An insight into biodiesel production from canola oil by homogeneously catalysed transesterification reaction in the presence of ethanol

By

Divashin Kowen Chinasamy

Bsc. Eng (Chemical)

Submitted in Fulfilment of the Academic Requirements for

Master of Science in Engineering

Discipline of Chemical Engineering

School of Engineering

College of Agriculture, Engineering and Science

University of KwaZulu-Natal

Howard College Campus

Durban, South Africa

April 2021

Supervisor: Prof Amir H. Mohammadi

Preface

The work presented in this dissertation was carried out in the analytical laboratory at the School of Engineering at the University of KwaZulu-Natal (Howard College Campus), Durban, from January 2020 to November 2020 under the supervision of Professor Amir H. Mohammadi.

This dissertation is submitted as the full requirement for the degree of Master of Science in Engineering (Chemical). All the work presented in this dissertation is original, unless otherwise stated. It has not (in whole or in part) been previously submitted to any tertiary institute as part of a degree.

_____

Divashin Kowen Chinasamy

As the candidate's supervisor, I agree to the submission of this dissertation:

_____

Prof Amir H. Mohammadi

Declaration

I, Divashin Kowen Chinasamy, declare that:

1. The research reported in this thesis, except where otherwise indicated, is my original research.

2. This thesis has not been submitted for any degree or examination at any other university.

3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

4. This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

a. Their words have been re-written but the general information attributed to them has been referenced

b. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks, and referenced.

5. This thesis does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

Signed

……

Acknowledgements

I would like to express my gratitude to the following individuals:

My supervisor, Prof Amir H. Mohammadi, for providing me with an interesting and important topic. His continuous support, guidance and expertise offered during this project have been invaluable.

Miss N. Hadebe, Mrs. T. Mofokeng & Mrs. P. Ntombela for their constant assistance and guidance in the laboratory and assistance in ordering the required chemicals.

My friend, Cameron Phekun, for his support and motivation during the project.

Lastly, my dear parents, Lesly and Charmaine Chinasamy, for always teaching me the importance of a good education and for affording me every opportunity to make a success of my career. I am where I am today thanks to them.

Abstract

The massive decline of fossil fuel resources in addition to the steady increase in the energy consumption rate over the past century has spurred research interest in alternative and renewable energy sources. A promising and sustainable alternative to fossil fuels is biodiesel. To raise market competitiveness for biodiesel, it is necessary to develop a cost-effective and technical processing schemes, to identify key related design criteria and optimize performance. In this study biodiesel is synthesized via transesterification reactions, through which triglycerides (vegetable oils) are converted to their alkyl esters (biodiesel) and glycerol as a by-product. This researched is aimed to investigate the homogenous catalysed transesterification reactions for biodiesel production using two different base catalyst, potassium hydroxide and sodium hydroxide, in the presence of canola oil and ethanol. The combination of the experimental conditions used to determine the optimal biodiesel yield was obtained by using the Box-Behnken experimental design. The Box-Behnken design was chosen as it generates a higher order response surfaces using fewer required runs than a normal factorial technique. The process variables that were considered for biodiesel production were the alcohol/oil molar ratio, catalyst loading, reaction temperature and the reaction time. Hence, the optimum conditions for biodiesel production through a homogenously catalysed transesterification reaction was proposed. The reason these process variables were chosen, were due to these variables having the largest impact on the production of biodiesel. The feedstock oil (canola oil) of this study had an acid number of 0.129 mg KOH/g, this ensured that a single step transesterification process could be utilised. An optimum yield of canola oil biodiesel produced using potassium hydroxide was 94.78%, while an optimum yield for canola oil biodiesel produced with sodium hydroxide was 95.78%. The biodiesel produced using the optimum experimental conditions were subject to basic property testing (such as density, viscosity, acid value, pH, pour point, flash point, etc), and blending with kerosene to produce bio-jet fuel (The 10% blend (BK10) which is 10% biodiesel and 90% kerosene and 20% blend (BK20) consisting of 20% biodiesel and 80% kerosene). The biodiesel samples (KOH and NaOH) met most of the ASTM standards, however the viscosity of the samples were 14.89 mm^2/s and 10.10 mm^2/s for KOH and NaOH biodiesel respectively which was beyond the 6 mm^2/s limit, hence further modification would be required before it can be utilised for diesel engines. It can be noted that this research found that NaOH would be better suited for biodiesel production in the presence of canola oil, as it produced a higher yield of ethyl ester of 95.78% and the viscosity of 10.10 mm^2/s obtained was closer to the acceptable range. The jet fuel samples did not meet all ASTM standard requirements; hence these are not recommended for use in an engine without further modification. A superficial feasibility study was conducted due to the lack

of studies regarding the cost analysis of biodiesel with the raw materials mentioned in this study, this study determined that the main factor influencing the economic viability of biodiesel is the feedstock cost.

TABLE OF CONTENTS

List of figures

List of tables

1. INTRODUCTION

1.1. MOTIVATION AND BACKGROUND

Throughout the past century, the demand for energy has progressively increased. Hence, the gap between supply and demand of petroleum oil raises concerns about fossil fuel depletion. The cause of the drastic increase of fossil fuel depletion is as a result of the significant growth in population and lifestyle changes. For many years, the increasing need for energy has been provided through the use of fossil fuels, this led to the crises of the depletion of fossil fuel, a rise in the fossil fuel prices and the serious environmental impacts such as global warming, acidification, deforestation as well as ozone depletion. The increased prices of petroleum-based fuels and growing environmental concerns have substantially amplified the public's attention to alternative and sustainable fuels. According to a study conducted by the World Energy Council (WEC), if there is a continuation in the current practice, worldwide energy demand in the year 2020 will be approximately 50-80% higher than it was in the early 1990's (Omer, 2008). Due to these reasons alternative energy sources have been studied in recent years.

Biodiesel is a solution to substitute fossil fuels due to a lower environmental impact, reduced emissions of particulate matter, carbon monoxide, total hydrocarbons as well as toxic aromatic and polyaromatic compounds (Lapuerta et al., 2008). Therefore, promotion of new applications for biodiesel can contribute to the accomplishment of sustainable development. Biodiesel by definition is a mixture of fatty acid alkyl esters which are commonly produced from triglycerides and alcohol in the presence of a catalyst through transesterification reaction. Biodiesel can be produced from vegetable oils, animal fats and waste cooking oils by transesterification. Biodiesel is a fuel that can be made from pure or waste vegetable oils such as soya and canola oil, mixed with methane and a small amount of lye. It runs a diesel engine just as petroleum-based diesel. Hence, it is necessary to study the potential of biodiesel, as well as its feasibility, to investigate a viable solution to alternative fuels in the future.

1.2. AIMS AND OBJECTIVES

The main aim for this study was to optimize the production of biodiesel using canola oil, in the presence of two different catalyst (Potassium hydroxide and Sodium hydroxide). The following are some of the additional aims and objectives for the research into biodiesel.

- To propose an ideal experimental procedure to produce biodiesel through transesterification using a single feedstock in the presence of various catalysts.

- To investigate the effect of various parameters such as the type of raw materials used, catalyst concentration, oil to alcohol ratio, reaction temperature and stirrer speed on the yield and quality of biodiesel produced.
- To determine theoptimum conditions for biodiesel production via the transesterification reactions.
- To determine the effects of different catalyst on the vegetable oil.
- To perform property testing to assess the quality of the biodiesel produced.
- To compare properties of biodiesel to commercial diesel.
- To conduct a kinetic study on the transesterification reactions.
- To investigate and determine the challenges, advantages, and disadvantages of using biodiesel.
- To determine the economic viability of the production of biodiesel.

Objectives:

- Conduct a detailed literature review to obtain all the necessary information and propose an efficient experimental method to produce biodiesel.
- Perform property tests on the raw materials to assess its quality.
- Conduct experiments to assess the optimal conditions for biodiesel production, and critically analyse the results obtained.

1.3. METHODOLOGY

The researched thesis is broken down into nine chapters. Each chapter covers an important aspect of this project. The following is a representation of the methodology used for the compilation of the researched topic.

Chapter 1 introduces the reader to the idea of the study. The background and motivation for the topic is presented so that the reader will understand there is a need for such a study. A list of the research aims, and objectives are also presented here to outline what the study intends to answer, and how this was achieved.

Chapter 2 is an extensive literature review, which was conducted to provide clarity and understanding, for the reader, of the theoretical background required to understand the research. This also covers aspects such as the methods of biodiesel production, catalysts used in biodiesel production, factors that affect the production of biodiesel as well as typical feedstocks biodiesel production.

Chapter 3 provides a list of the equipment as well as the raw materials required for the study. The chemicals used are provided along with the purity, supplier and the experimental apparatus used is described along with its purpose.

Chapter 4 focuses on the possible experimental design methods, as well as the experimental method used during this study. The experimental design obtained was vital to optimise the yield of biodiesel produced.

Chapter 5 presents the results and discussion of the homogenously base catalysed transesterification of canola oil using potassium hydroxide as the catalyst. The effects of the process variables were investigated, and a comprehensive discussion of the result was conducted.

Chapter 6 presents the results and discussion of the homogenously base catalysed transesterification of canola oil using sodium hydroxide as the catalyst. The effects of the process variables were investigated, and a comprehensive discussion of the result was conducted.

Chapter 7 describes the property testing methods used during the study and an illustration of the results of the property tests conducted on the optimal yield of biodiesel was produced along with the properties of various blends. The biodiesel was also analysed by GC-MS.

Chapter 8 focuses on a feasibility study conducted on biodiesel using many literature sources to determine if it is a feasible method for renewable energy.

Chapter 9 provides the conclusions drawn from this study and offers recommendations for future work that can be carried out in this field.

2. THEORETICAL BACKGROUND

2.1. HISTORY OF BIODIESEL

The first diesel engine was developed by Rudolph Diesel in the 1890s, this became the engine of choice for power, reliability, and high fuel economy around the world. Primary researchers on vegetable oil fuels included the French government and Dr. Diesel himself, who wished for pure vegetable oils to be used to power early diesel engines for agriculture in areas of the world, where petroleum was not available at that period (Jääskeläinen, 2019). Modern biodiesel has its roots in research conducted in the 1930s in Belgium. The reason for the development of the diesel engine was to improve inefficient and sometimes dangerous steam engines of the late 1800s. The diesel engine works on the principal of compression ignition, in which fuel is injected into the engine's cylinder after air has been compressed to a high pressure and temperature (Jääskeläinen, 2019) As the fuel enters the cylinder it self-ignites and burns rapidly, forcing the piston back down and converting the chemical energy in the fuel into mechanical energy. Dr. Rudolph Diesel, for which the engine is named, holds the first patent for the compression ignition engine, issued in 1893 (Demirbas, 2008).

Early diesel engines had complex injection systems and were designed to run on many different fuels, from kerosene to coal dust. It was only a matter of time before someone recognized that because of the high energy content, vegetable oils would make excellent fuel. The first public demonstration of vegetable oil based diesel fuel was at the 1900 World's Fair, when the French government commissioned the Otto company to build a diesel engine to run on peanut oil (Bondioli, 2007). Rudolph Diesel later did extensive work on vegetable oil fuels and became a leading proponent of such a concept, believing that farmers could benefit from producing their own fuel. However, it would take almost a century before such an idea became a widespread reality. With petroleum being available and cheap, the diesel engine design was changed to match the properties of petroleum diesel fuel.

Due to the widespread availability and low cost of petroleum diesel fuel, vegetable oil-based fuels gained little attention, except in times of high oil prices and shortages. Unfortunately, the newer diesel engine designs could not run on traditional vegetable oils, due to the much higher viscosity of vegetable oil compared to petroleum diesel fuel. Many methods have been proposed to lower the viscosity, including pyrolysis, blending with solvents, and even emulsifying the fuel with water or alcohols, none of which have provided a suitable solution (Demirbas, 2008)

A Belgian inventor in 1937 who first proposed using transesterification. The process of transesterification converts vegetable oil into three smaller molecules which are much less viscous and easy to burn in a diesel engine. In the early 1980s, concerns over the environment, energy security and agricultural overproduction once again brought the use of vegetable oils to the forefront. However, this time with transesterification as the preferred method of producing such fuel replacements (Bondioli, 2007).

Biofuel Type	Unit	2005–2010	2011–2015	2016–2025
Biodiesel	Percent consumption (of diesel fuel)	10%	15%	20%
	Amount (million kL)	2.41	4.52	10.22
Bioethanol	Percent consumption (of gasoline)	5%	10%	15%
	Amount (million kL)	1.48	2.78	6.28
Bio-oil/bio-kerosene	Amount (million kL)	1	1.8	4.07
Bio-oil/pure plantation oil (PPO)	Amount (million kL)	0.4	0.74	1.69
Biofuel	Percent consumption (of energy mix)	2%	3%	5%
	Amount (million kL)	5.29	9.84	22.26

Figure 2. 1: Roadmap for biofuel development (Elder et al., 2018)

2.2. WHY BIODIESEL?

2.2.1. Economical

Production of biodiesel can be done on a small scale and is relatively cheaper when compared to commercial diesel (Pal, 2011). With low prices, most people save a fortune on fuel bills. In some cases, it even goes into the thousands of Rands. With such a high rate of saving, most people regain their initial capital investment on the equipment required to make biodiesel within a matter of months.

2.2.2. Renewable

Biodiesel has been highly regarded for its renewable properties. It is an alternate method of producing fuel that replaces the making of fuel from a depleting resource such as crude oil. This means that it can be produced from things that can be regrown, reproduced, and reused. So, if there is a higher demand, it can just be grown from another crop of seeds for the oil.

2.2.3. Environmentally friendly

When Biodiesel is used to power diesel engines, the emissions at the tailpipe are significantly reduced. Studies by the US National Renewable Energy Lab indicate drops in several key areas' that help the

environment. Carbon Dioxide and Hydrocarbons are significantly reduced when Biodiesel is used. The use of biodiesel in older diesel engines such as indirect combustion diesels produce astounding results, indicating a reduction in the tailpipe emissions of nearly 90%. It also has a positive energy balance (Arshad, et al., 2018).

Benefits of the engine

Biodiesel has a significantly higher “lubricity” than Petro diesel. This implies that it is relatively more "slipperier" than normal diesel fuel. With the added "lubricity" of Biodiesel, engines have proved to experience less wear and tear when used on a regular basis. Biodiesel is also less polluting, hence easier on the engine.

2.2.4. The perfect alternative fuels

In comparison to other alternative fuels, Biodiesel is one of the front runners. Most alternative fuels require modifications to a vehicle for it to be used. Natural Gas and Propane require special tanks to be installed and changes to the fuel injection system must also be conducted. Ethanol also requires specialised changes to the fuel injection system. The use of electricity requires a completely different engine (Arshad, et al., 2018).

Physical and chemical properties of biodiesel and petro-diesel

Biodiesel has gained global attention as a blending component or a replacement for Petro diesel in the engine of vehicles. Due to this reason it is very important that the properties of both products are similar as this ensure both can be used in an engine. According to Siraj (2017), biodiesel is given the code B100 and must meet ASTM D 6751 and EN 14214 standards. The chemical, physical and thermal properties of biodiesel has a significant influence on the storage behavior and combustion flow of the substance. Table 2.1 gives some properties of biodiesel compared to Petro diesel. ASTM initiated the development of a standard for biodiesel by designating a task force and the first provisional biodiesel specification was released in 1999 known as the ASTM PS 121-99. After this the refining procedures for the standards continued and several precision and bias tests for the analytical methods were conducted. In March of 2002, the ASTM published its first full biodiesel standard, ASTM D6751.

Table 2. 1: Comparison of biodiesel and Petro diesel standards adapted from Siraj, (2017)

Property	Test method	Petro Diesel	Biodiesel
Flash point (˚C)	D 93	52 min	130 min
Water and sediments	D 2709	0.05 max % vol.	0.05 max % vol.
Kinematic viscosity @ 40 ˚C	D 445	1.3-4.1 mm^2/s	1.9-6.0 mm^2/s
Sulfated ash	D 874	-	0.02 max % vol.
Ash	D 482	0.01 max % vol.	-
Sulfur	D 5453	0.05 max % vol.	-
Sulfur	D 2622/129	-	0.05 max % vol.
Copper strip corrosion	D 130	No. 3 max	No. 3 max
Cetane number	D 613	40 min	47 min
Aromaticity	D 1319	35 max % vol.	-
Carbon residue	D 4530	-	0.05 max % mass
Carbon residue	D 524	0.35 max % vol.	-
Distillation temp.	D 1160	282 ˚C min -338 ˚C max	-

2.3. ADVANTAGES AND DISADVANTAGES OF BIODIESEL

Table 2.2 tabulates the advantages and disadvantages of biodiesel. The information in Table 2.2 was adapted from multiple sources such as Green Coast, (2020), Journey to Forever, (1999) and (Beer and Grant., n.d).

Table 2. 2: Advantages and disadvantages of biodiesel

Advantages	Disadvantages
Produced from renewable resources	Variation in the quality of biodiesel
Allows for longer engine lifespan as well as no engine modifications.	Cannot be used in low temperature conditions
It is environmentally friendly as it burns up to 75% cleaner than commercial diesel.	Due to high oxygen content, it produces high levels of NOx levels during combustion
Lower emissions of greenhouse gases since it is a plant-based energy source.	May cause clogging in the engine
Biodegradable and non-toxic	May cause food shortages as vegetables are used to produce these oils
Has a positive effect on economy	The use of fertilisers increase since the demand for vegetables will be higher
High cetane number, which allows for an improved engine performance and is a better lubricant.	The lower volumetric energy density of biodiesel means that more fuel needs to be transported for the same distance travelled
	A modified refueling infrastructure is needed to handle biodiesel, which adds to their total cost

2.4. MEANS OF BIODIESEL PRODUCTION

2.4.1. Chemical methods

Pyrolysis:

Pyrolysis refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oils are likely to approach diesel fuels. The pyrolysate has a lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolysate is lower. The pyrolysed vegetable oils contain acceptable amounts of sulfur, water and sediments which produce acceptable copper corrosion values but unacceptable ash, carbon residual and pour point (Jahirul et al., 2012). Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis.

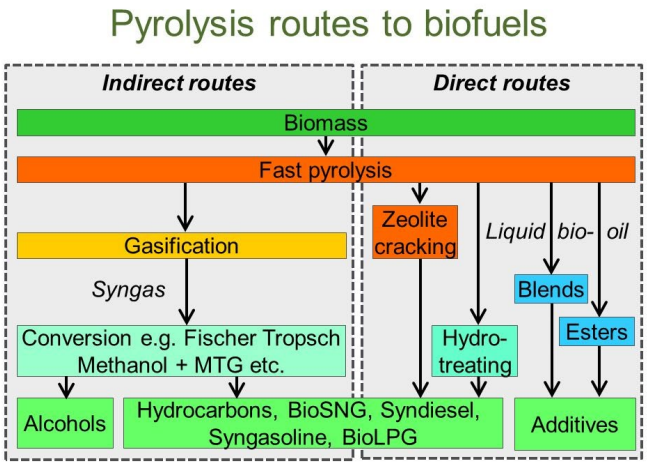


Figure 2. 2: Pyrolysis routes to biofuels (Bridgewater, 2015)

Transesterification:

Transesterification is a chemical reaction between an alcohol and vegetable oil in the presence of a catalyst. The products for the reaction require an ester and glycerol. The process generally consists of a series of three consecutive reversible reactions where initially triglycerides are converted to diglycerides. The next step involves the conversion of diglycerides into monoglycerides and the final step ensures the conversion of the monoglycerides into glycerol (Knothe, 2010). Alcohol is one of the main requirements for the reaction to occur. A wide variety of alcohols are used however, the alcohols commonly used are methanol, ethanol, propanol and butanol. The so called "ideal" alcohol to utilize is methanol, however for this project ethanol was required for the process. Methanol is made from fossil-origin raw materials, while ethanol can be obtained from renewable resources (Basque Research., 2014). Hence, ethanol was chosen for its renewable nature and using ethanol increases the speed of reaction is very much greater and, thus, there is a greater capacity of production (Basque Research., 2014).

The alcohol to oil molar ratio is one of the most significant factors. It plays a vital role in the efficiency and yield of the biodiesel produced. The stoichiometric ratio, according to the balanced reaction seen in figure 2.7, of alcohol to oil is 3-parts alcohol to 1-part oil, to advance immiscibility and improve the contact between the alcohol molecules and the triglyceride molecules (Sarin, 2000). Higher alcohol to oil ratio implies that the glycerin-fatty acid linkage breaks easier which in turn implies a greater conversion within a shorter period (Sarin, 2000). A higher molar ratio would also cause an increase in the yield as well as the purity of the biodiesel being produced. For this research topic, biodiesel was produced using this method as it is the most effective and efficient method of production. The reaction mechanism and thermodynamics

of this reaction will be discussed further in section 2.6. The following illustration is an example of the chemical reaction that takes place.

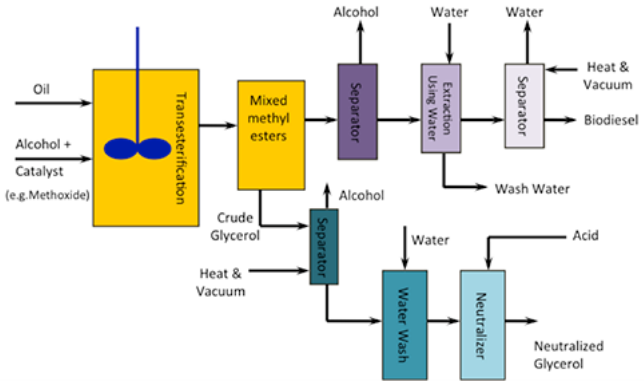


Figure 2. 3: Block diagram of a typical transesterification process (9.2 The Reaction of Biodiesel: Transesterification | EGEE 439: Alternative Fuels from Biomass Sources, n.d.)

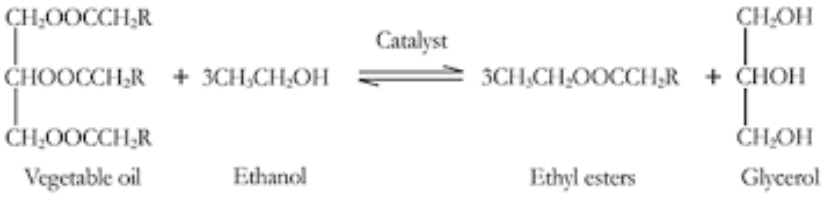


Figure 2. 4: Overall Transesterification reaction (Leung, et al., 2010)

2.5. REACTION MECHANISM AND THERMODYNAMICS

The reaction investigated in this study was the transesterification reaction. The production of biodiesel is not restricted to laboratory scale studies. Many industries use this process to produce various substances. The transesterification is an equilibrium reaction. The presence of a catalyst speeds up the reaction to favour the product side. To achieve a high yield of esters, the alcohol needs to be in excess (Pal, 2011). For a favorable forward reaction, the alcohol to oil ratio needs to be greater than the reaction stoichiometric ratio of 3:1. As stated by Pal (2011), the transesterification reaction is an exothermic reaction and immediately following the addition of catalyst, the temperature rises by approximately 1°C to 2 °C. Figure 2.7 illustrates the overall transesterification reaction.

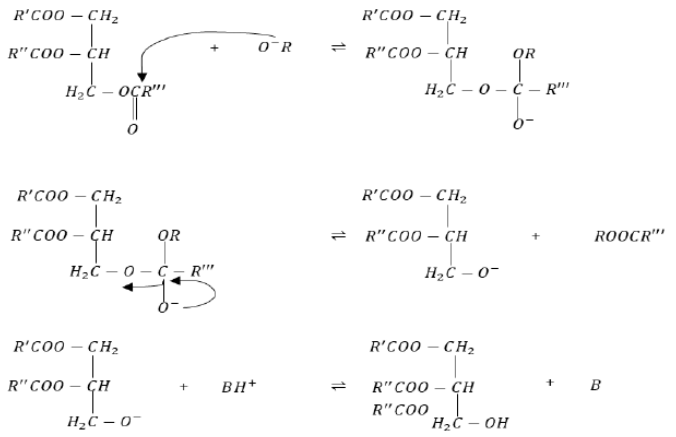


Figure 2. 5: Transesterification reaction mechanism (Leung, et al., 2010)

Furthermore, the three steps of transesterification are represented in figure 2.8 on an ionic level. Figure 2.8 shows the transfer of ions and the charge at each point of the reaction. R_1, R_2, and R_3 represent long-chain hydrocarbons, referred to as fatty acids, where R refers to the length of the alcohol chain. The alcohol breaks the fatty acid chains in the presence of a catalyst resulting in glycerol and a mixture of fatty acid alkyl esters (biodiesel) (Leung, et al., 2010). Figure 2.9 illustrates the reaction mechanism of the transesterification reaction, this figure shows the productions of the diglyceride and monoglyceride, and how the monoglyceride is converted into biodiesel (Ethyl ester) and glycerol.

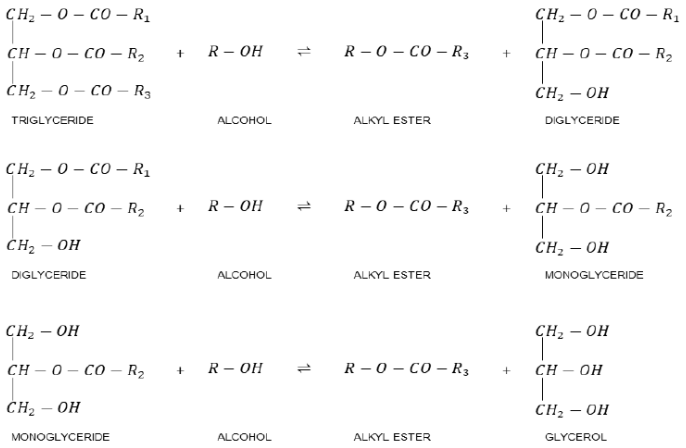


Figure 2. 6: Transesterification reaction mechanism (Leung, et al., 2010)

2.5.1. Homogenous base catalysed transesterification

Typically, homogeneous catalysts are dissolved in a solvent with the substrates, in the case of biodiesel, the base catalyst is dissolved in the alcohol required for productions. A homogeneous catalyst is generally

efficient in converting biodiesel with low FFA values. Lotero et al. (2005) stated that the main reason catalysts are widely used, include the fact that they are able to speed up the transesterification reaction at atmospheric pressure and at low temperature, in addition they are widely available and inexpensive which allows for high yields to be achieved in a short period of time. The most common homogeneous base catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH). Base catalysed transesterification reaction rates are approximately 4000 times faster than that of acid catalyzed reactions. However, these catalysts cannot be used for all vegetable oils as they are very sensitive to the FFA content of the oil. Wang et al. (2006) stated that homogenous base catalysts should only be used with oils that have an FFA content lower than 1 wt.%, while Felizardo et al. (2005) reported that homogenous base catalysts can be used in conjunction with oils that have an acid value below 2 $mg\ KOHg$. However, as tabulated in table 2.8, other researchers have recommended FFA values of up to 2 wt.%.

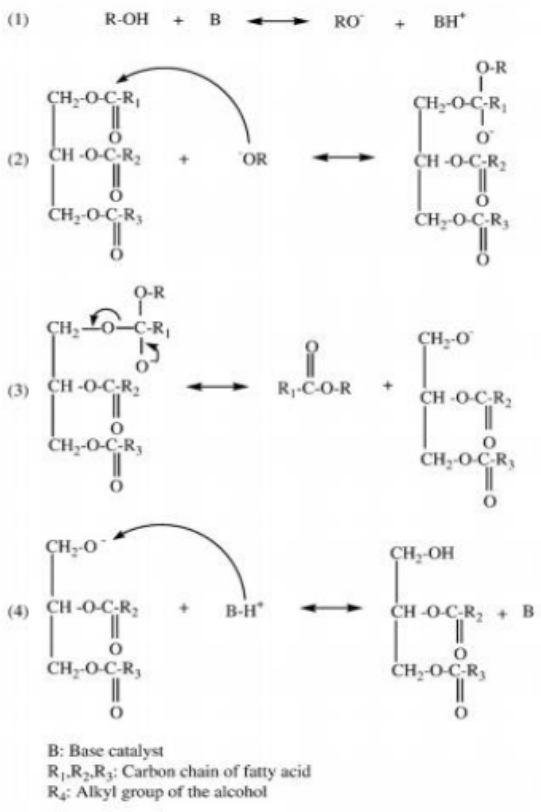


Figure 2. 7: Reaction mechanism for homogenous base catalysed transesterification (Lotero, et al., 2005)

2.5.2. Heterogeneous base catalysed transesterification

Heterogeneous catalyst is a recent development in the world of biodiesel production. Many solid (heterogenous) base catalysts such as basic zeolites, hydrotalcites and alkaline earth metals have been studied for biodiesel production using transesterification (Lam et al., 2010). Most heterogeneous catalysts

are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size then the larger the surface area for a given mass of particles. Zabeti et al. (2009) Calcium oxide (CaO) has a high basic strength, low solubility in methanol and can be synthesised via cheap sources such as limestone. Therefore, it has attracted a lot of attention as a potential catalyst for biodiesel production.

