2{}^-O{}^-COR^3
\end{array}
+\; CH_3OH \quad \Longleftrightarrow \quad
\begin{array}{c}
CH_2{}^-O{}^-COR^1 \\
| \\
CH_2{}^-OH \\
| \\
CH_2{}^-OH
\end{array}
+\quad R^2{}^-COOCH_3 \qquad (2)
$$

$$
\begin{array}{c}
CH_2{}^-O{}^-COR^1 \\
| \\
CH{}^-O{}^-COR^2 \\
| \\
CH_2{}^-O{}^-COR^3
\end{array}
+\; CH_3OH \quad \Longleftrightarrow \quad
\begin{array}{c}
CH_2{}^-OH \\
| \\
CH_2{}^-OH \\
| \\
CH_2{}^-OH
\end{array}
+\quad R^1{}^-COOCH_3 \qquad (3)
$$
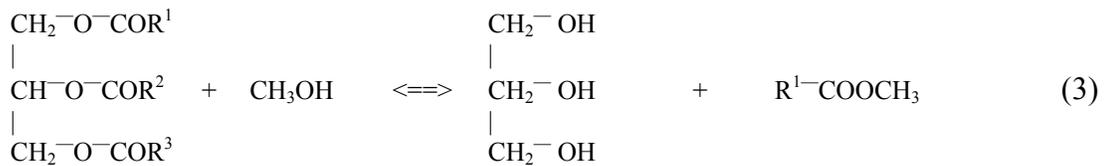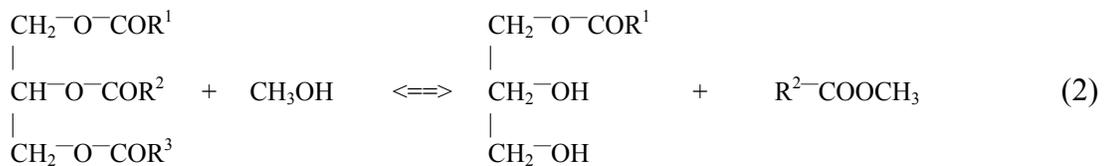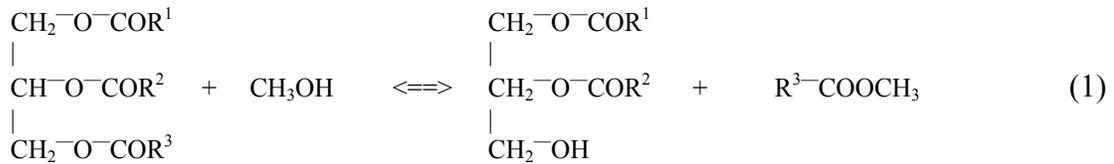
Equations (1), (2), and (3) detail the 3-step methanolysis reaction in which a triglyceride

molecule reacts with a methanol molecule to form a diglyceride plus a methyl ester

molecule (Equation 1), a monoglyceride plus a methyl ester molecule (Equation 2), and

finally a glycerin molecule plus a methyl ester molecule (Equation 3). The result is 3

methyl ester molecules plus one glycerin molecule. The reaction is reversible so excess

alcohol is typically used in practice to force the reaction towards ester production (Khan,

2002). The above equation formats were adapted from Mittelbach (2004).

2.4.2   ESTERIFICATION

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in a degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction.

The following formula shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule:

$$\underset{\text{ffa}}{R_1\text{-COOH}} + \underset{\text{methanol}}{CH_3OH} \overset{\text{sulfuric acid}}{\leftrightarrow} \underset{\text{methyl ester}}{R_1\text{-COO-CH}_3} + \underset{\text{water}}{H_2O} \tag{4}$$
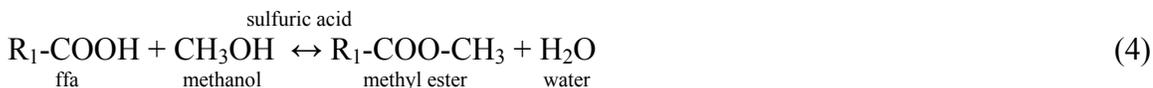
The above formula was adopted from Deshmane (2006) and represents the basic chemical reaction for all industrial esterification reactions using methanol as the alcohol. It is the formula for all reactions performed in the experimental section of this thesis.

2.4.2.1   Need for Esterification

Conventionally, virgin vegetable oils and high-grade animal fats are the feedstock of choice for biodiesel production due to low levels of impurities, such as free fatty acids and sulfated proteins, which can cause problems with processing and final product quality. Rapeseed alone comprises of roughly 84% of the lipid stocks used for biodiesel

17

production. By comparison, sunflower and palm oil each represent 13% of the feedstocks with soybean trailing with a 1% share. All other feedstocks such as waste fryer oils, animal fats, jatropha, peanut, mustard, etc. make up the remaining 2% (Pahl, 2005). With the economic and regulatory challenges outlined in the introduction, however, this trend is quickly changing (Biodiesel Magazine, 2008).

Second use oils such as yellow or brown grease are thermally- or chemically-degraded waste-oils that primarily contain grease collected from restaurant or industrial grease traps. Most of this oil is spent cooking oil from restaurants that has been thermally degraded by sustained high temperatures. It further degrades when in contact with water in the grease trap through a process known as hydrolysis (Montefrio, 2010). This degradation produces molecules known as free fatty acids. Fatty acids will chemically react with the typical alkaline catalysts used in base-catalyzed biodiesel reactions to form soap. Two problems result from this:

1. The catalyst is consumed resulting in either an increased catalyst requirement - and therefore higher chemical costs - or an incomplete or failed reaction.
2. The reaction between the fatty acid molecule and catalyst creates soaps which manifest themselves as impurities in the biodiesel and must be washed out (Lotero, 2005).

Free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional base-catalyzed reaction and will prevent the reaction from going to completion in almost all cases (Tyson, 2002).

Brown grease contains fatty acid concentrations in excess of 15% with typical values closer to 60%. It is not unusual for heavily degraded brown grease to contain nearly 100% free fatty acid (Tyson, 2002). These facts clearly imply that conventional methods of biodiesel production will be ineffective with brown grease or other ultra-high-FFA oils as feedstocks.

Acid-catalyzed esterification has been demonstrated be an effective method for converting moderately degraded feedstocks such as Yellow Grease and high-FFA animal fats into viable biodiesel. Yellow Grease primarily contains spent cooking oil that has not been hydrolyzed. For this reason, yellow grease rarely contains free fatty acid concentrations above 15% making it only moderately difficult to convert into biodiesel. Due to the greater FFA concentrations in brown grease, processing requires multiple esterification and dewatering stages as well as additional byproduct separation and purification steps (Tyson, 2002).

At present, conversion of ultra-high-FFA oils into biodiesel remains impractical and costly. Technology in existence today has failed to address three primary issues which

collectively contribute to the failure of widespread adoption of brown grease as a

principal feedstock for biodiesel:

1. Separation and purification of in-process biodiesel is challenging leading to inefficiencies, yield losses, and increased production costs.

2. Sulfur compounds remain in the finished product which fails to meet the ASTM D6751 specification of < 15 ppm of sulfur. Conventional attempts to distill the product to remove the sulfur are capital intensive and inefficient.

3. Brown grease processing can lead to waste-water discharge that is heavily contaminated and expensive to process/dispose of. High solid disposal and chemical costs exist for "dry wash" systems.

As previously discussed, the esterification reaction of free fatty acids directly into methyl

esters is a favored method of pre-treating degraded oils with high free-fatty acid

concentrations. Alternative methods involve the saponification and then washing, or

removal with water, of the resulting soaps. The removal of these soaps translates to a

yield loss and can only be economically accomplished with relatively low FFA

concentrations in the feedstock. It is not suitable for ultra-high-FFA oils.

2.4.3   INDUSTRIAL PROCESS

Industrially, both esterification and transesterification are employed in a two-step process

to first convert the FFA into alkyl esters and then to convert the remaining triglycerides

into methyl esters. An outline of the process follows:

1. The high-FFA oil is elevated in temperature and then methanol (Me OH) and sulfuric acid (H_2SO_4) are added in appropriate quantity. The reaction is allowed to progress for several hours until the FFA concentration is reduced to an acceptable level for base-catalyzed transesterification.

2. The methanol is decanted which carries the majority of the sulfuric acid and water with it. The methanol is either neutralized after decanting or neutralization is done prior to decanting with a base such as sodium hydroxide or potassium hydroxide. This converts the sulfuric acid into non-corrosive salts.

3. The esterified oil is then transferred to another reactor where additional methanol and a base catalyst is added to transesterify the remaining triglyceride.

4. Washing and other post-processing steps are done to prepare the resulting methyl esters for sale as biodiesel fuel. The glycerin byproducts are treated to remove the soaps and excess methanol (Zullaikah, 2005).

2.4.4 ALCOHOLS

The primary alcohols used for Biodiesel production in both transesterification and esterification reactions are of the lower types, namely methanol and ethanol (Mittelbach, 2004). Each has distinct advantages and disadvantages. They are described below in conjunction with an explanation of other possible alcohol species for the production of alkyl esters.

2.4.4.1   Methanol

Methanol is by far the most popular alcohol used in industrial Biodiesel production. The primary reasons for this are due to its low price and high reactivity. In conjunction with alkaline catalysts, practical yields greater than 100% are typical with 80 of the conversion occurring within the first 5 minutes (Mittelbach, 2004). Post-separation of the reacted products occurs at nearly the same rate as the reaction which eliminates process bottlenecks. Other advantages include the fact that methanol has less of an affinity to atmospheric moisture absorption and retention and can be obtained in anhydrous form. Moisture removal can be achieved by simple distillation.

Methanol is typically a petroleum-based product although some research has gone into the production of methanol from agricultural sources (Branson, 2002) from [Mittelbach, 47]. For that reason, it is considered less environmentally friendly than ethanol. Many complain that Biodiesel will not be a true agricultural fuel until ethanol is widely implemented in conventional processing techniques.

2.4.4.2   Ethanol

Ethanol is produced from the anaerobic fermentation of high-glucose carbohydrates followed by distillation. Also known as ethyl alcohol, ethanol is the alcohol found in alcoholic beverages for human consumption. The carbohydrate stock is typically derived from the germ of grains such as corn and wheat. Ethanol itself is used as an alternative fuel in gasoline engines. Ethanol can be blended as high as 10% in most gasoline engines and as high as 100 percent with minor modifications or in "flex fuel" vehicles. Though it

is considered a renewable resource, it is far more energy intensive to produce than

Biodiesel. Whereas Biodiesel has a positive energy balance as high as 3.5:1 (National

Biodiesel Board, 2008), ethanol has been reported to have an energy balance as low as

1.2:1 or even a negative balance (Journey to Forever, 2010). The energy balance of a

fuel is the ratio between the quantity of fossil energy units consumed in the production of

the fuel and the number of energy units yielded by the end use of the fuel. For this

reason, ethanol is far more expensive than methanol which is the primary reason for its

limited use as a reactant for Biodiesel production. Other advantages of ethanol besides

the environmental ones are the comparatively low toxicity in relation to methanol

(Wikipedia, 2010). Ethanol also has an additional carbon atom which has been shown to

increase the heat and cetane values of ethyl esters (Fillières et al., 1995). Other

disadvantages of ethanol are difficulty separating of the ester and glycerol phases, higher

reaction temperatures, reaction sensitivity to trace moisture, and lower conversion than

methanol (Mittelbach, 2004).

2.5   CHARACTERIZING THE ESTERIFICATION REACTION

The literature review produced no evidence of a formal attempt to characterize the

esterification reaction of free fatty acids in ultra-high-FFA oils using methanol as the

alcohol and sulfuric acid as the catalyst. The term "characterization" is used here to refer

to a comprehensive comparative study of the primary variables or factors that influence

the level of free fatty acid reduction in the sulfuric acid catalyzed esterification reaction.

As a product of the various investigations, however, some understanding was gained

about the effects of several variables of various unique reaction systems including those in oils containing elevated levels of FFA.

In studying the production of methyl esters from Nile tilapia (fish) oil using ultrasonic excitation, Santos et al. identified the methanol to FFA molar ratio to be the most important factor influencing the conversion of FFA to methyl esters followed by catalyst content. Response surface methodology was employed to determine an optimal operating condition of 9.0 alcohol to oil molar ratio and 2.0% wt/wt catalyst concentration at 30 ºC (Santos, 2010).

Cardoso et al. (2008) studied the effect of oleic acid concentration, catalyst concentration, and temperature in esterification reactions using $SnCl_2$ catalyst and ethanol as the alcohol. High FFA levels (up to 10%). All three factors were determined to have desirable effects on the esterification reaction and the study concluded that tin chloride was a suitable catalyst for esterification. In addition, the study determined that ethanol in high excess to oleic acid (>120:1 molar ratio) had no discernable effect on the reaction yield or rate at varied levels (Cardoso, 2008).

Ngo, et al. (2010) developed a process to manufacture biodiesel using waste greases with free fatty acid concentrations ranging from 10% to 90% using sustainable methods. The group characterized several catalysts and the resulting methyl ester products. The importance of this study was that it focused on low-cost feedstocks such as brown and yellow greases (Ngo, 2010).

The 2-step acid esterification / base transesterification of rendered pork lard with acid value of 14.57 mg KOH/g was studied by Dias et al. (2009). The team determined that the prevailing factors for the esterification reaction were sulfuric acid and temperature (Dias, 2009). Moisture or methanol content were not explicitly studied nor were interaction effects between factors.

Hahn et al. (2009) studied the effects of ethanol to oleic acid molar ratio, catalyst concentration, temperature, alcohol type, and free fatty acid type, on esterification reactions catalyzed by sulfuric acid under ultrasonic irradiation. Optimal conditions were found at ethanol to oleic acid molar ratio of 3:1, catalyst concentration of 3%, and reaction time of 2 hours at 60 ºC (Hahn, 2009).

Liu et al. (2006) studied the effects of water on the esterification of acetic acid using sulfuric acid as the catalyst. They demonstrated that catalytic activity was reduced by increased water content and determined its effect to be -0.83. The researchers presumed that the primary mechanism for this deactivation was solvation of the catalyst by water (Liu, 2006). This gives credence to the present study's examination of water content in the esterification reaction of ultra-high-FFA oils.

Many more such studies exist and support several of the postulates of this thesis; however the literature is lacking a comprehensive study to fully characterize the effects of the primary reaction components (alcohol level, catalyst level, water content, and temperature) of sulfuric acid catalyzed esterification of ultra-high FFA oils.

2.6   IMPROVING REACTION KINETICS

Stavarache et al. (2003) first reported that sonochemistry applied to the transesterification reaction could dramatically improve reaction time and yield. They concluded that low-frequency ultrasonic irradiation at both 28 and 40 kHz showed dramatic improvements over mechanical stirring (Stavarache, 2003). Others duplicated the effect in following years (Benitez 2004; Fang 2005; Colucci 2005). From 2006 until present, the number of papers on the topic increased dramatically with investigations in areas ranging from ultrasonically assisted exotic catalysis (Yue, 2006) to in-situ transesterification of sunflower oil using ultrasonic excitation (Georgogianni, 2008).

In, 2009, Lee et al. used ultrasonic excitation to prepare methyl via esterification of fatty acids. After resolving overheating problems, they determined that reaction time was shortened dramatically - 30 minutes for 93% yield (Lee, 2010). No consideration or comparison of mechanical or thermal energy input was made.

As mentioned in the previous section, Santos et al. studied the effects of ultrasonic excitation on Nile tilapia oil (2010). Comparisons were made between stirred and ultrasonically agitated reactions, however their study did not consider energy intensity in comparison to the stirred reactions.

As mentioned in the last section, Hahn et al. studied the effects of ethanol to oleic acid molar ratio, catalyst concentration, temperature, alcohol type, and free fatty acid type, on esterification reactions catalyzed by sulfuric acid under ultrasonic irradiation. Agitated

experiments were done with a stirrer with 35 watt output while sonication experiments were done with an ultrasonic cleaner outputting 700 watts (Hahn, 2009). Clearly, the improvement of ultrasonic irradiation over stirring was not examined as a function of energy input.

Deshmane, et al. studied the effects of ultrasonic irradiation on the esterification of palm fatty acid distillates at 30 ºC and 40 ºC with stirring, ultrasonic agitation, and a combination of both. The effects of ultrasound, methanol to distillate ratio, catalyst concentration, and reaction temperature, were studied. In addition, some kinetic modeling of the reaction was performed. The effect of artificial water addition was not studied, nor was the effect of energy input between the two agitation methods.

Clearly, though focused and highly valuable research has been accomplished in the area of ultrasonically assisted esterification reactions, there has been no attempt to reconcile the difference between stirring and sonication on an energy input basis in either transesterification reactions or esterification reactions in either high or ultra-high-FFA oils.

