A Study into Homogeneously and Heterogeneously Catalysed Transesterification of Waste Cooking Oil for the Production of Biodiesel

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This dissertation is submitted in fulfilment of the academic requirements of Master of Science in Chemical Engineering

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April 2024

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PREFACE

The research contained in this dissertation was completed by the candidate while based in the discipline of Chemical Engineering, School of Engineering of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College, Durban, South Africa. The research was financially funded by the University of Kwa-Zulu Natal: Strategic Funds and Fee Remission as well as supervisor's cost centre.

The contents of this work have not been submitted in any form to another university and, except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

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Signed: Prof Amir H. Mohammadi

Date: 3 May 2023

DECLARATION: PLAGIARISM

I, Keshav Rugnath, declare that

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Date: 3 May 2023

ACKNOWLEDGMENTS

Foremost, I would like to express my sincere gratitude to my supervisor, Prof Amir H. Mohammadi for his continuous support, guidance, expertise throughout the project, and financing my studies.

I want to thank Miss N Hadebe and Mrs T. Mofokeng for their guidance and continuous help.

Finally, I would like to thank my mother and late father, Sandhiya Rugnath and Ravin Rugnath, for always encouraging me to learn and grow, to develop my career and further my education. Without their support, I would not have been able to complete this project.

ABSTRACT

The ever-increasing population around the globe, along with the imbalances in food and fodder supply, the dwindling supply of fossil fuels, and the diminishing availability concerning natural resources have led to the emergence of significant energy challenges on a global scale. To address these issues, it is essential to pursue sustainably and economically viable growth, relying on domestic and renewable energy sources, to reduce the need for imported oil. An established renewable alternative to imported oil is biodiesel. For biodiesel to become market competitive with diesel, it is important to ensure the development of cost-effective processing schemes to optimize production. This research paper aims to determine whether heterogeneously and homogeneously transesterification of waste cooking oil can be used to produce biodiesel efficiently. The chosen homogeneous catalyst was Potassium Hydroxide, and the heterogeneous catalyst was Magnesium Oxide. The selected feedstocks were waste canola oil and ethanol. After a pre-treatment process, the acid value of the waste cooking oil was calculated to be 0.1167 mg KOH/g, indicating that a single step transesterification process can be used. The box-Behnken Design was utilised on Minitab Statistical Software to generate 27 different experiments using variations in the process variables. The process variables considered in this study were Catalyst Loading, Reaction Temperature, Reaction Time, and Alcohol to Oil Molar Ratio. The optimum yield for biodiesel produced from used canola oil utilising potassium hydroxide and magnesium oxide was 91.53% and 96.02%, respectively. From the various models explored, the full quadratic model most accurately fitted both experimental results with the KOH catalyst experimental data obtaining an R^2 value of 0.9575 and the MgO catalyst experimental data obtaining an R^2 value of 0.9710. Minitab calculated the optimal process variable conditions using the KOH catalyst to have a reaction temperature of 74 ^{o}C, a catalyst loading of 0.0673%, a total reaction time set at 84.55 minutes and an alcohol to oil molar ratio of 26:1. Minitab calculated the optimal process variable conditions using the MgO catalyst to have a reaction temperature at 54.41 ^{o}C, a catalyst loading of 1.44%, total reaction time set to be 120 minutes and alcohol to oil molar ratio to be 18.18:1. The kinematic viscosity was higher than the ASTM maximum limit of 6 mm^2/s for both the pure KOH and MgO Biodiesel samples at 8.29 mm^2/s and 15.24 mm^2/s, respectively. It was concluded that further modification would be required for direct use in an engine. The research for this study found KOH to be the most suitable catalyst for transesterification of waste cooking oil. This conclusion is drawn from the pure KOH biodiesel having a much lower viscosity than MgO biodiesel; KOH biodiesel also had a higher flash point than pure MgO biodiesel of 103.67 ^{o}C. The bio-jet fuel blends were not in accordance with many of the ASTM Standards. The acid values of the jet fuel blends (B10 and B20) from KOH and MgO samples were over the allowable limit set at 0.015 mg KOH/g oil. The pour point for Jet fuels should be approximately -47 ^{o}C. All the jet fuel blends (B10 and B20) exceeded the maximum limit. The critical success factors for biodiesel production in South Africa were determined.