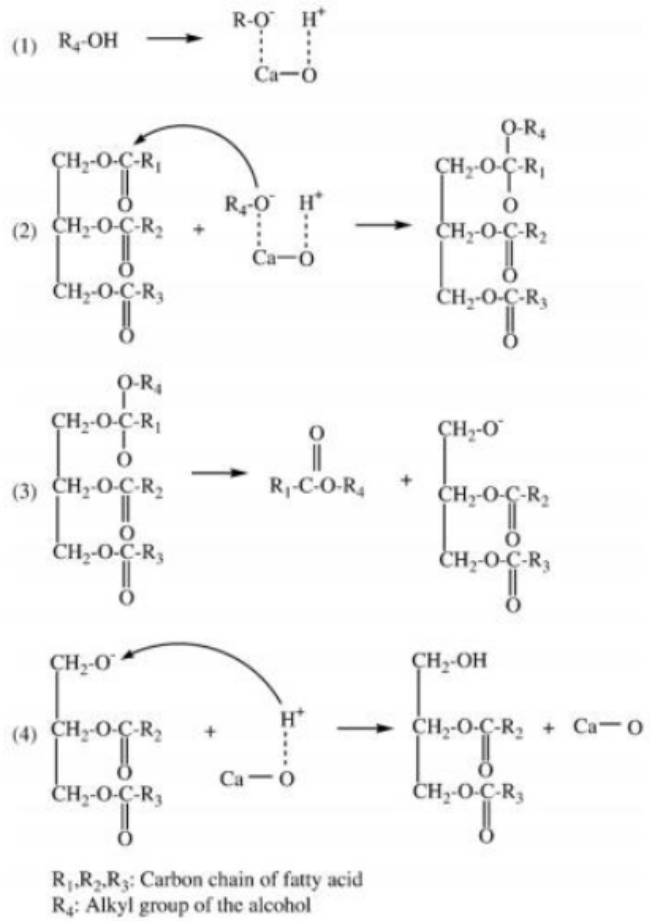


Figure 2. 8:Reaction mechanism for heterogeneous base catalysed transesterification (Lotero, et al., 2005)

2.5.3. Homogeneous acid catalysed transesterification

This method requires the use of an acid catalyst such as HCl or H_2SO4 to convert the triglycerides present in various vegetable oils into biodiesel and glycerol. Typically, this method is used as it is economically feasible when feedstocks with relatively high acid values are used for biodiesel production (Gebremariam and Marchetti, 2017). The presence of water in the reaction mixture may cause a reduction in the yield by competitive formation of carboxylic acids (Park et al., 2010). Due to the slow rate of reaction a relatively higher reaction time is required when acid catalysts are used, which poses a disadvantage, as the resulting

process conditions may not be feasible. However, this method is extremely useful for the conversion of high acid value feedstocks into biodiesel that meet the ASTM standards. Zhang et al. (2003) stated that since acid catalysed reactions are a one-step process, they are more feasible as compared to base catalysts which require two steps for vegetable oils with higher FFA content.

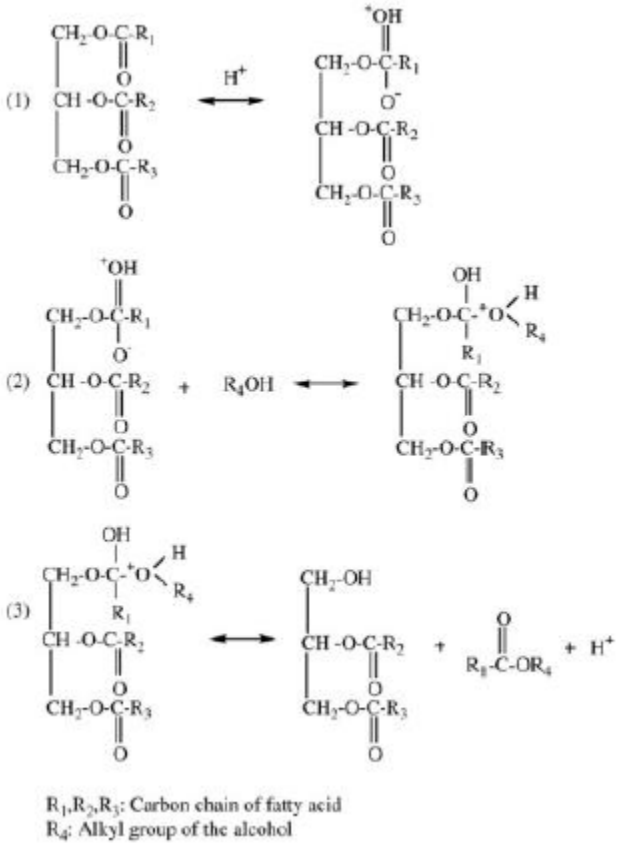


Figure 2. 9: Reaction mechanism for homogeneous acid catalysed transesterification (Lotero, et al., 2005)

2.5.4. Saponification and hydrolysis reaction

At times there may be some water which may be present in the feed stock and this may result in the formation of foams or gels that may cause difficulties in the separation of biodiesel from glycerol. A possible explanation for water content in the feedstock may be due to the process of extraction (Demirbas, 2005). Figure 2.12 illustrates a typical saponification reaction.

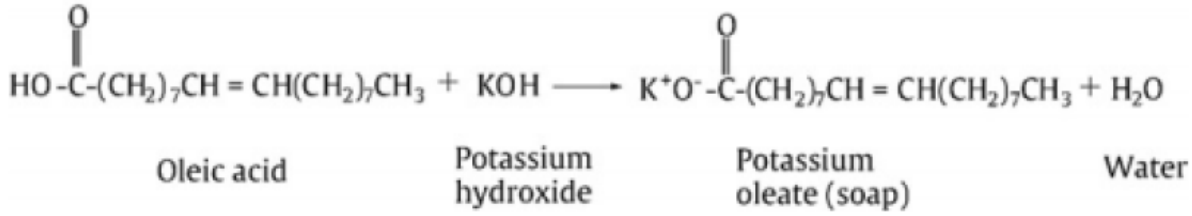


Figure 2. 10: Typical saponification reaction (Lam, et al., 2010)

Figure 2.13 shows that if water is present during the reaction process, it will then react with the triglyceride to form a diglyceride and fatty acid. This fatty acid will thereafter react with the base catalyst to form a soap (eg. potassium oleate) and water (as seen in Figure 2.12). If water were not present in the feedstock, then the triglyceride would not have reacted with it to form the fatty acid and therefore no soap would have formed. Therefore, the presence of water in a feedstock does indeed lead to soap formation. The soaps of saturated fatty acids typically solidify under ambient conditions, therefore a reaction mixture with a lot of soap may gel-up and form a semi-solid mass which is difficult to recover (Felizardo et al., 2005).

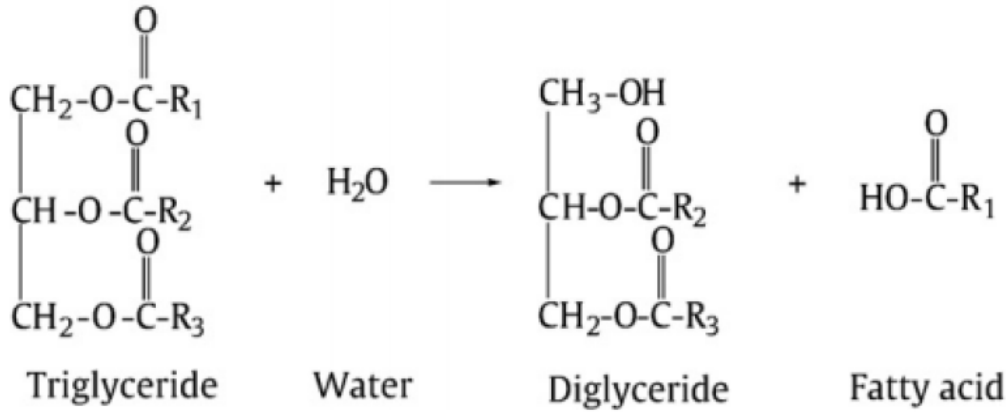


Figure 2. 11: Typical hydrolysis reaction of triglyceride to form free fatty acid (Lam, et al., 2010)

2.6. KINETICS AND MASS TRANSFER

2.6.1. Factors affecting kinetics and mass transfer

2.6.1.1. Reaction temperature

Temperature is an important process variable for the conversion of triglycerides into methyl/ethyl esters. It plays a vital role in affecting the kinetics of the transesterification reaction. Many studies are carried out between different temperature ranges (from 25 ºC to 200 ºC) to analyse the optimum temperature for the reaction to take place. Noureddini and Zhu (1997) investigated the effect of temperature dependency on the overall reaction rate of the system. This study was carried out for the temperature of 30, 40, 50 and 60ºC. It was deduced that an increase in temperature caused a decrease in the mass transfer regime in the early period of the reaction. The activation energies determined by the study indicated that the forward reaction rate increases with higher temperatures (Noureddini and Zhu, 1997). Similar results were confirmed by a study conducted by Darnoko and Cherian (2000) for the transesterification of palm oil. The rates of conversion increased with increasing the temperature (Darnoko and Cheryan, 2000). Although, it was reported in many instances that intensity of agitation was more important than the temperature for the transesterification of sunflower oil as the conversion results were similar for 25 ^{0}C and 65 ^{0}C for the mixing intensity of 600 rpm (Vicente et al., 2005). According to Klofular et al. (2010), the effect of temperature on the extent of mass transfer, the results of this study indicated that the rate of forward reaction was dominant over the rate of reverse reaction. Temperature was reported as an important factor for the reaction kinetics of waste sunflower oil and natural rapeseed oil (Klofular et al., 2010). Investigations have been carried out for the effect of low temperature on the kinetics for the methanolysis of sunflower oil for temperatures as low as 10,20 and 30 ºC. At these lower temperatures it was determined that initial drop size of the dispersed phase reduced up to 10 times as the reaction proceeded. With an increase in the reaction temperature, the droplet size decreases with the fast trend. Therefore, the total interfacial area increased with formation of stable emulsions, leading to enhance TG mass transfer rate (Stamenkovic et al., 2007). The kinetic behaviour for different systems with different reaction temperature is not the same, thus it is appropriate to consider the kinetic studies for each case separately. It can be concluded that reaction temperature plays a key role in the reaction kinetics.

2.6.1.2. Mixing speed

The degree of mixing between the triglyceride and alcohol phases is of great importance. Mechanical mixing is used as a method to increase the contact between the reactants. This process of mixing allows for an increase in the rate of mass transfer. Therefore, the change in the intensity of mixing in the reaction can cause the kinetics of the transesterification reaction to be changed (Noureddini and Zhu, 1997). Mixing

intensity can be reported by Reynolds number. NRe (dimensionless number) can be defined as the ratio of inertial forces to viscous forces as shown in equation 2.1.

$$Re = \frac{inertial\ force}{viscous\ force} = \frac{n \times {D_a}^2 \times \rho}{\mu} \quad (2.1)$$

Where n is the rotational speed of the impeller, Da is the impeller diameter, and ρ and μ are the fluid density and viscosity. The study conducted by Noureddini and Zhu (1997) investigated the effects of the RE on transesterification, this study was carried out for the rotational speed of 150, 300 and 600 rpm. The study showed that an increase in the Reynolds number caused a decreased viscosity of the biodiesel produced. For higher mixing intensities a shorter mass transfer region can be observed. A further study conducted by Ma et al. (1999) correlated drop size with the speed of mixing with mechanical agitation in the stirred reactor. This study stated that smaller droplet sizes increased the rate of reaction with stable emulsion (Ma et al., 1999). Thereafter, with the aid of experimental data it was proved that agitation plays an important role in the transesterification process and has a huge impact on the kinetics of the reaction (Alcantara et al., 2000; Noureddini et al., 2004). During the initial stages of the reaction limitations of mass transfer can be observed according to many kinetic studies. This initial limitation of the mass transfer regime was eliminated by speeding up the mixing speed of the reaction. Vicente et al. (2005) conducted a study for the kinetics of sunflower oil at higher agitation speeds to remove the mass transfer region. It was noted that the phase became homogenous due to the "self enhancement" of the interfacial area (Vicente et al., 2005). The droplet breakage was vigorous as the mixing was carried out at an elevated speed of 600 rpm. Stamenkovic et al. (2008) investigated the intensity of the agitation speed using sunflower oil as the feedstock. According to the study, the mean drop diameter and drop size distribution was observed at different mixing speeds. The reaction was performed at a relatively low temperature of 20 ^{o}C to increase the mass transfer regime and decrease the reaction rate in the initial stages to the reaction. Agitation speeds of 60 and 200 rpm was selected and the corresponding values of Reynolds numbers were in the range of 56 and 151. This indicates that the agitated solutions were in transition state, the flow was fully turbulent near the impeller and its behaviour became laminar away from the blade (Stamenkovic et al., 2007). It can also be noted that the by-products monoglycerides, diglycerides and soaps acted as emulsifying agents. This will enhance the stable emulsion of small drops leading to the progress of the reaction (Stamenkovic et al., 2007; Noureddini and Zhu., 1997). Increasing the intensity of agitation will cause an increase in the conversion of methyl esters, however the reaction time was stated as the controlling factor in terms of conversion (Slinn and Kendall, 2009). Recently mixing models were developed which shows the relation between mixing speeds and its effect on the transesterification reaction. Past models are specific and can be utilized only on the systems. This model has been confirmed by literature data and is claimed to be used on any transesterification systems (Brasio et al., 2011).

2.6.1.3. Alcohol to oil ratio

Studies in literature shows that a minimum molar ratio of 6:1 for alcohol to oil feedstock is preferred to favor the forward rate of reaction. According to the following studies conducted by Srivastava and Prasad (2000), Atadashi et al. (2011) and Balat and Balat (2008), this was also determined to be the optimum molar ratio for the conversion. An excess of alcohol is used to favour the reaction towards the forward reactions. Therefore, increasing the molar ratios to 12:1 has given a reasonable yield by increasing the conversion. In the study of transesterification of cynara oil, a range between 9:1 and 12:1 produced better results (Enciner et al., 2002). For higher molar ratio of 15:1, the separation of glycerin in the reaction becomes more difficult as the solubility increases due to the higher alcohol concentration. Freedman et al., (1984) conducted a study on the transesterification of soy oil using butanol and methanol with varying molar ratios of alcohol to oil between 30:1 to 6:1. At higher molar ratios of 30:1, the order of the reaction becomes pseudo first order, while at the molar ratios of 6:1, the order obtained was second and fourth order using butanol and methanol respectively (Freedman et al., 1984). As homogenous base catalyst, the studies were carried out using NaOH and KOH. Later the investigations were also carried out for the methoxides and ethoxides as the catalyst in the transesterification. Usually the catalyst and catalyst concentration are the least important factors to develop a model for the kinetics of methanolysis/ethanolysis. The molar ratios selected for almost all the studies were 6:1 for alcohol: oil. It was reported that the system follows a second order reaction rate for the ratios of 6:1. While for higher ratios of 10:1 and higher, pseudo first order reaction rate was observed.

2.7. KINETICS STUDY

Kinetic data is a vital factor in the process assessment and in the development of large-scale reactor systems. Kinetic models are key for designing chemical reactors, studying chemical reactions as well as side reactions and catalyst development. Many kinetic models have been studied and predicted for feed stocks such as work for soybean by Noureddini and Zhu (1997), a study of rapeseed oil by Klofutar et al. (2010), study of sunflower oil by Vicente et al. (2005) and an investigation into palm oil by Darnoko and Cheryan (2000). From research conducted in the duration of this study, there was a lack of kinetic studies and kinetic models for transesterification reactions. Little to no literature to date has been reported on the kinetic studies for canola oil as a feedstock according to research conducted during the time this project was conducted. However, certain articles did report kinetic studies for olive oil as a feed stock. Later, the models were developed including only second order reaction and second order reaction with side reactions.

Transesterification reaction progress is shown by three regimes. According to Pal (2011), these regimes are:

(1) Mass transfer controlled regime in the initial period of the reaction (slow).

(2) Chemically controlled regime for almost the entire period of reaction (fast).

(3) Equilibrium regime during the completion of the reaction (slow).

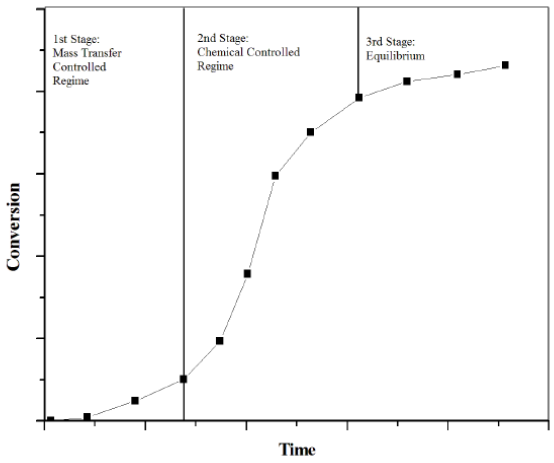


Figure 2. 12:General trend of alcoholysis of vegetable oil (Pal, 2011).

Freedman et al used the Arrhenius equation to relate reaction coefficients to temperature (Equation 2.2)

$$k = A\,exp(\frac{-E_a}{RT}) \tag{2.2}$$

where A is the Arrhenius pre-factor, Ea is the activation energy of the reaction, T is the temperature in kelvins and R is the universal gas constant.

A paper conducted in 1997 by Noureddini and Zhu, introduced the concept of Reynolds number and modified the equation. The authors of the study modified the equation by deriving a parameter "n" with experiments (Equation 2.3). The authors discovered that there was a correlation between the activation energy and the Reynolds number. By using the concept of shunt reaction and using n=1, the rate constants obtained were very small and were neglected. The results obtained from the studies were interesting as the rate constant for the reverse direction for the first two reactions were larger than the rate constant for the forward reaction (Noureddini and Zhu, 1997).

$$k = A\,T^2\,exp\,(-\frac{E_a}{RT}) \tag{2.3}$$

2.8. FEEDSTOCK AND PROCESS VARIABLES

Some of the parameters affecting the extent and rate of completion of the reaction include; the feedstock and alcohol used, type of catalyst and catalyst loading, molar ratio of alcohol to oil, reaction temperature and the in homogeneity of the reaction mixture (phase behaviour).

2.8.1. Feedstock

The most used compound for biodiesel production is vegetable oils, other compounds may be used for biodiesel can be fats and recycled greases. Biodiesel production ideally considered oils that had a low free fatty acid content. Table 2.5 shows the free fatty acid content of different feed stocks. Figure 2.7 indicates that the two main reactants required for biodiesel production, using the transesterification reactions, are an alcohol and a vegetable oil. Pinto, et al. (2005) stated that the feedstock to be used in the production of biodiesel is determined by various parameters such as the climate and the availability in each region. Pinto, et al. (2005) also stated that because of the higher price of edible vegetable oils as compared to non-edible oils, the latter is preferred for use as feedstock in the production of biodiesel. The use of non-edible oils or waste cooking oils prevents the issue of food against fuel. By converting edible vegetable oils into biodiesel, a huge chunk of food sources are being converted into automotive fuels and the large-scale production of biofuels from edible vegetable oils could bring about an imbalance to the food supply and demand market (Gui et al., 2008).

Selecting the type of vegetable oil used is a more involved process than choosing the alcohol due to numerous factors that need be considered. Knothe (2005) stated that cheaper vegetable oils are most likely of a lower quality and also has a relatively higher free fatty acid (FFA) content, which may cause the formation of soap during the transesterification reaction process, which is highly undesirable due to the reduction in the yield and the quality of the biodiesel produced. Another reason that choosing the oil is so important is that the quality of biodiesel obtained is largely dependent on the quality of the base oil used for production (Knothe, 2005). The transesterification of vegetable oils allows for a reduction of the viscosity, which allows for the use of these oils in diesel engines. Table 2.3 demonstrates the amount of oil and main producers of some of vegetable oil seeds

Table 2. 3: Main producers of some of vegetable oil seeds (O'Brien et al., 2000).

Seed	Amount of oil (%)	Productive areas
Canola	40-45	Canada, China, India, France, Austria, United Kingdom, Germany, Poland, Denmark, Chech, Republic.
Corn	3.1-5.7	USA, Mexico, Russia, Belgium, France, Italy, Germany, Spain, United Kingdom
Cotton	18-20	China, Russia, USA, India, Pakistan, Brazil, Egypt, Turkey.
Peanut	45-50	China, India, Nigeria, USA, Senegal, South Africa, Argentina.
Crocus	30-35	China, USA, Spain, Portugal
Soybeans	18-20	USA, Brazil, Argentina, China, India, Paraguay, Bolivia.
Sunflower	35-45	Russia, Argentina, Austria, France, Italia, Germany, Spain, United Kingdom.
Coconut	65-68	Filipinas, Indonesia, India, Mexico Sri Lan Ka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Republic of Cote d´Ivoire.
Olive	15-35	Spain, Italy, Italia, Greece, Tunes, Turkey, Morocco, Portugal, Syria, Algeria, Yugoslavia, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, USA, Australia.
Palm	45-50	Malaysia, Indonesia, China, Filipinas, Pakistan, Mexico, Bangladesh, Colombia, Nigeria, Republic of Cote d´Ivoire

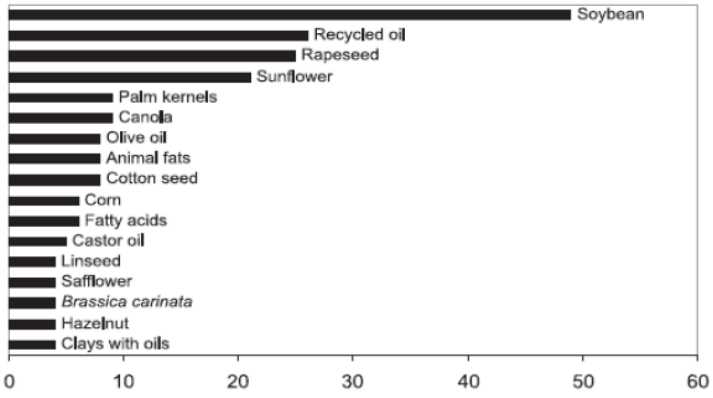


Figure 2. 13: Leading sources of biodiesel cited in scientific articles (Pinto, et al., 2005)

Table 2. 4: Yields of oil and meal obtained by extraction of different oilseeds (Gunstone, 2009)

Seed	Oil yield (%)	Meal yield (%)
Soybean	18.3	79.5
Cottonseed	15.1	57.4
Groundnut	40.3	57.2
Sunflower	40.9	46.9
Rapeseed	38.6	60.3
Palm	44.6	54.0
Copra	62.4	35.4
Linseed	33.3	64.2

Due to the properties of biodiesel being mainly dependent on the feedstock oil used for its production, it is reasonable to assume that future genetic engineering could have the ability to enhance the properties of the parent oil in order to produce biodiesel of much higher standards and better properties. The source of biodiesel used is dependent on the availability in each region (Pinto et al., 2005). The environmental conditions would also dictate the choice of oils, for example, palm oil may be used in regions with a warm climate while in regions with a colder climate it may prove problematic due to its high cloud point value. Table 2.4 shows the yield of oil obtained varies for different seeds and this is also a point of consideration when deciding on which oil to use for biodiesel production. The methods of oil extraction include chemical methods such as solvent extraction, as well as mechanical methods such as crushing or pressing (Gunstone, 2009).

Table 2. 5: FFA in different oil feedstocks (Singh & Singh, 2010)

Vegetable oil	Fatty acid composition (wt%)															
	12:0	**14:0**	**14:1**	**16:0**	**16:1**	**18:0**	**20:0**	**20:1**	**22:0**	**24:0**	**18:1**	**22:1**	**18:2**	**18:3**	**18:4**	**Others**
Cottonseed	-	0	-	28	-	1	0	-	0	0	13	0	58	0	-	-
Tabacco	-	0.09	-	10.96	0.2	3.34	-	-	-	-	14.4	-	69.49	0.69	-	0.69
Rapeseed	-	0	-	3	-	1	0	-	0	0	64	0	22	8	-	-
Safflower	-	0	-	9	-	2	0	-	0	0	12	0	78	0	-	-
Sunflower	-	0	-	6	-	3	0	-	0	0	17	0	74	0	-	-
Olive	-	-	-	5	0.3	1.6	-	-	-	-	74.7	-	17.6	0	0.8	-
Sesame	-	0	-	13	-	4	0	-	0	0	53	0	30	0	-	-
Linseed	-	0	-	5	-	3	0	-	0	0	20	0	18	55	-	-
Palm	-	-	-	35	-	7	-	-	-	-	44	-	14	-	-	-
Neem	-	0.2-0.26	-	13.6-16.2	-	14.4-24.1	0.8-3.4	-	-	-	49.1-61.9	-	2.3-15.8	-	-	-
Corn	-	0	-	12	-	2	-	-	0	0	25	0	6		-	-
Tallow	-	-	-	23.3	19.3	19.3	-	-	-	-	42.4	-	2.9	0.9	2.9	-
Hazelnut	-	-	-	4.9	0.2	2.6	-	-	-	-	83.6	-	8.5	0.2	0	-
Soya bean	-	-	-	14	-	4	-	-	-	-	24	-	52	-	6	-
Peanut	-	0	-	11	-	2	1	-	2	2	48	0	32	1	-	-
Coconut	48.8	19.9	-	7.8	0.1	3	-	-	-	-	4.4	-	0.8	0	65.7	6.2
Yellow grease	-	0.70	0	14.26	1.43	8.23	0.33	0.48	-	-	43.34	-	26.25	2.51	0.47	-

2.8.2. Reaction temperature

One of the most vital factors that affects the production and yield of biodiesel is the reaction temperature. Transesterification can occur at various temperatures ranges between room temperature to a temperature close to the boiling point of the alcohol used (1). Generally, the use of higher reaction temperature allows for more rapid reactions and shorter reaction times. Mathiyazhagan and Ganapathi. (2011) reported that using temperatures that are above the optimal temperature may results in a decrease in biodiesel yield, due to the fact that high temperatures accelerates the saponification of the triglycerides in the vegetable oil. An additional disadvantage of using temperatures above the boiling point of the alcohol, is that the alcohol would vaporize when added to the vegetable oil.

2.8.3. Alcohol/oil ratio

The molar ratio of alcohol to vegetable oil is an important factor affecting the yield of biodiesel. According to figure 2.8, for transesterification to occur successfully, it requires three moles of alcohol for every one mole of triglyceride (vegetable oil) to yield three moles of biodiesel (fatty acid alkyl esters) and one mole of glycerol. However, transesterification is an equilibrium reaction, so a large amount of excess alcohol is required to advance the reaction. A study conducted by Freedman, Pryde et al. (1984) illustrated the effects of a range of molar ratios of alcohol to triglyceride between 1:1 to 6:1 on the transesterification reaction by using different vegetable oils. For all the oils used for testing, the highest conversions (93% -98%) were achieved at a 6:1 molar ratio of alcohol to oil. Rashid and Anwar (2008) found the optimum yield (98%) of biodiesel was obtained at a 6:1 molar ratio of alcohol to oil. An increase in the ratio of alcohol to oil results in an increase in the biodiesel yield up to a certain optimal ratio after which a further increase in the oil to alcohol ratio does not increase the yield of biodiesel, but rather increases the difficulty and cost of separation of the biodiesel layer from the glycerol and unreacted alcohol layer (Mathiyazhagan and Ganapathi, 2011). According to the various literature sources, the optimum alcohol to oil molar ratio often lies between a range of 6:1 and 12:1, however, this was dependent on various factors such as type of catalyst used, alcohol used, etc. This is not to say that the optimum ratio would not lie in a range much higher than that seen in literature, as the type of feedstock used may require higher alcohol ratios.

2.8.4. Type of catalyst/ catalyst loading

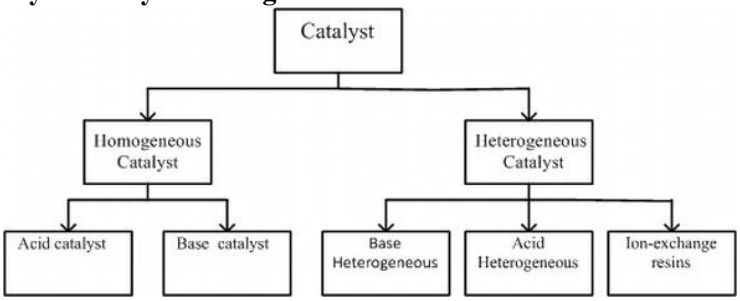


Figure 2. 14: Breakdown of different types of catalyst

Fukuda et al. (2001) reported that catalyst loading is the required amount of catalyst present during a reaction and is generally reported as a percentage of one of the reactants. The presence of a catalyst is vital for the transesterification process conducted under atmospheric conditions (Gunstone, 2009). Several types of catalysts have been studied, these include acidic, basic, homogenous and heterogenous catalysts.

2.8.4.1. Basic catalyst:

According to Guo (2011), the transesterification reaction may require catalyst such as alkaline metal oxides or alkoxides as well as potassium and sodium carbonates. This specific reaction, when a basic catalyst is required, needs to be carried out under excess alcohol, atmospheric pressure and temperature in the range of 60 to 65℃. When alkaline hydroxides are used the reaction time may exceed 90 minutes (Guo, 2011). Information obtained from Guo (2011) one major downside of using a basic catalyst for the transesterification reaction is that it cannot be applied directly to the vegetable oil as it contains a large amount of free fatty acids. When this catalyst is added to vegetable oil, which contains a high amount of free fatty acids, these acids neutralize to produce soap and water. When soap and water is produced it prevents the separation of glycerol from the mixture. Base catalysts tend to dissolve in glycerol as well as water which indicates they cannot be recycled (Guo, 2011).

2.8.4.2. Acidic catalyst:

Acid catalysts have not been used as widely as base catalysts. An acidic catalyst is usually favoured when using a vegetable oil with a relatively high composition of free fatty acids. Usually strong acids such a hydrochloric or sulphuric acid is favoured, since the reaction does not produce soap (Guo, 2011). The disadvantage of the use of an acid catalyst is that they are more sensitive to water and the moisture of a reaction. A small amount of moisture could severely decrease the yield of the product being produced. Other disadvantages of using an acid catalyst for the transesterification reaction include: a higher temperature range (from 80 to 100℃), a longer reaction time as well as the equipment being used may encounter some form of corrosion (Guo, 2011). The following table represents some of the advantages and disadvantages of using an acidic and basic catalyst.