2.7   SUMMARY OF THE LITERATURE REVIEW

Some history and background on both the science and history of biodiesel as an industry and as a process has been given. Justification for the use of second-use, high free-fatty acid feedstocks and the associated requirement for acid-catalyzed esterification has been explored. The literature review found a great deal of research in both the characterization

of certain components of the esterification reaction itself as well as sonochemistry as applied to the esterification reaction. It failed to find, however, a comprehensive exploration of the sulfuric acid catalyzed esterification reaction of ultra-high-FFA oils such as brown grease and fatty acid distillates. It also failed to find a dedicated comparison of the effects of agitation by stirring and by sonication on the basis of energy input. The remainder of this thesis seeks to reconcile these deficiencies in the current state of the art.

3.0 EXPERIMENTAL

From the literature review, it was discovered that the state of understanding about the relative effects between controllable factors in the esterification reaction of ultra-high-FFA oils such as brown grease is lacking both in academia and in industry. It is known that these factors all influence the reaction, however it is not known to what degree and to what extent some factors dominate the others. This information would be valuable to either the scientist or the captain of industry because it is a foundation upon which optimal operating conditions can be built. This foundation will be experimentally established as a product of this work.

In addition, with the many choices of second-generation reaction technologies, little guidance is offered as to whether these reaction technologies are worth the capital investment. A second experiment is presented here to demystify one particular reaction technology, sonication, and present its sole advantage in the context of its ability to input higher amounts of kinetic energy into the reaction matrix than conventional methods.

3.1   SCOPE OF EXPERIMENTS

The scope of the first experiment, esterification reaction characterization, is to establish a foundation for operational optimization. It is intended to identify the relative magnitudes of the four chosen experimental factors: sulfuric acid content, methanol content, water

content, and reaction temperature in reactions involving ultra-high-FFA oils. Brown grease was used in all experiments at an FFA concentration of ~85%. The experiment does not attempt to optimize the examined factors, nor does it strive to suggest that these are the only important elements. In addition, it evaluates only two levels for each factor and any conclusions drawn can only be applied to the range bracketed by the high and low level for each. Finally, the studied time range was the first 15 minutes of reaction. Typical esterification reactions in ultra-high-FFA oils can run for several hours and it is possible that the relative magnitudes of effects will differ from those found in this work. An assumption was made here that the relative magnitude of each effect remains proportional throughout the reaction.

The scope of the second experiment, enhanced reaction kinetics evaluation, is limited to the evaluation of sonication as a reaction enhancement technique against conventional stirring as a function of energy input. Two factors were varied: agitation type (sonication or stirring) and catalyst level. As mentioned in the introduction, energy input was held constant for both agitation methods as a way of filtering out the effect of mechanical and thermal energy input into the system from any other effect. If the agitation-method categorical factor effect was found to be significant at constant energy input, then it would suggest that sonication offers a benefit over and above its ability simply to add more mechanical energy to the reaction matrix. Interaction between this effect and catalyst treatment level was also examined. This experiment does not evaluate interactions between any of the other factors from the first experiment, nor does it attempt to optimize the power levels, frequency, or other sonication parameters for

sonochemistry. Since the power level of the sonication was held constant and only one level evaluated, this experiment does not identify any potential interaction effects that might occur at higher power levels. And as with the first experiment, conclusions and observations drawn from the experiment apply only to the regions bracketed by the factor levels.

3.2 DESIGN OF EXPERIMENT

The 2^k factorial design was chosen for the two primary experimental systems in this body of work. Both systems were completely randomized designs using the default random number generator in Minitab 16. The designs for each system are presented and discussed in the following sections.

3.2.1 ESTERIFICATION REACTION CHARACTERIZATION

There are four fundamental factors that potentially influence the rate and completeness of the esterification reaction of free fatty acids in waste oils:

1. Relative quantity of methanol
2. Relative quantity of sulfuric acid catalyst
3. Relative quantity of water
4. Temperature of the reaction system

A potential fifth factor is agitation speed, however the effect of this factor was thought to be minor and, in many existing industrial designs, difficult to alter. For this reason, agitation speed was fixed for the purpose of this experiment. Table 1 shows the factor levels and run order for the Esterification Reaction Characterization experiment.

Table 1: Esterification reaction characterization experiment

Run Order	Standard Order	Sulfuric Acid Addition	Water Addition	Methanol Addition	Temperature
1	27	+	−	−	+
2	20	−	+	−	−
3	18	−	−	−	−
4	28	−	+	−	+
5	26	−	−	−	+
6	33	+	+	+	+
7	19	+	−	−	−
8	24	−	+	+	−
9	25	+	+	+	−
10	30	−	−	+	+
11	22	−	−	+	−
12	23	+	−	+	−
13	31	+	−	+	+
14	29	+	+	−	+
15	21	+	+	−	−
16	34	0	0	0	0
17	32	−	+	+	+
18	12	+	+	−	+
19	14	+	−	+	+
20	10	+	−	−	+
21	4	+	+	−	−
22	11	−	+	−	+
23	1	−	−	−	−
24	2	+	−	−	−
25	17	0	0	0	0
26	16	+	+	+	+
27	5	−	−	+	−
28	8	+	+	+	−
29	9	−	−	−	+
30	13	−	−	+	+
31	6	+	−	+	−
32	3	−	+	−	−
33	15	−	+	+	+
34	7	−	+	+	−

A plus sign (+) indicates the high factor level, a minus sign (-) indicates the low factor level, and a zero (0) indicates the center point level (center points are discussed in future sections). Table 2 shows the corresponding treatment levels associated with the high, low, and center point levels.

Table 2: Treatment levels for factorial design

	+	−	0
Sulfuric Acid	500 µl	150 µl	350 µl
Water Addition	500 µl	0 µl	250 µl
Methanol	100 ml	50 ml	75 ml
Temperature	60 ℃	48 ℃	54 ℃

3.2.1.1 Justification for the Factorial Design

From the literature review, each of the listed factors is known to affect reaction efficiency, however the relative effects between them are not known. For instance, should an operator bother to increase reaction temperature or focus on reducing the water content of the lipid stock prior to starting the reaction? It was desired to determine the relative effects of the main factors and their interactions to gain a better understanding of where to focus time and capital in the optimization of real-world industrial systems.

Because this experiment is essentially a factor screening experiment, two treatment levels were chosen for each factor in order to simplify the design and minimize the number of required runs. Safeguards to test for curvature in the resulting model, which required the introduction of a few intermediate levels called center points, were also taken and this will be discussed in proceeding paragraphs.

33

Because there were more than one or two factors to evaluate and because it was desired to examine interactions between factors, a 2^4 factorial design was chosen for the experiment. The choice of a factorial design provided a relative efficiency of 2.5 compared to an experiment evaluating each independently (Montgomery, 2005). This means that a one-factor-at-a-time experiment would require 2.5 times the number of runs as the 2^4 factorial design that was chosen in order to evaluate the effects and interactions of each factor.

3.2.1.2   Choice of Levels

As outlined in Table 2, high, low, and center point levels were chosen for each of the four factors in the factorial design. The volume of oil used for all reactions for both experiments was 50 ml. The levels of each liquid reactant - sulfuric acid, water, and methanol - were chosen based on a volumetric percentage of the oil. Table 3 summarizes these percentages.

Table 3: Concentration of treatment levels by volume of oil

	+	–
Sulfuric Acid	1%	0.3%
Water Addition	1%	0%
Methanol	200%	100%

3.2.1.3   Randomization

As mentioned previously, the experiment was a completely randomized design.

Randomization was achieved using the default generator in Minitab 16. Experiments

were run in the exact order of the randomized output. This randomization can be

observed in Table 1. Other experimental elements such as human resource and

instrument allocation could not be randomized because, in each case, there was only one

instance of each element. Chemicals were drawn from lots and for this reason, blocking

was used as described in a later section.

3.2.1.4   Replicates

Determining the number of replicates was (and often is) an iterative process. From

Montgomery, we recall that a replicate is an independent repeat of a unique factor

combination (Montgomery, 2005). From a practical standpoint, replication is required to

rule out the possibility that an observed effect is caused by experimental error. It is the

fundamental technique for determining statistical significance. A replicate is not to be

confused with a repeated measurement, or "duplicate" as referred to in this text.

Duplication was used in these experiments to correct for variability caused by

instrumentation accuracy as well as identify possible botched measurements.

In order to estimate the number of required replicates, it was first necessary to determine

the standard deviation between identical factor combinations. Three identical runs were

made using the parameters in Table 4:

Table 4: Initial parameters to determine required replicates

Brown Grease	50 ml
Methanol	50 ml
Sulfuric Acid	250 µl
Water Addition	500 µl
Reaction Time	10 min.
Reaction Temp.	50 °C
Stir Rate	700 rpm

Two repeated measurements (duplicates) were taken after each run. The average value of each run is shown in Table 5 along with the associated standard deviation:

Table 5: Initial experimental standard deviation for esterification characterization

Sequence	Final FFA %
Run 1	28.892
Run 2	29.149
Run 3	30.189
S	0.68676

Once the standard deviation of successive identical runs was established, it was possible to arrive at an estimate of required replicates, or the sample size. Estimated sample size was determined using the "Power and Sample Size" tool in Minitab 16. An iterative approach was taken. It was desired to keep the sample size as low as possible to minimize the number of runs for the experiment. For this reason, it was deemed acceptable to choose the minimum possible number of replicates (2), enter the values for Power, Center Points, and the Standard Deviation, and calculate the minimum observable effect based on the significance level. This effect would then be evaluated with a practical eye to determine if it was appropriate for the experiment or if additional

replicates were needed.   The appropriate tool for 2-level factorial designs was selected

and the values entered as shown:
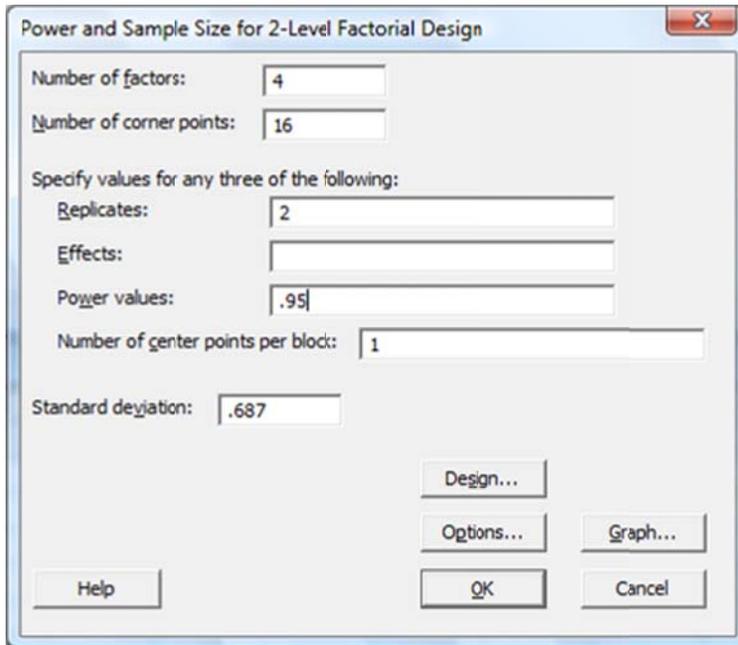
Figure 3: Power and sample size tool in Minitab 16

The design had 4 factors as previously stated and the number of corner points for a full-

factorial design is 4x4 = 16. A power value of 0.95 was considered sufficient to give

relative confidence that a real effect is not missed by the model.

Power = 1 - β   (5)

where β is the probability of not rejecting the null hypothesis when it is false

(Montgomery, 2005). From a practical standpoint, the power value is a measure of the

likelihood that an observed effect will be identified if it actually exists. A power value of

0.95 means that there is a 95% chance of identifying a real effect and a 5% chance of missing it even though it is real.

Blocking was anticipated (discussed in the next section), so 2 blocks were selected in the "Design…" option. A significance level (α) of 0.05 was entered under "Options…" The significance level is the probability of rejecting the null hypothesis if it is true. An α of 0.05 indicates that there is a 5% chance that an apparent effect is a product of statistical error and is not a real effect.

Both the power level and significance levels chosen for this design were the default values in Minitab and are common values in many statistical designs. Higher power levels and lower significance levels would be justified in optimization experiments where high certainty is required, however for the purposes and scope of this body of work and for determining the initial sample size, the default values were deemed to be adequate.

The tool iteratively determined a maximum detectible effect of 0.933 at an α level of 0.05 and a power level of 0.95 for a 2-level, 4-factor, full-factorial design with two blocks, one center point, and a standard deviation of 0.687. The power curve is seen in Figure 17.
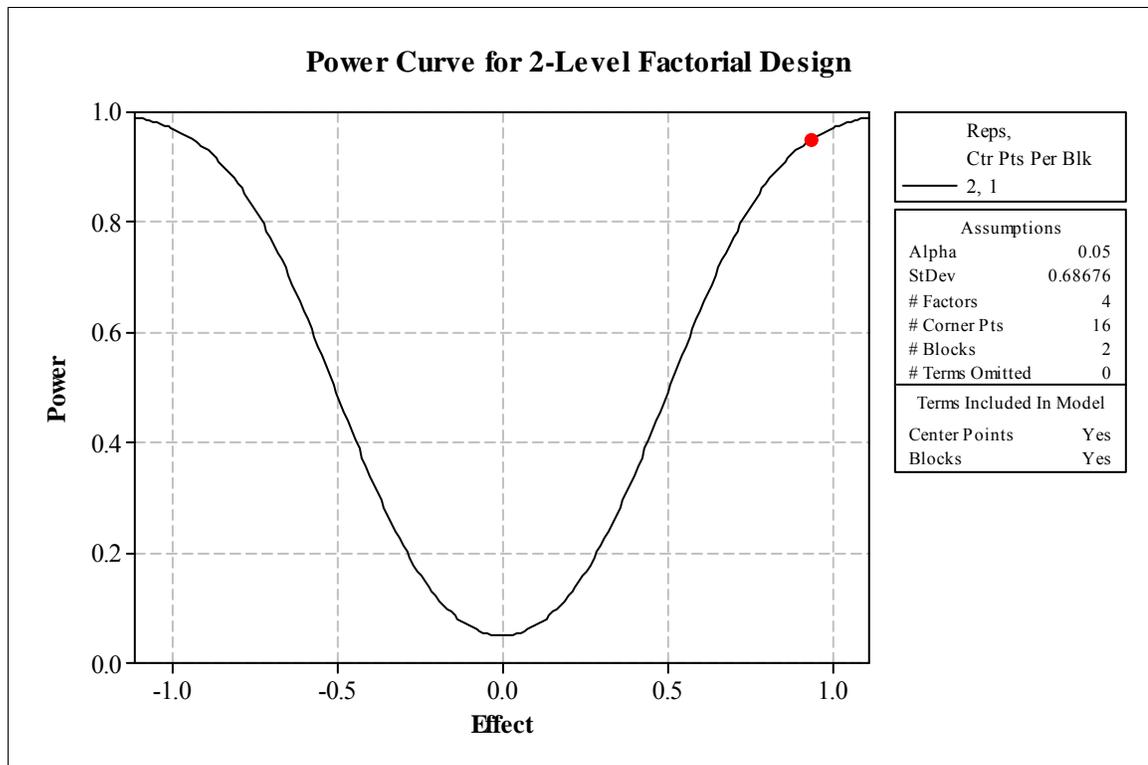
Figure 4: Power curve for the esterification reaction characterization experiment

Generally, from a practical standpoint, an effect with an impact on FFA percentage of less than about 3 would not be considered significant unless the cost to modify the factor(s) involved was minimal. Exceptions to this would be if the final FFA percentage was close to a spec which would determine the successful sale of product, or if no other methods existed to achieve a desired FFA percentage. This is discussed in more detail in the Results and Discussions section; however it was touched on briefly here in order to justify the choice of sample size.

Since the maximum detectible effect calculated by Minitab was ~1 and an effect less than 3 would generally be considered to be not useful, the initial selection of 2 replicates was considered to be sufficient for the experiment. Ultimately, the actual standard deviation

of the experiment was far greater than the initial estimate, and this affected the power

value for one of the effects, albeit not to the detriment of the experiment, as will be

discussed in the Results and Discussions section.

3.2.1.5   Consideration of the Fractional Factorial Design

A fractional factorial design was briefly considered for this experiment. Higher order

interactions were of no interest in this design and it was only desired to examine first

order interactions: that is, interactions between the main effects only. A resolution V

design would have been suitable since no main effect would have been aliased with any

other main effect or with any two-factor interactions, and aliasing would have existed

only with three factor interactions. A brief examination of Table 6 and recalling that

resolution V designs exist only in certain designs of 5 factors or more led to the nearly

immediate rejection of the possibility of using a fractional factorial design for this

experiment (Montgomery, 2005). A resolution IV, half-fraction design is possible with a

4-factor experiment; however aliasing between the 2-factor interactions would have led

to uncertainty about the significance of main-effect interactions. A full-factorial design

was the only reasonable possibility given the objectives of the experiment.