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NOMENCLATURE

Symbol	Description
A	Temperature (°C)
AV	Acid value (mg KOH/g)
B	Catalyst loading (%)
BK	Biodiesel blend (%)
C	Reaction time (minutes)
C_0	Central points
D	Alcohol to oil molar ratio
Da	Impeller diameter (m)
K	Factors chosen
M	Concentration (M)
m	Mass (g)
mg KOH/g	Milligrams of KOH per gram of sample
MM	Molar mass (g/mol)
mm^2/s	Kinematic viscosity
N_s	Rotational speed of impeller (s^{-1})
N	Experiments
n	Number of moles (mol)
N_{Re}	Reynold’s number
°C	Temperature
Ppm	Parts per million (w/w)
R’	Short alkyl group
R”	Fatty acid chain
R^2	Coefficient of determination
RPM	Revolutions per minute
SV	Saponification value (mg KOH/g)
V_1	Volume (L)
x_i	Code values of transesterification variable
x_j	Code values of transesterification variable
β_0	Constant coefficient

β_i	Linear effect
β_{ii}	Square effect
β_{ij}	First-order interaction effect
ρ	Fluid density (kg/m^3)
$	Dollar
% wt.	Percentage based on weight
μ	Viscosity (Pa.s)

CHAPTER 1: Introduction

2.1) Background and Topic Motivation

Fossil fuels are derived from non-renewable resources and the combustion of these fuels makes up 98% of the world’s carbon emissions (Aransiola, 2012). Due to the great concern and the greatly diminishing supply of petroleum, many researchers have begun the search for renewable and limited toxicity biofuels (Hill et al., 2006). The ever-increasing demand for energy makes the utilisation of renewable fuels a well discussed topic (Kiss, Dimian, and Rothenburg, 2008). The renewable alternative fuel source needs to be economically feasible, readily available, and environmentally friendly, thus leading to biodiesel being widely publicised as an established alternative fuel. A new cause for escalation in the search for alternate fuel stems from the escalating conflict between Russia and Ukraine, raising the price of petrol greatly and is set to climb depending on further hostilities hence a need for alternative resources is greatly required (Bishop, 2022).

Multiple methods have been created using various feedstocks to produce biodiesel fuel. These methods are micro-emulsion, pyrolysis and transesterification. The most common production process for biodiesel is transesterification as this process results in greater yields and quality (Chilabade, 2018). During this process, a chemical reaction between a natural oil and an alcohol occurs. This reaction takes place with a catalyst producing glycerol and biodiesel as products (Mishra and Goswami, 2017). Biodiesel is produced from virgin vegetable oil, and because of this, there are ongoing research on these feedstocks competing with food source supplies. If this were to happen, virgin vegetable oil, which is the most common feedstock in biodiesel production, will significantly increase in price. These issues created the idea of utilising used cooking oil as a replacement for vegetable oil. Millions of people use vegetable oils to cook food and discard the waste oil afterwards. Waste cooking oil is substantially cheaper than fresh vegetable oils and eliminates the financial burden of paying to dispose the oil. Utilising waste cooking oil would also eliminate the need for farmlands required to grow a feedstock for producing biodiesel on a large scale (Talebian-Kiakalaieh, Amin and Mazaheri, 2013). All these challenges can be converted into environmental and economic advantages. Used vegetable oil and alcohols need to be investigated to maximise the return by optimising the process variables. The following parameters greatly influence the production of biodiesel: Free fatty acid (FFA) content, physical properties, oil to alcohol ratio, presence of water, catalyst loading, duration of reaction, temperature of reaction, and stirrer speeds (Motasemi and Ani, 2012). An investigation on which catalyst, homogeneous or heterogeneous, best suits this process needs to be conducted. The ability to use a substance that is typically discarded in homes worldwide as a source of production for biodiesel makes this feedstock a very favourable substitute for virgin cooking oil. Used vegetable oil removes the food vs. fuel issue surrounding biodiesel research. This in turn makes biodiesel a very suitable alternative for petro-diesel.

1.2) The purpose of this research work:

1.2.1) Aims of this research study:

- To determine whether heterogeneously and homogeneously catalysed transesterification of waste cooking oil can be used to produce biodiesel efficiently.

1.2.2) Objectives of this research study

- To investigate the effect of the chosen process parameters on the biodiesel product's production and quality.
- To determine whether the produced biodiesel and biodiesel blends (B10 and B20) are in accordance with ASTM Standards for biodiesel.
- To determine whether heterogeneously or homogeneously catalysed transesterification is most suitable for the chosen feedstock.

1.2.3) Tasks for this research study

- To conduct a basic superficial kinetic study from literature for transesterification reactions.
- To conduct a basic economic analysis from literature for biodiesel production determining the critical success factors of biodiesel production in South Africa
- To complete a detailed literature review in order to gain the necessary insight required to create a well-planned procedure to produce biodiesel from used cooking oil utilising both homogenous and heterogeneous catalysts.
- To propose a well-planned pre-treatment method for used cooking oil.
- To conduct experiments to find optimal process conditions to maximise the yield of biodiesel production through homogenously and heterogeneously catalysed transesterification reactions.