2.8.4.3. Homogenous catalyst

Homogenous catalysts are typically broken down into either base or acid. The most common base catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (CH_3NaO) and potassium methoxide (CH_3KO) (Carter and Halle, 2005). The most common acid catalysts are hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and sulphonic acid (RSO_3H) (Carter and Halle, 2005).

2.8.4.4. Heterogenous catalyst

This type of catalyst is usually a solid, in the form of powder and offers more feasible reaction conditions in comparison to homogeneous catalyst. Acid heterogeneous catalysts can be used for the esterification reaction because the acid catalyst can catalyze the FFA content present in the reaction mixture and base catalysts are used in transesterification reactions to allow for the conversion of triglycerides into fatty acid esters and glycerol (Ma and Hanna, 1999). In addition, heterogeneous catalysts are highly selective and can be reusable once recovered. The potential for separation by filtration or centrifugation eliminates the need for wastewater treatment and reduces product contamination by catalyst. The major disadvantage of heterogeneous catalysts is deactivation, which occurs over time due to poisoning, coking, leaching and sintering.

Table 2. 6: Advantages and disadvantages of different types of catalyst

Type of catalyst	**Advantages**	**Disadvantages**
Homogeneous base	• Does not form water during the transesterification reaction • Two-step alkaline-catalysed transesterification from used vegetable oil is an economic method for biodiesel production • Reaction can occur at mild reaction condition and thus less energy required	• Very Sensitive to FFA content in the oil • Saponification can occur if the FFA content in the oil is more than 2 wt.% • Produce more wastewater from purification

	• NaOH and KOH are economically feasible and widely available.	
Heterogeneous base	• Faster reaction rate than acid catalysed transesterification. • Less energy is required for the reaction and it can occur in milder conditions. • Catalyst is reusable. • Considerably easier separation	• When exposed to ambient air, catalyst may be poisoned. • Catalyst leaching may result in the contamination of products. • Soap formations decreases biodiesel yield.
Heterogeneous acid	• Mainly used for low grade oils. • Insensitive to FFA and water content. • Easy separation of catalyst. • Esterification and transesterification occur simultaneously • Catalyst reusable	• Requires higher alcohol to oil molar ratios and higher reaction temperatures. • Energy intensive • Difficult catalyst synthesis methods may lead to higher costs.
Heterogeneous acid	• Insensitive to FFA and water content. • Esterification and transesterification occur simultaneously • Mainly used for low grade oils.	• Slow rate of reaction • May cause corrosion of equipment • Problematic to separate catalyst from the product
Enzyme	• Easy purification steps required • Insensitive to FFA and water content • Mainly used for low grade oils.	• Slow rate of reaction, slower than acid catalysed transesterification. • Higher costs • Highly sensitive to alcohols

2.8.5. Reaction time

The rate of conversion of a vegetable oil to biodiesel approaches equilibrium with the increased reaction time. According to Jagadale and Jugulkar, (2012), the reaction goes; thus, diglycerides and monoglycerides at the beginning of the reaction increases and then decreases. The amount of monoglycerides was found to be higher than diglycerides and monoglycerides required for the transesterification at the end of the reaction. Freedman et al. (1986) stated that the maximum ester conversion was achieved in less than 90 minutes. Increases in reaction time beyond the optimal level results in the reduction of biodiesel due to the reverse reaction resulting in a loss of alkyl esters, as well as soap formation (Jagadale and Jugulkar, 2012).

2.8.6. Type of alcohol

The most used alcohols for transesterification are methanol and ethanol, however, methanol is preferred mainly due to its lower cost (Carter and Halle, 2005). According to Leung et al. (2010) ethanol has a much lower reactivity than that of methanol during the process of transesterification. Longer chain alcohols are rarely used mainly due to their higher cost; however, it is possible to use these alcohols in the transesterification process (Freedman et al., 1986). The higher conversion rates for the longer chain alcohols are most likely due to the higher reaction temperatures which is possible due to their higher boiling points.

Table 2. 7: The effect of the alcohol type on the conversion rate and biodiesel density (Balat and Balat, 2010).

Alcohol	**Boiling point (K)**	**Reaction Temperature (K)**	**Conversion (%)**	**Specific gravity**
Methanol	338	333	87.8	0.8876
Ethanol	351.5	348	95.8	0.8814
2-propanol	355.4	348	92.9	0.8786
1-butanol	390	383	92.1	0.8782

2.8.7. Acid value

The acid value is used to determine the acidity of a substance. The acid value is defined as the weight of base in mg needed to neutralise the organic acids present in 1g of fat and it is a measure of the free fatty acids (FFA) present in the fat or oil (Sattanathan, 2015).

2.8.8. Free fatty acid and moisture content

For base catalysed transesterification, the vegetable oils used for the reaction is very sensitive to the FFA content, and all materials should be substantially anhydrous (Wright, Segur et al.1944). The presence of FFA and water in the reaction may cause an unwanted side reaction with the catalyst and produce soaps. Therefore, the effectiveness of catalyst is reduced, and the formed soaps drastically increases the viscosity of the mixture. Higher viscosity may lead to the formation of gels, which will make separation of glycerol extremely difficult. Meher, Vidya Sagar et al. (2006) stated that the FFA and moisture contents are vital parameters for determining the economic viability of the transesterification process. It is suggested that the FFA content of the feedstock used in the transesterification process should be as low as possible, typically below 1% (or acid value less than 2 mgKOH/g).

Table 2. 8: Recommendations for different FFA% required for transesterification

Reference	**Recommended FFA (wt. %)**
Ma and Hanna (1999)	< 1
Ramdhas et al. (2005)	≤ 2
Zhang et al. (2003)	< 0.5
Freedman et al. (1984)	< 1
Tiwari et al. (2007)	< 1
Sahoo et al. (2007)	≤ 2
Wang et al. (2006)	< 0.5

The high water content in the vegetable oils may have an impact on the yield of the biodiesel produced. According to a study conducted by Lam et al. (2010) the presence of water in the reaction can hydrolyse triglycerides to diglycerides and form free fatty acids, this is most likely to occur at high temperatures. Figure 2.14 shows a typical hydrolysis reaction. As seen, this reaction results in the formation of free fatty acids which will then go on to react with the base catalyst to form soap as seen in Figure 2-7. It can therefore be concluded that the presence of water in the vegetable oil will result in the excessive formation of soap.

2.9. BIODIESEL PROPERTIES

The properties of biodiesel present many issues that may be difficult to overcome to meet American, European and South African fuel standards. These properties arise from the vegetable oils and alcohols used to produce biodiesel. According to Marwaha et al. (2018) the structural features such as degree of unsaturation, chain length and branching of the vegetable oil and alcohol affects properties of biodiesel such as viscosity, cetane number, heat of combustion and oxidative stability. There are many factors that influence the properties of biodiesel and these factors are discussed in this chapter.

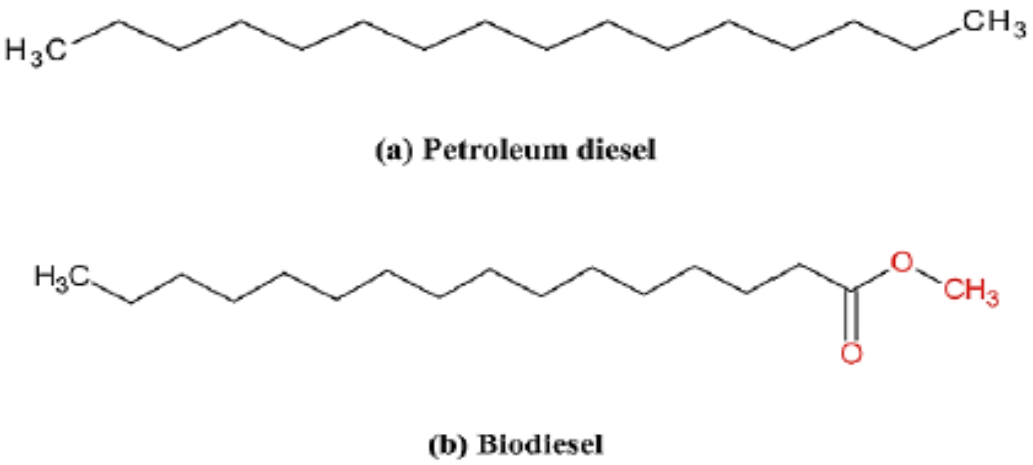


Figure 2. 15: Chemical formula for petrol and biodiesel

2.9.1. Density

Density is an important biodiesel parameter, with impact on fuel quality. Blangino et al. (2008) stated that the density of biodiesel is mainly dependent on the feedstock used during the production process as well as the alkyl ester profile of the biodiesel in addition degree of unsaturation is a huge influence on the density of biodiesel, this implies that a higher degree of unsaturation results in a higher density. According to Bianchi et al. (2011), the density dictates the energy content of a fuel, where higher densities indicate a higher amount of thermal energy for the same amount of fuel, resulting in a better fuel economy. Fuel density is a weight of unit volume of fuel. The minimum value of density is desirable to obtain the maximum engine power through the fuel flow control in the injection pump. It also required minimising the smoke formation when operating with maximum power (Yasin et al., 2013). Yasin et al. (2013) also stated that density is an important fuel property because injection systems and pumps must deliver a precisely adjusted amount of fuel to provide proper combustion. The density of biodiesel is generally slightly higher than that of commercial diesel. Chain length also affects biodiesel density with an increase in chain length leading

to a decrease in density (Saxena et al., 2013). According to ASTM D6751 standards, the density of biodiesel at 40 °C is 0.82 to 0.9 g/cm^3.

2.9.2. Viscosity

Saxena et al. (2013) defines viscosity as "a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another". Saxena et al. (2013) also stated that the viscosity of biodiesel is higher than that of commercial diesel by roughly a factor of two. The kinematic viscosity determines the degree of atomization that biodiesel has inside the combustion chamber (Anguebes-Franseschi et al., 2019). Fuel viscosity can be significantly lowered by using the transesterification process. Viscosity has a greater impact under low temperatures that resist the fuel to flow smoothly from the storage tank into the engine. Higher viscosity causes poorer atomization of the fuel spray and inaccurate fuel injectors operation (Yasin et al., 2013). The main issue with the direct use of vegetable oils as fuels is the high viscosity. Kumar et al. (2017) noted that the mean diameter of the fuel droplets from the injector and their penetration increases with increasing viscosity. This may lead to nozzle clogging, injector choking and incomplete combustion within the engine (Kumar et al., 2017). The previously mentioned problems can result in a lower engine lifespan. Viscosity increases as the chain length (number of carbon atoms) of an organic molecule increases. Viscosity also increases with an increasing degree of saturation (Knothe, 2005). Bianchi et al. (2011) claim that the necessary fuel characteristics are dependent on the intended application of the fuel, for instance, engines used for the production of energetic power allow the use of fuels with a higher viscosity.

2.9.3. Cetane number

The cetane number is an indication of a fuels readiness to auto ignite after it has been injected into the diesel engine. Diesel fuels are required to have a cetane number greater than 40 and most refineries produce diesel with cetane numbers within the range of 40 and 45. Biodiesel has a higher cetane number than commercial diesel, its range is between 46 and 60. However, the cetane number of biodiesel depends on the feedstock used. The biodiesel range for the cetane number shortens the ignition delay in the engine which improves the combustion characteristics (Biodiesel Education, 2006).

2.9.4. Acid Value

The acid value (AV) measures the content of acidic substances in biodiesel and is also used to monitor the degree of degradation that may occur during storage (Anguebes-Franseschi, et al., 2019). Anguebes-Franseschi, et al. (2019) defines the acid value as the amount of base (in mg of KOH) required to neutralize the FFA in 1 gram of oil. Original oils (Canola and soybean) have relatively lower acid values than that of waste cooking oils, which may require acid esterification to lower its acid value.

2.9.5. Saponification value

The saponification value (SV) refers to all fatty acids present in the sample (free and esterified). To determine SV, the sample is completely saponified with an excess of alkali, which excess is then determined by titration (in mg KOH/g). The saponification number depends on the molecular weight and the percentage concentration of fatty acid components present in FAMEs of oil. The SV is effectively used to determine the average relative molecular mass of oils and fats (Ismail and Ali, 2015).

2.9.6. Heating value

The heating value is also known as the heat of combustion, and in the case of biodiesel it depends mainly on the oil source used for production. The heating value of a fuel affects both the brake thermal efficiency and combustion characteristics of an engine. Its value for fuel blend cannot be calculated based on the blend ratio even though the heating values of blend fuels are known (Heating value of biodiesel: An empirical and theoretical exploration, 2020). Due to the high oxygen content of biodiesel, it has lower mass energy values than petroleum diesel (Ismail and Ali, 2015). Ismail & Ali also stated that as the length of the chain increases for a constant level of unsaturation, the amount of oxygen decreases resulting in an increase in heating value.

2.9.7. Flash point

The flash point of a fuel is the lowest temperature at which vapours of the fuel will ignite when given an ignition source (Anguebes-Franseschi et al., 2019). The flash point of a fuel is inversely related to its volatility, and the specifications for flash point are meant to guard against contamination by highly volatile impurities (Ismail and Ali, 2015). The flash point values of biodiesel produced from vegetable oils are lower than the flash point of the vegetable oil from which they are synthesized (Ma and Hanna, 1999).

2.9.8. Cloud point

The cloud point (CP) is defined as “the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under controlled conditions during standard tests” (Anguebes-Franseschi et al., 2019). This is an important parameter as the presence of solidified waxes can thicken the fuel and clog the fuel filters and injectors in engines (Ismail and Ali, 2015). Biodiesel has a higher cloud point than petroleum diesel (Singh and Singh, 2010).

2.9.9. Pour point

A report by Singh and Singh (2010) indicated that the Pour Point (PP) is the temperature at which the amount of wax out of solution is sufficient to gel the fuel. Singh and Singh (2010) stated that biodiesel has a higher PP than petroleum diesel.

2.9.10. Sulphur content

According to SAPIA (2018), since the beginning of 2005 the sulphur content of fossil diesel has to be below 50 ppm as high sulphur contents in fuels have been connected with negative health effects and an increased service frequency on vehicles. Biodiesel is essentially seen as sulphur free when made from fresh vegetable oil

2.10. OTHER MEANS OF REDUCTION OF VISCOSITY FOR VEGETABLE OILS

2.10.1. Physical methods

2.10.1.1. Blending:

The purpose of blending is to manipulate a property of the raw material used. In this case, the vegetable oil is the raw material in question. The dilution of vegetable oils can be accomplished with materials such as diesel fuels, solvent or ethanol. Dilution results in the reduction of viscosity and density of vegetable oils. The addition of 4% ethanol to diesel fuel increases the brake thermal efficiency, brake torque and brake power, while decreasing the brake specific fuel consumption. Since the boiling point of ethanol is less than that of diesel fuel, it could assist the development of the combustion process through an unburned blend spray. EPA research shows that biodiesel reduces most emissions from unmodified diesel engines. The amount by which emissions are reduced, depends on the blend level (Biodiesel Blends (Clean City Fact Sheet), 2005). This effect is linear with the blend level so a B5, which is obtained by blending 95% petrodiesel with 5% biodiesel blend reduces life cycle CO_2 emissions by 3.8%. Low-level blends will also cause small reductions in emissions of hydrocarbons, carbon monoxide, particulate matter, and harmful air toxics (Biodiesel Blends (Clean City Fact Sheet), 2005).

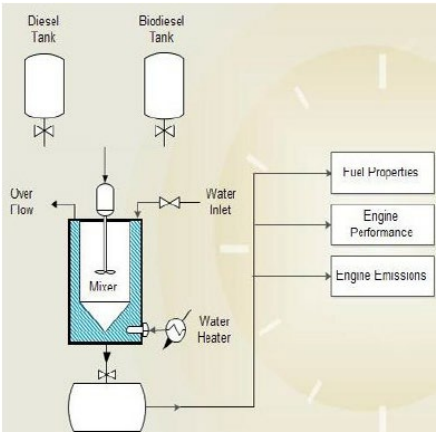


Figure 2. 16: The process of blending (Khalid,.et al 2014).

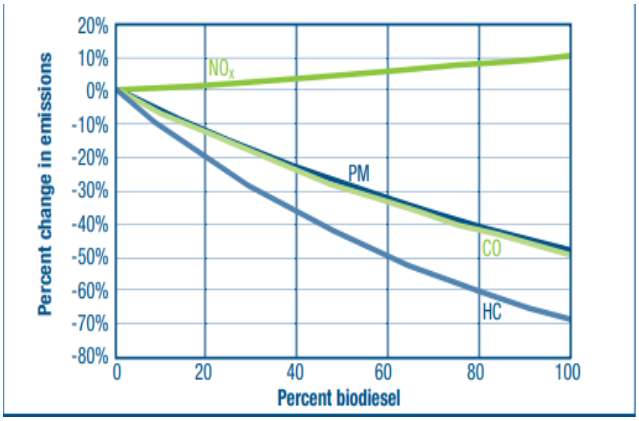


Figure 2. 17: The basic emissions of different blends (Biodiesel Blends (Clean City Fact Sheet), 2005).

2.10.1.2. Microemulsion:

The formation of micro emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersion. The droplet diameters in micro-emulsions range from 100 to 1000 Å. Micro-emulsion can be produced from vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, and alcohol and a surfactant and acetane improver, with or without diesel fuels (Arpornpong, Sabatini, Khaodhiar and Charoensaeng, 2015). All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel. The 2-octanol was an effective amphiphile in the micellar solubilisation of methanol in triolein and soybean oil

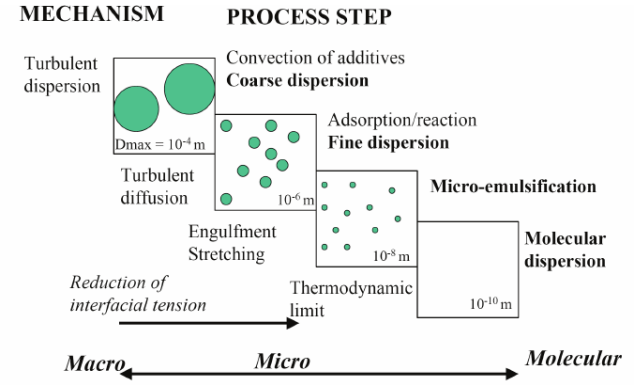


Figure 2. 18: Process mechanism of micro-emulsion (Jankowski.,2011).

3. EQUIPMENT & FEEDSTOCK DESCRIPTION

3.1. MATERIALS AND EQUIPMENT

This section mainly focuses on providing a comprehensive description of the materials used and the equipment set up used. The vegetable oil chosen for this study was canola oil. This oil was a reactant in the transesterification reaction in the presence of Ethanol and Potassium Hydroxide and sodium hydroxide as the catalyst to produce biodiesel. Table 3.1 shows the chemicals and equipment used during this research study.

3.1.1. MATERIALS USED

The following table represents the raw materials used for this study. Potassium hydroxide was used as the titrant when combined with water to form a 0.1 M solution. Ethanol and hydrochloric acid were used with potassium hydroxide to determine the saponification value of the oils

Table 3. 1:List of chemicals used during the production of biodiesel

Chemicals	Suppliers	Purity
Canola oil	Suncat Catering Supplies cc	100%
Sodium hydroxide	Radchem	Analytical Reagent (AR)
Ethanol	Laboquip	99.9%
Potassium Hydroxide	Radchem	Analytical Reagent (AR)
Phenolphthalein	Libro Chemical and Laboratory supplies	1% in 96% ethanol
Propanol	Radchem (Pty) Ltd	Analytical Reagent (AR)
Kerosene	Libro Chemical and Laboratory supplies	
Toluene	Merck	99%
Hydrochloric acid	Sigma-Aldrich	Analytical Reagent (AR)

3.1.2. EQUIPMENT USED AND SETUP USED

The following equipment was used to facilitate the transesterification of canola oil and olive oil. Figure 3.1 is to be used in conjunction with the table below:

Table 3. 2: List of the equipment used for the transesterification reaction

Equipment	Description
Heating mantle and magnetic stirrer	Provides heat for the reaction mixture
Magnetic stirrer bar	Provides intensive stirring to the reaction vessel
Thermometer	Measure temperature of reaction mixture to allow for temperature control
Separation funnel (500 ml -1 L)	Allows biodiesel to easily settle at the top of the funnel for easy removal of the bottom glycerol
Rotary evaporator	To remove excess water and ethanol after hot water washing
Scale	To measure the mass of samples
Glass beaker	The vessel for the reaction to occur in
Parafilm	To cover the reaction vessel
Volumetric cylinder	To measure out the required oil quantity
Volumetric flask	To mix alcohol and catalyst
Burette	For titration to determine acid value
Dropper	Used to add indicator to the sample being titrated
Viscometer	Measure viscosity
Hydrometer	Measure specific gravity
pH meter	Measure pH
Refractometer	Measure refractive index

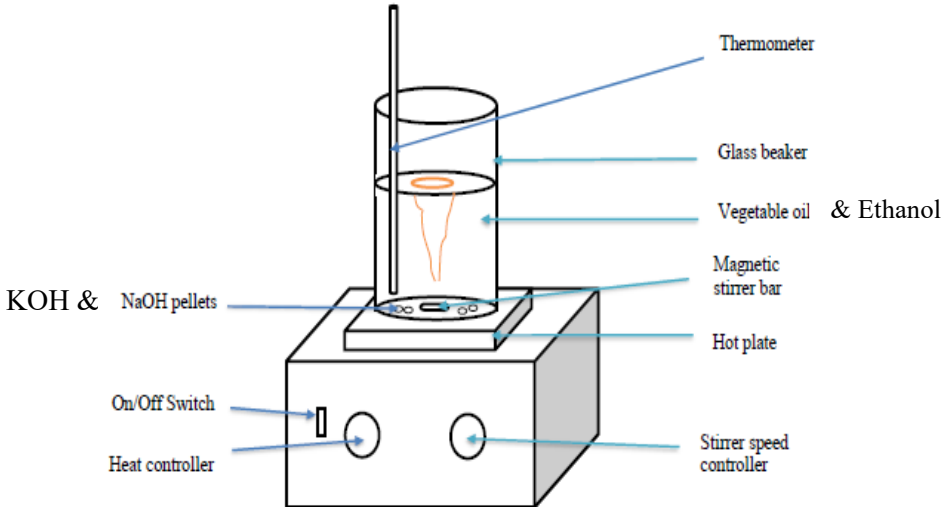


Figure 3. 1: *Experimental setup of the biodiesel production.*

Figure 3.2: (a) Canola oil (KOH) biodiesel and glycerol layer (b) Canola oil (NaOH) biodiesel and glycerol layer

4. EXPERIMENT DESIGN & METHOD

4.1.1. EXPERIMENTAL DESIGN OF EXPERIMENTS

4.1.1.1. OVAT

One Variable at a Time (OVAT) was very popular scientific method dominated until early nineteen century. In this method one variable/factor is tested at a time while the other variables are constrained except the investigated one (Durakovic, 2017). In literature this method of optimisation is regarded as the most basic form of optimisation and functions. This method of optimisation makes investigating the optimal conditions easier as one may be able to see which variable produces the largest impact on the yield of biodiesel. Since other variables are fixed when the effect of the changing variable is plotted against the yield of biodiesel, it will be clear from the plot where the optimal condition that results in the highest yield lies.

4.1.1.2. Factorial design

For a factorial design, the influences of all experimental variables and interaction effects on the response or responses are investigated. If the combinations of k factors are investigated at two levels, a factorial design will consist of 2k experiments Ferreira et al. (2007), Figure 4.1 shows, the factorial designs for 2, 3 and 4 experimental variables can be observed. The levels of the factors are given by – (minus) for a lower level and + (plus) for a higher level. A zero-level is also included (a centre) in which all variables are set at their median value. Three or four centre experiments must always be included in any type of factorial designs, for the following reasons (Durakovic, 2017):

• The risk of missing non-linear relationships in the middle of the intervals is minimized

• Repetition allows for determination of confidence intervals. What - and + should correspond to for each variable is defined from what is assumed to be a reasonable variation to investigate.

Two variables			Three variables				Four variables				
Exp. no.	Variables		Exp. no.	Variables			Exp. no.	Variables			
	x_1	x_2		x_1	x_2	x_3		x_1	x_2	x_3	x_4
1	−	−	1	−	−	−	1	−	−	−	−
2	+	−	2	+	−	−	2	+	−	−	−
3	−	+	3	−	+	−	3	−	+	−	−
4	+	+	4	+	+	−	4	+	+	−	−
			5	−	−	+	5	−	−	+	−
			6	+	−	+	6	+	−	+	−
			7	−	+	+	7	−	+	+	−
			8	+	+	+	8	+	+	+	−
							9	−	−	−	+
							10	+	−	−	+
							11	−	+	−	+
							12	+	+	−	+
							13	−	−	+	+
							14	+	−	+	+
							15	−	+	+	+
							16	+	+	+	+

Figure 4. 1: Factorial design table (Durakovic, 2017)

4.1.1.3. Box-behnken design

The Box-Behnken design is an independent quadratic design, this means that it does not contain an embedded factorial or fractional factorial design. These types of designs are used to generate much higher response surfaces, while using a lower quantity of runs than a normal factorial approach. In this type of design, the treatment combinations are at the midpoints of edges of the process space and at the center. These designs are rotatable (or near rotatable). The designs have limited capability for orthogonal blocking compared to the central composite designs. This and the central composite techniques essentially suppress selected runs to maintain the higher order surface definition. An important advantage of the Box Behnken Design (BBD) is the efficiency for the estimation of the regression coefficients for a regression model. According to a study conducted in Ferreira et al. (2007), the BBD easily estimates regression parameters for a full quadratic model and allows for the building of sequential designs by the use of multiple blocks. Furthermore, this design model is able to determine the lack of fit of the model to the data set (Ferreira et al., 2007).

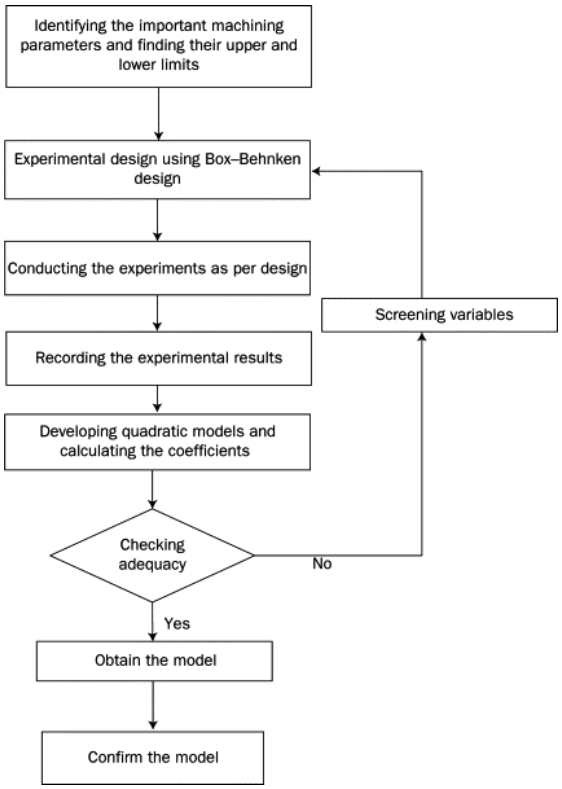


Figure 4. 2: Methodology for box-behnken design (Rao and Kumar, 2012)

4.1.2. EXPERIMENTAL DESIGN

Design of experiment (DOE) is a scientific method of conducting experiments, which ensures that the experimenter draws a valid reading for unknown parameters based of data collected through experiments (Eldin, 2011). The use of the DOE allows for the researcher to be purposeful, organised, and increase the productivity of the work as well as the reliability of the results obtained. The techniques for carrying out experiments when many factors are involved, has been known for a long time and is popularly known as the factorial design of experiments (Eldin, 2011). This afore mentioned method helps the researcher to determine the possible combinations of factors and to identify the best combination for desired results. However, for this study the Box-Behnken Design (BBD) method was used. The BBD is a statistical method; hence it can be used to reduce the number of experiments required to obtain accurate results during the optimisation process. The Box-Behnken approach was employed as it avoids using a combination of the extreme values of all variables simultaneously and hence avoids experiments performed under extreme conditions which are costly and may exhibit unsatisfactory results (Ferreira et al., 2007). The number of experiments (N) required for a Box-Behnken design can be calculated as follows (Ferreira et al., 2007):

$$N=2(k-1)+C_0 \quad (3.1)$$

Where N is the number of experiments, k is the number of factors and C_0 is the number of central points. For this study, 4 factors with 3 central points are used therefore, the number of experiments required would be:

$$N=2\times4(4-1)+3=27 \quad (3.2)$$

The experimental design and optimisation were done on Minitab software (version 17). Four factors were varied: reaction time, reaction temperature, catalyst loading and alcohol to oil molar ratio. This resulted in a total of 27 experimental runs, including 3 replicates which help improve accuracy. The figure below represents the illustration of the BBD.

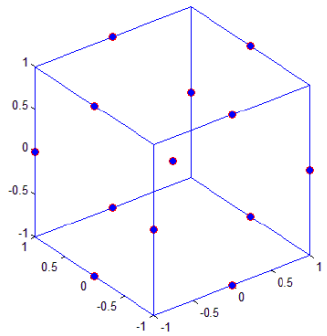


Figure 4. 3: Box-Behnken Design

The conditions used below was guided by preliminary experimental results as well as literature data.