Table 6: Available factorial designs (Minitab 16)

	Factors													
Run	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	Full	III												
8		Full	IV	III	III	III								
16			Full	V	IV	IV	IV	III	III	III	III	III	III	III
32				Full	VI	IV	IV	IV	IV	IV	IV	IV	IV	IV
64					Ful	VII	V	IV	IV	IV	IV	IV	IV	IV
128						Full	VIII	VI	V	V	IV	IV	IV	IV

40

3.2.1.6   Test for Curvature

As mentioned previously, it was also desired to test for curvature in the design. Because a 2^k factorial design assumes linearity by its nature (predictive intermediate points would fall along a line drawn between the two factor levels), a test for curvature is valuable if the experimenter suspects non-linearity in the model or simply wishes to test for its existence (Montgomery, 2005).

Center points are added to the model to test for the existence of quadratic effects in the fitted data. These second-order effects will cause a twisting of the plane generated by the interaction terms (Montgomery, 2005). Graphically, curvature would be observed if the center points do not lie near the plane passing through the factorial points. True center points will be treatment levels that are equidistant from each high and low treatment level. These have the advantage of not affecting the standard effects estimates in the 2^k design (Montgomery, 2005). To have true center points, all factors must be numerical, not categorical, factors. Center points can be simulated in experiments that have one or more categorical factors as will be seen in sections dealing with the sonication experiment. For this design, one center point was chosen per block as a simple test for curvature. The center points can be observed in Table 4 and the center point levels can be seen in Table 5.

3.2.1.7   Blocking

A 2^4 full-factorial design with no blocking or center points would yield $2^{4-1} = 16$ unique runs or factor combinations. Adding one replicate would result in 32 runs. Dividing the

experiment into two blocks and adding one center point per block resulted in a total of 34 unique factor combinations.

Blocking was chosen for two primary reasons:

1. Dividing the experiment into two blocks would result in 16 runs per block. At approximately 30 minutes total cycle time per run (reaction, sampling, analysis), this fit nicely into an 8-hour day. By completing one block inside of one day, the influence of performing the runs on different days could be adequately controlled for in the statistical analysis.

2. The quantities in each container of the various reagent chemicals used for the reactions and analyses were not sufficient for 34 complete runs. For instance, the container of reagent alcohol used as the solvent in the FFA measurement was 1 gallon or 3.8 liters. Recall that measurements were run in duplicate for a total of 68 total measurements barring any mistakes. Each measurement required 100 ml of reagent alcohol for a total requirement of 6.8 liters of reagent alcohol. Similarly, about 4 liters of titrant was needed for the measurements, and the volume of each bottle of titrant was 2 liters. By dividing the experiment into 2 blocks, each block could be run with 1 batch of chemicals.

The end result was that several potential nuisance factors could be statistically eliminated from the experimental results. The number of blocks was equal to the number of

replicates, so each replicate occurred in a different block. As a result, no confounding existed with this design.

3.2.2   ENHANCED REACTION KINETICS EVALUATION

An additional objective of this study was to examine a reaction kinetics enhancement technology, ultrasonically induced cavitation, from a total energy input standpoint. The literature review showed several instances of sonochemistry being applied to both transesterification and esterification reactions of low and high free fatty acid oils respectively. None, however, attempted a comparative examination of the technique under the lens of energy input. It is the belief of the author that the single advantage of sonochemistry in esterification and transesterification reactions is that the technology possesses the ability to deliver more mechanical energy to the reactants than conventional stirring methods. Some claims of catalyst activation and complex hydroxyl reactions induced by sonication have been made (Mason, 1990), but the author challenges these claims as having any significant impact on reaction rate improvement. It became an objective of this study to demonstrate that reaction acceleration is a function of energy input only and that any means for inputting an equivalent amount of energy (high-shear mixing for instance) is just as suitable as sonochemistry. The author regrets that he must spoil the ending to some degree in order to continue the current discussion because a significant portion of this experimental design was based on the findings of the first experiment from the preceding section.

As seen in further detail in the Results and Discussion section, the Esterification Reaction Characterization experiment concluded that sulfuric acid (catalyst) addition rate had the single greatest impact on final FFA content after 15 minutes of reaction time. This was followed by temperature and water addition rate (negative magnitude). Methanol content in the range and reaction period evaluated had negligible effect. A primary interaction between temperature and catalyst also existed but was determined to be of no practical significance. Due primarily to experimental logistics, a 2^2 factorial design was chosen with agitation method (sonication or stirring) at a common energy level and sulfuric acid content as the controllable factors. This choice is justified as follows:

1. A 2^2 design would give the minimum number of experimental runs while still demonstrating the primary objective.

2. Methanol content could not be practically varied because this would change the volume of the reactant mixture and therefore influence the energy content required to agitate the mixture. This would make it difficult to fix the energy input for each level.

3. Temperature could not be easily varied between runs because the sonication reaction generated the heat for the reaction through mechanical excitation as an influence of the cavitation itself. The only way to vary the temperature would be to induce additional cooling which would effectively remove energy from the system. This would cause the observer to draw false conclusions about the energy/agitation method relationship.

4. Energy input was not chosen as a variable factor because, in addition to it being difficult to change, due to the range of energy use between the highest and lowest stirring settings, the difference in levels would have been so small that a significant effect would have had little chance of being identified.

5. Varied sulfuric acid levels would result in minute volumetric differences between levels and therefore could have potentially impacted the required energy input to agitate the bulk material just as changing methanol volume would, however the order of magnitude between the sulfuric acid volume (μl) and the reaction volume (ml) was thought to be negligible and within the range of variability between reaction volumes of different experimental runs. For this reason, and because it was the single most significant effect, sulfuric acid addition rate was chosen as the second controllable variable for the 2-level, 2-factor design.

Table 7: Reaction acceleration evaluation experiment

Run Order	Standard Order	Agitation Type	Sulfuric Acid
1	5	−	−
2	9	−	0
3	2	+	−
4	1	−	−
5	4	+	+
6	8	+	+
7	3	−	+
8	10	+	0
9	6	+	−
10	7	−	+

Table 8: Reaction acceleration experiment treatment levels

	+	−	0
Agitation Type	Sonication	Stirring	N/A
Sulfuric Acid	500 μl	150 μl	325 μl

3.2.2.1   Design Choices

Since most of the background on the various design choices was covered in the

Esterification Reaction Characterization section, the design choices are covered more

concisely in a single section here.

A full factorial 2^2 design required only 2x2 = 4 runs. It was desired to test for curvature,

however since one of the factors (agitation method) was categorical and not numerical,

pseudo-center points were added to the model. Pseudo-center points are the center points

for the numerical factors at each combination of the categorical factors (Minitab Help,

2010). In the 2^2 design, only two numerical factor combinations existed yielding only

two pseudo-center points to simulate a single center point for the model.

A similar series of identical experimental runs as in the Esterification Reaction

Characterization was used to establish the required sample size for the Enhanced

Reaction Kinetics Evaluation. Reaction parameters are summarized in Table 9 and the

results of the runs and resulting standard deviation are summarized in Table 10.

Table 9: Initial parameters to determine required replicates

Brown Grease	50 ml
Methanol	50 ml
Sulfuric Acid	325 μl
Reaction Time	15 min.
Reaction Temp.	60 °C

Table 10: Initial experimental standard deviation for sonication experiment

Sequence	Final FFA %
Run 1	26.49537
Run 2	26.41208
Run 3	26.79163
Run 4	27.24879
S	0.378094

The 2-Level Factorial Design Power & Sample Size tool in Minitab 16 yielded the following power curve for a 2^2 design with no blocks, a significance level (α) of 0.05, a power level of 0.95, and a standard deviation of 0.378094:
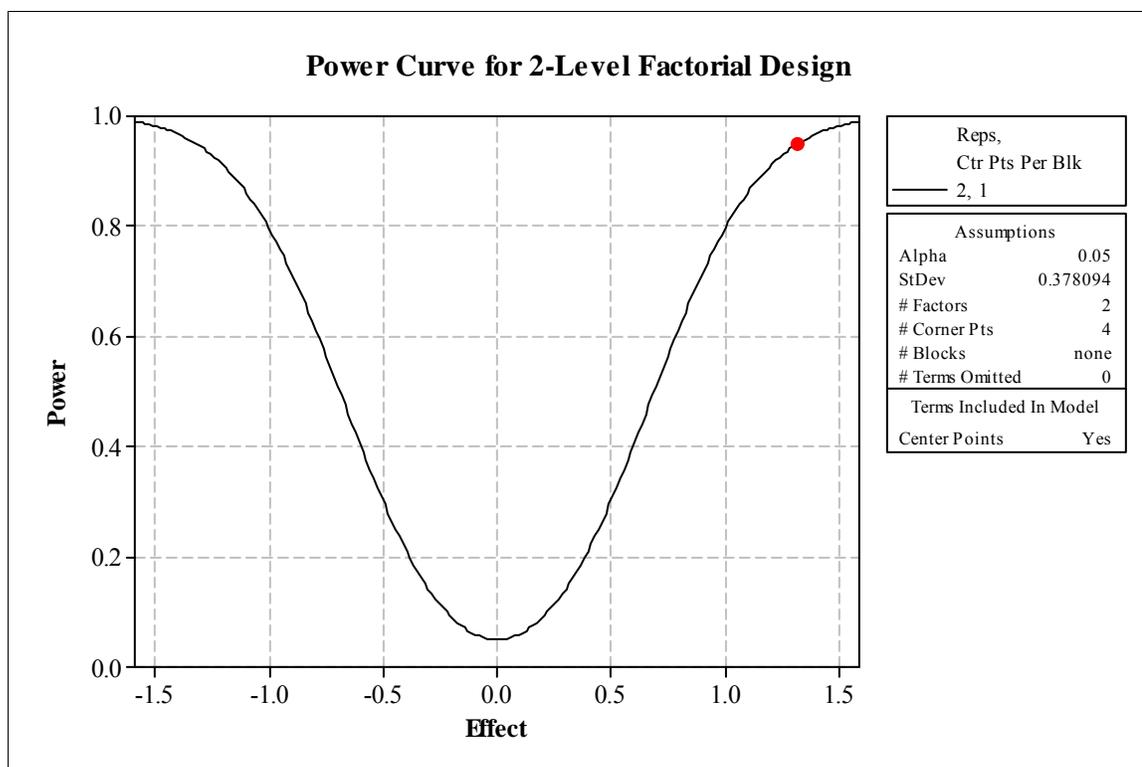
Figure 5: Power curve for the sonication experiment

From Figure 18, an effect of 1.31751 can be observed with only two replicates. Though higher than the observable effect with the Esterification Characterization Experiment, it still falls within the practical level of 3 referenced earlier.

With the addition of the two pseudo-center points, the total number of runs for the enhanced reaction kinetics evaluation experiment is 10. Because of the relatively small number of runs, and referring to the justification for blocking in the Esterification Reaction Characterization section, blocking was not used in this design.

3.3 EQUIPMENT

3.3.1 SONICATOR

As mentioned previously, the sonicator used for experimentation was a Misonix XL2020 with a driver frequency of 20 kHz and maximum power output of 600 W. Table 11 shows the basic specifications of the device and related peripherals.

Table 11: Specification for XL2020 sonicator

Generator	
Input Voltage	200-260 Vac @ 50/60 Hz
Full Load Current	7.5 Amps
Fuse Rating	8 Amps (GDB8)
Weight	16.5 lbs. (7.4Kg)
Dimensions	7.5"x18.5"x11.6" (WxLxH)
Output Voltage	1500 V rms (max.)
Output Frequency	20 KHz (nom.)
Convertor	
Weight	2 lbs. (0.9 Kg)
Dimensions	8" L x 2.5" Dia.
Materials	Aluminum
Standard Horn	
Weight	0.5 lbs. (0.45Kg)
Dimensions	5" L x1.5" Dia.
Materials	Titanium Alloy

3.3.2 GLASSWARE

Standard laboratory glassware was used for measuring and reacting the various chemicals for these experiments. Table 12 shows a list of the specific glassware used and the purpose of each.

Table 12: Glassware used in experimentation

Glassware	Purpose
140 ml Beaker	Reaction vessel for stirred reactions,
100 ml Graduated Cylinder (1 ml graduations)	Measurement of methanol, lipid stock, and reagent alcohol for FFA analysis
500 ml beaker	Intermediate holding vessel for lipid stock, reaction vessel for reaction curve derivation
4 oz. glass jar	Reaction vessel for sonication reactions
5 ml. pipette	Measurement and dispensing of sulfuric acid for reaction curve derivation experiment

3.3.3 PIPETTING SYSTEM

Figure 6: Adjustable pipetter

A Fisherbrand™ Finnpipette II (fishersci.com catalog number 21-377-822) single-channel pipetter with an adjustable volume of 200 – 1000 μl was used for measuring and dispensing sulfuric acid and deionized water in the stirred reactions and for dispensing sulfuric acid in the sonication reactions. The measurement accuracy was ±6.00 to 1.80 μl (±0.9 to 0.6% of range) and the precision was 2.00 to 0.6 μl (0.3 to 0.2% of range). Thermo Scientific™ Finntip 1000 pipette tips (Thermo Scientific item #9401070) were used in conjunction with the pipetter.

3.3.4   STIR BARS

Figure 7: Magnetic stir bar

Magnetic stir bars were used to agitate the stirred reactions. For the reactions involved in the factorial experiments, a Fisherbrand™ Polygon Stir Bar (fishersci.com catalog number 14-512-126) with dimensions 9.5 mm D x 25.4 mm L was used for agitating the reactants. For pre-reaction lipid stock stirring and for the reaction rate curve derivation reactions, an 8 mm D x 50 mm L magnetic stir bar (fishersci.com catalog number 14-512-127) was used.

3.3.5   BALANCE

A digital laboratory balance with an accuracy of ±0.01 g was used for weighing samples for FFA analysis and for weighing reactor quantities before and after reaction to determine methanol loss.

3.3.6   HEATED STIR PLATE

A Fisher Scientific Isotemp magnetic stirrer with maximum rotational output of 1400 RPM was used for conducting the stirred reactions. The plate has unidirectional temperature control which means that it has heating ability, but not cooling ability. The

Isotemp has a thermocouple temperature probe for the purposes of loop thermal control and temperature monitoring.

3.3.7 AUTO TITRATOR

An 809 Titrando potentiometric auto-titrator manufactured by Metrohm of Sweden was used for the FFA measurements. The device was controlled by the Tiamo 1.1 computer interface software. Additional information on the Titrando can be found in the Appendix. Descriptions of the use and setup of the device are covered in future sections.

3.3.8 POWER METER

Power measurements were taking for the reaction kinetics enhancement evaluation experiments using a Watts Up? Pro electricity monitor manufactured by Electronic Educational Devices. Data acquisition was accomplished by a USB connection from the Watts Up? meter to a laptop computer running the Watts Up Real Time version 0.10.7.14 data logging software.

3.3.9 KARL FISHER MOISTURE ANALYZER

Moisture analyses were conducted using a Karl-Fisher moisture analyzer.

3.4   MATERIALS

3.4.1   METHANOL

The methanol used for the esterification reactions in both the esterification characterization experiment and the enhanced reaction kinetics evaluation experiment was provided by Univar. The lot number was JO09880613 and the product number was 298001. The methanol was analyzed by Karl Fisher in duplicate for an average of 0.1339% moisture.

3.4.2   BROWN GREASE

Brown grease was used as the high FFA feedstock for all esterification reactions and was provided by CHP ByProducts, LLC. The grown grease was tested for FFA using the 809 Titrando automatic titrator in duplicate for an average of 85.348% FFA. The moisture content of the brown grease was tested by Karl Fisher in duplicate for an average of 0.4956% moisture.

3.4.3   REAGENT ALCOHOL

Ethanol Government Formula C was used as the reagent alcohol solvent for the FFA titrations. The reagent alcohol (lot number 8Z040809182, product number 763541) was manufactured by Univar.

3.4.4 SULFURIC ACID

Sulfuric acid 98% (manufacturer EMD Chemicals, fishersci.com catalog number 50-947-796) was used as the catalyst for the esterification.

3.4.5 DEIONIZED WATER

Deionized water was used in the esterification reaction characterization experiments to test water content as a factor. The water was produced with a US Filter laboratory deionization system.