Table 4. 1: Experimental design for the transesterification of canola oil with KOH

Run order	Temperature (ºC)	Catalyst loading (wt.% oil)	Reaction time (mins)	Alcohol/Oil Molar Ratio
1	52	0.020	30	18
2	52	0.085	75	18
3	30	0.085	75	26
4	52	0.085	75	18
5	52	0.020	120	18
6	52	0.085	30	26
7	52	0.150	120	18
8	74	0.085	75	10
9	74	0.085	75	26
10	74	0.085	120	18
11	30	0.085	75	10
12	52	0.150	75	26
13	52	0.085	30	10
14	52	0.020	75	10
15	52	0.150	75	10
16	74	0.020	75	18
17	30	0.150	75	18
18	30	0.085	30	18
19	30	0.085	120	18
20	52	0.085	120	10
21	52	0.085	120	26
22	74	0.085	30	18
23	52	0.085	75	18
24	52	0.020	75	26
25	30	0.020	75	18
26	52	0.150	30	18
27	74	0.150	75	18

Table 4. 2: Experimental design for the transesterification of canola oil with NaOH

Run order	Temperature (°C)	Catalyst loading (wt.% oil)	Reaction Time (mins)	Alcohol/Oil Molar Ratio
1	30	0.15	75	18
2	52	0.085	75	18
3	52	0.15	120	18
4	52	0.02	75	10
5	30	0.085	75	26
6	30	0.085	120	18
7	74	0.085	120	18
8	52	0.085	30	26
9	52	0.15	30	18
10	74	0.02	75	18
11	30	0.085	30	18
12	52	0.15	75	26
13	52	0.085	120	10
14	52	0.02	75	26
15	30	0.02	75	18
16	74	0.15	75	18
17	52	0.085	75	18
18	52	0.15	75	10
19	74	0.085	30	18
20	52	0.085	75	18
21	74	0.085	75	10
22	52	0.085	30	10
23	74	0.085	75	26
24	52	0.085	120	26
25	52	0.02	30	18
26	52	0.02	120	18
27	30	0.085	75	10

4.2. EXPERIMENTAL PROCEDURE

Due to the relatively low acid value recorded for canola oil (Antolin et al., 2002), a 2-step method was not required to be employed. Therefore, canola oil transesterification with base catalyst (Potassium Hydroxide and Sodium Hydroxide) would be used to produce biodiesel. The following steps were conducted for transesterification of Canola oil:

- Initially, 200 ml of oil was weighed, and this mass was converted into moles (the calculations can be seen in appendix a). The oil was then heated while being stirred.
- Using the appropriate molar ratio of alcohol to oil, the mass of ethanol required was obtained.
- The amount of catalyst required (as a weight percentage of oil used) was weighed and dissolved into the ethanol.
- Once the oil reached the desired temperature, the alcohol and catalyst mixture was added to the oil.
- After the appropriate reaction time had elapsed, the mixture was poured into a separation funnel, which allowed the separation of the glycerol layer and biodiesel layer.
- Two distinct layers were observed in the funnel, the top layer being biodiesel and the bottom layer being glycerol.
- After the removal of the bottom glycerol layer from the funnel, hot water was added to remove any additional impurities from the biodiesel as biodiesel is insoluble in water.
- The biodiesel was then further purified in a rotary evaporator at 150 mbar and 70 ℃.
- The sample was set and allowed to cool after being purified by the rotary evaporator, thereafter the sample was weighed to calculate the yield.
- The mass of the biodiesel sample was then recorded and used to determine the yield of biodiesel.
- According to Fereidooni, *et al*., (2017) the equation to calculate the yield of biodiesel is as follow:

$$Yield(\%) = \frac{mass\ of\ biodiesel\ produced}{mass\ of\ oil\ used} \times 100$$

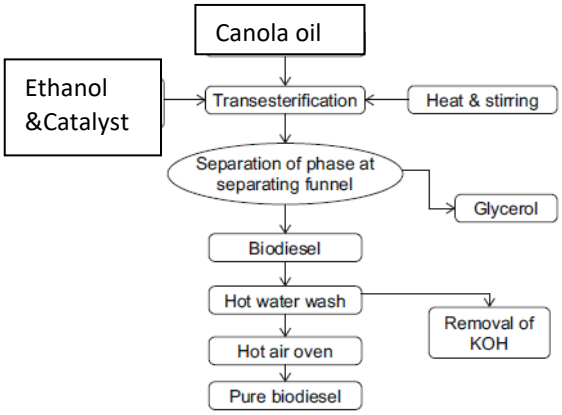


Figure 4. 4: Production method flowchart

5. CANOLA OIL TRANSESTERIFICATION (WITH POTASSIUM HYDROXIDE): RESULTS & DISCUSSION

This study aims to use potassium hydroxide (KOH) as a basic catalyst for the transesterification of canola oil with ethanol. After an extensive literature review it was noted that the Box-Behnken design method would be ideal for designing the experiment. This design was done using the Minitab (V.17) software and the information gathered from the software was used to identify the ideal conditions to produce biodiesel from canola oil. Four factors were used to determine the optimum conditions: temperature, catalyst loading, reaction time and alcohol/oil molar ratio. The boiling point of ethanol is 78.37 ^{o}C and according to Mathiyazhagan and Ganapathi (2011), it is recommended that the reaction temperature should not exceed the boiling point of ethanol as this would result in the ethanol to be vaporised and therefore decreased contact between the oil and alcohol. Canola oil is also relatively cheaper than other vegetable oils, it is easily obtained and its low acid value of 0.129 $mg\ KOH/g$ oil which indicated that it could be transesterified using a base catalyst to produce biodiesel in a single step reaction resulting in lower production costs as compared to other oils. Due to the low acid value the catalyst loading varied between 0.02 wt% of oil to 0.15 wt% of oil. According to the chemical reaction formula for transesterification, a stoichiometric ratio of 3:1 is required for production. However, with research it can be noted that an excess of alcohol shifts the equilibrium to the right and favours the forward reaction. Therefore, the alcohol to oil ratio varied from 10:1 to 26:1. Reaction time was varied from 30 minutes to 2 hours. Many research papers suggested that the optimum time is 90 minutes, however it was decided that the range should be longer to ensure more accurate results. The separation time utilised in this study was approximately 4 hours. The reason for the longer separation time was due to the fact that high alcohol molar ratio was used, as for higher molar ratio of 15:1 and a higher separation of glycerol in the reaction becomes more difficult as the solubility increases due to the higher alcohol concentration.

Property testing for canola oil indicated that its properties were highly desirable, therefore it would be one of the most ideal feedstocks for biodiesel production. A study conducted by Antolin et al. (2002) indicates that the main issue with the direct use of vegetable oils in diesel engines is their high viscosity. However, canola oil has a low dynamic viscosity (which is tabulated in Table 5.1), made it an ideal feedstock for biodiesel production.

Table 5. 1: Properties of Canola oil

Property	Value
Density (kg/m3)	917
Refractive index	1.466
Viscosity (cP)	54.5
Acid value (mg KOH/g)	0.129
FFA %	0.0645

Table 5. 2: Composition of canola oil (Pal, 2011)

Fatty Acid	Molecular weight (g/mol)	%molar	%mass
Miristic	228.38	0.0575	0.0469
Palmitic	256.43	7.3757	6.7565
Palmitoleic	254.41	0.1910	0.1736
Stearic	284.48	2.0964	2.1305
Oleic	282.47	48.0179	48.4533
Linoleic	280.45	31.9683	32.0275
Linolenic	278.44	9.2860	9.2365
Arachidic	312.54	0.4809	0.5369
Behenic	340.59	0.2960	0.3602
Erucic	338.58	0.2303	0.2785

The use of the Box-Behnken design model, used a maximum of 27 runs to complete the study on canola oil. For accuracy and repeatability, the runs were done twice to ensure the results were reliable. When the experimental phase was completed, the Minitab software was used to fit a regression equation to the experimental data. For simplicity, each factor used for the experimental procedure was allocated a symbol as follows:

A = Temperature (°C)

B = Catalyst loading (%)

C = Reaction time (min)

D = Alcohol/oil molar ratio

Run number	A	B	C	D	Experimental	Predicted
1	52	0.02	30	18	0.8711	0.8607
2	52	0.085	75	18	0.9023	0.9094
3	30	0.085	75	26	0.8999	0.9179
4	52	0.085	75	18	0.9047	0.9094
5	52	0.02	120	18	0.9221	0.9152
6	52	0.085	30	26	0.905	0.9298
7	52	0.15	120	18	0.7758	0.7830
8	74	0.085	75	10	0.7719	0.7502
9	74	0.085	75	26	0.9478	0.9278
10	74	0.085	120	18	0.8561	0.8646
11	30	0.085	75	10	0.8247	0.8410
12	52	0.15	75	26	0.8667	0.8471
13	52	0.085	30	10	0.7612	0.7832
14	52	0.02	75	10	0.7785	0.7816
15	52	0.15	75	10	0.7556	0.7403
16	74	0.02	75	18	0.8945	0.9177
17	30	0.15	75	18	0.8999	0.8965
18	30	0.085	30	18	0.9457	0.9211
19	30	0.085	120	18	0.9001	0.9030
20	52	0.085	120	10	0.7912	0.7865
21	52	0.085	120	26	0.8959	0.8943
22	74	0.085	30	18	0.8981	0.8787
23	52	0.085	75	18	0.9212	0.9094
24	52	0.02	75	26	0.9302	0.9291
25	30	0.02	75	18	0.8875	0.8798
26	52	0.15	30	18	0.8659	0.8696
27	74	0.15	75	18	0.7501	0.7777

Table 5. 3: Results obtained for transesterification of canola oil with KOH

Table 5. 4: Model summary for the results obtained

Terms	S	R^2	R^2 (adj)	R^2 (pred)
Linear	0.0412	0.6369	0.5709	0.4586
Linear + square	0.0338	0.8005	0.7119	0.5512
Linear + interactions	0.0378	0.7774	0.6383	0.3964
Full quadratic	0.0225	0.9410	0.8722	0.6675

Table 5.3 shows the maximum yield of 0.9478, which was obtained at run nine that had a temperature of 74, catalyst load of 0.085%, reaction time of 75 minutes and an alcohol to oil molar ratio of 26:1. On the other hand, the lowest yield was 0.7501, and can be seen at run 27, which had a temperature of 74, catalyst load of 0.15%, reaction time of 75 minutes and finally an alcohol to oil molar ratio of 10:1. The main factors for the lower yield could be the lower alcohol ratio as well as the high temperature which could have evaporated the alcohol upon contact with the oil, as well as the high amounts of catalyst which could have caused the formation of soap during the reaction process. Table 5.4 shows the different methods that could have been used to predict the yield. Qiu et al. (2013) defines the correlation coefficient of determination (R^2) value as "the ratio of the explained variation to the total variation and is a measure of the degree to which the regression equation fits the data". Joglekar and May (1987) stated that an R^2 value of at the minimum of 0.8 represents of a good fit to a model. The results displayed on table 5.4 indicates that the linear + square model along with the full quadratic model had an R^2 value of at least 0.8, however the values for the full quadratic model was significantly higher. Hence that implies that a full quadratic model provides the best fit to the data obtained and can therefore be used to effectively predict the yield of biodiesel within the range of this study. The results from table 5.4 indicates that the full quadratic response model attainted in this study represents the transesterification of canola oil in the presence of potassium hydroxide very well, with an R^2 value of 0.9410 and an adjusted R^2 value of 0.8722 at a 95% confidence level. The good fit of the full quadratic model to the data obtained from the study can be seen in Figure 5.4 . However, with respects to the predicted R^2 value of 0.6675, this represents that the quadratic model may only be roughly 66.75% accurate when used to predict the yield of biodiesel produced outside the range of the study. This value is considerably lower than the R^2 and adjusted R^2 value, this lower value could be a sign that the quadratic model obtained during analysis is tailored particularly to the results and data obtained in this specific study, therefore the model can only be used to correctly predict the yield of biodiesel within the range of this study. The standard deviation is represented by the S-value in table 5.4, this value represents the standard deviation of the distance between the data values and the fitted values. The extremely low

standard deviation of 0.0225 represents a low deviation of data points from the predicted responses. This therefore indicates that the regression equation (5.3) obtained for this study, fits the data obtained extremely well. The model is also very significant, as indicated by a very low probability (p) value of 0 (seen in table 5.5). For a 95% confidence level, a p-value less than 0.05 indicates statistical significance, while a value higher than 0.1 indicates statistical insignificance (Zhang and Zheng, 2009).

From the four methods used to predict the data, the best prediction was shown using the quadratic equation. The full quadratic equation was used to determine the predicted yield and the coefficients was found using Minitab. The following equation was adapted from Halder, et al, (2015):

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i X_i + \sum_{i=1}^{k} \beta_{ij} X_i X_j \quad (5.1)$$

The fully expanded version of equation 5.1 can be seen below:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11}(X_1)^2 + \beta_{22}(X_2)^2 + \beta_{33}(X_3)^2 + \beta_{44}(X_4)^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (5.2)$$

The regression equation obtained via multiple regression analysis is shown below using the symbols for each factor of the experiment, where A, B, C and D represent Temperature, Catalyst loading, Reaction time and Ethanol/Oil molar ratio, respectively.

$$Y = 0.381 - 0.00051A + 3.740B + 0.00233C + 0.03051D - 0.000007A^2 - 9.02B^2 - 0.000007C^2 - 0.000731D^2 - 0.02741AB + 0.000001AC + 0.000143AD - 0.01206BC - 0.0195BD - 0.000027CD \quad (5.3)$$

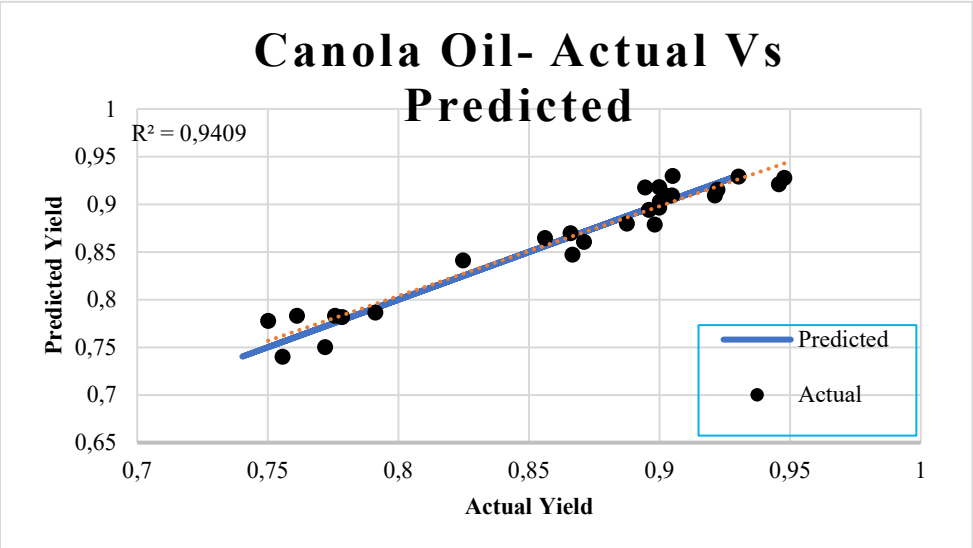


Figure 5. 1: Experimental vs Predicted data for Biodiesel with KOH

Table 5. 5: ANOVA analysis of results and model

ANOVA analysis for canola oil with KOH					
Source	**Degree of freedom**	**Sum of squares**	**Mean squares**	**p-value**	**Characteristics**
Model	14	0.0968	0.0069	0	Significant
Linear	4	0.0196	0.0049	0.001	Significant
A	1	0.0063	0.0063	0.004	Significant
B	1	0.0079	0.0079	0.002	Significant
C	1	0.0051	0.0051	0.008	Significant
D	1	0.0003	0.0003	0.478	Not Significant
Square	4	0.0168	0.0004	0.002	Significant
A^2	1	0.0001	0.0005	0.740	Not Significant
B^2	1	0.0077	0.0077	0.002	Significant
C^2	1	0.0011	0.0011	0.167	Not Significant
D^2	1	0.0117	0.0117	0	Significant
2-way interaction	6	0.0145	0.0024	0.010	Significant
AB	1	0.0061	0.0061	0.004	Significant
AC	1	0.00001	0.00001	0.938	Not Significant
AD	1	0.0025	0.0025	0.045	Significant
BC	1	0.0050	0.0050	0.009	Significant
BD	1	0.0004	0.0004	0.384	Not Significant
CD	1	0.0004	0.0004	0.402	Not Significant
Error	12	0.0061	0.0005		
Lack of fit	10	0.0059	0.0006	0.163	Not Significant
Pure error	2	0.0002	0.0001		
Total	26	0.1029			

Table 5.5 shows the ANOVA analysis conducted on the quadratic model. The purpose of an ANOVA analysis is to determine if there are any statistically significant differences between three or more unrelated groups of data. The test produced a p-value to determine whether the relationship between the factors used in the experiment are significant or not.

Table 5.5 shows that three out of four coefficients for the linear terms are significant, the only term that is not significant is that of alcohol to oil molar ratio, this entails that the molar ratio for transesterification in this study does not have a very significant impact on the results which had been predicted by the quadratic model. The coefficients for the linear terms of the other variables such as temperature, catalyst loading and alcohol molar ratio, are all very significant indications that these variables play an important role on the impact of the yield of biodiesel obtained from canola oil when using a potassium hydroxide as the catalyst,

as predicted by the proposed full quadratic model equation. Table 5.5 also denotes the coefficient for the quadratic terms, the results for temperature as well as the reaction time are not significant, however the remaining two quadratic coefficients for catalyst loading (p- value = 0.002) and the alcohol to oil molar ratio (p-value = 0) are very significant indicating that the quadratic coefficient of temperature and reaction time does not have great impact on the predicted yield which has been expressed by the model as significantly as the quadratic coefficients of the other variables. It can be seen that the interaction between temperature (A) and reaction time (C) has a p-value of 0.938, catalyst loading (B) and molar ratio (D) with a p- value of 0.385 and reaction time (C) and molar ratio (D) with a p-value of 0.402. These coefficients indicate that the interactions between these variables are not significant while the interactions between all the other variables are highly significant when using the full quadratic model. The lack of fit for the model expressed a p-value of 0.163, this denotes that the lack of fit is not significant, this further supporting the observation that the quadratic model is a good fit for the data. Due to the inclusion of the few insignificant terms in the statistical analysis of the quadratic model, this may have been a cause for the relatively lower predicted R^2 value of 0.6675. If the insignificant terms were to be removed from the analysis the value could have been improved. The current predicted value was lower than the recommended value of 0.8 (Joglekar and May, 1987), and for the purpose of this study it was deemed more important to understand the effects of the process variables within the range of the study and for this purpose the unmodified model was still a good fit to the data. Furthermore, modification of the model does not mean that it could be used to determine the yield of biodiesel produced outside the range of the study, further experiments would need to be conducted in order to verify this justification.

The optimum conditions to maximise the yield of canola oil biodiesel was obtained with the help of the Minitab software and produced via the transesterification process. The results obtained for the optimised reaction conditions can be seen in table 5-6 below:

Table 5. 6: Optimum conditions obtained from Minitab

Temperature	**Catalyst loading (%)**	**Time (mins)**	**Molar ratio**	**Experimental yield**	**Predicted yield**
74.0	0.020	102.73	26.0	0.9662	0.9901

The Minitab software was used to identify the conditions for the optimal conditions to produce the highest yield, the yield was determined to be 0.9901. However, when using the same conditions to produce biodiesel

in the lab, the yield was determined to be 0.9662. This shows an approximate error of 2.41 %, which is relatively small therefore gives a further justification that the quadratic model is a good fit for this study.

The effects of the four reaction parameter used in this study to determine the optimum yield of biodiesel obtained from canola oil are represented using surface response plots and contour plots illustrated in Figures 5.3 to 5.8. Each plot shows the effect of two variables across their range within the study, with the other two variables kept constant at their median value. The response surface visually represents the tendency of each factor to influence the yield. The shape of the contour plots are an indication of the extent and nature of the interactions between the factors. According to studies conducted by Qiu, et al., (2013) a noticeable interaction is indicated by an elliptical contour plot, whereas a more circular contour plot represents a negligible interaction.

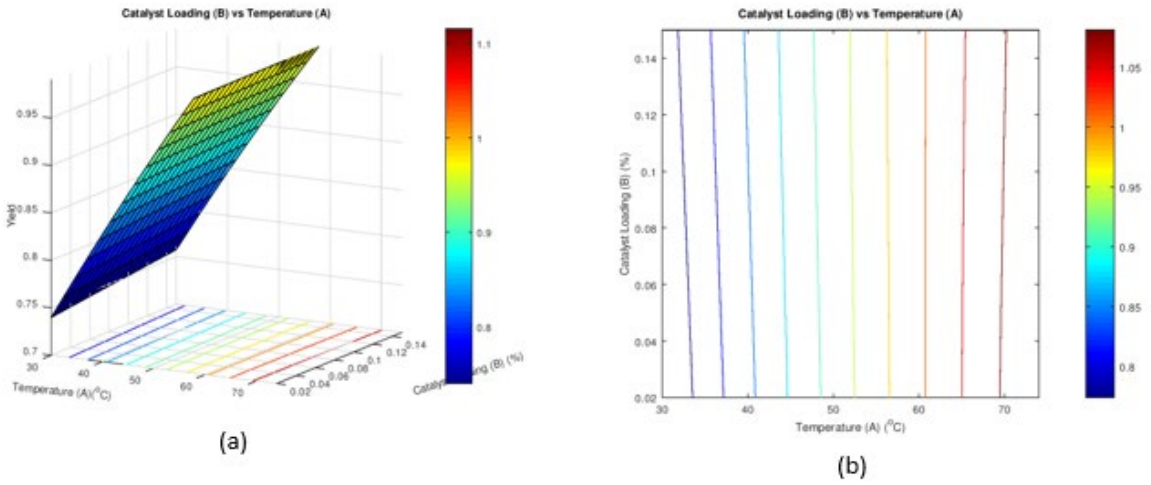


Figure 5. 2: (a) Surface response plot of catalyst loading and temperature on yield of biodiesel from KOH (b) Effect of catalyst loading and temperature on yield of biodiesel from KOH contour plot

Figure 5.3(a) represents a three-dimensional response surface interaction between the catalyst loading (B) and the reaction temperature (A). According to the figure, it can be noted that the yield of biodiesel increases with an increase in temperature and is relatively constant with regards to catalyst loading. This shows a directly proportional effect of temperature on the yield of biodiesel produced. This behavior of the system could be because transesterification is endothermic in nature (Antolin et al., 2002), which means that the endothermic reactions absorb energy and relatively high temperatures favour these types of reactions. A large quantity of base catalysts may result in the formation of soap and this may cause a reduction in the yield of biodiesel (Rahimi et al., 2014), however in this case that may not be a factor as the yields seems

more or less constant with regards to the catalyst loading increases. It can be noted that high biodiesel yields can be obtained when using low catalyst loading combined with high reaction temperatures. With regards to table 5.5, a p-value of 0.004 was obtained which suggests that these parameters are statistically significant. Figure 5.3(b) indicates a quite contradictory result; it shows straight contour that means the interaction between temperature and catalyst loading does not have a significant impact on the yield of biodiesel.

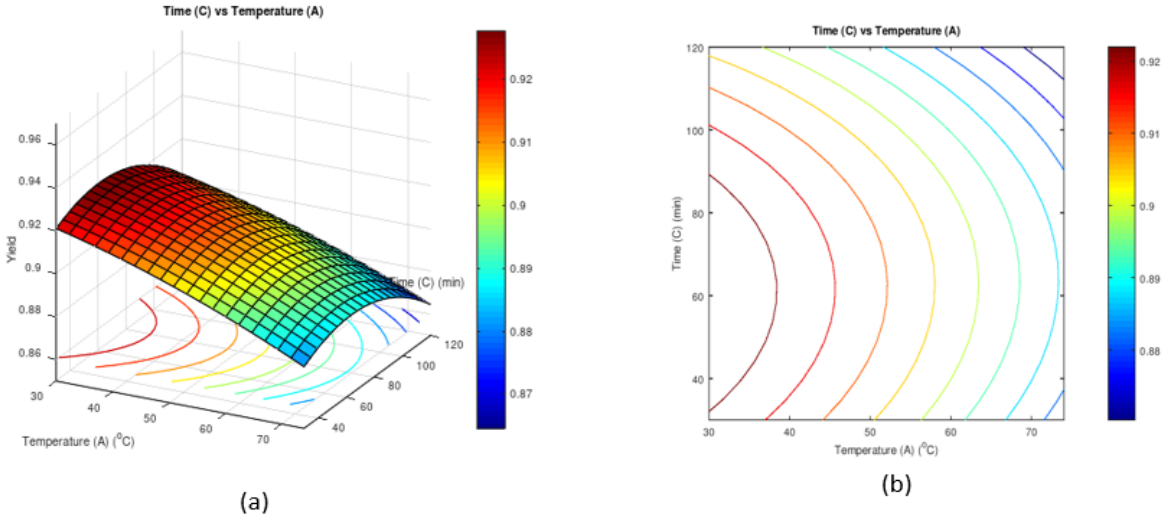


Figure 5. 3: (a) Surface response plot of reaction time and temperature on yield of biodiesel from KOH (b) Effect of Reaction time and temperature on yield of biodiesel from KOH contour plot

Figure 5.4(a) indicates a three-dimensional surface response that illustrates the effects of temperature (A) and reaction time (C) on the yield. This figure shows that as the temperature of the system increases the yield produced gradually decreases, however, it is clear from this surface response plot that the reaction time has a more significant effect on the yield. The yield can be seen to increase with time up to a point, after which a further increase in temperature results in a decrease in yield possibly due to the reverse reaction resulting in a loss of esters and formation of soap. Table 5.5 shows the interaction between these two values has a p-value of 0.938, which indicates that this interaction is statistically insignificant. Figure 5.4(b) displays a circular shape, indicating that the interaction between temperature and time is not significant, which further supports the results obtained from the statistical analysis obtained in table 5.5.

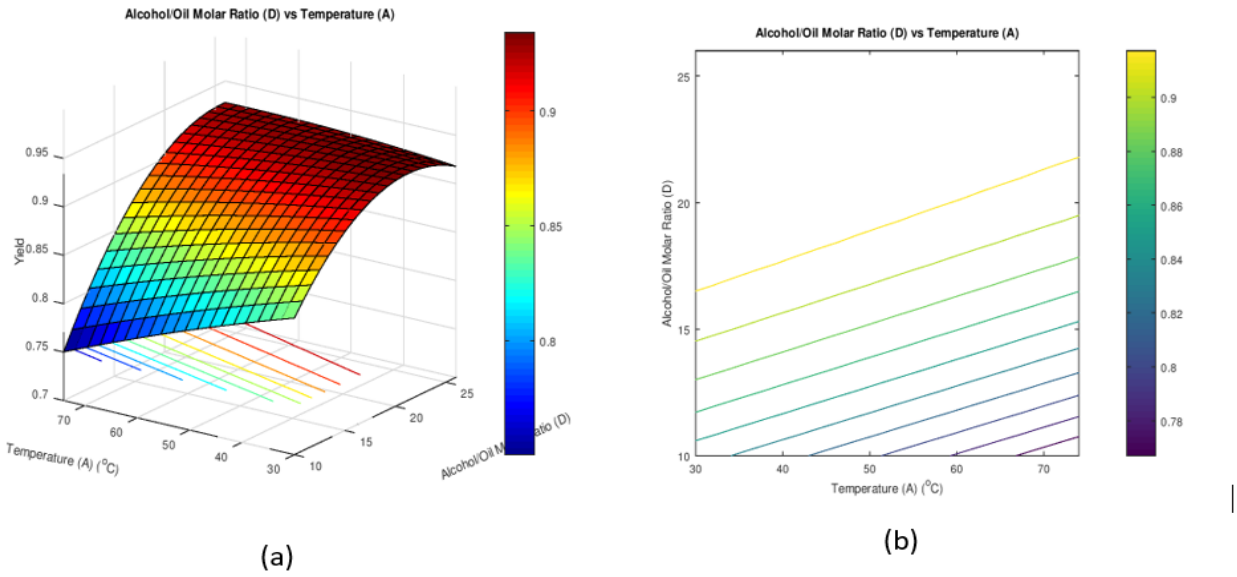


Figure 5. 4: (a) Surface response plot of alcohol/oil molar ratio and temperature on yield of biodiesel from KOH (b) Effect of alcohol/oil molar ratio and temperature on yield of biodiesel from KOH contour plot

Figure 5.5(a) shows the surface response plot for the effect of alcohol/oil molar ratio (A) and temperature (A) on the yield of biodiesel produced. This figure notes that the ethanol/oil molar ratio has a parabolic effect on the yield of biodiesel. Initially, an increase in the ratio results in an increase in yield, however after a point an increase in the ratio results in a decrease in the yield of biodiesel produced. Many studies suggest that an excess amount of alcohol is required to favour the forward reaction. According to Le Chatelier's principle, an increase in the amount of ethanol beyond an optimal point interferes with the separation of the glycerol layer from the biodiesel layer resulting from an increase in solubility, which means longer separation time is required due to the difficulty of separation of ethanol and glycerol (Kafuku and Mbarawa, 2010); the glycerol layer that interacts with the biodiesel solution layer shifts the equilibrium back to the left, which favours the reverse reaction and reduces the amount of biodiesel produced. Figure 5.5 (a) illustrates that lowest yields can be observed when using a high temperature combined with a low alcohol/oil molar ratio, this is due to the low alcohol to oil ratios being insufficient to drive the forward reaction. Table 5.5 recorded a p-value of 0.045, which translate to the results being statistically significant. Figure 5.5(b) indicates that the interaction between the alcohol/oil molar ratio and temperature has a significant effect on the yield of biodiesel.