3.5 REACTOR DESIGN

3.5.1 STIRRED REACTOR DESIGN

The stirred reactor setup is shown in Figure 8. All stirred reactions were conducted using this design.
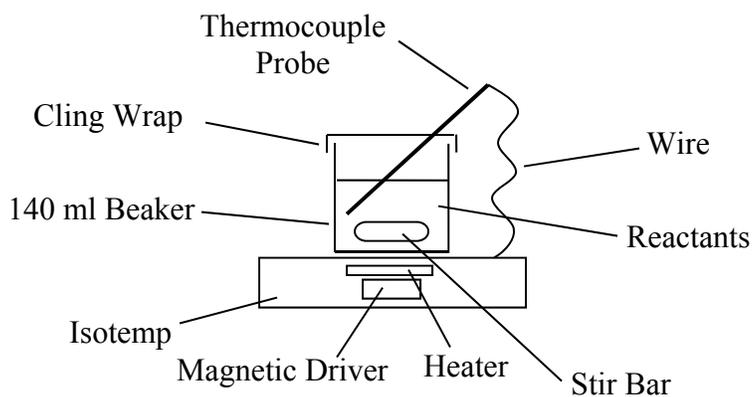

Figure 8: Stirred reactor setup

The stirred reactor design consists of a 140 ml beaker atop a heated stir plate. Reactants

(brown grease, methanol, sulfuric acid, and deionized water) are added to the beaker in

quantities determined by the experimental design. The beaker is covered with cling wrap

which provides a superior barrier for inhibiting the escape of methanol vapors from the

reaction zone. Stirring is accomplished with a 9.5 mm diameter, 25.4 mm long magnetic

stir bar driven by a magnetic stirrer within the hot plate. Heating is provided by an

electric resistance heater within the hotplate controlled by feedback from a thermocouple

probe. The probe is submerged beneath the liquid level to provide an accurate

temperature readout of the reactant system. A control loop maintains temperature at the

desired setpoint.

3.5.2   SONICATION REACTOR DESIGN

The design of the sonication reaction vessel underwent several incarnations during the

course of the current research. A basic schematic of the final setup is shown in Figure 9.
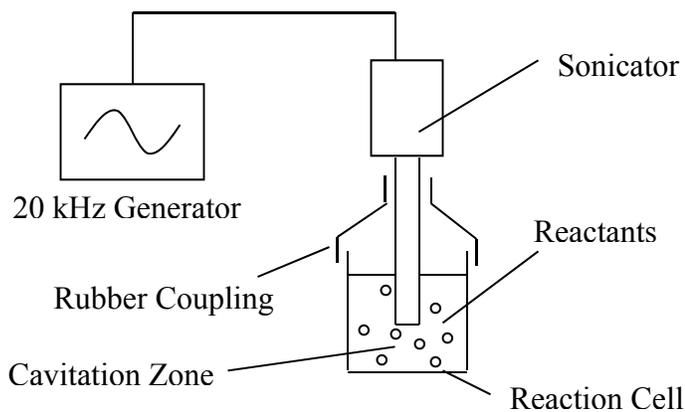

Figure 9: Sonication reactor setup

The sonicator is connected to the 20 kHz power supply and lowered into the reaction cell at a fixed depth provided by the rubber coupling. The reaction cell consists of a 4 oz. glass jar mounted below the sonicator probe. The reaction cell is coupled to the sonicator probe with a 1 ¼" X 1 ½" rubber coupling. The coupling is secured with pipe clamps to the probe neck as well as to the jar rim. Reactants (high FFA oil, methanol, and sulfuric acid) are added to and contained within the reaction cell. The coupling inhibits the escape of methanol vapor as well as focuses the sonic energy into the reaction cell. This accomplishes two things: it retards the evaporation of methanol and prevents sonic energy from reflecting out of the reaction cell. Both provide better experimental control and enhanced repeatability. In addition, the rubber coupling serves as a suitable spacer to ensure a standard probe depth for all reactions. A thermocouple wire (not shown in Figure 9) is inserted between the probe neck and the 1 ¼" end of the rubber coupling with the junction end submerged beneath the liquid level. The thermocouple wire is connected to a digital thermocouple analyzer for temperature readout, and monitoring.

The basic components of the above setup remained the same; however several revisions were made in order to promote stable reaction conditions. Early experiments resulted in a high degree of inconsistency of performance. This was a result of crude and non-repeatable apparatus setups. Initially, the probe was lowered into a 140 ml glass beaker. The probe was mounted on a stand with clamps that made it difficult to control the probe depth. Parafilm® was used to cover the glass beaker and a small hole was punched in the film to allow for probe insertion. Methanol vapors easily escaped from around the edges of this hole resulting in incomplete and non-repeatable reactions. The rubber coupling

56

design was eventually implemented and solved both the methanol escape and sound reflection issues.

Initial experiments made no provision for temperature control and it was soon found that the effects of the initial exothermic energy release elevated temperatures near or beyond the boiling point or methanol. Most of the methanol was allowed to escape from the reaction vessel before a good reaction was produced. Attempts were made to control the temperature with a water bath, however simplicity prevailed and the final setup consisted of an electric fan positioned to blow directly on the reaction cell. Cooling was occasionally assisted by squirting a small amount of anhydrous methanol directly on the cell to provide evaporative cooling. This method of control was manual, however required only occasional attention and was typically only used at the beginning of the reaction to correct for the initial exothermic energy release. Temperature was maintained to within 1 °C for the duration of the reaction using this method.

3.6   METHODOLOGY

3.6.1   EXPERIMENTAL SEQUENCE

Experiments were run on a laboratory scale using standard laboratory glassware and equipment. The basics steps for the experiments are listed below:

1. Oil and methanol are measured up in the volumes and order specified by the experimental design and placed into the appropriate reaction vessel.

2. In the stirred reactions, a magnetic stir bar is added.

3. The reaction vessel is weighed and the weight recorded. This step is to monitor methanol loss during the reaction.

4. Agitation is started and, with the stirred reactions, the appropriate temperature set point specified by the experimental design is selected and heating is started.

5. The oil/methanol mixture is allowed to heat to the temperature setpoint. With the sonication reactions, the ultrasonically induced cavitation generates the required heat without the need for external heating.

6. Once the temperature set point is reached, the water is added if required by the design.

7. After the water is added, the sulfuric acid is added in the volume required by the design and the timer is simultaneously started. The power measurement data acquisition program is also started for the enhanced reaction kinetics experiment only.

8. The esterification reaction is exothermic and will generate heat. For the stirred reactions, the control loop will reduce the heat input to maintain the temperature setpoint. For the sonication reactions, trim cooling may be required. The trim cooling process is described in section 3.3.2, Sonication Reactor Design.

9. After the 15 minute reaction time period has elapsed, the alarm will sound and two duplicate samples are immediately drawn from the reaction mixture with a 1 ml transfer pipet. The samples are placed into two separate pre-weighed 140 ml beakers.

10. The beakers are re-weighed and their final weight is recorded. The final weight is subtracted from the initial weight to calculate the weight of the sample.

11. As quickly after the sample is drawn as possible, 100 ml of reagent alcohol is added to the 140 ml beaker containing the sample. This halts any continued reaction as well as eliminates the evaporation of methanol from the sample. The reagent alcohol acts as the solvent for titration analysis.

12. A stir bar is added to the two prepared duplicate samples.

13. The samples are analyzed for FFA using the titration procedure outlined in X using the Metrohm 809 Titrando automatic titrator.

14. The FFA percentages produced are the free fatty acid % by weight of the total reaction system (oil, methanol, sulfuric acid, and water) in the ratios specified by the experimental design for that particular run. The weights of the other reactants must be mathematically reduced to leave only the FFA% of the oil component. This is done by simple arithmetic using a Microsoft Excel™ spreadsheet.

15. The calculated final FFA% of the oil is entered into the factorial table in Minitab 16 and the effects analyzed using ANOVA and regression analysis to determine the statistically significant factor effects.
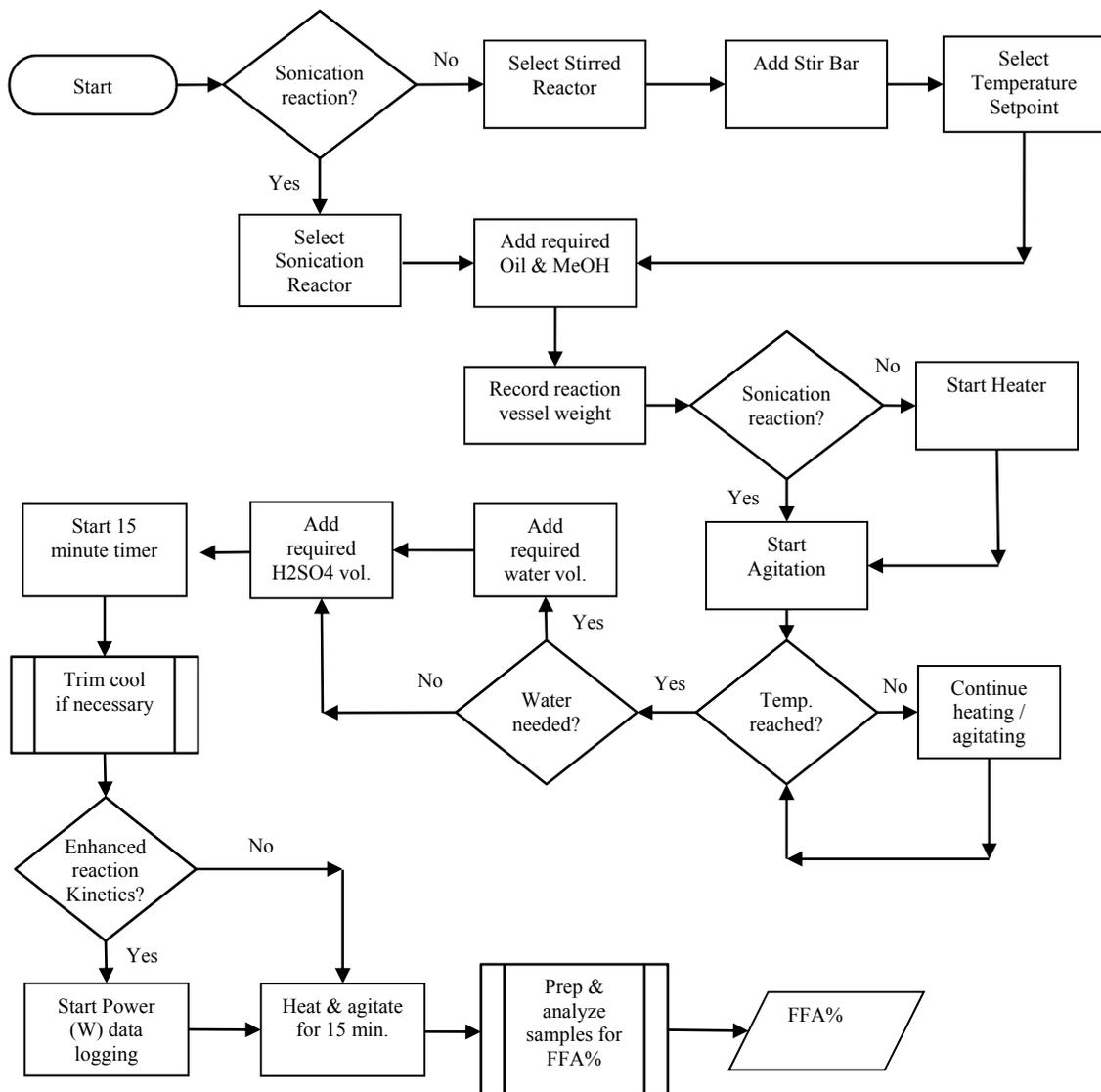
Figure 10: Experimental flowchart

3.6.2   REACTION PARAMETERS

The parameters for the esterification reaction characterization and the enhanced reaction

kinetics evaluation are shown in Tables 13 & 14 below.

Table 13: Fixed reaction conditions for esterification reaction characterization

	Level
Brown Grease	50 ml
Agitation Rate	700 rpm

Table 14: Fixed reaction conditions for enhanced reaction kinetics evaluation

	Level
MeOH Content	50 ml
Brown Grease	50 ml
Power Level	33 W

The variable factors were varied according to the experimental design for each experiment discussed in section 3.2.

3.6.3   MEASUREMENTS

The experimental component of this thesis required two primary categories of measurements to be taken:

1. Free Fatty Acid % for all reactions
2. Rate of energy input for the enhanced reaction kinetics evaluation

Other measurements such as weights, temperature, and moisture content were made, however these were secondary to the experimental goals and served as support to the laboratory activities. Two software packages were used in conjunction with the respective instruments for which they were designed. They are detailed in the following sections.

3.6.3.1   Free Fatty Acid Measurements

Measurements of final free fatty acids content in reaction samples were with the

Metrohm 809 Titrando automatic titrator. Standard wet titration methods were adapted to

the Tiamo 1.1 computer interface software designed specifically for the Titrando. A

screenshot of the main graphical user interface for the Tiamo software is shown in Figure

11.
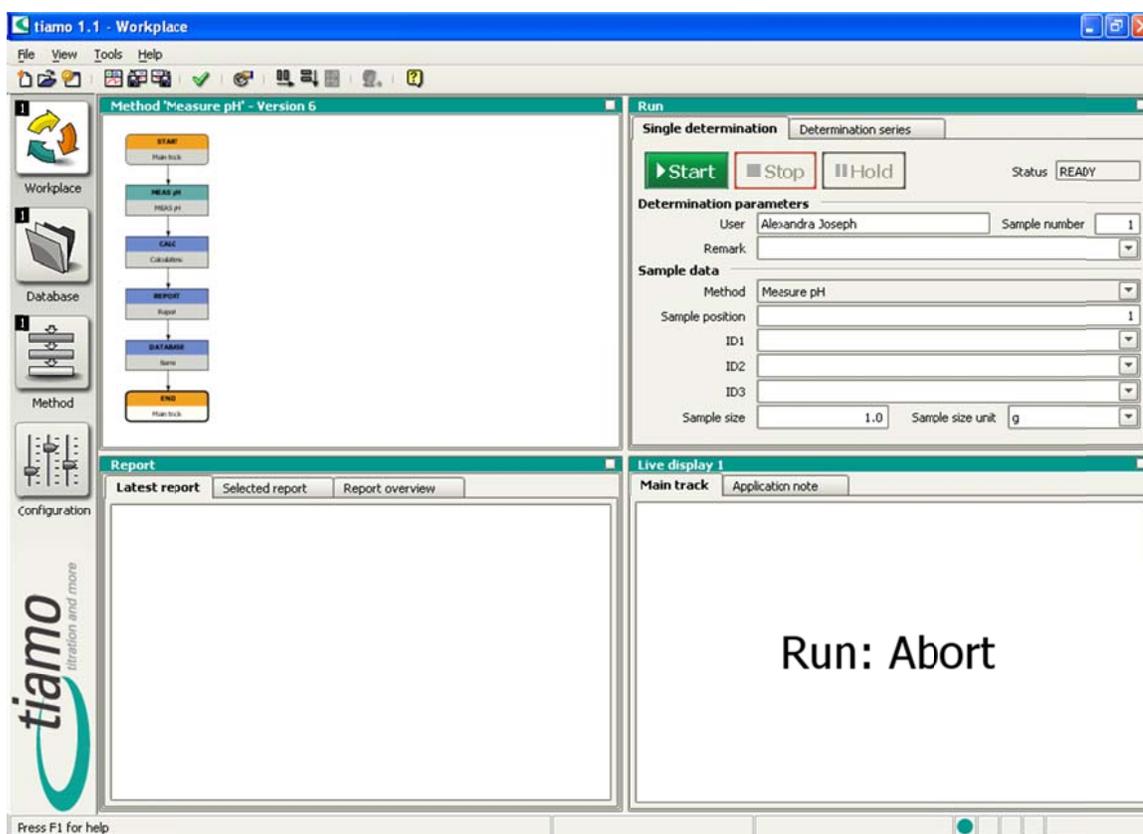
Figure 11: Tiamo 1.1 workplace GUI

Calculations for the final FFA% were done automatically by the software using the following formula:

$$('\text{DET U.EP}\{2\}.\text{VOL}' - '\text{DET U.EP}\{1\}.\text{VOL}' - '\text{CV.FFAbk}')$$
$$* '\text{DET U.CONC}' * 28.2 / '\text{MV.Sample size}' \qquad (6)$$

Where:

'DET U.EP{2}.VOL' is the volume of titrant dispensed at the second inflection point

'DET U.EP{1}.VOL' is the volume of titrant dispensed at the first inflection point

'CV.FFAbk' is the volume of titrant dispensed with a solvent blank titration

'DET U.CONC' is the normality of the titrant

28.2 is the molecular weight of oleic acid divided by 10

and

'MV.Sample size' is the user inputted sample weight

As the titration runs, the voltage is measured with respect to time and plotted. Two inflection points will occur: one when the sulfuric acid endpoint is reached, and the other when the FFA endpoint is reached. Equation 6 calculates the FFA based on these two endpoints. A plot of a typical titration curve with the sulfuric acid and FFA endpoints is shown in Figure 12.
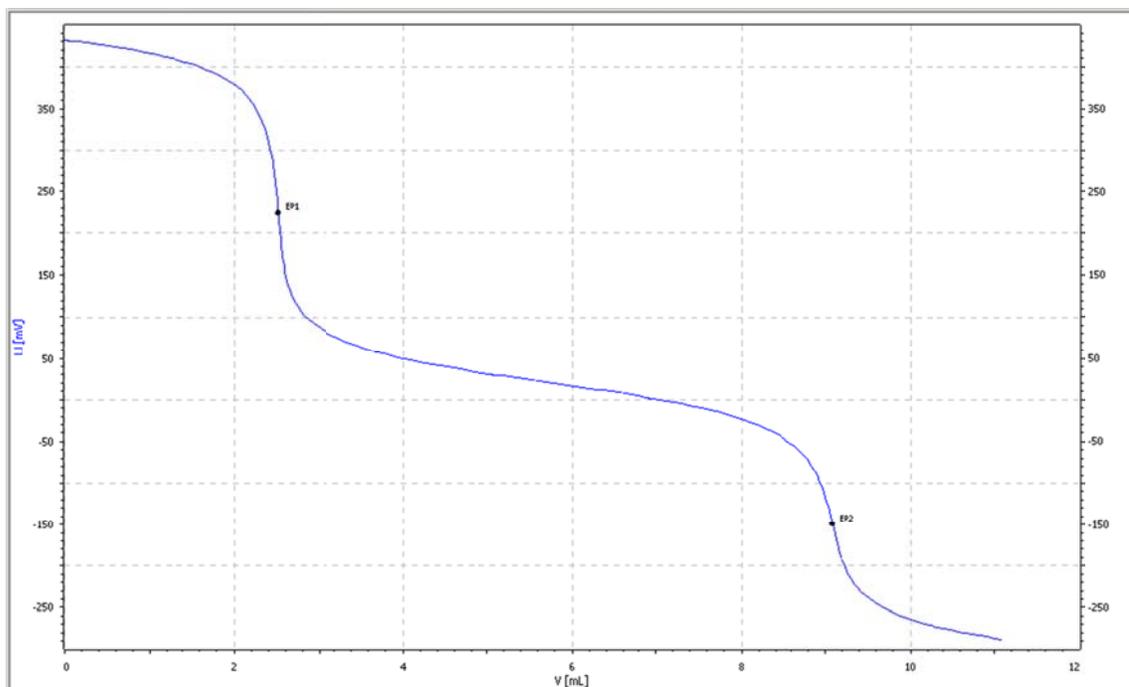
Figure 12: Tiamo 1.1 titration plot

EP1 is the sulfuric acid endpoint and EP2 is the FFA endpoint. A similar curve was evaluated for every FFA analysis. A major advantage of this titration method is that the FFA can be differentiated from the sulfuric content. This is impossible with manual titrations using an indicator solution as the FFA endpoint determinant.

3.6.3.2   Energy Input Measurements

The energy input for the Enhanced Reaction Kinetics experiments was measured with the Watts Up? Pro meter and software. The baseline power draw for each equipment setup was measured and recorded. The baseline power draw is defined as the power drawn by all pieces of equipment associated with either experimental setup detailed in section 3.5. The baseline power draw was different for each experimental setup and this value as accounted for when tuning the power consumption for each experiment as it was only

64

desired to measure the power drawn for the reactions, not that of the equipment itself. In

addition, power measurement was started after the reactants, equipment, and glassware

was allowed to heat up and reach setpoint. This eliminated the measurement of non-

steady state energy consumption.

The author acknowledges that energy losses will exist for each of the experimental setups

and that these losses may be different. The losses are defined for each setup as follows:

1. Stirred Reactions

    a. Radiative and convective thermal losses from the hotplate surface

    b. Radiative and convective thermal losses from the beaker walls

    c. Evaporative losses from the methanol vaporization

2. Sonication Reactions

    a. Sound reflection from the reaction vessel

    b. Radiative and convective thermal losses from the beaker walls

    c. Evaporative losses from the methanol vaporization

Though the sources of loss are somewhat different between setups, recall that the primary

objective is to determine any superiority of ultrasonic irradiation over conventional

stirring over and above its ability to deliver more energy to the reaction system. This

includes losses, be they for better or for worse. In addition, the configurations are

thought to approximate those seen in large-scale industrial environments. For instance,

where thermal losses from the surface of the hotplate might be significant, it is no less so

than losses from the surface of jacketed tank heaters, steam boilers, heat exchangers, etc. seen in industrial processes. It was desired to accommodate these losses in the experiment, and any differences between losses of the two experimental setups would adequately account for those seen on an industrial scale.

4.0 RESULTS AND DISCUSSION

4.1 ESTERIFICATION CHARACTERIZATION

Table 15 shows a table of estimated effects and coefficients for the esterification

characterization experiment from the ANOVA output in Minitab 16.

Table 15: Minitab output of the estimated effects

```
--------------------------------------------------------------------------------
Estimated Effects and Coefficients for FFA (coded units)

Term                                Effect    Coef  SE Coef        T      P
Constant                                     40.62   0.4804    84.56  0.000
Block                                         1.27   0.4661     2.73  0.015
Sulfuric Acid Content               -33.18  -16.59   0.4804   -34.53  0.000
Water Content                         6.50    3.25   0.4804     6.77  0.000
Methanol Content                      0.69    0.35   0.4804     0.72  0.481
Temperature                         -13.93   -6.97   0.4804   -14.50  0.000
Sulfuric Acid Content*Water Content   0.47    0.24   0.4804     0.49  0.630
Sulfuric Acid Content*               -0.70   -0.35   0.4804    -0.73  0.478
  Methanol Content
Sulfuric Acid Content*Temperature    -2.49   -1.24   0.4804    -2.59  0.020
Water Content*Methanol Content       -0.06   -0.03   0.4804    -0.06  0.950
Water Content*Temperature            -0.85   -0.43   0.4804    -0.88  0.389
Methanol Content*Temperature         -0.51   -0.25   0.4804    -0.53  0.605
Sulfuric Acid Content*Water Content*  0.40    0.20   0.4804     0.42  0.682
  Methanol Content
Sulfuric Acid Content*Water Content*  1.13    0.56   0.4804     1.17  0.258
  Temperature
Sulfuric Acid Content*               -1.40   -0.70   0.4804    -1.46  0.165
  Methanol Content*Temperature
Water Content*Methanol Content*       1.22    0.61   0.4804     1.27  0.223
  Temperature
Sulfuric Acid Content*Water Content* -0.38   -0.19   0.4804    -0.39  0.699
  Methanol Content*Temperature
Ct Pt                                        -9.77   1.9808    -4.93  0.000


S = 2.71759     PRESS = 742.588
R-Sq = 98.94%   R-Sq(pred) = 93.34%   R-Sq(adj) = 97.82%
--------------------------------------------------------------------------------
```

An examination of the P-values for each effect located along the right-hand column of

Table 9 reveals several significant effects. Significance, which is the notion that the

observed response is not likely a product of chance as described in section 3.1.2.4, is

determined by comparing the P-value to the significance level (α).   Recall from section

3.1.2.4 that the significance level used for this experiment is $\alpha = 0.05$. Effects with P-

values less than α are considered to be *statistically* significant.

4.1.1   STATISTICAL RESULTS

4.1.1.1   Interaction Effects

Only one interaction effect, Sulfuric Acid Content*Temperature, was found to be

statistically significant with a P-value of 0.02. The 2-way interaction terms can be

evaluated visually in Figure 13.
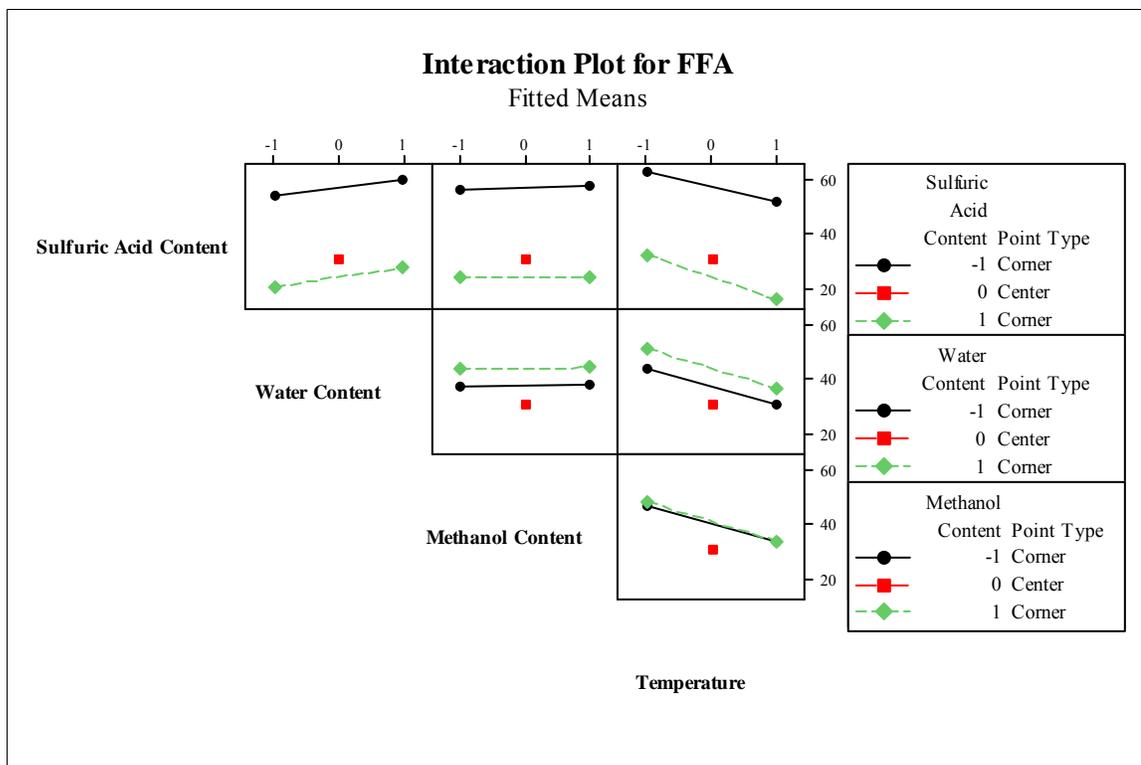
Figure 13: Interaction effects plots for the esterification characterization experiment

The interaction effects plots are interpreted by looking at how the lines fall in each plot. Nearly parallel lines indicate no interaction where non-parallel or intersecting lines suggest interaction. As can be seen, only the Sulfuric Acid Content*Temperature interaction term (upper right-hand plot) is appreciably non-parallel and therefore shows slight interaction. As will be discussed in the Practical Evaluation section, however, this effect is minor and is of no practical significance.

4.1.1.2   Main Effects

The main effects Sulfuric Acid Content, Water Content, and Temperature, all of which had P-values of 0.00, were all significant. Figure 14 graphically summarizes these effects.
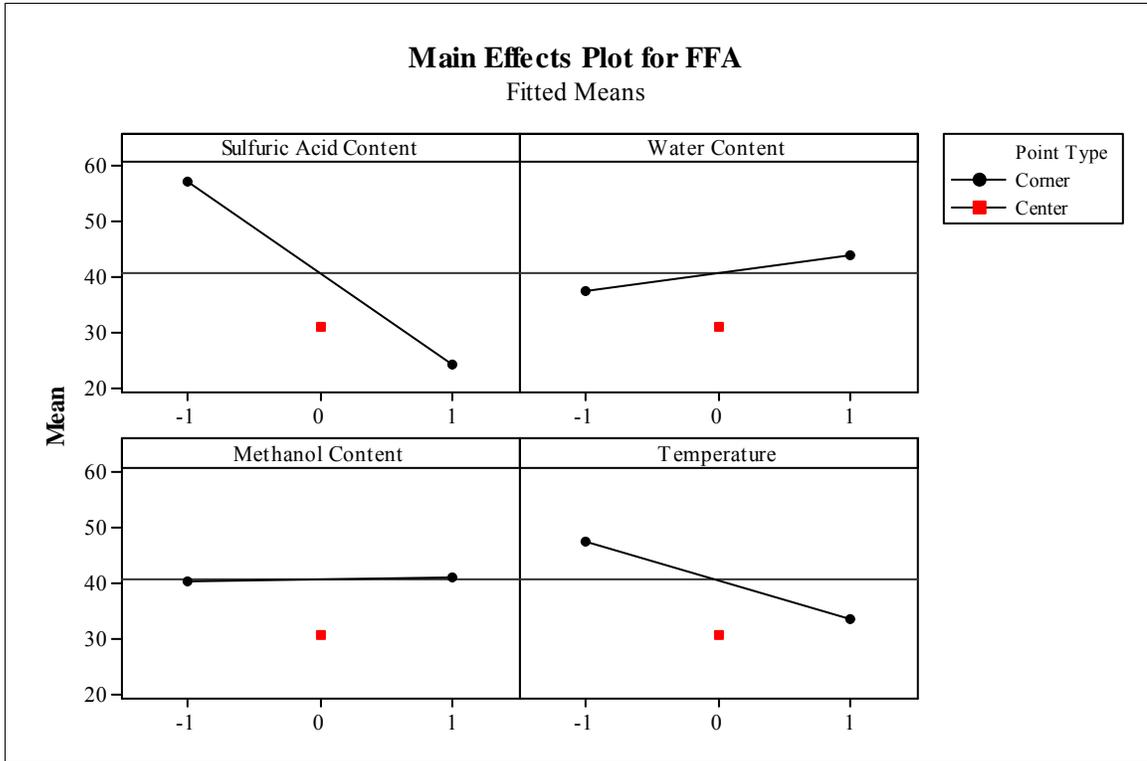
Figure 14: Main effects plots for the esterification characterization experiment

The coded variables are plotted against the grand mean. The grand mean is the "mean of all observations across all factor levels" (Minitab 16 Help, "grand mean") rather than the mean of observations within each factor setting. A negative slope indicates a factor that results in a lower FFA concentration after the 15 minute reaction time at its highest level and a higher FFA content at its lowest level. A positive slope indicates the inverse. A

70

nearly horizontal line indicates that the factor has no effect on the system within the studied region.

Since the goal is to reduce FFA concentration, negative slopes are considered desirable and positive slopes are considered undesirable. Steeper slopes suggest a greater effect on the final FFA concentration. Again, Sulfuric Acid Content and Temperature both accelerate FFA reduction while Water Content retards FFA reduction. Methanol Content was not significant with a P-value of $0.481 > 0.05$. This came as a surprise as will be testified to in the Practical Interpretation section.

4.1.1.3 Covariate Effects

Initially, a covariate, *methanol loss*, was added to the model. During the experiment, a certain amount of methanol evaporated from the reaction chamber. This had the potential to affect the outcome of the design so the loss was measured and added as a covariate to the model. Methanol loss was shown to have no statistically significant effect and was subsequently removed and the data refitted without the term to provide a cleaner fit with less statistical noise. From the data, the fact that methanol loss had no statistically significant effect is not surprising since the main effect of methanol content was not significant. Covariates were also added to the Sonication Experiment as will be seen later.

4.1.1.4 Blocking Effects

As mentioned previously, blocking was used to rule out influences on the model caused by performing the reaction on different days and by using different chemical lots during the experiment. This proved to be a good design choice since the Block effect term has a P-value of 0.015 and is therefore considered a significant effect. It is not known whether the effect came from the use of different chemical lots or from performing two halves of the experiment on different days since the effect is a composite of the two variables.

4.1.1.5 Center Point Effects

As described in section 3.2.1.6, center points were used in the design to test for curvature. As with blocking, this design choice proved to be a fortunate one as the model distinctly revealed the center point term to have a significant effect at a P-value of 0.00.

The center points are also shown within the main effects plot. Recall that curvature exists when the center point does not lie along the line drawn between the two factor levels. Figure 14 clearly reveals the curvature in the fitted data.

4.1.1.6 Relative Effects

Figure 15 shows a normal probability plot of the effects of the esterification characterization experiment. The normal probability plot more clearly shows that sulfuric acid content, temperature, water content, and an interaction between temperature and sulfuric acid content have significant effects on the esterification reaction within the

72

chosen level ranges. Within the chosen range of 50 ml to 100 ml of methanol content

(100% to 200% of the volume of oil used), no effect was observed due to methanol.