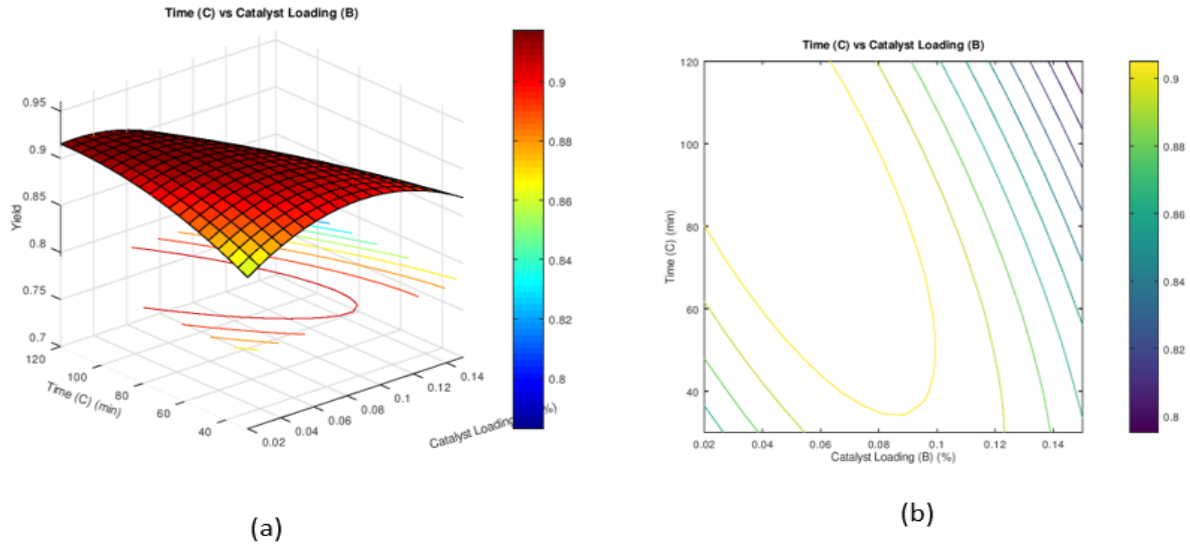


Figure 5. 5: (a) Surface response plot of reaction time and catalyst loading on yield of biodiesel from KOH (b) Effect of reaction time and catalyst loading on yield of biodiesel from KOH contour plot

Figure 5.6(a) represents the surface response of the effect of catalyst loading (B) and reaction time (C) on the yield of biodiesel. The results obtained from the response plot shows that the yield of biodiesel obtained from canola oil, using KOH as the catalyst, increases with both time and catalyst loading up to a certain peak, thereafter it begins to gradually decrease. This may be due to the fact that while enough time is required for the reaction to continue to completion, as time passes and more products are formed, the equilibrium shift to favour the reverse reaction which therefore causes a reduction in the yield of biodiesel produced. Similarly, a small amount of catalyst is required to drive the reaction to favour the forward reaction, but the use of high amounts of base catalysts result in the formation of soap which reduces the biodiesel yield. Results shown in table 5.5 show that the interaction between these parameters has a p-value of 0.009, which indicates that it is statistically significant. Figure 5.6(b) shows that the interaction between the catalyst loading and time has a significant impact on the yield of biodiesel obtained from canola oil with KOH.

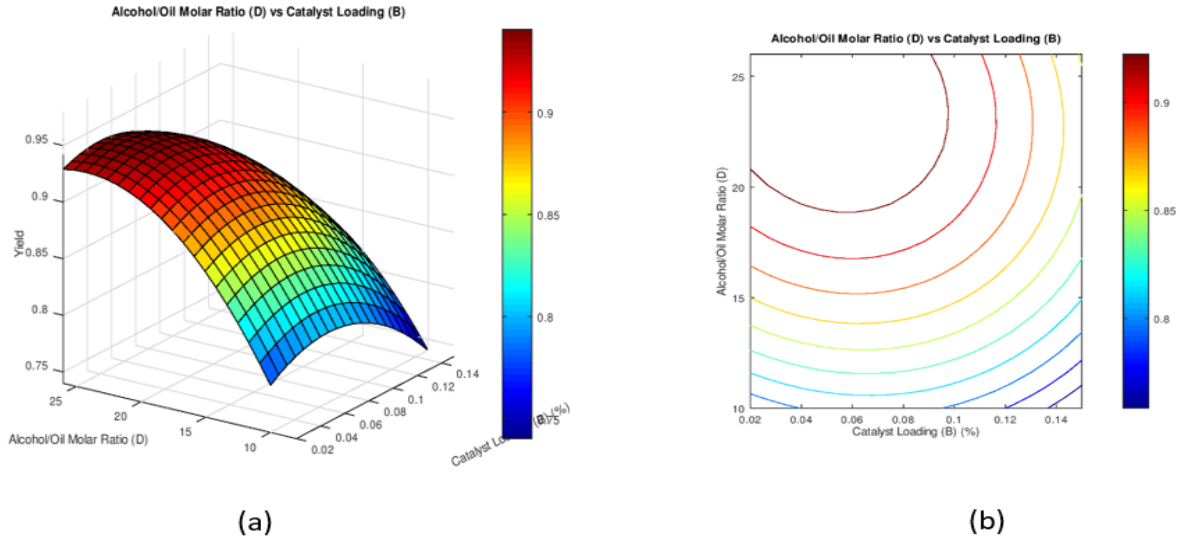
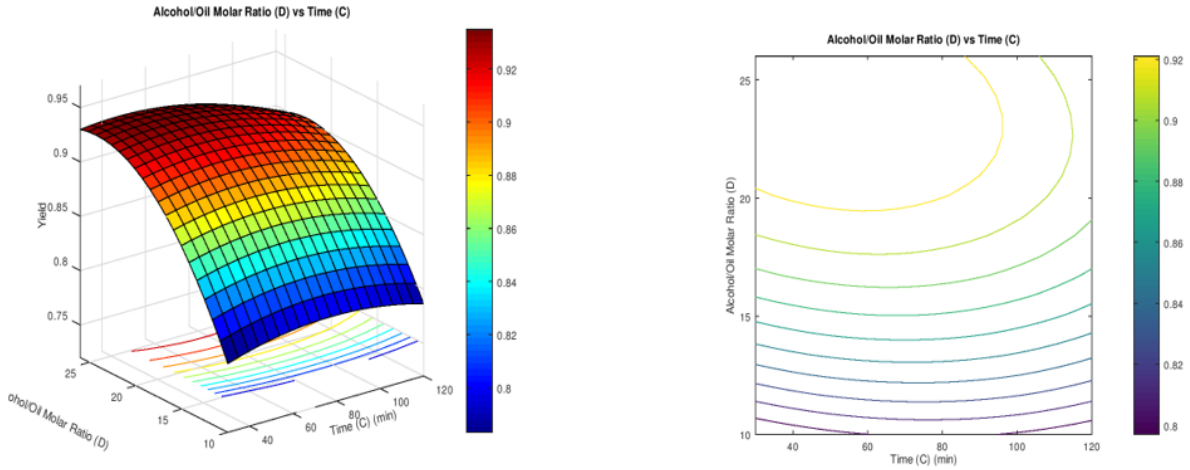


Figure 5. 6: Surface response plot of alcohol/oil molar ratio and catalyst loading on yield of biodiesel from KOH (b) Effect of alcohol/oil molar ratio and catalyst loading on yield of biodiesel from KOH contour plot

Figure 5.7(a) shows the effect of the interactions between the ethanol/oil molar ratio (D) on catalyst loading (B) on the yield of biodiesel produced. From figure 5.7 (a) it can be noted that the biodiesel yield increases with both the ethanol to oil ratio and catalyst loading up to an optimum point, thereafter the yield starts to gradually decrease with a further increase in the ethanol ratio and catalyst loading. An excess of ethanol and small quantities of catalyst is required to drive the forward reaction. Increasing both these parameters above the optimal points may cause the formation of soap and favours the reverse reaction, which will in turn reduce the yield of biodiesel. A study conducted by Fereidooni et al, (2017) stated that the addition of high amounts of base catalyst results in a biodiesel product with a high viscosity which complicates the separation of the biodiesel layer from glycerol layer, and high viscosity biodiesel is undesirable for use in diesel engines, hence it should be avoided. From table 5.5, we see that the p-value obtained for this interaction of parameters is 0.384, which means that this interaction is statistically insignificant. Figure 5.7 (b) shows a circular contour, which backs up the results obtained in table 5.5, showing the results for this interactive pair is insignificant.



(a) (b)

Figure 5. 7: Surface response plot of reaction time and alcohol/oil molar ratio on yield of biodiesel from KOH (b) Effect of reaction time and alcohol/oil molar ratio on yield of biodiesel from KOH contour plot

The effect of the interaction between the alcohol/oil molar ratio (D) and reaction time (C) on the yield of biodiesel is shown visually in Figure 5.8(a). From this figure it can be observed that the yield of biodiesel obtained increased as the alcohol to oil ratio and reaction time increased up to an optimum point, thereafter the yield slowly decreases. The lowest yields are obtained at low ratios of alcohol to oil and lower reaction times due to an insufficient amount of ethanol to drive the forward reaction and a too short period of reaction time for the reaction to reach completion. At longer reaction times, more soap formation was observed during the water washing process caused by the hydrolysis of esters which cause the fatty acids to form soap. As seen in table 5.5, the results obtained for the interaction between parameter CD, gave a p-value of 0.402, which is statistically insignificant. Figure 5.8(b) produced almost circular contours which support the findings in table 5.5, that the interaction is insignificant to the study.

The parabolic shape of most of the surface plots denotes that there is an optimum point at which the yield of biodiesel obtained is a maximum and any further increases result in a decrease in the biodiesel yield.

Figures 5.9 to Figure 5.12 illustrates the main effects of each variable on the yield of biodiesel produced. These figures were obtained by varying on variable at a time, while the other variables remained fixed at their median values. The median values are as follows:

Temperature: 52ºC Catalyst loading: 0.085%

Reaction time: 75 minutes Alcohol/oil molar ratio: 18

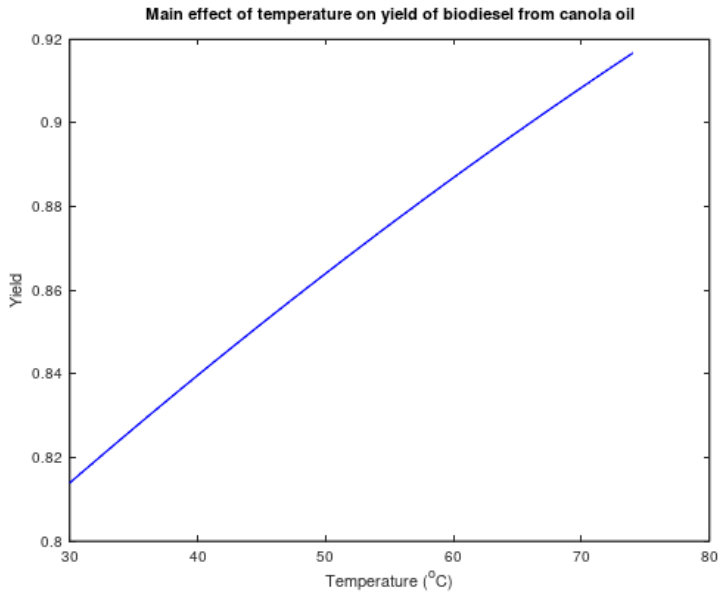


Figure 5. 8: main effect of temperature on biodiesel yield

Figure 5.9 illustrates the main effect of the reaction temperature in percentage of the biodiesel yield produced. The results suggest that as the temperature was increased the yield increased as well, however it is important to note that had the temperature exceeded 78ºC the yield would have drastically dropped due to the evaporation of ethanol. At low temperature, the reaction rate was relatively slow and with increasing temperature, the percentage yield of biodiesel remarkably increased. According to Rahimi et al. (2014), the effect of temperature is mainly due to the transesterification reaction being an endothermic reaction, as the increase in temperature favours an endothermic reaction process. It was found that the maximum percentage of methyl esters for canola oil using KOH was obtained at 74ºC.

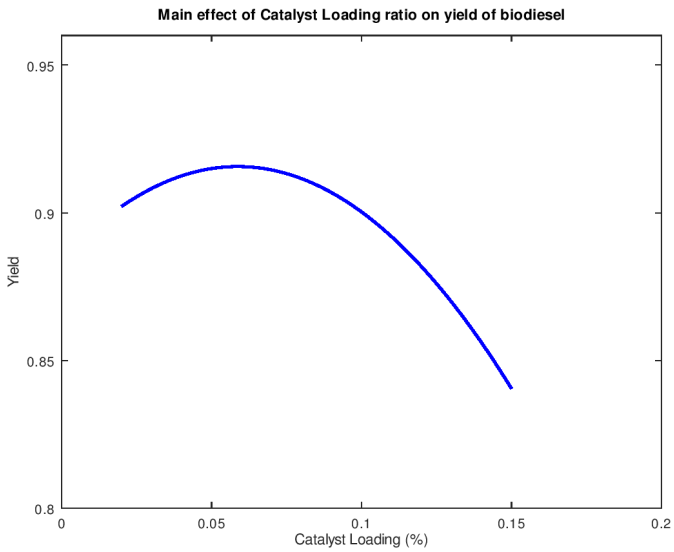


Figure 5. 9: main effect of catalyst loading on biodiesel yield

In general, the catalyst concentration/loading is an important factor to be considered during the transesterification process and the cost of production depends on it and extra catalyst will increase the complexity of product separation (Rahimi et al., 2014). Figure 5.10 illustrates the main effect of the amount of catalyst used on the yield of the biodiesel produced. It can be seen for canola oil that the yield of biodiesel drastically decreased as the catalyst loading percentage increased. This is because high amounts of alkaline catalyst allows for the formation of soap, which thereby reducing the yield of biodiesel obtained.

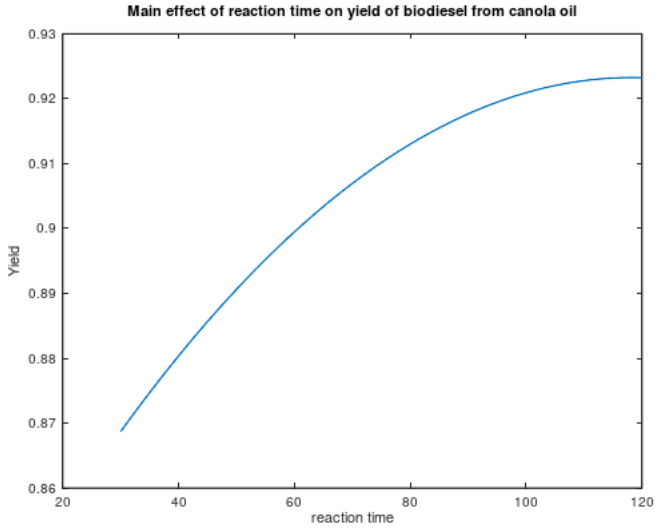


Figure 5. 10: main effect of reaction time of biodiesel yield

Figure 5.11 shows the main effect of the reaction time on the yield of biodiesel that is produced. The results illustrated that the reaction time has a parabolic effect on the yield. After 100 minutes, the yield of biodiesel starts to decrease as time increased. The reason for this may be due to the fact that as time passes more glycerol is formed causing the equilibrium to shift to the left and favouring the reverse reaction, which may cause the yield of biodiesel produced to decrease.

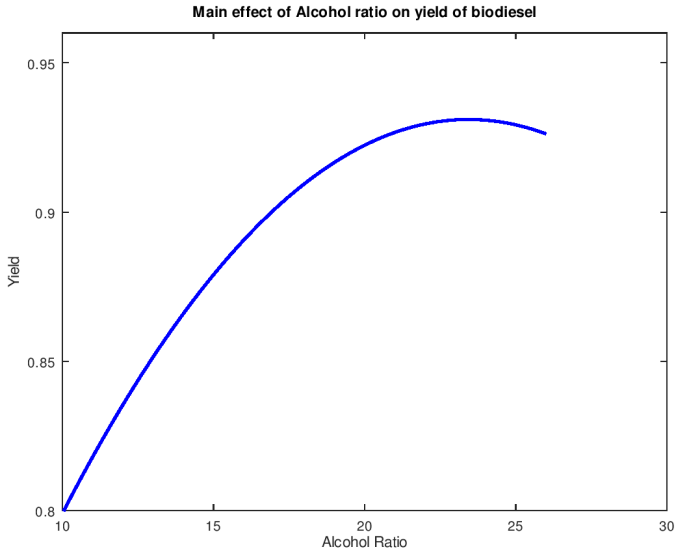


Figure 5. 11: main effect of molar ratio on biodiesel yield

According to Figure 5.12, the yield of biodiesel initially increases drastically as the alcohol to oil molar ratio increases up to a value of approximately 16, thereafter, a further increase in the ratio results in a much lower increase in the yield, and thereafter reaches a point where the yield will drop significantly. This is because high alcohol to oil ratios, such as ratios above 15:1, cause increased solubility of glycerol in biodiesel thereby increasing the separation difficulty causing a reduction in the yield of biodiesel obtained.

Findings recorded by Rahimi et al. (2014) as well as Demirbas (2007) support the results obtained during this study. It should be noted that the main effect plots are mainly to understand the effect of one variable while the others remain fixed, these plots were not used to determine the optimum conditions to produce biodiesel. Truly optimised conditions can only be determined by varying all the variables and considering all their interactions therefore, the Box-Behnken design, and the response optimiser was used on Minitab. The yield was constrained on Minitab to lie between 0 and 1, as yields higher than 1 are not possible, and all process variables were constrained to lie between their minimum and maximum values used in this study because the model may not be able to accurately represent the trends that may be observed outside the range considered in this study.

6. CANOLA OIL TRANSESTERIFICATION (WITH SODIUM HYDROXIDE): RESULTS & DISCUSSION

Table 6. 1: Biodiesel from NaOH results

Run number	A	B	C	D	Experimental	Predicted
1	30	0.15	75	18	0.9557	0.9105
2	52	0.085	75	18	0.9478	0.9358
3	52	0.15	120	18	0.7212	0.7627
4	52	0.02	75	10	0.7595	0.7379
5	30	0.085	75	26	0.8927	0.9049
6	30	0.085	120	18	0.8934	0.8782
7	74	0.085	120	18	0.8995	0.8802
8	52	0.085	30	26	0.9102	0.9169
9	52	0.15	30	18	0.8576	0.8615
10	74	0.02	75	18	0.9578	0.9776
11	30	0.085	30	18	0.9311	0.9326
12	52	0.15	75	26	0.7912	0.7976
13	52	0.085	120	10	0.7715	0.7384
14	52	0.02	75	26	0.9501	0.9602
15	30	0.02	75	18	0.8899	0.8684
16	74	0.15	75	18	0.7514	0.7474
17	52	0.085	75	18	0.9192	0.9358
18	52	0.15	75	10	0.7375	0.7122
19	74	0.085	30	18	0.8767	0.8759
20	52	0.085	75	18	0.9515	0.9358
21	74	0.085	75	10	0.7177	0.7241
22	52	0.085	30	10	0.7415	0.7436
23	74	0.085	75	26	0.9499	0.9184
24	52	0.085	120	26	0.9012	0.8728
25	52	0.02	30	18	0.9055	0.8814
26	52	0.02	120	18	0.9175	0.9310
27	30	0.085	75	10	0.7417	0.7915

By using the Box-Behnken design model, it was noted that a maximum of 27 runs was to be done to complete the study on canola oil using NaOH as a catalyst. For accuracy and repeatability, the runs were done three times to ensure the results were reliable. The reasons for choosing the experimental conditions are the same as those discussed in chapter 5. When the experimental phase had been completed, the Minitab

software was used to fit a regression equation to the experimental data. For simplicity, each factor used for the experimental procedure was given a symbol as follows:

A = Temperature (°C) B = Catalyst Loading (%)

C = Reaction time D = Alcohol molar ratio

Table 6. 2: Model summary for the NaOH results

Terms	S	R^2	R^2 (adj)	R^2 (pred)
Linear	0.0639	0.5295	0.4440	0.3082
Linear + square	0.0498	0.7662	0.6623	0.4740
Linear + interactions	0.0603	0.6952	0.5047	0.2074
Full quadratic	0.0329	0.9319	0.8524	0.6191

Table 6.1 shows that maximum yield of biodiesel produced was 0.9578. which was obtained at run ten that had a temperature of 74 °C, catalyst load of 0.02%, reaction time of 75 minutes and an alcohol to oil molar ratio of 18:1. The high temperature in this case favoured the forward reaction, while the alcohol ratio and catalyst loading was sufficient to drive the reaction to its forward reaction, while simultaneously decreasing the formation of soap. On the other hand, the lowest yield was 0.7177. The lowest yield can be seen at run 21, which had a temperature of 74 °C, catalyst load of 0.085%, reaction time of 75 minutes and finally an alcohol to oil molar ratio of 10:1. The main factors causing a lower yield could be the lower alcohol ratio, which does not drive the reaction towards the forward reaction as well as the high temperature which could have evaporated the alcohol upon contact with the oil, and finally the high amount of catalyst which could have caused the formation of soap during the reaction process. Table 6.2 shows the different methods that could have been used to predict the yield. The results displayed in table 6.2 indicates that the full quadratic model had an R^2 value greater than 0.8. Hence, that implies that a full quadratic model provides the best fit to the data obtained and can therefore be used to effectively predict the yield of biodiesel within the range of this study. The results from table 6.2 that the full quadratic response model attained in this study represents the transesterification of canola oil in the presence of sodium hydroxide very well, with an R^2 value of 0.9319 and an adjusted R^2 value of 0.8524 at a 95% confidence level. The good fit of the full quadratic model to the data obtained from the study can visually be seen in Figure 6.1. However, with regards to the predicted R^2 value of 0.6191, this represents that the quadratic model may only be roughly 61.91% accurate when used to predict the yield of biodiesel produced outside the range of the study. The

standard deviation is represented by the S-value in table 6.2, this value represents the standard deviation of the distance between the data values and the fitted values. The extremely low standard deviation of 0.0329 represents a low deviation of data points from the predicted responses. This therefore indicates that the regression equation (6.3) obtained for this study fits the data obtained extremely well.

From the four methods used to predict the data, the best prediction was shown using the quadratic equation. The full quadratic equation was used to determine the predicted yield and, the coefficients was found using Minitab. The following equation was adapted from Halder, et al. (2015):

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i X_i + \sum_{i=1}^{k} \beta_{ij} X_i X_j \quad (6.1)$$

The fully expanded version of equation 5.1 can be seen below:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11}(X_1)^2 + \beta_{22}(X_2)^2 + \beta_{33}(X_3)^2 + \beta_{44}(X_4)^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (6.2)$$

The regression equation obtained via multiple regression analysis is shown below using the symbols for each factor of the experiment, where A, B, C and D represent Temperature, Catalyst loading, Reaction time and Ethanol/Oil molar ratio, respectively.

$$Y = -0.068 + 0.00315A + 5.75B + 0.00276C + 0.0605D - 0.000028A^2 - 10.96B^2 - 0.000015C^2 - 0.001368D^2 - 0.0476AB + 0.000015AC + 0.000115AD - 0.01268BC - 0.0658BD - 0.000027CD \quad (6.3)$$

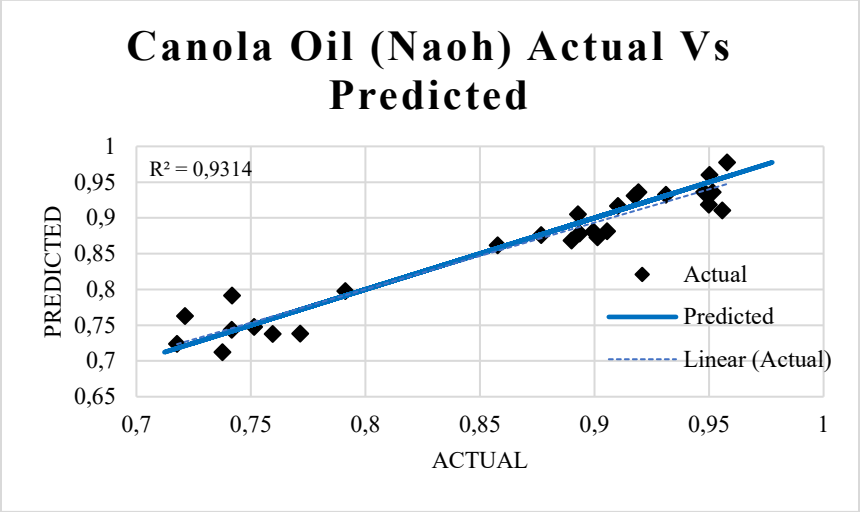


Figure 6. 1: Actual vs predicted results for NaOH biodiesel

Table 6. 3: ANOVA analysis of results and model

ANOVA analysis for canola oil with NaOH					
Source	**Degree of freedom**	**Sum of squares**	**Mean squares**	**p-value**	**Characteristics**
Model	14	0.1781	0.0127	0	Significant
Linear	4	0.0421	0.0105	0.001	Significant
A	1	0.0214	0.0214	0.001	Significant
B	1	0.0145	0.0145	0.003	Significant
C	1	0.0058	0.0058	0.039	Significant
D	1	0.0013	0.0013	0.298	Not Significant
Square	4	0.0452	0.0113	0.001	Significant
A^2	1	0.0010	0.0010	0.363	Not Significant
B^2	1	0.0114	0.0114	0.007	Significant
C^2	1	0.0047	0.0047	0.059	Not Significant
D^2	1	0.0409	0.0409	0	Significant
2-way interaction	6	0.0317	0.0053	0.010	Significant
AB	1	0.0185	0.0185	0.001	Significant
AC	1	0.0009	0.0009	0.378	Not Significant
AD	1	0.0016	0.0016	0.241	Not Significant
BC	1	0.0055	0.0055	0.044	Significant
BD	1	0.0047	0.0047	0.05	Significant
CD	1	0.0004	0.0004	0.565	Not Significant
Error	12	0.01301	0.0011		
Lack of fit	10	0.0123	0.0012	0.218	Not Significant
Pure error	2	0.0006	0.0003		
Total	26	0.1911			

Table 6.3 shows the ANOVA analysis conducted on the quadratic model obtained using the Minitab software. Table 6.3 shows that alcohol ratio coefficients for the linear terms is not significant, this entails that the molar ratio for transesterification in this study does not have a very significant impact on the results which had been predicted by the model. It can also be noted that the coefficient for the quadratic terms for temperature and reaction time are both not statistically significant due to the high p-values, this indicates that the quadratic coefficient of temperature and reaction time does not have great impact on the predicted yield which has been expressed by the model as significantly as the quadratic coefficients of the other variables. It can be seen that the interaction between temperature (A) and reaction time (C) has a p-value of 0.378, temperature (A) and molar ratio (D) with a p- value of 0.241 and reaction time (C) and molar ratio (D) with a p-value of 0.565. These coefficients indicate that the interactions between these variables are not significant while the interactions between all the other variables are highly significant when using the full

quadratic model. The lack of fit for the model expressed a p-value of 0.218, this denotes that the lack of fit is not significant, this further supporting the observation that the quadratic model is a good fit for the data.

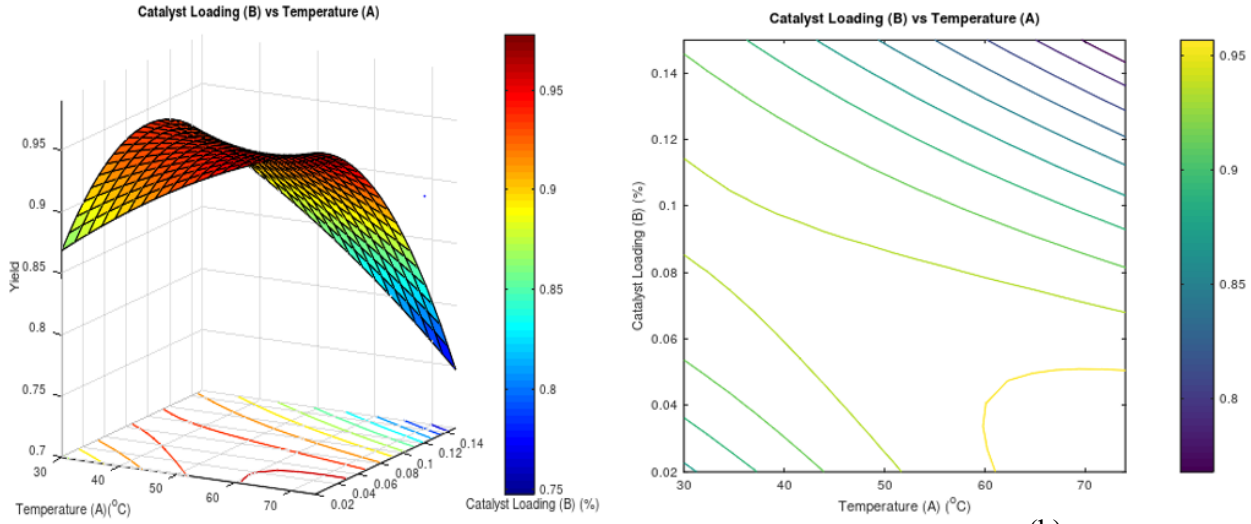
The optimum conditions to obtain the maximum yield of canola oil biodiesel using sodium hydroxide was obtained with the help of the Minitab software and produced via the transesterification process, the results obtained for the optimised reaction conditions can be seen in table 6.4 below:

Table 6. 4: Optimum conditions obtained from Minitab

Temperature (^{o}C)	**Catalyst loading (%)**	**Time (mins)**	**Molar ratio**	**Experimental yield**	**Predicted yield**
74	0.02	110.60	18.18	0.9697	0.9999

The Minitab software was used to identify the conditions for the optimal conditions to produce the highest yield, the yield was determined to be 0.9999. However, when using the same conditions to produce biodiesel in the lab, the yield was determined to be 0.9697. This shows an approximate error of 3.02%.