Effects with negative values are considered to be beneficial because the practical

objective is to reduce FFA concentration. Inversely, effects with positive values are

considered to be counteractive to the goal of reducing FFA concentration.
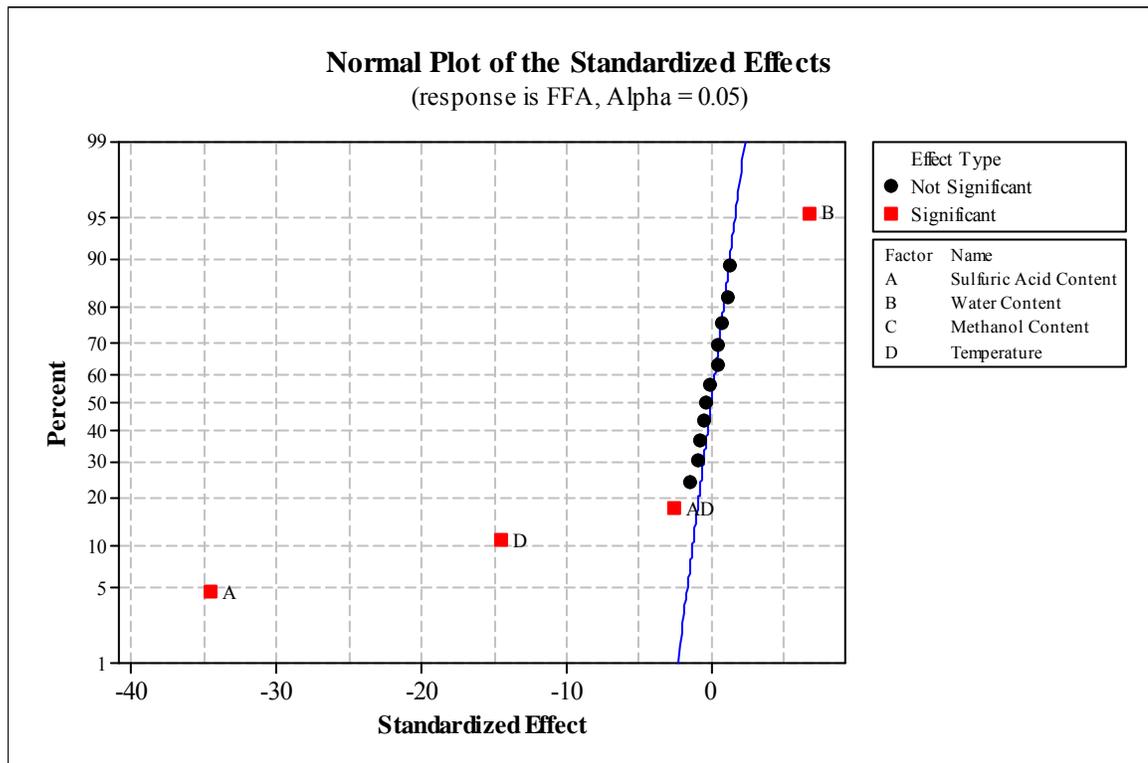

Figure 15: Normal probability plot of the effects of the esterification characterization
experiment

Sulfuric acid content had the greatest beneficial effect relative to the other effects at a

standardized value of -33.18 followed by temperature at -13.93 and then the 2-way

interaction between temperature and sulfuric acid content at -2.49. Water content had a

counteractive effect of 6.50. Sulfuric acid content had, by far, the greatest effect at nearly

twice the next most significant effect. The half-normal probability plot of the effects is

73

given in Figure 16. The relative magnitudes of the effects are more easily visualized in the half-normal plot. Again, sulfuric acid content is shown to have the greatest effect accounting for over 95% of the total variability of the model.
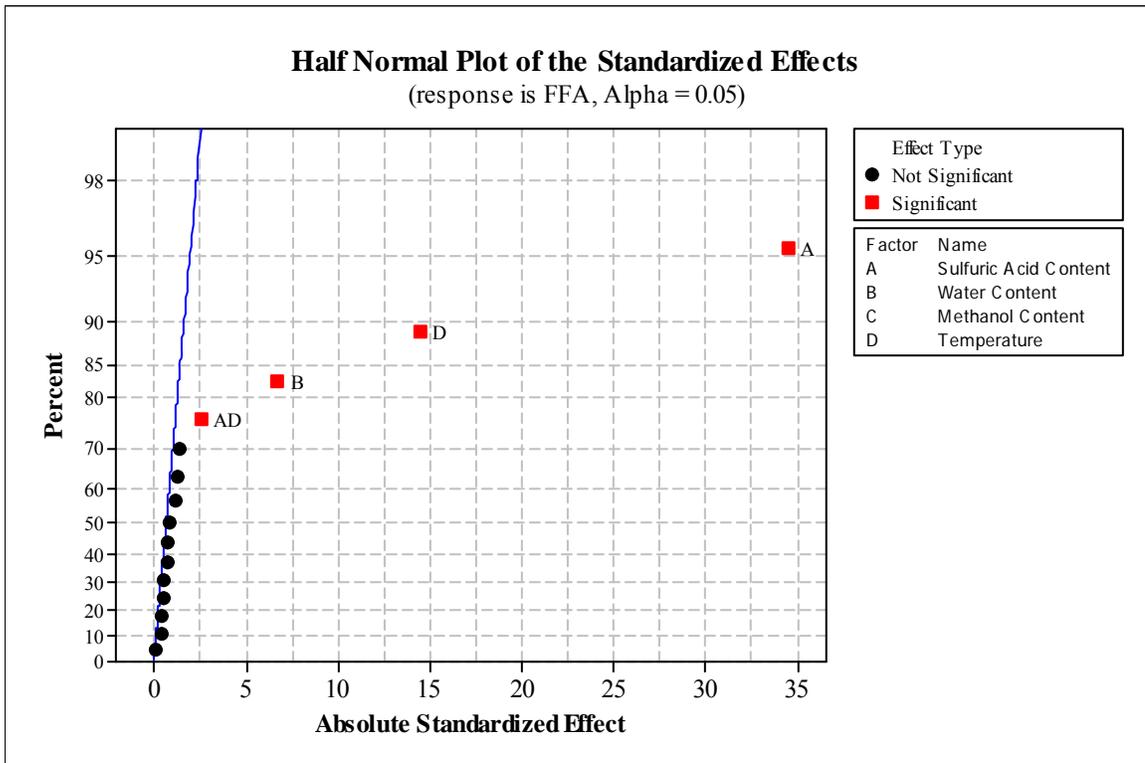

Figure 16: Half-normal probability plot of the effects of the esterification characterization experiment

A pareto chart is another useful way to view the fitted data. Figure 17 shows a pareto chart of the standardized effects of the esterification characterization experiment. The error term was calculated from the difference between the two replicates and was used to draw the significance line on the Pareto chart. Factors and their interactions with an effect of magnitude above the error term of 2.12 as indicated on the chart are considered to be statistically significant while factors or interactions with an effect of magnitude

below 2.12 are not considered to be statistically significant. This provides a quick, visual

way to determine which effects are significant without having to look at the P-values.
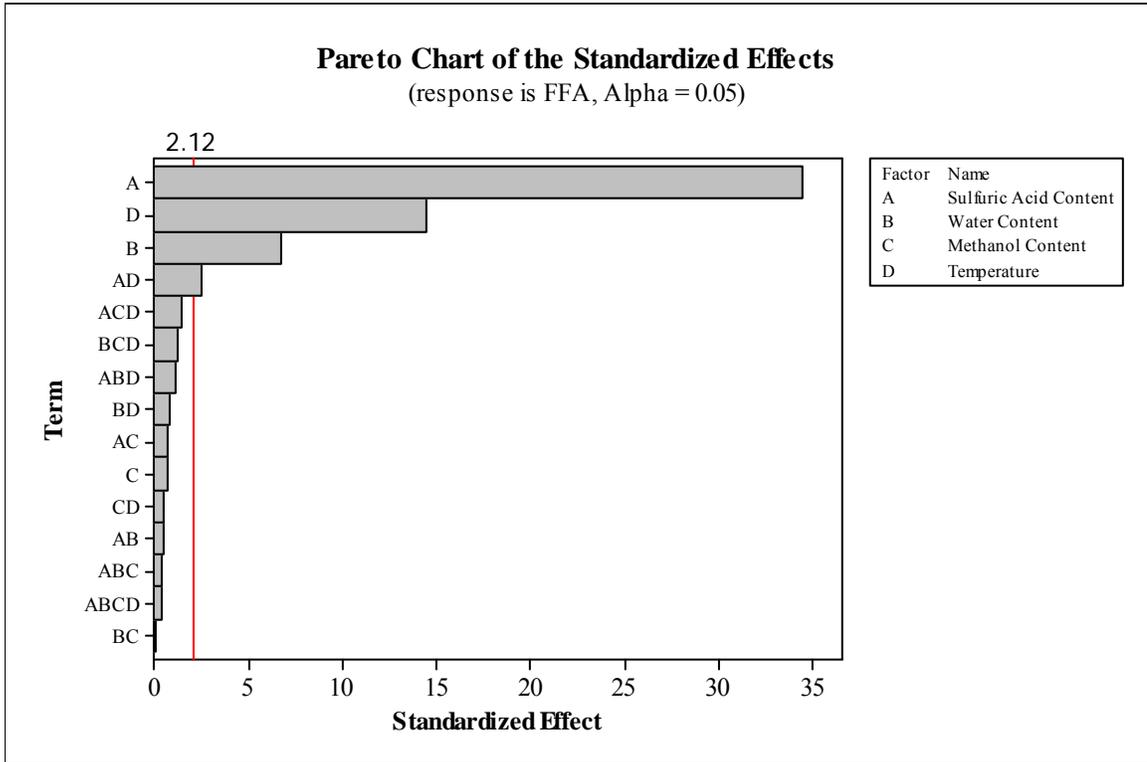
Figure 17: Pareto chart of the effects of the esterification characterization experiment

Clearly, Figure 17 reveals sulfuric acid content to be twice the magnitude of the next

greatest effect, temperature. In addition, the interaction between sulfuric acid content and

temperature is revealed to be of marginal statistical significance. All other two-, three-,

and four-way interactinos are of no statistical significance.

4.1.1.7 Regression Equation

In order to obtain a cleaner regression equation with better fit, the model was refitted

excluding the statistically non-significant terms. Table 16 shows the Minitab 16 output

of the refitted regression data.

Table 16: Minitab output of refitted data

```
----------------------------------------------------------------------
Estimated Effects and Coefficients for FFA (coded units)

Term                               Effect    Coef  SE Coef       T      P
Constant                                    40.62   0.4510   90.08  0.000
Block                                        1.27   0.4375    2.91  0.007
Sulfuric Acid Content              -33.18  -16.59   0.4510  -36.78  0.000
Water Content                        6.50    3.25   0.4510    7.21  0.000
Temperature                        -13.93   -6.97   0.4510  -15.44  0.000
Sulfuric Acid Content*Temperature   -2.49   -1.24   0.4510   -2.76  0.010
Ct Pt                                       -9.77   1.8594   -5.25  0.000


S = 2.55112     PRESS = 480.486
R-Sq = 98.42%   R-Sq(pred) = 95.69%   R-Sq(adj) = 98.07%
----------------------------------------------------------------------
```

As can be seen, the standard deviation and R^2 terms are improved over the fit that

incorporates all of the non-significant terms (Table 14). From the Coef column in Table

15, coefficients for the regression equation are listed.

4.1.1.8 Model Adequacy Check

Residual plots were used to check the adequacy of the regression model. Figure 18

shows four diagnostic plots that are useful in evaluating whether the regression

assumptions apply to the data. Residuals are simply the difference between the fitted

response data and the observed values. They are indicative of how well the fitted model

represents the real-world data.

76
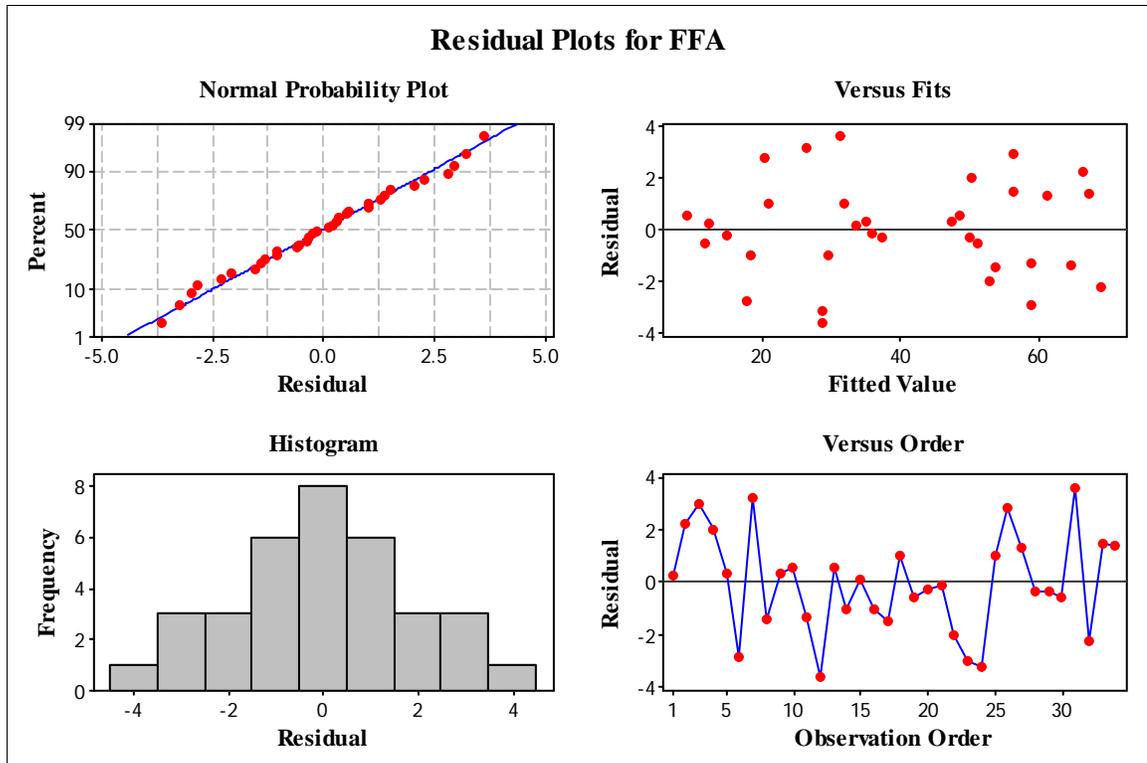
Figure 18: Residual plots for the esterification characterization experiment

The normal probability plot in the upper left of the four plot display of Figure 18 shows the residuals falling along a relatively straight line indicating that the data is normally distributed. There is slight curvature at the tails of the plot which indicates only minor skewness in the data suggesting that the model is relatively symmetrical. There are no outliers and there is no diverging slope to the plotted residuals which indicates that there are no unidentified variables influencing the design.

The versus fits plot in the upper right hand quadrant of the four plot display of Figure 18 shows a plot of residuals vs. the fitted response values. The variance of the residuals seems to be randomly distributed with respect to final FFA% indicating constant variance in the error term, no missing quadratic terms, and no outliers.

The histogram in the lower left quadrant of Figure 18 is perfectly bell-shaped and confirms the lack of outliers or skewness in the fitted data. Long tails or disconnected bars would indicate skewness or outliers respectively and this is not the case with the histogram suggesting that experimental technique was satisfactory.

The versus order plot in the lower right quadrant of Figure 18 shows a plot of the residuals vs. the order of the experimental observations. Patterns in this plot would indicate that the order of the measurements had an influence on the final FFA%. The plot shows relative randomness and therefore indicates that the order of the runs did not greatly affect the final FFA concentration.

The examination of the four residual plots in Figure 18 show a model well suited to ANOVA and regression analysis and gives confidence in the design choices for the factorial design as well as the experimental technique used in the acquisition of the data.

4.1.1.9 Power Analysis

As described in section 3.2.1.4, an estimate of the standard deviation of the model was used to determine the sample size at an acceptable power level. It is now time to reevaluate the power curve using the actual standard deviation of the experimental data to determine whether the initial sample size assumption was correct. From Table 15, the standard deviation of the fitted data of the esterification reaction characterization experiment is 2.71759 vs. the original estimate of 0.687 from Table 5. Since the standard

deviation directly influences the sample size, this raises a concern that the initial choice

of sample size for the experiment was sufficient to detect the desired change.
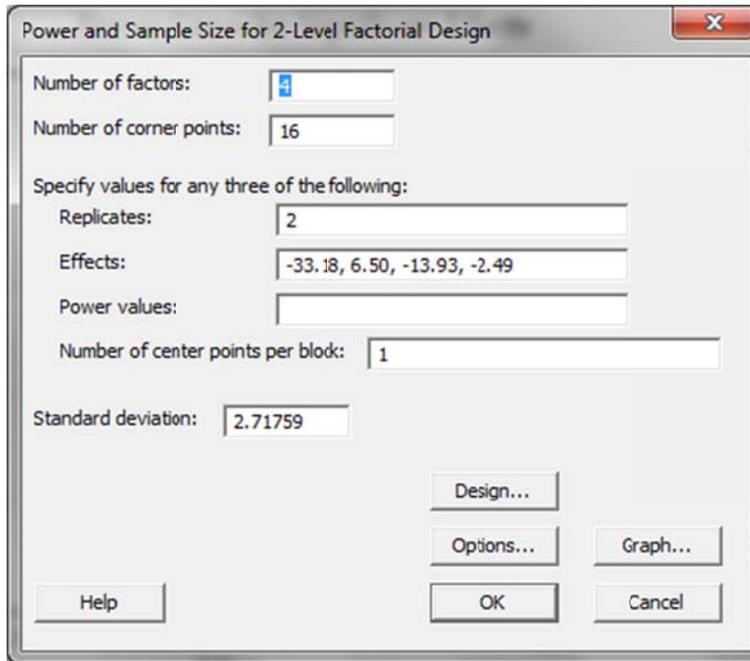

Figure 19: Power and sample size window

Figure 19 shows the inputs for the Power and Sample Size tool in Minitab 16 for the 2-

level factorial design. The four significant effects were input into the "Effects" field as

shown along with the other required data in their respective fields. The tool was run and

a power curve for the four effects was generated.
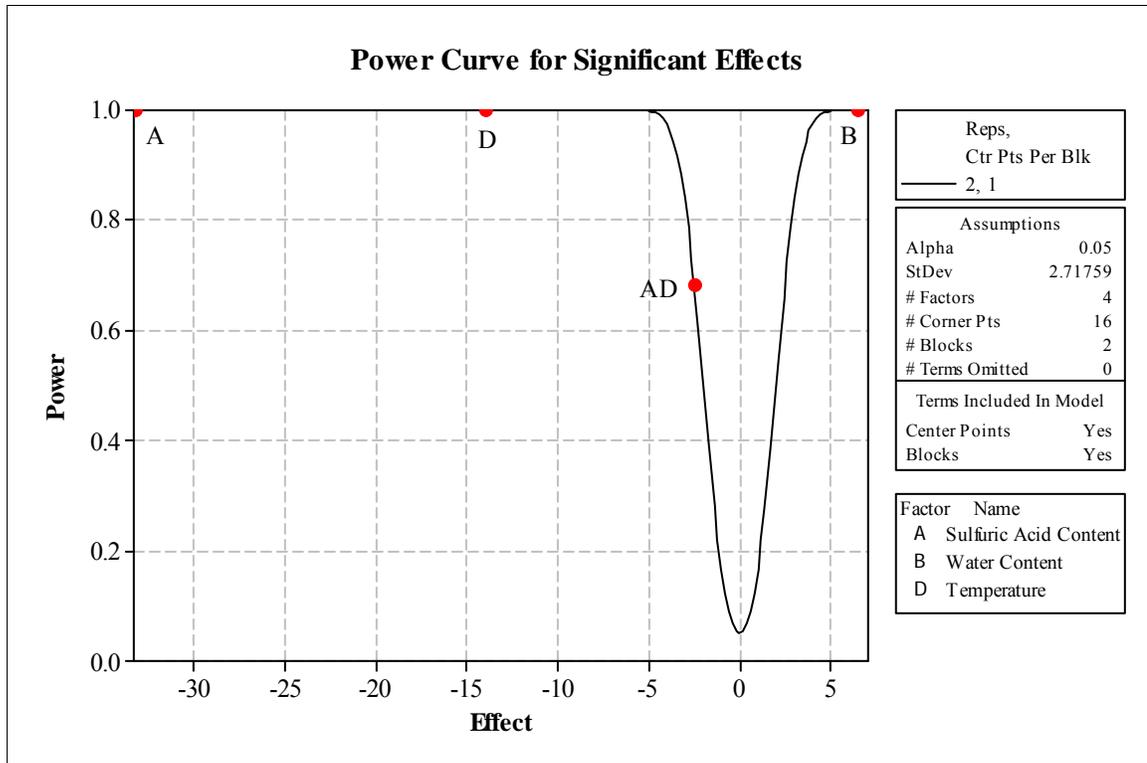
Figure 20: Power curve for the four significant factor effects

Figure 20 shows the power curve of the experiment using the new standard deviation. The main effects all have close to 100% probability of being real effects, however the Sulfuric Acid Content*Temperature (AD) interaction has only a 68% chance of being a real effect. Table 17 shows the Minitab output of the power data.

Table 17: Minitab output of power analysis

```
------------------------------------
Center
Points
   Per                 Total
 Block  Effect  Reps   Runs    Power
     1  -33.18     2     34  1.00000
     1    6.50     2     34  0.99999
     1  -13.93     2     34  1.00000
     1   -2.49     2     34  0.68221
------------------------------------
```

What this means is that the sample size was not large enough to identify the AD

interaction with the desired power of 0.95 at the realized standard deviation of 2.71759.

Two possible remedies for this conundrum exist:

1. Rerun the experiment with a larger sample size.

2. Accept the uncertainty of the interaction effect.

The second option could only be used if the effect was considered to be insignificant by

another means. If the effect were of interest, it would be required to rerun the entire

experiment with more replicates or better repeatibility to reduce the standard deviation of

the sample set. In fact, the experiment was salvageable because the interaction term is

indeed insignificant from a practial standpoint as has been mentioned and as will be

discussed in more detail in the next section.

4.1.2   PRACTICAL INTERPRETATION

Statistical methods can be very useful for identifying significant trends from voluminous

sets of data. There is, however, often a sharp contrast between statistical significance and

practical significance. The ultimate question that must be asked when a trend or effect is

plucked from the sea of data by a soulless software package is, "do we care?" With that

in mind, this section endeavors to examine the results of the analysis with a practical eye

and to build a framework upon which the data can be applied to real world processes.

4.1.2.1 Limitations of the Design

Without a consideration of the initial experimental assumptions, an observer could draw false conclusions about the scope of the experimental results. One must recall that the experimental data is limited to the first 15 minutes of reaction time. Also, the conclusions only apply to the ranges bracketed by the treatment levels outlined in Figure 5. General conclusions about the data outside of these ranges are in potential error.

Figure 21 shows a comparison between two different reaction rate curves at two different factor combinations. Additionally, it shows the associated moisture increase for one of the two reactions. Figure 21 was attained by running an additional experiment involving two esterification reactions at two different factor combinations. One reaction was run with the highest levels of sulfuric acid and methanol and the lowest level of water. The other reaction was run at the lowest levels of sulfuric acid and methanol and the highest level of water. Both reactions were run at the highest temperature level. Please refer to Table 6 for the associated treatment levels. Free fatty acid percentages were measured at various intervals during each reaction until the reactions slowed appreciably. The moisture concentration for the first reaction described above was also measured.
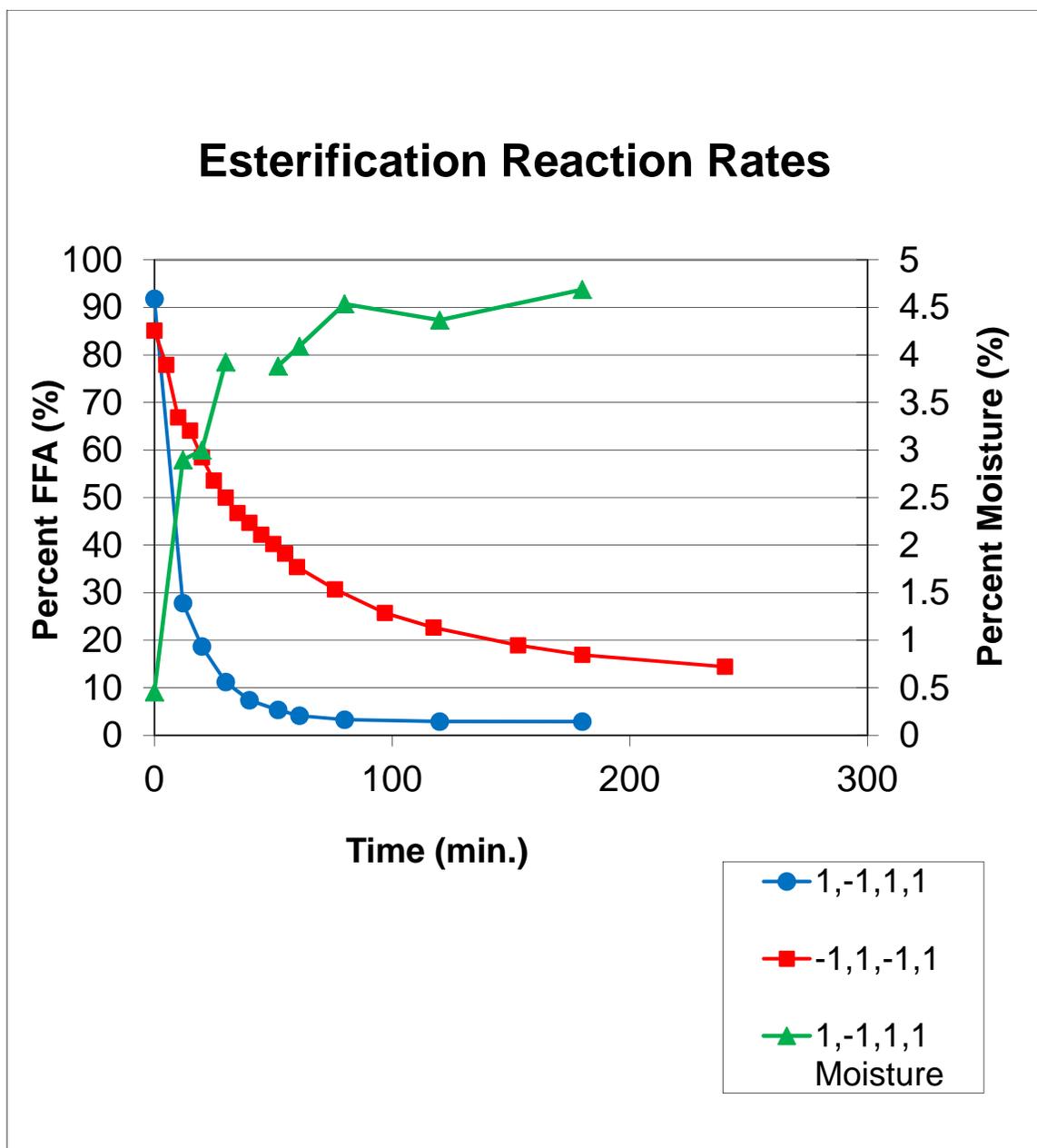
Figure 21: Esterification reaction rate for two factor combinations

From the curves, it can be observed that the rate of FFA reduction with time is not linear.

An initial steep decline quickly changes slope until negligible reaction occurs with time.

A 15 minute reaction period was chosen so that the total factorial experiment could be

achieved within a reasonable timeframe, however the assumption must be made that the relative effects are seen throughout the duration of the reaction.

4.1.2.2   Sulfuric Acid Content

Clearly, sulfuric acid content was identified as having the most significant effect on the system response. This may lead a student of this thesis to conclude that the most advantageous thing to do would be to increase the sulfuric acid addition rate in order to accelerate the reaction and reduce the FFA concentration. This is true to a point; however said student should be aware of the fact that the sulfuric acid must be neutralized in post-processing. After the reaction has completed, agitation is stopped and the excess methanol rises to the top of the oil phase carrying most of the sulfuric acid with it in solution. The methanol/sulfuric acid solution is then decanted and neutralized prior to recovery of the methanol for reuse. The neutralization of the sulfuric acid with sodium hydroxide generates sodium sulfate salts which can prove operationally problematic in sufficient quantity. If the quantity of salts exceeds the capacity for the remaining water to dissolve them, then they will settle out in process vessels, foul heat exchangers, abrade pump seals, and clog piping. This suggests that care must be taken when choosing sulfuric acid addition rates in industrial applications.

Additionally, it should be remembered that sulfuric acid was shown to have a significant effect within the region studied which was between 150 μl and 500 μl or 0.3% and 1.0% of the volume of oil used. There is likely a point beyond which adding additional sulfuric acid will result in no further reduction in FFA after a 15 minute reaction period. This

point should be identified with a path of steepest ascent experiment or similar

optimization experiment.

4.1.2.3   Temperature

The analysis suggests that increasing temperature will accelerate the reaction rate within

the 15 minute reaction period studied. Two temperature levels were used for this factor:

48 ºC and 60 ºC. Because of the curvature term, it is expected that this relationship

increases exponentially between the two levels. A physical limit exists, however, and

that is the boiling point of methanol or 64.7 ºC at atmospheric pressure. As the boiling

point is approached, methanol evaporation will increase and then no further temperature

increase will be possible as the methanol begins to change into the vapor phase. After the

entire volume of methanol has vaporized, temperature increase will once again be

possible, however it will be a pointless action since the primary reactant is no longer

present. For several reasons, this is an undesirable event and the reaction temperature

should be limited to a point below the boiling point and below which evaporation

becomes excessive.

4.1.2.4   Water Content

The data suggest that water content has a negative impact on reaction rate. One must be

aware that the "water content" term is somewhat of a misnomer because the factor

evaluated was simply an addition of a certain volume of water. Two levels were studied:

0 μl and 500 μl. This does not account for the water already present in the methanol

(0.1339%) and the brown grease (0.4956%). The experiment is measuring the effect of the *additional* water on the response.

Within the studied range of water addition (0% to 1% of the volume of brown grease) the water was shown to inhibit the FFA reduction. This was expected and supported by Liu et al. in the literature review (2006).   No limit to this relationship is anticipated: in other words, reduction of the total system water content down to zero percent will result in the best reaction rate as it relates to water content and further increases in water content will result in further inhibition and potential stalling of the FFA conversion.

Additionally, water is created as a byproduct of the esterification reaction of free fatty acids into methyl esters. This water gradually slows the reaction as can be seen in Figure 21. From Figure 21, the associated moisture rise with FFA reduction is clearly visible.

What this all means is that the operator should take great care to reduce initial moisture content when performing esterification reactions. Obviously, water should never be intentionally added to the reactants!

4.1.2.5   Methanol Content

As mentioned earlier, it came as a great surprise that methanol content was shown to have no significant effect on the experimental response. Methanol Content was expected to have a large effect based on practical experience. It is likely that this resulted from a level choice which fell above the point at which the path of steepest ascent is observed.

The path of steepest ascent is used in optimization experiments to determine the point at which further increase in a treatment level results in no further response from the system. Practical experience shows that increased methanol content will result in increased reaction rates at methanol volumes below 100% of the volume of high FFA oils. From the experimental results, however, it is evident that methanol content has little effect within the region between 100% and 200% of the volume of oil, which was the region tested. An optimization study should be conducted to determine the point at which additional methanol addition results in no further FFA reduction.

4.1.2.6   Sulfuric Acid Temperature Interaction

As mentioned, one interaction term was determined by the regression analysis to be statistically significant: Sulfuric Acid*Temperature. The magnitude of this term was also shown to be problematic as described in section 4.1.1.9 since its power was lower than the 0.95 threshold below which significance is in question. The answer to the previously pondered question, "do we care?" is simply, "no". The reason for this is twofold:

1.   The interaction term is a combination of sulfuric acid and temperature, two factors which would already be maximized within practical constraints based on the analytical conclusions.

2.   The effect of the interaction term is marginal. As stated earlier in section 3.2.1.4, an effect of less than 3 would generally be ignored unless there was an economic reason to consider it (e.g. borderline spec). The number is rather arbitrary and

would be subject to the demands of the specific situation; however it serves as a good rule of thumb for process planning. The absolute contribution of the interaction effect was 2.49 < 3 and therefore not generally considered to be practically significant.

Given the above evaluation, the high uncertainty associated with the interaction term is of little concern from a practical vantage point.