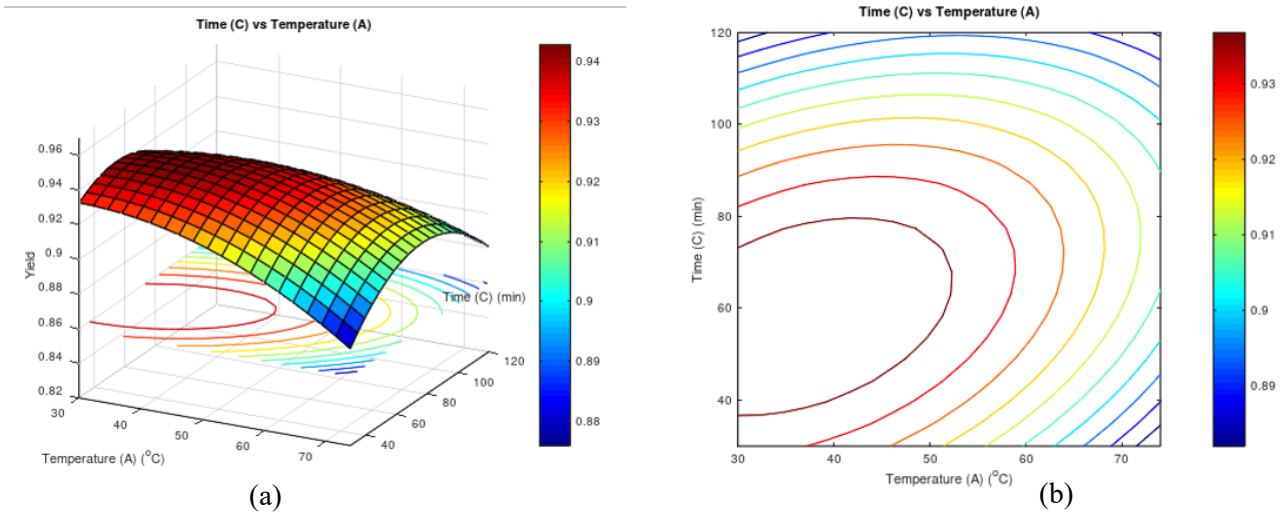
The effects of the four reaction parameter used in this study to determine the optimum yield of biodiesel obtained from canola oil are represented using surface response plots and contour plots that can be seen in Figures 5.2 to 5.7 below. Each plot shows the effect of two variables across their range within the study, with the other two variables kept constant at their median value



(a) (b)

Figure 6. 2:(a) Surface response plot of catalyst loading and temperature on yield of biodiesel from NaOH (b) Effect of Catalyst loading and temperature on yield of biodiesel from NaOH contour plot

The plots depicted in figure 6.2 (a)illustrates the response plot of temperature and catalyst loading on the yield of biodiesel produced. From the plot it can be noted that as the catalyst loading increases it causes the yield of biodiesel to decrease, conversely it can be seen that as the temperature increases, the yield of biodiesel increases. The decrease due to catalyst loading mainly attributes to the formation of soap, which causes the yield to decrease. However, the increase in yield due to temperature is caused by the fact that higher temperatures allows for the forward reaction to be driven, this also attests to the endothermic nature of the transesterification reaction. Figure 6.2 (b) shows that an elliptical contour forms, which suggest that the interaction is significant, can also be seen in table 6.3 which illustrates a p-value of 0.001 for the AB interaction.



(a) (b)

Figure 6. 3:(a) Surface response plot of time and temperature on yield of biodiesel from NaOH (b) Effect of time and temperature on yield of biodiesel from NaOH contour plot

Figure 6.3(a) shows the response of the interactions between the reaction time and temperature on the yield of biodiesel. The yield decreases as the temperature of the reaction increased, this suggest that the higher temperatures caused the alcohol to evaporate, leading to the insufficient amount of alcohol to drive the reaction towards the forward reaction. It is also important to note the parabolic nature of the reaction time response, which shows that after the peak was reached the yield decreased with time, this can be attributed to the reverse reaction; as time passes and the reaction reaches equilibrium, the reverse reaction becomes more prominent resulting in a decreased yield. The contour plot shown in Figure 6.3(b) indicates that the interactions between time and temperature have a significant effect on the yield of biodiesel due to the elliptical nature of the contours, however the results obtained in table 6.3 is contradictory as it shows a p-value of 0.378, which indicates that the data for the AC interaction is statistically insignificant.

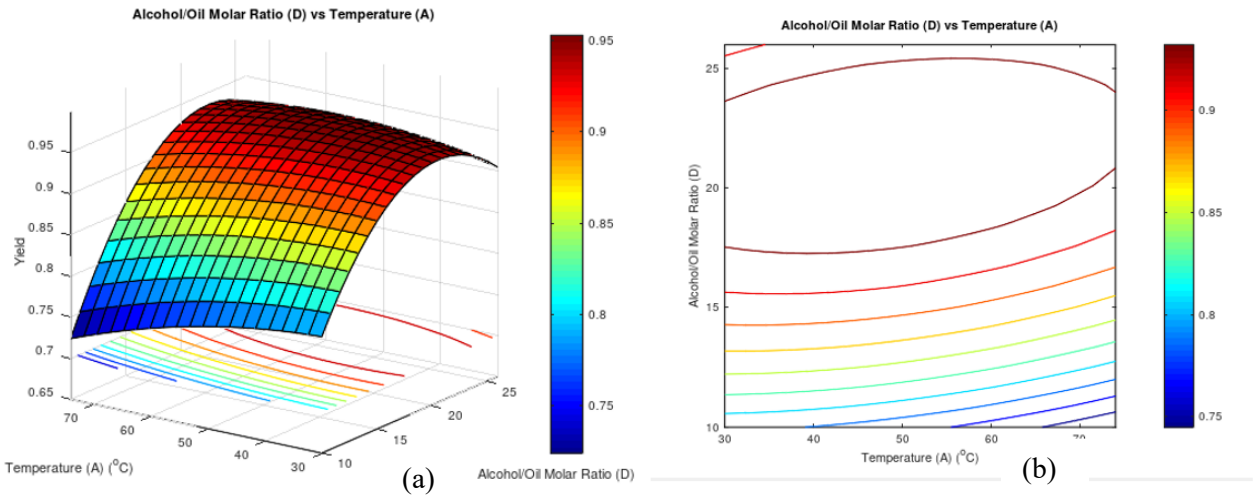
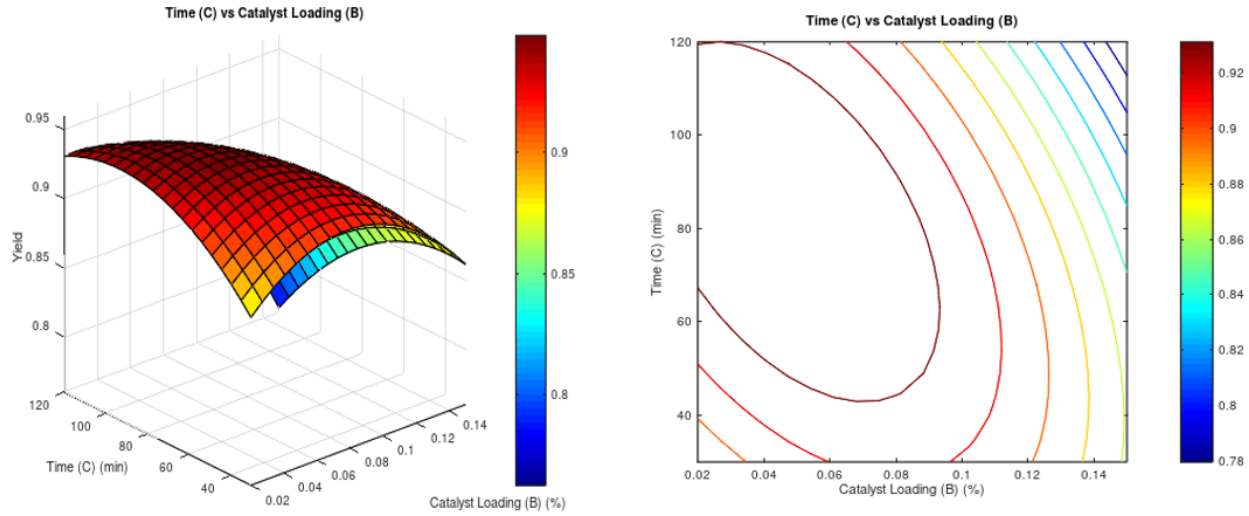


Figure 6. 4:(a) Surface response plot of alcohol/oil molar ratio and temperature on yield of biodiesel from NaOH (b) Effect of alcohol/oil molar ratio and temperature on yield of biodiesel from NaOH contour plot

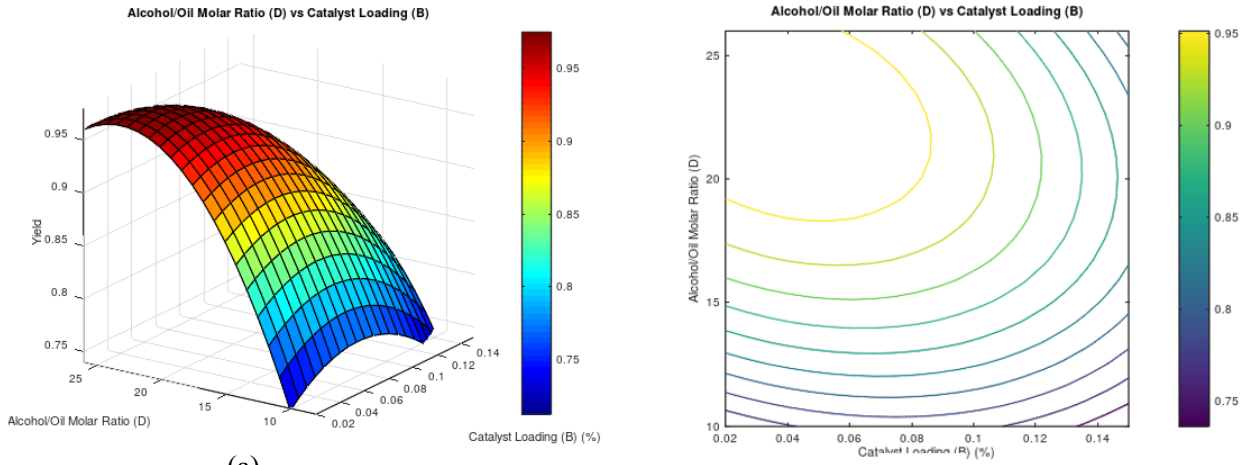
Figure 6.4(a) shows the 3D response surface effects between the alcohol molar ratio and temperature on the biodiesel yield. At higher temperatures, a higher yield can be obtained with high alcohol molar ratios. This is because the alcohol is more likely to evaporate at high temperatures, therefore more alcohol would be required to drive the reaction towards the forward reaction. The maximum temperature used for the reaction during this study was 74 °C, the temperature control system was manual and hence the reaction temperature may have reached the boiling point of ethanol (78.37°C) during any stage of the reaction. If ethanol did evaporate, there would be a small amount of time with reduced contact between the alcohol and oil. The highly elliptical nature of contours obtained in Figure 6.4(b) means that the interactions between the alcohol to oil molar ratio and temperature have a significant impact on the yield of biodiesel, which is also contradictory to the results obtained in table 6.3, which shows a p-value of 0.241 for the AD interaction.



(a) (b)

Figure 6. 5:(a) Surface response plot of catalyst loading and time on yield of biodiesel from NaOH (b) Effect of Catalyst loading and time on yield of biodiesel from NaOH contour plot

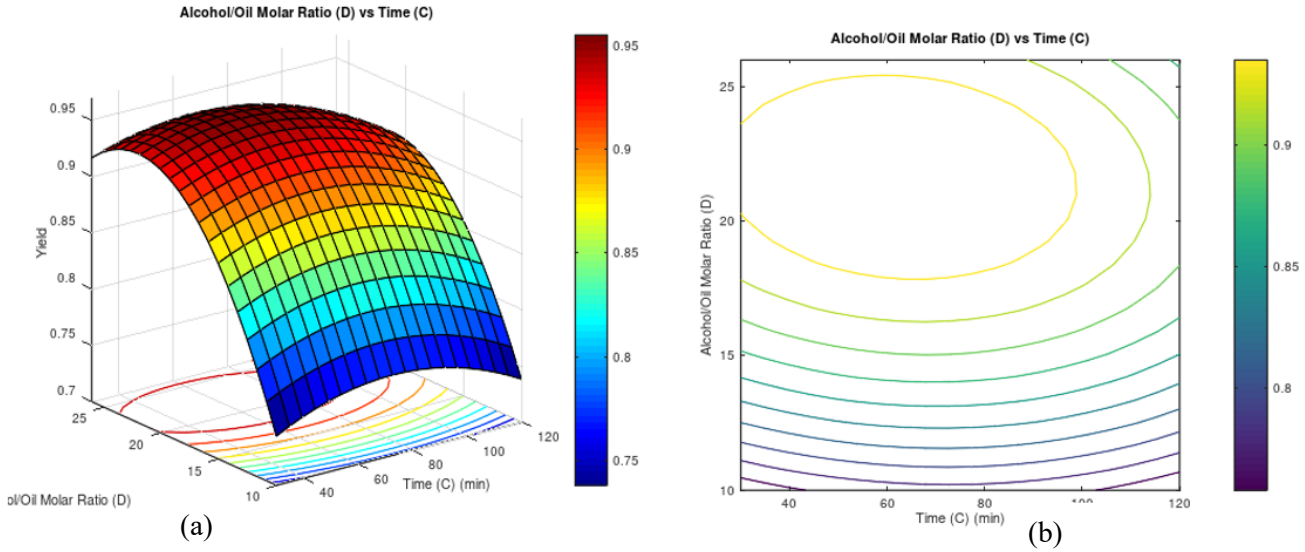
The relatively parabolic shape of Figure 6.5(a) implies that the interactions between reaction time and catalyst loading does significantly impact the yield of biodiesel. This is further supported by the elliptical nature of Figure 6.5(b), this is further justified with the results obtained in table 6.3, which indicates a p-values of 0.044. It can still be noted that high yields can be obtained in high amounts of time, with low values of catalyst loading.



(a) (b)

Figure 6. 6:(a) Surface response plot of catalyst loading and alcohol/oil molar ratio on yield of biodiesel from NaOH (b) Effect of Catalyst loading and alcohol/oil molar ratio on yield of biodiesel from NaOH contour plot

The surface response for the interactions between catalyst loading and alcohol to oil molar ratio on the yield of biodiesel is illustrated in Figures 6.6 (a) and (b). The lowest yield occurs at the lowest alcohol molar ratio and at high catalyst loading values. The parabolic nature of both factors indicates that after equilibrium is obtained the yield drastically drops. This combination of factors significantly hinders the forward reaction; the low amount of alcohol is not sufficient to drive the forward reaction and the high amount of base catalyst promotes the formation of soap. This combination should be avoided. Figure 6.6 (b) shows that the interactions between the ratio of alcohol to oil and catalyst loading significantly impacts the biodiesel yield, which can also be justified by the p-value of 0.05 obtained in table 6.3.



(a) (b)

Figure 6. 7:(a) Surface response plot of time and alcohol/molar ratio on yield of biodiesel from NaOH (b) Effect of time and alcohol/oil molar ratio on yield of biodiesel from NaOH contour plot

Figure 6.7(a) depicts the effect of the interactions between the alcohol molar ratio and time on the yield of biodiesel in the form of a 3D surface response plot. A combination of a low alcohol molar ratio and large and/or less amount of time corresponds to the lowest yield and hence, this combination of factors should be avoided. This can be because with the passage of time and the formation of glycerol, the glycerol tends to dissolve in the ethanol reducing the rate of the forward reaction, while a low alcohol to oil molar ratio is not sufficient to shift the equilibrium to the right. The contours obtained in Figure 6.7(b) implies that the interactions between the alcohol molar ratio and time have a significant impact on the yield of biodiesel obtained. The results in table 6.3 provides a p-value of 0.565 which contradicts the data obtained by the contour plots.

The main effect plots shown in figures 6.8 to 6.11 were obtained by varying one variable, while holding the other variables at their median values. The main purpose of these plots is to investigate the effect that each variable has on the yield and these plots were not used in the optimisation as these plots do not consider the interactions between the variables.

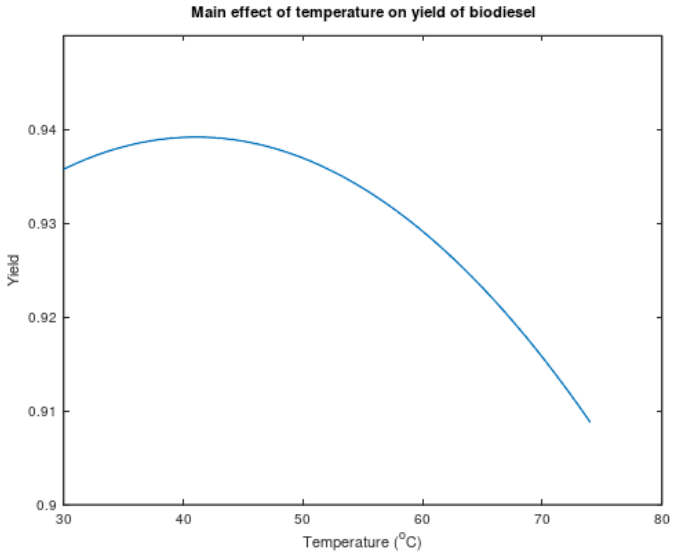


Figure 6. 8: Main effect of temperature

Figure 6.8 shows that initially there is a slight increase in the yield with the increasing temperature, and then the yield decreased as temperature increased. However, the difference between the highest and lowest yield value is approximately 0.03% and this may suggest that the effect of temperature on the yield of biodiesel obtained from canola oil using a sodium hydroxide catalyst, is not prominent. As mentioned previously, the reason for the decrease in yield may be the evaporation of ethanol at elevated temperatures.

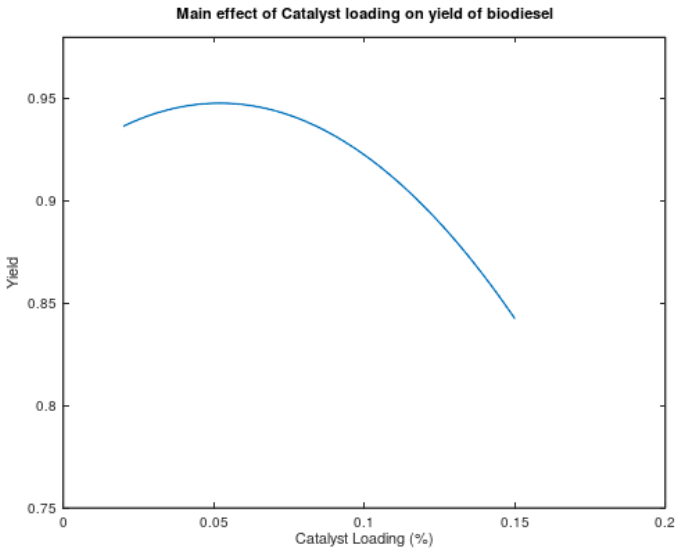


Figure 6. 9: Main effect of catalyst loading

Figure 6.9 shows that the yield of biodiesel has a slightly parabolic shape. After a peak has been reached there is a decrease in the yield of biodiesel; as the catalyst loading increases. A possible explanation for this effect is that high amounts of base catalyst allows for the formation of soap, which decreases the production of biodiesel resulting in a decrease in yield. A difference of approximately 0.12between the peak and lowest point can be noted which may suggest that catalyst loading has a prominent effect on biodiesel yield.

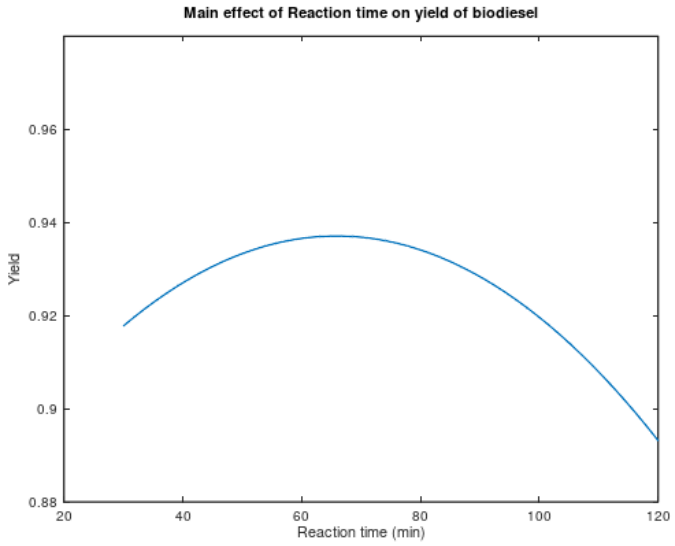


Figure 6. 10: Main effect of reaction time

The main effect of reaction time on the yield of biodiesel can be seen in figure 6.10. The difference between the peak and lowest yield values is less than 0.05, indicating that the effect of time on the yield of biodiesel obtained from canola oil using sodium hydroxide as a catalyst is not significant.

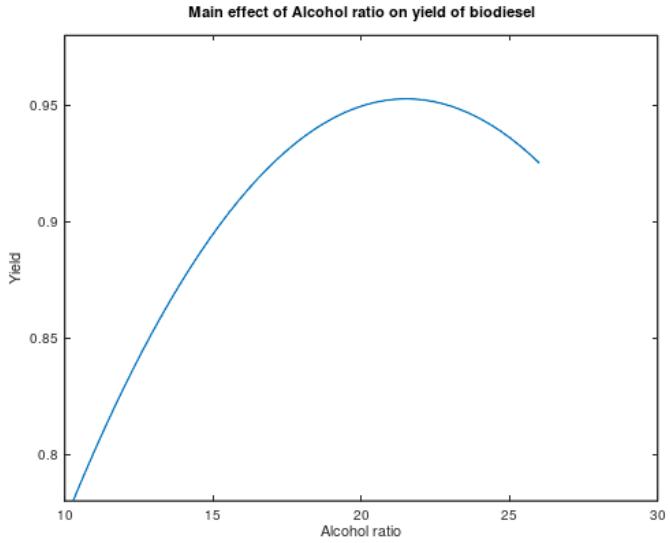


Figure 6. 11:Main effect of alcohol/oil molar ratio

Figure 6.11 illustrates the effect of the alcohol/oil molar ratio on the yield of biodiesel. The alcohol/oil ratio has the most significant effect on the yield of biodiesel, with a difference of roughly 0.18 between the peak and lowest yield values. The yield of biodiesel first increases as the ratio increases, however, after reaching its peak at around a molar ratio of 21, the yield begins to decrease as the ratio increases. Once again, this is due to the excessive amount of alcohol contributing to the difficulty in separation of the biodiesel from the glycerol layer, thereby decreasing the yield.

7. PROPERTY TEST

In this chapter, simple property testing was conducted on the biodiesel produced during this study, to determine whether the biodiesel met the international standards and classify if it could be used in diesel engines without any further modification. Properties of the feedstocks as well as the biodiesel produced from these feedstocks were assessed. The property testing was conducted on the runs that produced the optimum yield for biodiesel while using potassium hydroxide and sodium hydroxide as the catalyst for the reaction. Tests were also conducted on blends of biodiesel of 10% and 20%. The 10% blend (BK10) consisted of 10% biodiesel and 90% kerosene while the 20% blend (BK20) consisted of 20% biodiesel and 80% kerosene.

7.1. DENSITY

The density of the sample was measured using a device called the Mettler Toledo density meter easy D40. A sample of the biodiesel was first set aside in a 10 ml syringe. The device was switched on and dried in order to make sure no residue from the previous use was in the tubing. If a density of 0.0016 g/cm^3 or lower was recorded after drying, then the device was considered dry. Thereafter, the syringe was placed in the device and the biodiesel sample was injected into the device to be measured and recorded. This process was repeated three times to calculate an average to ensure accuracy of the results. The density of all samples was measured at a standard reference temperature of 15 ℃ as specified according to ASTM D941. According to ASTM D941 the limit for density is 900 kg/m^3. The accuracy of the device is ± 0.0005 g/cm^3.

Table 7. 1: Density results

Sample	**Density (g/cm^3)**			**Average density (g/cm^3)**
	Run 1	**Run 2**	**Run 3**	
Canola oil	0.9160	0.9160	0.9160	0.9160
KOH biodiesel	0.8915	0.892	0.8918	0.8918
NaOH biodiesel	0.8838	0.8837	0.8837	0.8837
KOH biodiesel BK 10	0.8182	0.8188	0.8182	0.8184
KOH biodiesel BK 20	0.8216	0.8215	0.8215	0.8215
NaOH biodiesel BK 10	0.8124	0.8123	0.8124	0.8124
NaOH biodiesel BK 20	0.8192	0.8198	0.8197	0.8196

7.2. ACID VALUE

Acid value tests were conducted in accordance with the method outlined in ASTM standard D974. Before the test could be conducted, a titration solvent was prepared by mixing toluene, water and isopropyl alcohol in the ratio 100:1:99. A 0.1 M potassium hydroxide (KOH) solution was also prepared and added into a burette. A blank titration of the titration solvent was then conducted to determine the amount of reactive substances in the titration solvent. The blank titration was conducted as follows: 100 mL of titration solvent was added to an Erlenmeyer flask followed by 5 drops of phenolphthalein indicator and a blank titration of the titration solvent was conducted. The volume of the KOH solution required to titrate the titration solvent was recorded. The following procedure was followed to determine the acid value as outlined by ASTM standard D974: 20g of the sample was weighed into an Erlenmeyer flask along with the titration solvent and 5 drops of indicator. The sample was titrated against the KOH solution until the solution reached a pale pink color, which held for approximately 1 minute. The volumes used where recorded and used in equation 7.1 to determine the acid value.

$$acid\ value\ \left(\frac{mg\ KOH}{g\ oil}\right) = \frac{(x-y)M\times 56.1}{W} \tag{7.1}$$

where x is the volume of KOH solution required for the actual titration (mL), y is the volume required for the blank titration (mL), M is the molarity of the KOH solution and W is the weight of the sample (g)

Table 7. 2: Acid value test results

Sample	Acid Value (mg KOH/g)			Average acid value (mg KOH/g)
	Run 1	Run 2	Run 3	
Canola oil	0.1290	0.1346	0.1234	0.1290
KOH biodiesel	0.1795	0.2132	0.2010	0.1982
NaOH biodiesel	0.1627	0.1683	0.1683	0.1664
KOH biodiesel BK 10	0.2805	0.2749	0.2019	0.2525
KOH biodiesel BK 20	0.3197	0.2805	0.2637	0.2879
NaOH biodiesel BK 10	0.1290	0.1346	0.1290	0.1309
NaOH biodiesel BK 20	0.1038	0.1122	0.1066	0.1075

7.3. pH

Firstly, the pH meter was calibrated. The calibration consisted of exposing the device to standard solutions of different pH levels. A sample of biodiesel was placed within a small beaker. The probe of the pH meter was then inserted into the sample and the pH of the biodiesel was recorded. The pH meter had an uncertainty value of ± 0.01.

Table 7. 3: pH results

Sample	pH			Average pH
	Run 1	Run 2	Run 3	
Canola oil	7.62	7.70	7.71	7.67
KOH biodiesel	7.92	7.84	7.84	7.87
NaOH biodiesel	7.57	7.55	7.59	7.57
KOH biodiesel BK 10	8.52	8.59	8.72	8.61
KOH biodiesel BK 20	8.55	8.66	8.67	8.63
NaOH biodiesel BK 10	8.21	8.22	8.3	8.24
NaOH biodiesel BK 20	8.40	8.44	8.44	8.43

7.4. REFRACTIVE INDEX

A calibration was also performed for the refractometer. The calibration was performed using deionised water to zero the refractometer. Once the calibration was completed, three drops of the biodiesel sample was placed onto the device. The reading was then obtained from the refractometer. Three readings were recorded for each run to calculate an average. The uncertainty of the refractometer had a value of ± 0.00002.

Table 7. 4: Refractive index results

Sample	Refractive index			Average Refractive index
	Run 1	Run 2	Run 3	
Canola oil	1.47305	1.47305	1.47305	1.47305
KOH biodiesel	1.45667	1.45662	1.45665	1.45665
NaOH biodiesel	1.45553	1.45541	1.45551	1.45548
KOH biodiesel BK 10	1.45967	1.45993	1.45952	1.45971
KOH biodiesel BK 20	1.45914	1.45864	1.45878	1.45885
NaOH biodiesel BK 10	1.44748	1.44863	1.44875	1.44829
NaOH biodiesel BK 20	1.44762	1.44712	1.44757	1.44744

7.5. VISCOSITY

A viscometer was utilised to measure the dynamic viscosity of the samples. To maintain constant desired temperature, a water bath was used (40 ℃ for biodiesel, 25 ℃ for oils and 20 ℃ for jet fuels) before recording the measurement. Spindle S21 was used to measure the viscosity of the oil, however for the viscosity of the blends and biodiesel spindle 1 had to be used. Once the sample was set at the desired temperature required for the test, the spindle was placed into the sample and the rotation speed was set to 100 rpm. The dynamic viscosity was then recorded in centipoise (cP) and this value was divided by the density of the sample to obtain the kinematic viscosity (mm^2/s). The kinematic viscosity limit for biodiesel according to ASTM D445 is 6 mm^2/s, while for jet fuel the limit is 8mm^2/s according to ASTM D1665. The apparatus used to measure the viscosity had an uncertainty value of ± 0.02 mm^2/s.

Table 7. 5: Viscosity results

Sample	Kinematic Viscosity (mm^2/s)			Average Kinematic Viscosity (mm^2/s)
	Run 1	Run 2	Run 3	
Canola oil	59.50	59.50	59.50	59.50
KOH biodiesel	14.90	14.89	14.89	14.89
NaOH biodiesel	10.33	9.99	9.99	10.10
KOH biodiesel BK 10	7.14	7.13	7.14	7.14
KOH biodiesel BK 20	8.20	8.21	8.21	8.21
NaOH biodiesel BK 10	6.77	6.85	6.81	6.82
NaOH biodiesel BK 20	7.01	7.02	7.00	7.01

7.6. API VALUE

The API value was calculated using the three specific gravity readings obtained during the density tests conducted in section 7.7. This value was only calculated for the blends of biodiesel and kerosene. The API value was calculated using an equation obtained from Speight, (2002), the equation is as follows:

$$API\ value\ = \frac{141.5}{Specific\ gravity\ of\ biodiesel} - 131.5 \qquad (7.2)$$

Table 7. 6: API values of the blends

Sample	API values			Average pH
	Run 1	Run 2	Run 3	
KOH biodiesel BK 10	41.44	41.31	41.44	41.40
KOH biodiesel BK 20	40.72	40.75	40.75	40.74
NaOH biodiesel BK 10	42.68	42.70	42.68	42.68
NaOH biodiesel BK 20	41.23	41.10	41.12	41.15

7.7. POUR POINT

For the pour point test, the samples of biodiesel were placed into a beaker, which was surrounded by ice. According to ASTM D1655, the pour point for jet fuel is approximately at a temperature of -47 ℃ and due to limitations on the laboratory equipment, this could not be tested. Therefore, only the pour point of the biodiesel samples was tested. The ASTM D6751 stated that the pour point value should be between the temperature range of -15 ℃ to 10 ℃.

Table 7. 7: Pour point results

Sample	Pour Point (°C)			Average Pour Point (°C)
	Run 1	Run 2	Run 3	
KOH biodiesel	-2.60	-2.50	-2.80	2.63
NaOH biodiesel	-3.30	-3.20	-3.60	3.37

7.8. HEAT OF COMBUSTION

Similarly, as the API value, the three specific gravity values were obtained from section 7.1, and the heat of combustion was determined for the jet fuel samples using a formula obtained from Speight, (2002):

$$Heat\ of\ combustion = \ 12400 - 2100(SG^2) \tag{7.3}$$

Table 7. 8: Heat of combustion results

Sample	Heat of combustion (BTU/lb)			Average Heat of combustion (BTU/lb)
	Run 1	Run 2	Run 3	
KOH biodiesel BK 10	10994.15	10992.09	10994.15	10993.46
KOH biodiesel BK 20	10982.44	10982.79	10982.79	10982.67
NaOH biodiesel BK 10	11014.01	11014.35	11014.01	11014.13
NaOH biodiesel BK 20	10990.71	10988.65	10988.99	10989.45

7.9. FLASH POINT

A flash point apparatus was used to identify the flash point of the optimum sample of biodiesel along with its jet fuel blends. A small volume of the sample was placed in a cup in the flash point apparatus. The cup was then covered with a lid. The sample was heated within the cup and the lid of the cup was opened in 1 °C intervals and the sample was exposed to an ignition source. The lowest temperature at which the vapour above the fuel flashed, was recorded as the flash point. The flash point equipment used provides results with an uncertainty of ± 0.01 °C.

Table 7. 9: Flash point results

Sample	Flash point (°C)			Average Flash point (°C)
	Run 1	Run 2	Run 3	
KOH biodiesel	100	101	101	100.7
NaOH biodiesel	98	96	98	97.3
KOH biodiesel BK 10	53	55	54	54.0
KOH biodiesel BK 20	58	59	59	58.7
NaOH biodiesel BK 10	43	44	44	43.7
NaOH biodiesel BK 20	49	51	51	50.3

7.10. GC ANALYSIS

The following section illustrates the results obtained for the optimum sample of biodiesel produced, using the conditions stated in table 5.6 for biodiesel produced using KOH and table 6.4 for biodiesel produced using NaOH. The compositions of each sample were analysed using a Shimadzu gas chromatography- mass spectrometry (GC-MS). Below are the column specifications as well as the conditions of the column for the results obtained:

Table 7. 10: GC-MS column specifications

Name	Ultra-Alloy
Length	30.0 m
Thickness	0.25µm
Diameter	0.25 µm

Table 7. 11: conditions of the GC

Injection temperature (°C)	250
Column oven temperature (°C)	120
Injection mode	Split
Carrier gas	Helium
Flow control mode	Linear velocity
Pressure (kPa)	80.6
Total flow ($\frac{mL}{min}$)	34.0
Linear velocity ($\frac{cm}{s}$)	37.5
Purge flow ($\frac{mL}{min}$)	3.0
Split ratio	30
Column flow ($\frac{mL}{min}$)	1

Table 7. 12: GC temperature program

Rate	Final temperature	Hold time
-	120	0
10	180	1
1	215	0
2	260	0

7.10.2. KOH biodiesel

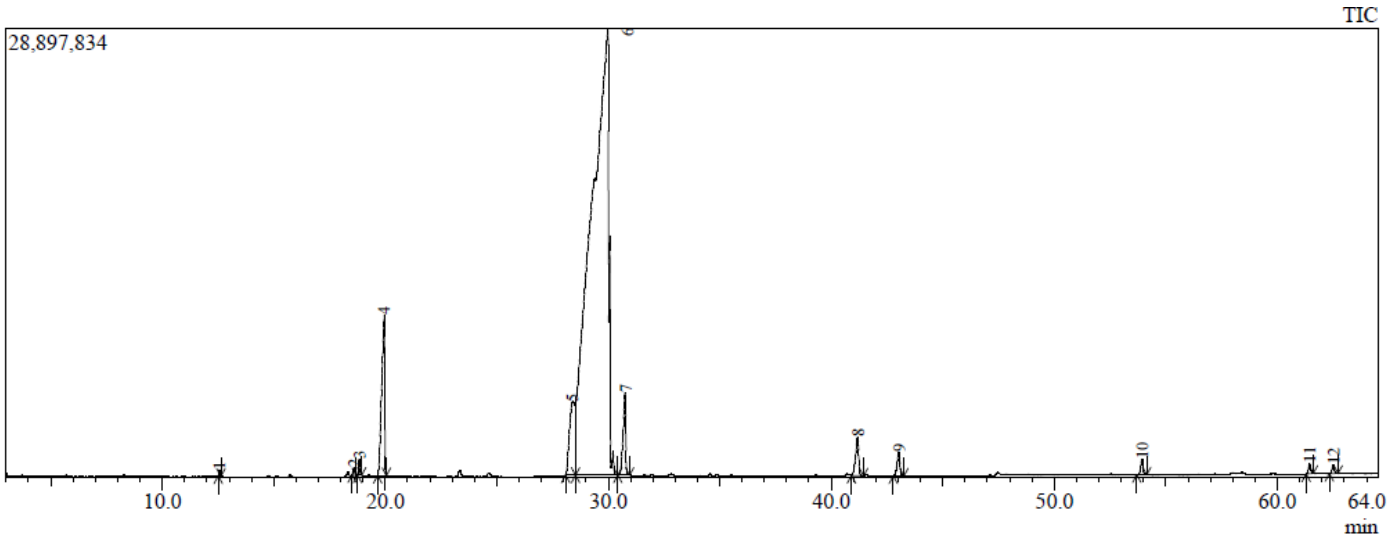


Figure 7. 1: KOH biodiesel chromatogram

Table 7. 13: GC-MS Results

Peak number	Retention time (Min)	Area (%)	Name of compound	Chemical formula
1	12.569	0.07	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$
2	18.599	0.13	9,12,15-Octadecatrienoic acid, ethyl ester (Z,Z,Z)	$C_{20}H_{34}O_2$
3	18.850	0.27	Ethyl 9-hexadecenoate	$C_{18}H_{34}O_2$
4	19.971	5.05	Hexadecenoic acid, ethyl ester	$C_{18}H_{34}O_2$
5	28.375	4.31	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$
6	30.016	85.04	(E)-9-Octadecenoic acid ethyl ester	$C_{20}H_{38}O_2$
7	30.789	2.38	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$
8	41.196	1.28	(E)-9-Octadecenoic acid ethyl ester	$C_{20}H_{38}O_2$
9	43.042	0.71	Eicosanoic acid, ethyl ester	$C_{22}H_{44}O_2$
10	53.925	0.39	Docosanoic acid, ethyl ester	$C_{24}H_{48}O_2$
11	61.437	0.20	Cis-15-Tetracosenoic acid, ethyl ester	$C_{24}H_{46}O_2$
12	62.491	0.18	Ethyl tetracosanoate	$C_{26}H_{52}O_2$

7.10.3. NaOH Biodiesel

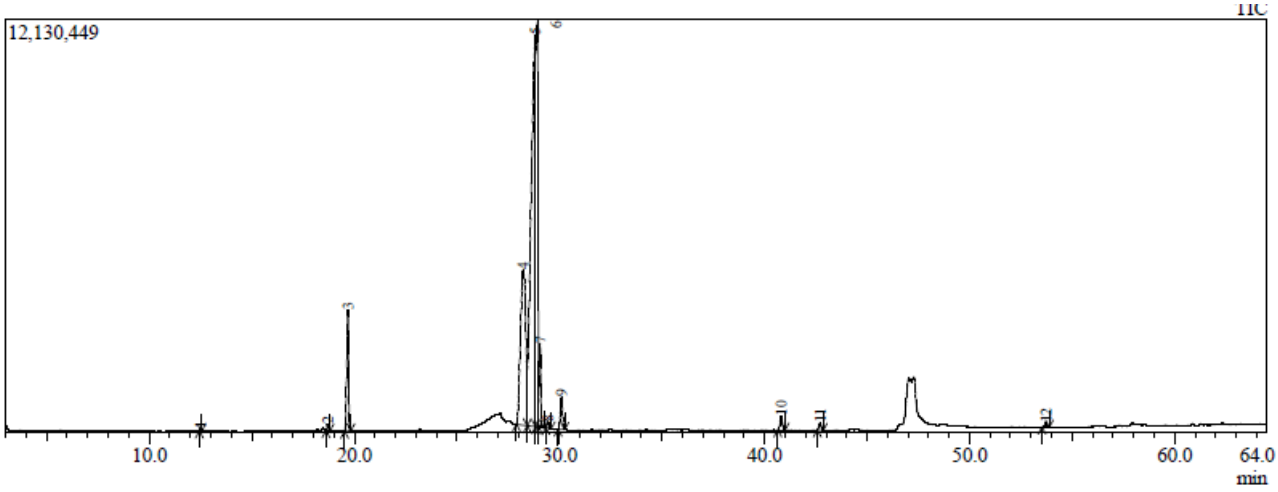


Figure 7. 2: NaOH biodiesel chromatogram

Table 7. 14: GC-MS results for NaOH

Peak number	Retention time (Min)	Area (%)	Name of compound	Chemical formula
1	12.487	0.06	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$
2	18.707	0.22	Ethyl 9-hexadecenoate	$C_{18}H_{34}O_2$
3	19.688	5.35	Hexadecenoic acid, ethyl ester	$C_{18}H_{34}O_2$
4	28.224	21.07	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$
5	28.817	45.09	Ethyl oleate	$C_{20}H_{38}O_2$
6	28.937	21.54	Ethyl oleate	$C_{20}H_{38}O_2$
7	29.057	3.18	(E)-9-Octadecenoic acid ethyl ester	$C_{20}H_{38}O_2$
8	29.446	0.25	Ethyl-9,12,15-octadecatrenoate	$C_{20}H_{34}O_2$
9	30.106	1.74	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$
10	40.818	0.89	Ethyl 9-hexadecenoate	$C_{18}H_{34}O_2$
11	42.704	0.41	Eicosanoic acid, ethyl ester	$C_{22}H_{44}O_2$
12	53.730	0.21	Docosanoic acid, ethyl ester	$C_{24}H_{48}O_2$

7.11. PROPERTY TEST DISCUSSION

As previously mentioned, this chapter focuses on the property testing conducted on the optimum sample of biodiesel produced using both KOH and NaOH. A further objective was achieved in this study as the properties of blends of biodiesel and kerosene (Jet fuel) was conducted. The first test conducted was the determination of the density of the samples. According to ASTM D941, the limit for biodiesel density is 0.9 g/cm^3. The biodiesel for this study produced an average density of 0.8918 g/cm^3 and 0.8837 g/cm^3 for biodiesel produced from KOH and NaOH respectively. These densities are within the range set out by the American standard for biodiesel testing methods. The significant drop in density for the blends can be accounted for by the higher volumes of kerosene in the blend mixture. An important property to be tested for the oil feedstock and biodiesel samples is the acid value, as this determines the number of steps required to produce biodiesel. An acid value of less than 1%, translates to the use of transesterification as the production method. The canola oil used in this study presented an acid value of 0.1290 %, which was a further justification of the use of transesterification for this study. The acid values recorded for the biodiesel samples as well as the blend was relatively low, as tabulated in table 7.2. The main objective of transesterification is to reduce the viscosity of the vegetable oil, for the use in diesel engines. Therefore, the test conducted for viscosity was the defining moment to determine if the vegetable oil would be suitable. The limits for biodiesel was 6 mm^2/s and the limit for jet fuel was 8 mm^2/s, as described by ASTM D445 and ASTM D1665 respectively. The results showed that transesterification did reduce the viscosity of the oil, however the results obtained in table 7.5 illustrate that neither the biodiesel produced from KOH, NaOH fell within the acceptable range. The jet fuel blend for NaOH however, did fall within the accepted range. It was also clear that the biodiesel produced with NaOH dropped the viscosity of the vegetable oil significantly more than the biodiesel produced by KOH. The tests of the API value and the heat of combustion was calculated using equation 7.2 and 7.3 respectively, and the results can be found in tables 7.6 and 7.8 respectively. The refractive index (RI) is a parameter that relates to molecular weight, fatty acid chain length, degree of unsaturation, and degree of conjugation of the biodiesel sample (Ismail and Ali, 2015). In addition, the RI also depends on the concentration of saturated and unsaturated fatty acids. Thus, it is a useful parameter for standardisation of the product. According to Dominguez et al. (1996), pure biodiesel has a refractive index value in the range of 1.45, with a limit of approximately 1.4590. The results obtained in table 7.4, shows that all the RI values are within the range stated. According to a study conducted by Andualem and Gessesse. (2012), the pH of biodiesel according to USA and Europe is 8.9. The results obtained in this study, as can be seen in table 7.3, falls below the accepted range specified. The pour point of the two biodiesel samples were determined using ice, and it was seen by ASTM D1655 that the range for the pour point is between -15°C to 10°C. The results obtained in table 7.7, shows that the values recorded, fell well within the range specified. The final property test conducted was for the flash

point, this was conducted on both biodiesel samples as well as the kerosene blends samples. According to ASTM D93 the range for the flash point for biodiesel lies between 93 ^{o}C to 170 ^{o}C, while the flash point for jet fuel should exceed 38 ^{o}C according to ASTM D1655. The results provided in table 7.9 shows that for both biodiesel and the jet fuel blend the values were in accordance with ASTM standards.

8. ECONOMIC ANALYSIS

8.1. BIODIESEL IN SOUTH AFRICA

8.1.2. Energy situation in South Africa

A study conducted by Wilson et al. (2005), revealed that South Africa is the largest emitter of greenhouse gases in Africa as well as one of the top twenty carbon intensive countries in the world. Around 14% of the total primary energy supply in the country is imported in the form of crude oil. South Africa's liquid fuels are manufactured by feedstock consisting of more than 50% imported crude oil, 30% coal, 10% domestic crude oil and 8% natural gas.

According to the South African Petroleum Industry Association (SAPIA), South Africa consumed approximately 12.54 billion litres of diesel in 2018 (SAPIA 2018 annual report, 2018). Figure 8.1 along with Table 8.1 shows the trend of diesel and other petroleum products, consumption between 2008-2018. Diesel prices have reached a selling price of about R14.78/litre at the coast (5 August 2020) due to an all-time high global oil price caused by various political factors as well as the COVID-19 pandemic. During the COVID-19 pandemic, lockdown, the price of diesel drastically declined. However, as the lockdown was eased to open the economy the price of diesel and petroleum increased as well. Taking the volatile crude oil price and fluctuating Rand/Dollar exchange rate into account, a diesel pump price of R20.00 per litre does not seem feasible in the foreseeable future.

Table 8. 1: petrol and diesel consumption (SAPIA 2018 annual report, 2018)

	Millions of litres					
Year	**Petrol**	**Diesel**	**Paraffins**	**Jet fuel**	**Fuel oil**	**LPGs**
2008	11069	9762	532	2376	555	613
2009	11321	9437	551	2349	724	554
2010	11455	10170	545	2308	468	612
2011	11963	11225	581	2434	477	717
2012	11714	11262	470	2367	568	656
2013	11153	11890	530	2233	523	485
2014	11344	13169	558	2197	487	389
2015	12072	14178	573	2441	591	588
2016	10160	10846	558	2121	562	557
2017	11174	12147	648	2713	523	551
2018	11142	12539	702	2346	552	504

8.1.3. Driving force of biodiesel in South Africa

The following are problems that many countries face worldwide, and biodiesel maybe be the solution to many of these issues.

1. A decrease in the dependency of imported fuels in South Africa.
2. Promotion of a renewable energy source.
3. Decrease of the greenhouse effect as well as a drop in the rate of pollution.
4. Assist South Africa in achieving the objectives of the White Paper on Renewable Energy, which stated that by 2013, SA should be generating around 10,000 GWh of energy from renewable sources (Wilson et al., 2005)

8.2. BIODIESEL FEASIBILITY STUDY

A report conducted by Murugesan et al. (2009) shows that diesel fuels have a huge impact on the economies of developing countries. According to Mulugetta (2008), road transport is the most reliable means of moving goods and services in Africa, this means accounting for almost 85 % of the total fossil fuel consumed in the transport sector, of which roughly 55 % comprise of diesel fuels. This shows the importance of diesel fuels as well as the great dependency on diesel fuels in the African continent. In South Africa, the dependency on diesel is no different, with an estimated 11142 million litres of petrol and 12539 million litres of diesel being consumed in 2018 (SAPIA, 2018). Table 8.2 lists the top ten nations ranked in terms of overall biodiesel production volume potential. The development of the biodiesel industry on the African continent, however, is still in its infancy.

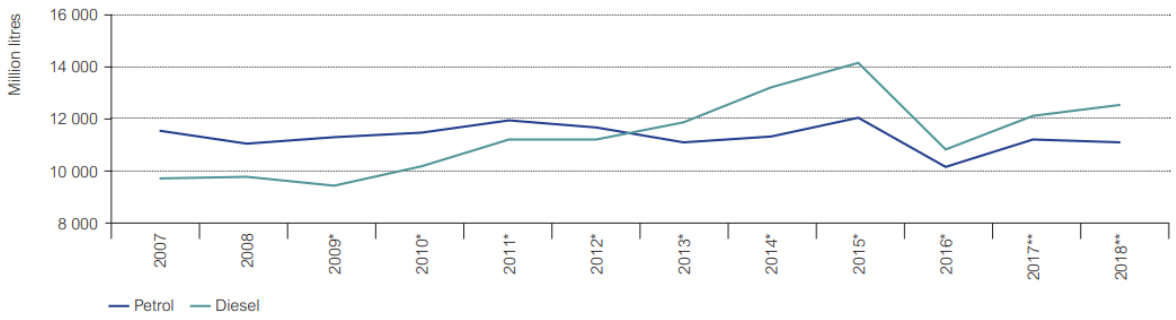


Figure 8. 1: Petrol and diesel production (SAPIA 2018 annual report, 2018)

Table 8. 2: Production cost of diesel in the top 10 countries (Sharma et al., 2009).

Rank	Country	Volume potential (per million L)	Production ($/L)
1	Malaysia	14540	0.53
2	Indonesia	7595	0.49
3	Argentina	5255	0.62
4	USA	3212	0.70
5	Brazil	2567	0.62
6	Netherlands	2496	0.75
7	Germany	2024	0.79
8	Philippines	1213	0.53
9	Belgium	1213	0.78
10	Spain	1073	1.71

8.2.2. Biodiesel Production Process

According to Amigun et al. (2008), a significant economic consideration in the production of biodiesel is the choice of the production process, as significant capital and operating cost differences exist with different processes. The technologies required for changing vegetable oils into biodiesel have been researched extensively as examined in Zhang et al. (2003) and Basha et al. (2009). Biodiesel may be obtained by four primary means, these being: (i) direct use and blending of oils; (ii) microemulsions of oil; (iii) pyrolysis of vegetable oil; and (iv) transesterification. The most common and frequent means to produce biodiesel is to transesterify triacylglyerols in vegetable oils with an alcohol, in the presence of either an acid or base catalyst (You et al., 2008). The type of feedstock along with its quality decides the choice of chemical technology needed in production plants. Further research revealed that the scale of production as well as the conversion technology directly influences both the capital costs and the operating costs. Studies conducted by Zhang et al. (2003) and Amigun et al. (2008) stated that the alkali-catalysed transesterification is the most used process for commercially produced biodiesel. This is mainly due to its faster reaction rate than acid-catalysed transesterification (Zhang et al., 2003). The reaction occurs at a lower temperature and pressure, which allows for lower capital and operating costs (Amigun et al., 2008). Similarly, Zhang et al. (2003) stated that the capital costs are much lower for alkali-catalysed processes. Therefore, the alkali-catalyzed transesterification process is typically the most economical means of producing biodiesel (Amigun et al., 2008).

Amigun et al. (2008) stated that a vital technological issue in biodiesel production is to know if either batch or continuous flow plant should be designed. A study conducted by Eidman (2007) stated that most of the biodiesel plants in the United States currently use continuous flow processes. For large-scale operations, continuous flow plants appear to be the preferred choice (Amigun et al., 2008) and can produce continuously within set parameters. Due to the larger scale of biodiesel production, continuous flow processes have higher capital costs than batch processes (Eidman, 2007). According to Eidman (2007), higher capital outlays may be mitigated by several important operational advantages, such as lower processing costs and generally more consistent output than batch processes. Lower processing costs may arise from the ability to reuse catalysts and other chemicals which is often infeasible in batch processes (Amigun et al., 2008).

Batch processes allow a quantity of biodiesel to be processed in separate areas. Amigun et al. (2008) stated that lower initial capital requirements and the ability to regulate production within demand results in batch processes being better suited for smaller scale production, therefore favorable to be used in the African continent. These reports suggested that since government energy policies in Africa are often regarded to be quite uncertain and unpredictable, investors may combat risk by favouring research with lower capital outlays.

8.2.3. Biodiesel Production Cost

Biodiesel production costs typically vary according to the geographic region and the choice of feedstock (Johnston and Holloway, 2007). Mulugetta (2008) stated that the factors involved to produce biodiesel in Sub-Saharan Africa and in other developing countries are most likely to be different from those in developed countries, due to the differences in technologies and managerial capabilities. The labour portion of the production costs depends on the production capacity, the degree of automation, the type of process (batch or continuous) and the feedstock variety processed (Amigun et al., 2008). Mulugetta (2008) noted that due to a general lack of empirical experience with respect to biodiesel production in Africa, local studies often make use of production data from Europe and North America.

The cost share of feedstock typically varies by study and feedstock variety. A study conducted by Tareen et al. (2000) stated that the price of soybean accounted for roughly 75 % of the soybean-based biodiesel production costs. However, according to Haas et al. (2006), this study estimated that the cost may be as high as 88 % using crude soybean oil as the feedstock. Withers and Noordam (1996) found that feedstock costs made up roughly 64 % and 70 % of total costs, respectively, using rapeseed oil as the feedstock. Mulugetta (2008) estimated that palm oil as a feedstock makes up for more than 85 % of production costs

in Ghana. Therefore, Amigun et al. (2008) stated that the cost of feedstock is generally the most vital factor that influences the economic feasibility of the production of biodiesel. Despite capital expenditure being the primary barrier that must be overcome in establishing a biodiesel production plant, the long term success of such ventures are frequently more dependent on the daily operating efficiency than on the initial capital expenditure (Amigun et al., 2008).

Kenkel and Holcomb (2006) noted that the vital factors influencing the economics of locating and operating biodiesel plants include: (i) feedstock availability; (ii) access to market centers for biodiesel; (iii) access to markets for by-products; (iv) utility costs and availability; and (v) state/local incentives. The feedstock costs make up a huge proportion of the total biodiesel production costs. Many researchers found that the future promotion of the production of biodiesel should target the reduction of feedstock costs by developing new technologies which could increase the yields of available feedstocks, as well as allow the use of lower cost alternative methods (Zhang et al., 2003; Amigun et al., 2008; You et al., 2008).

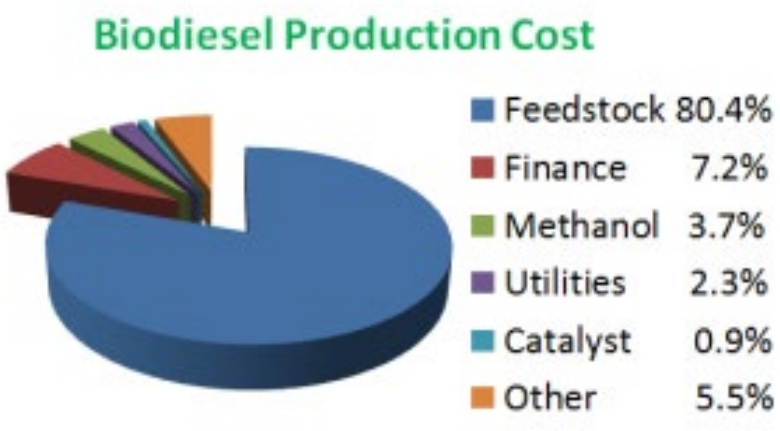


Figure 8. 2: Biodiesel production cost distribution (Esterification - SRS Biodiesel, 2020)

8.2.4. Feasibility study

A very common argument against the use of various types of biofuels are the high production costs, although this is not the case for sugarcane-based bioethanol produced in Brazil (van den Wall Bake et al., 2009). Many studies are in agreement that a significant barrier to the commercialisation of biodiesel is its higher production cost as compared to commercial diesel fuel (Zhang et al., 2003; You et al., 2008). The neo-classical economic principles propose that "if two inputs (e.g., biodiesel and conventional diesel) are perfect substitutes in production, the first-order condition of least-cost production is simplified to a direct comparison of input costs" (Tareen et al., 2000). Several studies have concluded that biodiesel is more costly to produce than conventional diesel and therefore concluded that the production of biodiesel is not

economically feasible (Griffin et al., 1985; Withers and Noordam, 1996; Haas et al., 2006; Eidman, 2007; Nolte, 2007; Sawyer, 2007; Amigun et al., 2008).

From a South African perspective, the cost of production for both bioethanol and biodiesel will most likely play a vital role in terms of competitiveness, especially in export markets (Funke et al. 2009). Funke et al. (2009) also stated that the fact that biodiesel is generally more expensive to produce than its commercial diesel counterpart, "creates a significant challenge for the successful marketing of biodiesel in South Africa, and could hamper the successful development of a biodiesel market, especially in light of voluntary blending as stipulated in the biofuel strategy. It further indicates that the SA industry might face a serious threat if local blending mandates are imposed" (Funke et al., 2009: 231). According to figure 8.3 and 8.4, the profitability is mainly dependent on the type of feed stock, these are values adapted from Nolte, (2007) For two biodiesel plant. They show that the production and profitability is highly unpredictable. Figure 8.5 shows some of the manufacturing costs of the feedstock for two different plants. Figures 8.3 to 8.5 was obtained from Nolte, (2007), which was conducted for a study during 2007, hence the values illustrated was conducted at that time. It would be from an educated guess that the production cost in today's market would be much higher due to inflation, as well as the shortages of certain resources.

Figure 8. 3: The profitability of a canola SEBP plant for various biodiesel selling prices

Biodiesel Selling Price	Profit per litre before tax	Net Profit after 29% income tax	Rate of Return on Investment
R/litre	*R/litre*	*Thousand Rand*	*%*
6.50	0.69	10906	10%
7.00	1.19	18810	17%
7.50	1.69	26713	25%
8.00	2.19	34616	32%
8.50	2.69	42519	39%

Figure 8. 4: The profitability of a soybean SEBP plant for various biodiesel selling prices

Biodiesel Selling Price	Profit per litre before tax	Net Profit after 29% income tax	Rate of Return on Investment
R/litre	*R/litre*	*Thousand Rand*	*%*
6.50	-1.20	-18,968	-13%
7.00	-0.70	-11,064	-8%
7.50	-0.20	-3,161	-2%
8.00	0.30	4,742	3%
8.50	0.80	12,645	9%

Figure 8. 5: Manufacturing cost at different plants for different feed stocks

SEBP Plant		COBP Plant	
Local Feedstock	**Manufacturing Cost**	**Imported Feedstock**	**Manufacturing Cost**
Canola	R4.81/litre	Palm Oil	R6.62/litre
Sunflower seeds	R6.67/litre	Soybean Oil	R6.89/litre
Soybeans	R6.70/litre	Sunflower Oil	R7.48/litre
		Rapeseed Oil	R9.28/litre

9. CONCLUSION AND RECOMMENDATIONS

9.1. CONCLUSION

Upon completion of this study, the following conclusions were drawn:

- Canola oil was chosen as the feedstock for the study, with an acid value of 0.129 mg KOH/g recorded. The low acid value ensured that a single step alkaline catalysed transesterification reaction was required.
- When experimental work was concluded for runs comprising of canola oil, ethanol, and potassium hydroxide, it was noted that the highest yield was 0.9478 which was obtained at a temperature of 74 ^{o}C, catalyst load of 0.085%, reaction time of 75 minutes and an ethanol/canola oil molar ratio of 26:1.
- A statistical analysis was conducted on the result, and it was found that a full quadratic model best fitted the experimental data as it showed a strong coefficient of determination (R^2) value of 0.9410.
- Minitab was used to determine that the predicted optimum yield was 0.9901, which could be obtained using a temperature of 74 ^{o}C, a catalyst loading of 0.02%, reaction time of 102.73 min and a molar ratio of 26:1. However, when using the same conditions experimentally the yield determined was 0.9662 which was lower than the optimum predicted value.
- Therefore, for the study of canola oil, ethanol and potassium hydroxide it can be concluded that the optimum yield was obtained using the conditions obtained using the minitab software.
- The next step of the study required an alternative homogenous base catalyst to be used, the catalyst chosen was sodium hydroxide and due to the low acid value of canola oil a single step transesterification reaction was required.
- Upon completion of experimental work for the NaOH catalyst, it was noted that the optimum yield was 0.9578. which was obtained at a temperature of 74 ^{o}C, catalyst load of 0.02%, reaction time of 75 minutes and an alcohol to oil molar ratio of 18:1.
- Similarly, for the NaOH catalyst it was found that the full quadratic model best suited the experimental data with a R^2 value of 0.9319.
- Minitab predicted that the optimum yield would be 0.9999 at a temperature of 74 ^{o}C, catalyst loading of 0.02%, time of 110.60 min and an alcohol/oil molar ratio of 18.18. However, using the same conditions experimentally gave a yield of 0.9697 which was lower than the predicted values.
- Therefore, it was concluded that the optimum yield was obtained using the conditions acquired from the minitab software.