4.2   ENHANCED REACTION KINETICS

Figure 22 shows the main effects plots of the enhanced reaction kinetics experiment.
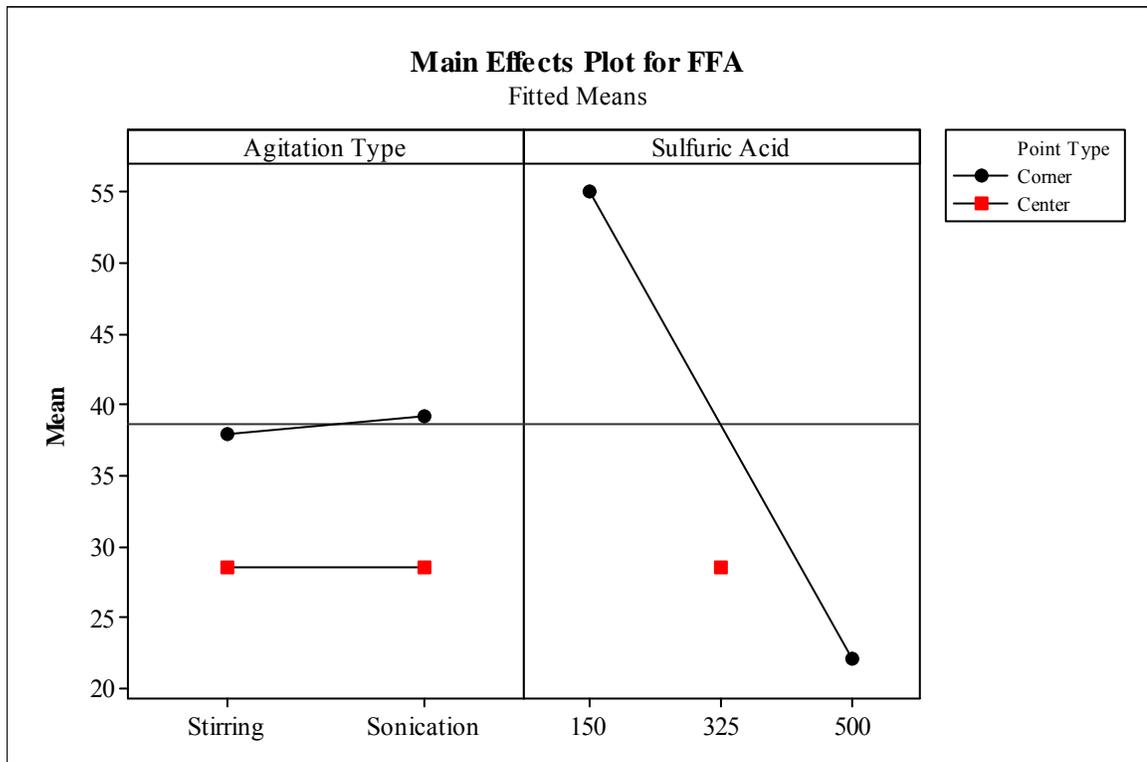
Figure 22: Main effects plot for the reaction kinetics enhancement experiment

From the above figure, the magnitude of the main effect between sonication and stirring is relatively minor. The magnitude of the effect between the high and low levels of sulfuric acid concentration is, once again, dramatic. From Figure 23, no evidence of interaction at either high or low levels of sulfuric acid content exists.
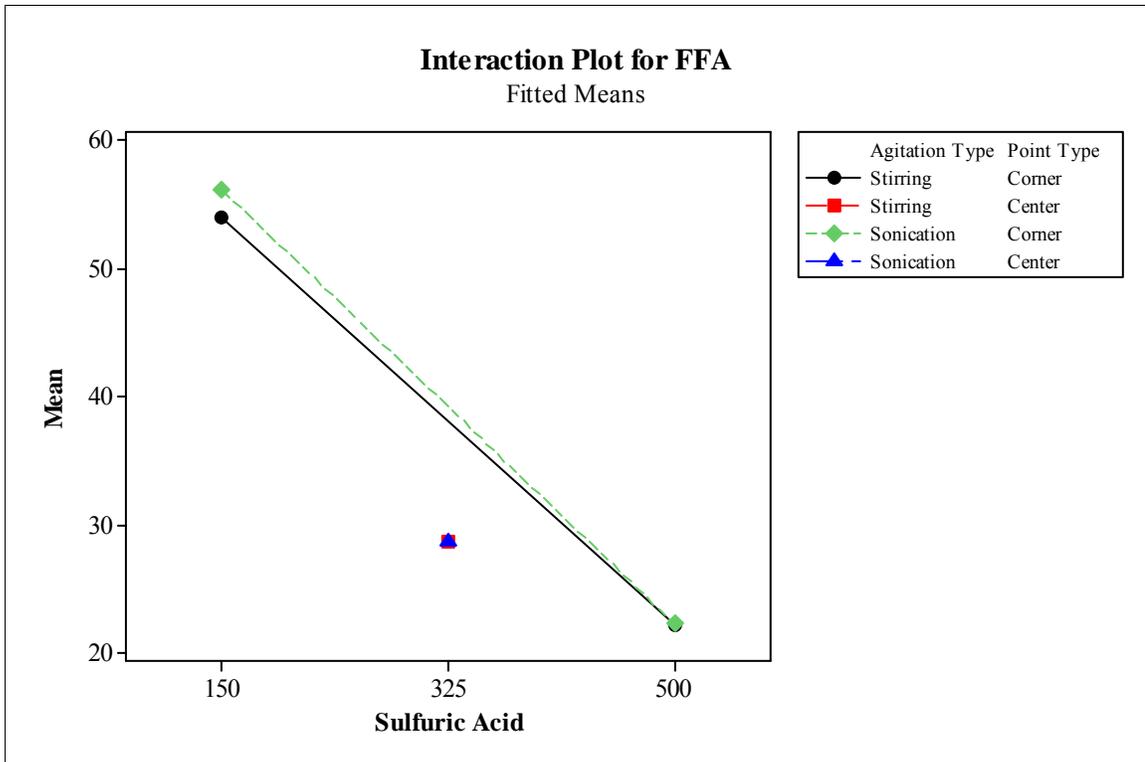

Figure 23: Interaction plot for the reaction kinetics enhancement experiment

The lines for stirring and sonication and the related center points nearly overlap which shows a largely identical effect between sonication and stirring at both the high and low levels of sulfuric acid concentration. No discernable interaction exists between the two main effects.

The pareto chart of the standardized effects in Figure 24 shows the sulfuric acid factor

effect to be the only significant effect based the effect magnitude threshold of 3.18

calculated from the P-values as described in section 4.1.1.6.

Pareto Chart of the Standardized Effects
(response is FFA, Alpha = 0.05)

| Factor	Name
A	Agitation Type
B	Sulfuric Acid
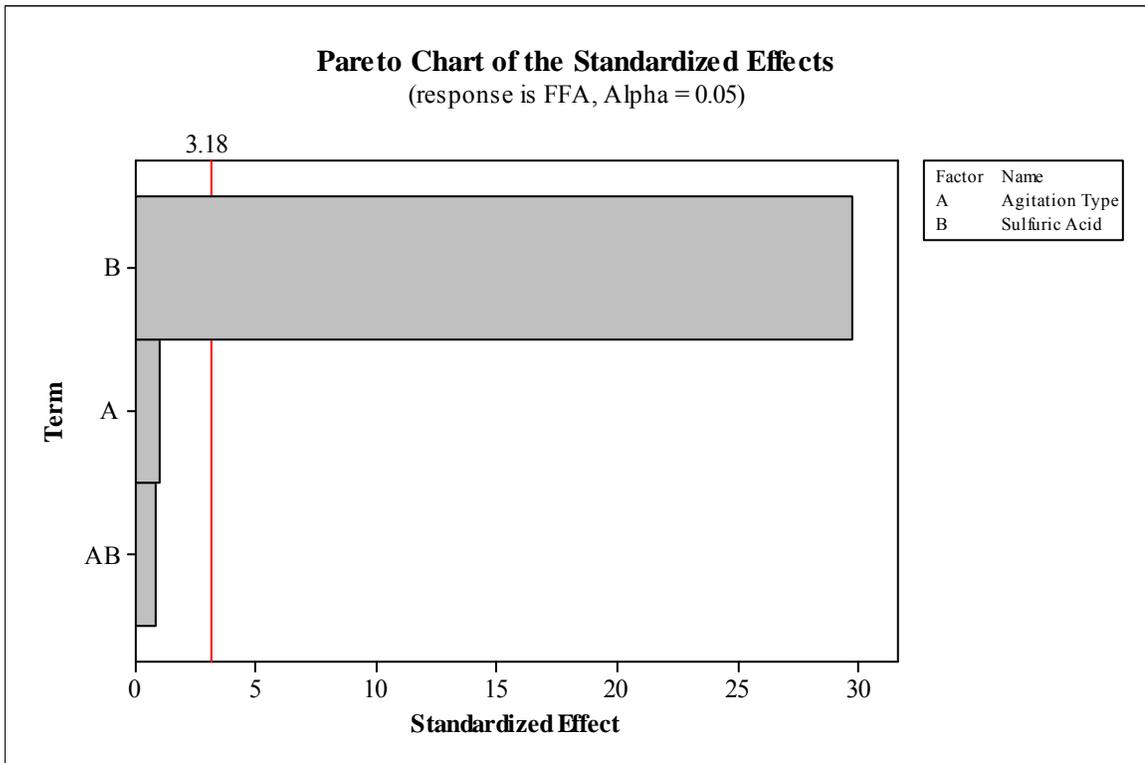
Figure 24: Pareto chart for the reaction kinetics enhancement experiment

The power curve in Figure 25 shows that the model is powerful enough to detect real

effects when they exist with the sulfuric acid effect having a 95% chance of being real.

Power Curve for 2-Level Factorial Design

Reps,	
Ctr Pts Per Blk	
— 2, 1	

| Assumptions	
Alpha	0.05
StDev	1.33243
# Factors	2
# Corner Pts	4
# Blocks	none
# Terms Omitted	0
Terms Included In Model	
Center Points	Yes
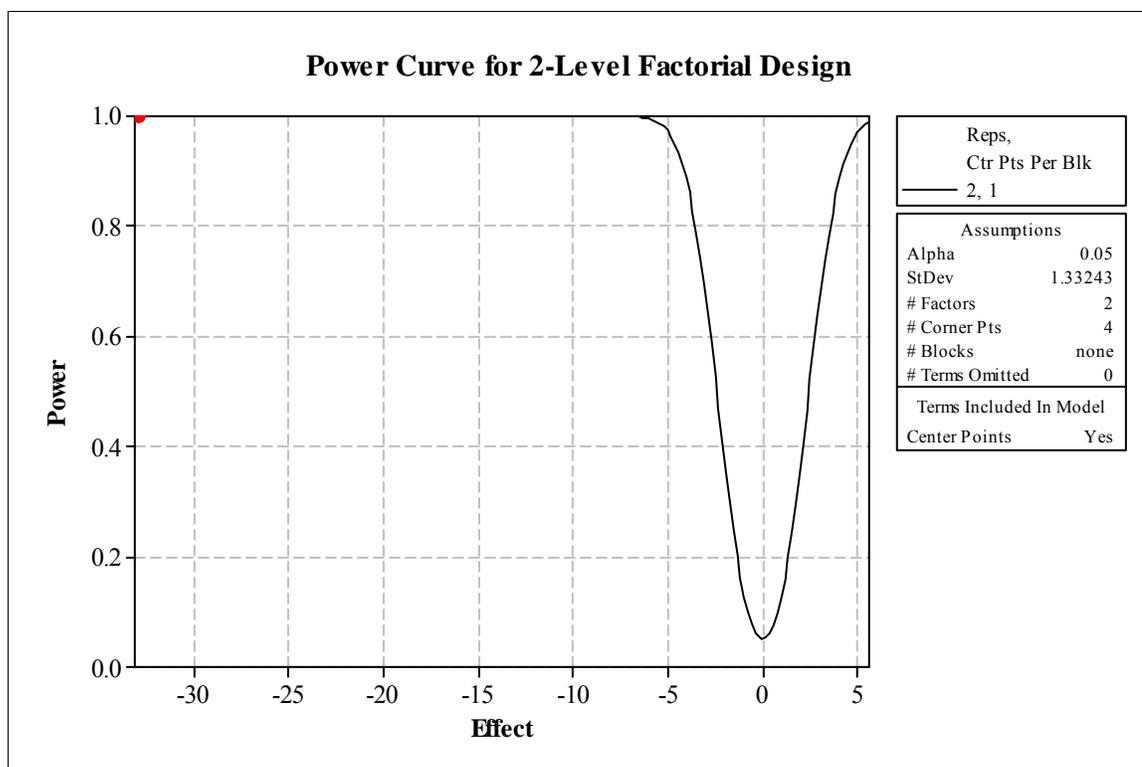
Figure 25: Power curve for the reaction kinetics enhancement experiment

The primary conclusion to be drawn from the data is that, at a fixed power (wattage) level of 33 watts of combined mechanical and thermal energy input, no statistically significant difference exists between the agitation methods of sonication and stirring. This suggests that the observations seen in the literature review are solely a function of the ability of sonicators to administer dramatically increased rates of mechanical energy into the reaction system.

91
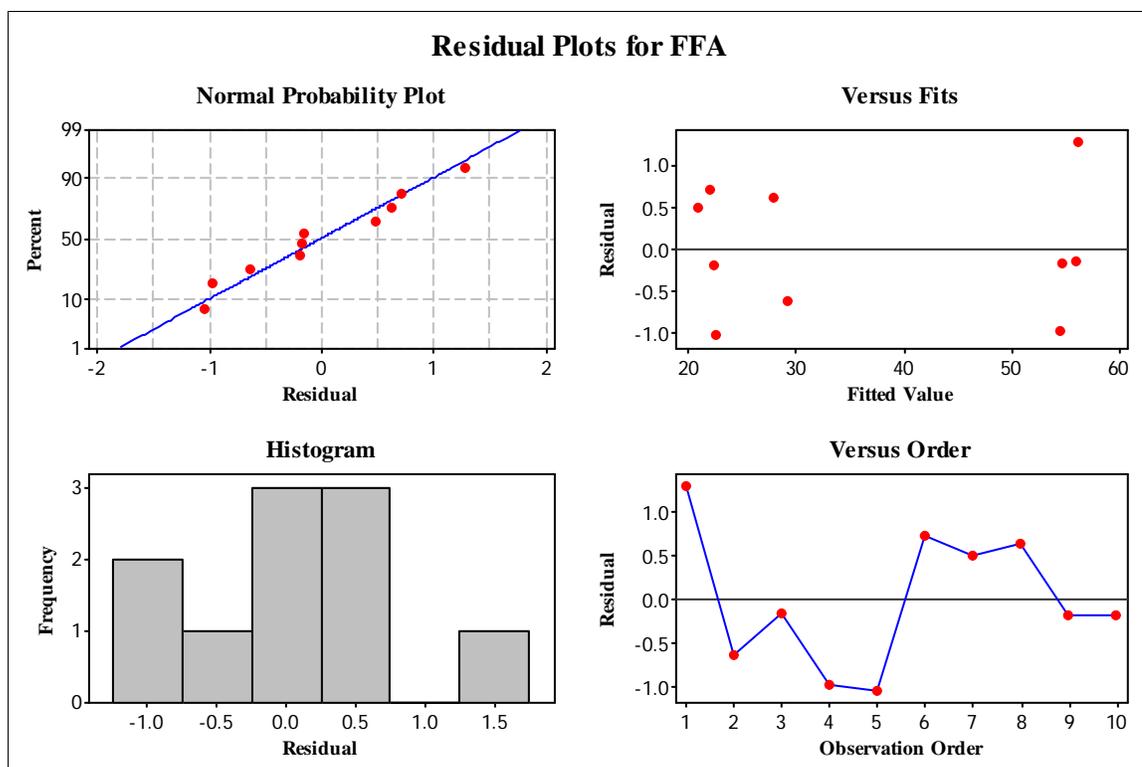
Figure 26: Residual plots the reaction kinetics enhancement experiment

The residual analysis is shown in Figure 25. While there appears to be some indication of outliers, and evidence of skewness, suggesting a less than perfect fit for the regression analysis, these disparities are likely the result of the extremely small number of experimental runs (10).

5.0 CONCLUSIONS

A study of the esterification reaction in ultra-high-FFA oils using methanol as the reacting alcohol and sulfuric acid as the catalyst was presented herein. It first sought to characterize the major reaction elements and determine their relative effects on the final FFA% after 15 minutes of reaction time. In addition, a comparison of a claimed reaction acceleration technique - agitation by ultrasonic irradiation – to conventional stirring was performed at constant energy input to evaluate the potential merits of sonication beyond its ability to input more energy into the reaction matrix. A literature review provided direction as well as suggested that additional work in the two areas of study herein was warranted. The experimental section and resulting analysis concluded that catalyst concentration (sulfuric acid) and reaction temperature had the greatest effects on the final FFA content after 15 minutes of reaction time. This was supported by Dias et al. (2009). Water addition was shown to have a retarding effect on the final FFA content and was supported by the work of Liu et al. (2006). Methanol was shown to have no significant effect on the final FFA content after 15 minutes of reaction time which is inconsistent with some of the other findings (Santos, 2010) but supported by others (Cardoso, 2008). The author concludes that the acceptance of the null hypothesis in this case is due to the relatively high volumetric ratio of methanol to oil. Effects would likely have been observed within a lower region. Finally, ultrasonic irradiation was shown to have no significant effect after 15 minutes of reaction time when the stirring and sonication power levels were held constant. This clearly demonstrates that the sole advantage of sonication

as an agitation method for the esterification of ultra-high-FFA oils such as brown grease

is its ability to introduce higher levels of mechanical energy into the reaction system.

6.0 RECOMMENDATIONS

Further areas for research include the optimization of all of the factor levels identified as being significant in the study. The author also believes that it would be beneficial to evaluate the region of oil to methanol volumetric ratio from 2:1 to 1:1. It is clear that methanol has no effect in the region of ratios from 1:1 to 1:2, however based on some of the findings in the literature, there is indication that methanol does have an impact on final FFA concentration in ultra-high-FFA feedstocks such as brown grease and fatty acid distillates. Finally, additional study of the sonication reaction as a function of power level is warranted. A larger experiment at multiple levels for power level, methanol content, and sulfuric acid content should be conducted. Optimization of any findings should also be conducted.

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ABOUT THE AUTHOR

Lucas Altic received his Bachelors in Mechanical Engineering in the Spring of 2004. Shortly thereafter, he began his career in renewable fuels, specifically biodiesel development and production. He has worked as a process engineer, project manager, plant manager, and independent contractor at biodiesel manufacturing facilities in Florida, Georgia, and South Carolina. His areas of focus are process management and control. He was a speaker at the Siemen's Automation Summit, Orlando, FL on the topic of process automation in 2008 and also presented at the annual Florida Farm to Fuels summit in August 2009. Upon completion of this Thesis, Lucas received his Masters degree in Mechanical Engineering from the University of South Florida. Lucas' wife, Lara, recently gave birth to their new baby boy, Jackson Joseph Altic.