- For the biodiesel obtained using both catalysts, property tests were conducted according to the ASTM standards.
- The property of the kinematic viscosity was beyond the ASTM standard limit for both biodiesel samples, therefore further modifications would be required before it could be used in a diesel engine.
- However, it can be noted that NaOH was found to be the better suited catalyst with regards to the transesterification of canola oil. This is due to the higher yields produced using NaOH as well as the lower viscosity of biodiesel produced.
- Finally, a feasibility study was conducted on biodiesel in general and it was found that the profitability of the production of biodiesel mainly depended on the type of feedstock used. As the feedstock prices accounted for majority of the manufacturing cost.

9.2. RECOMMENDATIONS

- Different feedstock of blends of feedstock should be studied.
- Other catalysts as well as longer chained alcohol should also be considered.
- Other types of methods should be investigated such as pyrolysis as well as methods that take other factors such as pressure into account.

REFERENCES

Alcantara R., Amores J., Canoira L.; Fidalgo E.; Franco M.; Navarro A., 2000. *Catalytic production of biodiesel from soybean oil, used frying oil and tallow.* Biomass and Bioenergy. **18**: p. 515-527.

Amigun B, Müller-Langer F and von Blottnitz H., 2008. *Predicting the Costs of Biodiesel Production in Africa: Learning from Germany. Energy for Sustainable Development 12 (1): 5-21.*

Andualem, B. and Gessesse, A., 2012. Production and Characterization of Biodiesel from Brebra (M. ferruginea) Seed Non-edible Oil. *Biotechnology(Faisalabad)*, 11(4), pp.217-224.

Anguebes-Franseschi, F. et al., 2019. Physical and Chemical Properties of Biodiesel Obtained from Amazon Sailfin Catfish (Pterygoplichthys pardalis) Biomass Oil. *Journal of Chemistry,* pp. 1-12.

Antolin, G. et al., 2002. Optimisation of biodiesel production by sunflower oil transesterification. *Bioresource Technology,* 83(2), pp. 111-114.

Arpornpong, N., Sabatini, D., Khaodhiar, S. and Charoensaeng, A., 2015. Life cycle assessment of palm oil microemulsion-based biofuel. *The International Journal of Life Cycle Assessment*, 20(7), pp.913-926.

Arshad, M., Zia, A. M., Shah, F. A. & Ahmad, M., 2018. An Overview of Biofuel. In: M. Arshad, ed. Perspectives on Water Usage for Biofuels Production. Lahore: Springer, pp. 1- 37.

Atadashi I., Aroua M & Aziz A., 2011. Biodiesel Separation and purification: A review. Renewable Energy. ***36****: p. 437-443.*

Balat M & Balat H., 2008. A critical review of bio-diesel as a vehicular fuel. Energy Conservation and Management. ***49****: p. 2727–2741.*

Basha SA, Gopal KR and Jebaraj S., 2009. A Review on Biodiesel Production, Combustion, Emissions and Performance. *Renewable and Sustainable Energy Reviews* 13: 1628-1634**.**

Basque Research. (2014, November 12). Ethanol and heterogeneous catalysts for biodiesel production. *ScienceDaily*. Retrieved April 12, 2021 from www.sciencedaily.com/releases/2014/11/141112084246.htm

Bianchi, C. L. et al., 2011. Non Edible Oils: Raw Materials for Sustainable Biodiesel. In: M. Stoytcheva & G. Montero, eds. *Biodiesel: Feedstocks and Processing Technologies.* Croatia: InTech, pp. 3-22.
Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield Md. Enamul Hoque*, Amrit Singh, Yong Leng Chuan Department of Mechanical, Materials & Manufacturing

Engineering, University of Nottingham Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor Darul Ehsan, Malaysia

Blangino, E., Riverós, A. F. & Romano, S. D., 2008. Numerical expressions for viscosity, surface tension and density of biodiesel: analysis and experimental validation. *Physics and Chemistry of Liquids,* 46(5), pp. 527-547.

Brásio A., Romanenko A & Santos L.; Fernandes N., 2011. Modeling the effect of mixing in biodiesel production. Bioresource Technology. ***102****: p. 6508–6514.*

Bridgewater, T., 2015. *Fast pyrolysis for bioenergy and biofuels - ppt video online download*. [online] Slideplayer.com. Available at: <https://slideplayer.com/slide/9340560/> [Accessed 12 April 2020].
Carter, D. & Halle, J., 2005. *How to Make Biodiesel.* Pennsylvania: Low-Impact Living Initiative.

Darnoko D & Cheryan M., 2000. *Kinetics of Palm Oil Transesterification in a Batch Reactor.* Journal of American Oil Chemist Society. **77**(10): p. 1263-1266.

Demirbas , A., 2005. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science,* 31(5-6), pp. 466-487.

Demirbas, A., 2008. Biodiesel: A Realistic Fuel Alternative For Diesel Engines. London: Great Britain: Springer.

Domínguez L Á A, 1996. Biofuels: Use of Vegetable Oils as Renewable Energy. Madrid: Ministry of Agriculture, Fisheries and Food.

Eidman VR., 2007. Economic Parameters for Corn Ethanol and Biodiesel Production. *Journal of Agricultural and Applied Economics* 39(2): 345-356.

Elder, M., Romero, J., Bhattacharya, A., Sano, D. and Matsumoto, N., 2018. Socioeconomic Impacts of Biofuels in East Asia: Holistic Perspectives for Policy-making. *Biofuels and Sustainability*, pp.87-118.

Eldin, A., 2011. General Introduction to Design of Experiments (DOE).

Enciner J et al., 2002. Biodiesels fuel from vegetable oils: transesterification of Cynara cardunculus L. oils with ethanol Energy Fuels. ***16****: p. 443-450.*

Felizardo, P. et al., 2005. Production of biodiesel from waste frying oils. *Waste Management,* 26(5), pp. 487-494.

Fereidooni, L., Hosseini, S. N. & Mehrpooya, M., 2017. Production of green diesel through isopropanolysis of waste cooking oil via reflux system in presence of sodium hydroxide. *The first International Congress on Engineering Sciences.*

Ferreira, S., Bruns, R., Ferreira, H., Matos, G., David, J., Brandão, G., da Silva, E., Portugal, L., dos Reis, P., Souza, A. and dos Santos, W., 2007. Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta*, 597(2), pp.179-186.

Freedman, B., Butterfield, R. O. & Pryde, E. H., 1986. Transesterification Kinetics of Soybean Oil. *Journal of the American Oil Chemists' Society,* 63(10), pp. 1375-1380.

Freedman, B., Pryde, E. H. & Mounts, T. L., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society,* 61(10), pp. 1638-1643.

Funke T., 2010**.** Personal Communication. The Bureau for Food and Agricultural Policy (BFAP), Department of Agricultural Economics, Extension and Rural Development, University of Pretoria, South Africa.

Gebremariam, S. & Marchetti, J., 2017. Biodiesel production technologies. *AIMS Energy,* 5(3), pp. 425-457.

Green Coast. (2020). *Facts about Biodiesel: Understanding the Advantages and Disadvantages*. [online] Available at: https://greencoast.org/facts-about-biodiesel/ [Accessed 2 Mar. 2020].

Griffin RC, Lacewell RD and Collins GS., 1985. Impacts of Substituting Plant Oils for Diesel Fuel. *Western Journal of Agricultural Economics* 10(2): 401-412.

Gui, M. M., Lee, K. T. & Bhatia , S., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy,* 33(11), pp. 1646-1653.

Guo, F., 2011. *Biodiesel Production with Solid catalyst.* INTECH Open access publisher

Haas MJ, McAloon AJ, Yee WC and Foglia TA., 2006. A Process Model to Estimate Biodiesel Production Costs. *Bioresource Technology* 97: 671-678.

Halder, S., Dhawane, S. H., Kumar, T. & Halder, G., 2015. Acid-catalyzed esterification of castor (Ricinus communis) oil: optimization through a central composite design approach. *Biofuels,* 6(3-4), pp. 1-11.

Ismail, S. A.-e. A. & Ali, R. F. M., 2015. Physico-chemical properties of biodiesel manufactured from waste frying oil using domestic adsorbents. *Science and Technology of Advanced Materials,* 16(3), pp. 1-9.

Jääskeläinen, H., 2019. Early History of the Diesel Engine. [Online] Available at: https://www.dieselnet.com/tech/diesel_history.php [Accessed 26 August 2019].

Jahirul, M., Rasul, M., Chowdhury, A. and Ashwath, N., 2012. Biofuels Production through Biomass Pyrolysis —A Technological Review. *Energies*, 5(12), pp.4952-5001.

Jankowski, Antoni. (2011). Influence of chosen parameters of water fuel micro emulsion on combustion processes, emission level of nitrogen oxides and fuel consumption of CI engine. 18.

Joglekar, A. M. & May, A. T., 1987. Product excellence through design of experiments. *Cereal Food World,* Volume 32, pp. 587-868.

Johnston M and Holloway., 2007. A Global Comparison of National Biodiesel Production Potentials. *Environmental Science and Technology* 41(23): 7967- 7973.

Kafuku, G. & Mbarawa, M., 2010. Alkaline catalyzed biodiesel production from moringa oleifera oil with optimized production parameters. *Applied Energy,* Volume 27, p. 2561–2565.

Kenkel P and Holcomb RB., 2006. Challenges to Producer Ownership of Ethanol and Biodiesel Production Facilities. Journal of Agricultural and Applied Economics 38(2): 369-375.

Khalid, Amir & Md Nor Anuar, Mohamad & Ishak, Yusri & Manshoor, Bukhari & Sapit, Azwan & Leman, Mutalib & Zaman, Izzuddin. (2014). Emissions Characteristics of Small Diesel Engine Fuelled by Waste Cooking Oil. MATEC Web of Conferences. 13. 06006. 10.1051/matecconf/20141306006.

Klofutar B.; Golob J.; Likozar B.; Klofutar C.; Z˘agar E.; Poljanšek I., 2010. The transesterification of rapeseed and waste sunflower oils: Mass-transfer and kinetics in a laboratory batch reactor and in an industrial-scale reactor/separator setup. Bioresource Technology. **101**: p. 3333–3344.

Knothe, G,.2010. *The Biodiesel Handbook, Second Edition.* Taylor & Francis

Kumar, V., Kant, P. & Chaudhary, A. P., 2017. BIODIESEL: REDUCING ENVIRONMENT POLLUTANT AND DEPENDENCY ON PETROLEUM DIESEL. *Petroleum and Coal,* 59(1), pp. 89-99.

Lam, M. K., Lee, K. T. & Mohamed, A. R., 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances,* 28(4), pp. 500-518.

Lapuerta, M., Armas, O. and Rodríguez-Fernández, J., 2008. Effect of biodiesel fuels on diesel engine emissions. *Progress in Energy and Combustion Science*, 34(2), 198-223.

Leung, D. Y. C., Wu, X. & Leung, M. K. H., 2010. A review on biodiesel production using catalyzed transesterification. *Applied Energy ,* 87(4), pp. 1083-1095.

Lotero, E. et al., 2005. Synthesis of Biodiesel via Acid Catalysis. *Industrial & Engineering Chemistry Research,* 44(14), pp. 5353-5363.

Ma F., Clements L., Hanna M., 1999. *The effect of mixing on transesterfication of beef tallow.* Bioresouce Technology. **69**: p. 289–293.

Ma, F. & Hanna, M. A., 1999. Biodiesel production: a review. *Bioresource Technology,* 70(1), pp. 1-15.

Mathiyazhagan, M. & Ganapathi, A., 2011. Factors Affecting Biodiesel Production. *Research in Plant Biology,* 1(2), pp. 1-5.

Mulugetta Y., 2008. Evaluating the Economics of Biodiesel in Africa. *Renewable and Sustainable Energy Reviews* 13: 1592-1598.

Murugesan A, Umarani C, Chinnusamy TR, Krishnan M, Subramanian R and Neduzchezhain N., 2009. Production and Analysis of Bio-Diesel from Non-Edible oils – A Review. *Renewable and Sustainable Energy Reviews* 13: 825-834.

Nolte, M., 2007. COMMERCIAL BIODIESEL PRODUCTION IN SOUTH AFRICA: A PRELIMINARY ECONOMIC FEASIBILITY STUDY. [online] Available at: <http://academic.sun.ac.za/crses/html/research_topics_files/pdf/Mirco_Nolte.pdf> [Accessed 12 April 2021].

Noureddini H and Zhu D., 1997. *Kinetics of Transesterification of Soybean Oil.* Journal of *Transesterification of Soybean Oil.* Journal of American Oil Chemist Society. **74**(11): p. 1451463.

Noureddini H., Hardey D., Gutsman R., 2004. *A continous process for the glycerolysis of soyabean oil.* Journal of American Oil Chemist Society. **81**: p. 1-5.

Nrel.gov. 2005. *Biodiesel Blends (Clean City Fact Sheet)*. [online] Available at: <https://www.nrel.gov/docs/fy05osti/37136.pdf> [Accessed 17 March 2020].

Nwakuba N, Obasi S, Enem J., 2000. Effect of Reaction Time on the Yield of Biodiesel from Neem Seed Oil Abba

Omer, A.M., 2008. Energy, environment and sustainable development. *Renewable and Sustainable Energy Reviews*, 12(9), 2265-2300.

Pal, Krupal, "Investigations of transesterification of canola oil with methanol and ethanol for a new efficient method of biodiesel production" (2011). Electronic Thesis and Dissertation Repository. 325. https://ir.lib.uwo.ca/etd/325

Park, J., Wang, Z., Kim, D. & Lee, J., 2010. Effects of water on the esterification of free fatty acids by acid catalysts. *Renewable Energy,* 35(3), pp. 614-618.

Pinto, A. C. et al., 2005. Biodiesel: An Overview. *Journal of the Brazilian Chemical Society,* 16(6), pp. 1313-1330.

Qiu, P. et al., 2013. Application of Box-Behnken design with response sirface methodology for modeling and optimizing ultrasonic oxidation of arsenite with H2O2. *Central European Journal of Chemistry,* 12(2), pp. 164-172.

Rahimi, M., Aghel, B., Alitabar, M., Sepahvand, A. and Ghasempour, H., 2014. Optimization of biodiesel production from soybean oil in a microreactor. *Energy Conversion and Management*, 79, pp.599-605.

Rao, J. and Kumar, B., 2012. 3D Blade root shape optimization. *10th International Conference on Vibrations in Rotating Machinery*,.

Rashid, U. & Anwar, F., 2008. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel,* 87(3), pp. 265-273.

Sahoo, P. K., Das, L. M., Babu, M. K. G. & Naik, S. N., 2007. Biodiesel Development from High Acid Value Polanga Seed Oil and Performance Evaluation in a CI Engine. *Fuel,* Volume 86, pp. 448-454.

SAPIA. 2018. *SAPIA 2018 Annual Report*. [online] Available at: <https://www.sapia.org.za/Portals/0/Annual-Reports/SAPIA_AR%202018_FA.pdf> [Accessed 19 August 2020].

Sarin, A., 2000. *Biodiesel*. Royal Society of Chemistry

Sattanathan, R., 2015. Production of Biodiesel from Castor Oil with its Performance and Emission Test. International Journal of Science and Research, 4(1), pp. 273-279.

Saxena, P., Jawale, S. & Joshipura, M. H., 2013. A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Engineering,* Volume 51, pp. 395-402.

Sharma YC, Singh B., 2009. Development of biodiesel: Current scenario. Renewable and Sustainable Energy Reviews 13, 1646-1651.

Singh, S. P. & Singh, D., 2010. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews,* 14(1), pp. 200-216.

Siraj, S., 2017. Effects of Thermal, Physical, and Chemical Properties of Biodiesel and Diesel Blends. *American Journal of Mechanical and Industrial Engineering*, 2(1), p.24.

Slinn M.& Kendall K., 2009. *Developing the reaction kinetics for a biodiesel reactor.* Bioresource Technology. **100**: p. 2324-2327.

Speight, J., 2002. *Chemical and process design handbook.* s.l.:The McGraw-Hill Companies.

*Srivastava A.; Prasad R., Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews., 2000. **4**: p. 111-113.*

SRS Biodiesel. 2020. *Esterification - SRS Biodiesel*. [online] Available at: <http://www.srsbiodiesel.com/technologies/esterification/> [Accessed 11 November 2020].

*Stamenkovic O et al., 2008. Kinetics of sunflower oil methanolysis at low temperatures. Bioresource Technology. **99**: p. 1131-1140.*

*Stamenkovic´ O et al., 2007. The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil. Bioresource Technology. **98**: p. 2688-2699.*

Tareen IY, Wetzstein ME and Duffield JA., 2000. Biodiesel as a Substitute for Petroleum Diesel in a Stochastic Environment. *Journal of Agricultural and Applied Economics* 32(2): 373-381.

Tiwari, A. K., Kumar, A. & Raheman, H., 2007. Biodiesel production from jatropha oil (Jatropha curcas) with high free fatty acids: An optimized process. *Biomass and Bioenergy,* 31(8), pp. 569-575.

Van den Wall Bake JD, Junginger M, Faaij A, Poot T and Walter A., 2009. Explaining the Experience Curve: Cost Reductions of Brazilian Ethanol from Sugarcane. *Biomass and Bioenergy* 33: 644-658.

*Vicente G.; Martinez M.; Aracil J.; Esteban A., Kinetics of sunflower oil methanolysis. Ind. Eng. Chem. Res, 2005. **44**: p. 5447-5454.*

Wang, Y. et al., 2006. Comparison of Two Different Processes to Synthesize Biodiesel by Waste Cooking Oil. *Molecular Catalysis,* 252(1), pp. 107-112.

Wang, Y. et al., 2006. Comparison of Two Different Processes to Synthesize Biodiesel by Waste Cooking Oil. *Molecular Catalysis,* 252(1), pp. 107-112.

Wilson, S. C., Matthew, M., Austin, G. and von Blottnitz, H. 2005. *Review of the Status of Biodiesel Related Activities in South Africa.* Report for the City of Cape Town, South Africa, 76

Withers RV and Noordam M., 1996. *Biodiesel from Canola: An Economic Feasibility Analysis*. In: *Liquid Fuels and Industrial Products from Renewable Resources*, *Proceedings of the Third Liquid Fuel Conference, 15-17*

Yasin, M., Mamat, R., Yusop, A., Rahim, R., Aziz, A. and Shah, L., 2013. Fuel Physical Characteristics of Biodiesel Blend Fuels with Alcohol as Additives. *Procedia Engineering*, 53, pp.701-706.

You YD, Shie JL, Chang CY, Huang SH, Pai CY, Yu YH and Chang CH., 2008. *Economic Cost Analysis of Biodiesel Production: Case in Soybean Oil. Energy & Fuels 22: 182-189.*

Zabeti, M., Daud, W. M. A. W. & Aroua, M. K., 2009. Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology,* 90(6), pp. 770-777.

Zhang Y, Dubé MA, McLean DD and Kates M., 2003. Biodiesel Production from Waste Cooking Oil: 2. Economic Assessment and Sensitivity analysis. Bioresource Technology 90: 229-240.

Zhang, Y., Dube, M. A., McLean, D. D. & Kates, M., 2003. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology,* 89(1), pp. 1-16.

Zhang, Z. & Zheng, H., 2009. Optimization for decolorization of azo dye acid green 20 by ultrasound and H2O2 using response surface methodology. *Journal of Hazardous Materials,* 172(2-3), pp. 1388-1393.

APPENDIX A: SAMPLE CALCULATIONS

All sample calculations are shown with respect to Canola oil with respect to potassium hydroxide. The same method had been used for the sodium hydroxide catalyst.

Molar mass

According to a study conducted by Huaping, et al., (2006) the molar mass of a vegetable oil can be determined according to the following equation:

$$Molar\ mass\ = \frac{56.1 \times 1000 \times 3}{SV - AV}$$

Where SV represents the saponification value, and AV represents the acid value of the oil, both in units of $mg\ KOH/g$. The saponification value was determined according to the method suggested by Muhammad, et al. (2019). Initially, approximately four to five drops of phenolphthalein indicator was added to a mixture which consisted of 2g of oil and 25mL of a 0.1N ethanol and potassium hydroxide solution. The solution turned pink upon adding the indicator, which indicated a neutralisation of the acid in the solution. The solution was then titrated with a 0.5M hydrochloric acid solution until the pink colour disappeared, and this volume was recorded as the volume titrated. A blank titration of the ethanol and KOH solution was also done, and the saponification value was calculated according to the following equation (Muhammad, et al., 2019):

$$SV\ = \frac{56.1 \times 0.5 \times (V_b - V_t)}{m}$$

Where Vb is the volume titrated during the blank titration, Vt is the volume titrated and m is the mass of sample. The blank titration volume was 20.2 mL, while the volume titrated for canola oil was 6.48 mL. The calculation for the saponification value of canola oil is shown below:

$$SV_{Canola\ oil} = \frac{56.1 \times 0.5 \times (20.2 - 6.48)}{20} = 192.12 \frac{mg\ KOH}{g}$$

How the acid value was determined, can be seen in chapter 7. The sample calculation for canola oil is shown below:

$$Acid\ value\ = \frac{(0.97 - 0.5) \times 0.1 \times 56.1}{20} = 0.129 \frac{mg\ KOH}{g}$$

The molar mass of canola oil was therefore:

$$MM_{Canola\ oil} = \frac{56.1 \times 1000 \times 3}{(192.12 - 0.129)} = 876.6\ \frac{g}{mol}$$

Amount of alcohol required

200 mL of sunflower oil weighed 179.9g. The number of moles of sunflower oil was calculated as follows:

$$n_{oil} = \frac{mass}{Molar\ mass} = \frac{179.9}{876.5} = 0.2052\ mol$$

For an alcohol to oil molar ratio of 10, the amount of alcohol required is:

$$n_{alcohol} = 10 \times 0.2052 = 2.0525 mol$$

Ethanol has a molar mass of 46.07 g/mol. The mass of ethanol required is calculated as follows:

$$m_{alcohol} = 2.0525 \times 46.07 = 94.56\ g$$

Amount of catalyst required

For a catalyst loading of 0.02%, the mass of catalyst required is:

$$m_{catalyst} = 0.0002 \times 179.9 = 0.03598 g$$

Yield

The yield for experiment 1 of canola oil transesterification was calculated as follows:

$$Yield = \frac{mass\ of\ biodiesel\ produced}{mass\ of\ oil\ used} \times 100 = \frac{156.71}{179.9} \times 100 = 87.11\%$$

APPENDIX B: RAW DATA

Table B. 1: KOH biodiesel raw data

Run	Temperature (°C)	Catalyst loading (g)	Reaction time (min)	Alcohol ratio (g)	Run 1	Run 2	Run 3	Average yield
1	52	0.03598	30	170.1847	0.8652	0.8745	0.8737	0.8711
2	52	0.152915	75	170.1847	0.892	0.9125	0.9024	0.9023
3	30	0.152915	75	245.8223	0.9057	0.8825	0.9115	0.8999
4	52	0.152915	75	170.1847	0.9122	0.9055	0.8964	0.9047
5	52	0.03598	120	170.1847	0.9301	0.9225	0.9140	0.9221
6	52	0.152915	30	245.8223	0.8897	0.9128	0.9125	0.905
7	52	0.26985	120	170.1847	0.7612	0.7665	0.7995	0.7758
8	74	0.152915	75	94.54703	0.7635	0.7789	0.7722	0.7719
9	74	0.152915	75	245.8223	0.9459	0.9317	0.9658	0.9478
10	74	0.152915	120	170.1847	0.8596	0.8567	0.8520	0.8561
11	30	0.152915	75	94.54703	0.7915	0.8535	0.8291	0.8247
12	52	0.26985	75	245.8223	0.8755	0.8615	0.8611	0.8667
13	52	0.152915	30	94.54703	0.7440	0.7815	0.7581	0.7612
14	52	0.03598	75	94.54703	0.7589	0.7971	0.7795	0.7785
15	52	0.26985	75	94.54703	0.7512	0.7598	0.7558	0.7556
16	74	0.03598	75	170.1847	0.9001	0.8996	0.8838	0.8945
17	30	0.26985	75	170.1847	0.9057	0.8889	0.9050	0.8999
18	30	0.152915	30	170.1847	0.9479	0.9399	0.9494	0.9457
19	30	0.152915	120	170.1847	0.8910	0.9102	0.8992	0.9001
20	52	0.152915	120	94.54703	0.7995	0.7812	0.7929	0.7912
21	52	0.152915	120	245.8223	0.8915	0.9001	0.8961	0.8959
22	74	0.152915	30	170.1847	0.8965	0.8962	0.9017	0.8981
23	52	0.152915	75	170.1847	0.9227	0.9198	0.9212	0.9212
24	52	0.03598	75	245.8223	0.9302	0.9300	0.9305	0.9302
25	30	0.03598	75	170.1847	0.8987	0.8871	0.8767	0.8875
26	52	0.26985	30	170.1847	0.8413	0.8161	0.9404	0.8659
27	74	0.26985	75	170.1847	0.7399	0.7600	0.7505	0.7501

Table B. 2: NaOH biodiesel raw data

Run	Temperature (°C)	Catalyst loading (g)	Reaction time (min)	Alcohol ratio (g)	Run 1	Run 2	Run 3	Average yield
1	30	0.26985	75	170.184661	0.9556	0.9559	0.9555	0.9557
2	52	0.15292	75	170.184661	0.948	0.9478	0.9476	0.9478
3	52	0.26985	120	170.184661	0.7218	0.7212	0.7207	0.7212
4	52	0.03598	75	94.547034	0.7598	0.7594	0.7592	0.7595
5	30	0.15292	75	245.822288	0.893	0.8928	0.8924	0.8927
6	30	0.15292	120	170.184661	0.8952	0.8923	0.8928	0.8934
7	74	0.15292	120	170.184661	0.9021	0.8984	0.898	0.8995
8	52	0.15292	30	245.822288	0.9106	0.9101	0.9102	0.9102
9	52	0.26985	30	170.184661	0.8577	0.8575	0.8576	0.8576
10	74	0.03598	75	170.184661	0.958	0.9575	0.9578	0.9578
11	30	0.15292	30	170.184661	0.9318	0.9309	0.9308	0.9311
12	52	0.26985	75	245.822288	0.7906	0.7912	0.7918	0.7912
13	52	0.15292	120	94.547034	0.772	0.7706	0.7718	0.7715
14	52	0.03598	75	245.822288	0.951	0.9492	0.9501	0.9501
15	30	0.03598	75	170.184661	0.8906	0.889	0.8902	0.8899
16	74	0.26985	75	170.184661	0.7431	0.7591	0.7521	0.7514
17	52	0.15292	75	170.184661	0.9201	0.9205	0.9171	0.9192
18	52	0.26985	75	94.547034	0.7385	0.7359	0.7381	0.7375
19	74	0.15292	30	170.184661	0.875	0.8791	0.8761	0.8767
20	52	0.15292	75	170.184661	0.9522	0.9511	0.9512	0.9515
21	74	0.15292	75	94.547034	0.7178	0.7169	0.7184	0.7177
22	52	0.15292	30	94.547034	0.7424	0.7412	0.741	0.7415
23	74	0.15292	75	245.822288	0.9502	0.9501	0.9495	0.9499
24	52	0.15292	120	245.822288	0.9011	0.9012	0.9012	0.9012
25	52	0.03598	30	170.184661	0.9057	0.9055	0.9054	0.9055
26	52	0.03598	120	170.184661	0.9182	0.9172	0.9172	0.9175
27	30	0.15292	75	94.547034	0.7425	0.7413	0.7414	0.7417

Table B. 3: Acid value raw data

sample	Initial value (mL)			Final value (mL)			Difference (mL)			Average (mL)
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	
Blank	4.2	4.48	4.58	4.70	4.98	5.10	0.5	0.5	0.52	0.51
Canola oil	6.82	7.28	7.56	7.78	8.26	8.52	0.96	0.98	0.96	0.97
KOH biodiesel	7.98	8.20	8.54	9.12	9.46	9.78	1.14	1.26	1.24	1.21
NaOH biodiesel	0.80	4.02	7.20	1.88	5.12	8.32	1.08	1.10	1.12	1.1
KOH biodiesel BK10	12.20	11.90	12.26	13.88	13.38	13.50	1.50	1.48	1.24	1.41
KOH biodiesel BK20	14.28	15.84	16.72	15.92	17.34	18.18	1.64	1.50	1.46	1.53
NaOH biodiesel BK10	2.02	5.12	13.50	2.98	6.10	14.48	0.96	0.98	0.98	0.97
NaOH biodiesel BK20	2.98	6.10	14.48	3.85	7.00	15.38	0.87	0.90	0.90	0.89

APPENDIX C: PROPERTY TESTING EQUIPMENT

Figure C. 1: Schematic of pH meter used

Figure C. 2: Schematic of a refractometer (Sciencecompany.com, 2019).

Figure C. 3: Flash Point Apparatus

Figure C. 4: GC/MS

(a) (b)

Figure C. 5: Density Apparatus