2.2) Thesis Breakdown

This thesis is made up of five different chapters. Every individual chapter discusses crucial aspects of the study. Below is a brief description of what each chapter entails.

Introduction: This chapter gives an introduction to the thesis. This chapter discusses the motivation and the background of the research topic. A detailed list of this study's aim, objectives, tasks, and purpose is provided.

Literature Review: This chapter gives the reader background information, clarity and understanding of the research topic. This chapter discusses various methods of producing biodiesel, different types of catalysts, various feedstocks, and property testing of biodiesel. A basic superficial feasibility study was completed on biodiesel production investigating the expense of producing biodiesel, cost of raw materials and factors affecting biodiesel production in Africa.

Materials, Equipment and Experimental Method: This chapter discusses the raw materials and chemicals used with details about the supplier and purity. This chapter discusses the reason for choosing the experimental apparatus and the various potential experimental design methods that could be used. The experimental method and design are discussed with the purpose of finding the optimal parameters to produce biodiesel.

Discussion and Results: Detailed discussion explaining the ANOVA Analysis, interactions between process variables, and each process parameter's effect on the transesterification reaction. This chapter also discusses the results of the property testing methods used. A series of simple property tests were completed on the pure biodiesel created from the optimal process variable conditions and the bio-jet fuel blends (B10 and B20). GC-MS analysis was also conducted in this chapter.

Conclusion and Recommendations: Detailed conclusions on the thesis and recommendations for future studies are given.

CHAPTER 2: Literature Review

2.1) Historical Background of Biodiesel

In 1893, an original compression-ignited diesel engine was created with the hands of a German engineer, Rudolph Diesel. Well known for its reliability, power, and high fuel economy worldwide, Rudolph Diesel believed in the possibility that vegetable oil could be utilised to power diesel engines for agriculture (Jääskeläinen, 2019). At the World's fair in Paris in 1900, a peanut oil-fuelled diesel engine was displayed by the French Otto Company (Knothe, Krahl and Gerpen, 2015). Years later, India began researching vegetable oil conversion into diesel to overcome the fuel shortages caused by World War II. The growing attention placed on vegetable oil diesel was stopped after a reduction in the prices of petrol diesel was reported in that period (Singh and Walia, 2016). In 1937, the earliest documented biodiesel generation was patented by a Belgian Scientist named George Chavanne (Knothe, Krahl and Gerpen, 2015).

Biodiesel is seen as a highly promising substitute to fossil fuels as ever-increasing attention is placed on the environmental repercussions of petroleum diesel and the limited supply of petroleum resources. Biodiesel, also known as mono alkyl ether, started to be produced on a large scale in the 1990s and has since increased in production significantly. In parts of Europe, biodiesel was publicized as an opportunity to stop the decline of rural areas and increase energy levels (Mishra and Goswami, 2017). After 2001, biodiesel grew in popularity because of the increased awareness of energy security and the extremely high foreign oil prices (Singh and Walia, 2016). One method to produce biodiesel is through the transesterification process. The transesterification process chemically combines a natural oil of edible or non-edible origin, or animal fat with an alcohol, utilising a catalyst to produce biodiesel (Mishra and Goswami, 2017).

2.2) Dilution/Blending

The usage of vegetable oil and biodiesel directly has been deemed ineffective and unfeasible for diesel engines. This is due to their high viscosities, higher pour points, lower calorific values, and lower volatilities. Direct use may lead to corrosion of components and increased polymerization of sump oil resulting in the need to change the oil more often in the engine. Therefore, for the above reasons it is accepted that blends of diesel with roughly 10-20% vegetable oil could be utilised exempt from any modifications in engines (Rakopoulos et al., 2006). The fuel injection systems from newer engines are very vulnerable to fuel viscosity fluctuations. Due to the viscosity of vegetable oils being much higher than diesel, usage could cause poor fuel atomization, causing poor combustion, injector coking, deposits, and injector pump failure. Therefore, fuel modification techniques such as pyrolysis, micro-emulsion and transesterification are designed to lower the viscosity to eliminate flow and atomization related issues (Krishna, Bandewar and Dongare, 2014). Polymerisation occurring during storage and combustion can also result in challenges (Srivastava et al., 2018).

2.3) Biodiesel Production Processes

The feedstocks of biodiesel are broken down into four major groupings: Edible and non-edible virgin vegetable oil, used oil, and animal fat. With advancements in technology, various methods have been created to utilise these feedstocks in order to produce a fuel that diesel engines can utilise. These methods are: Pyrolysis, Micro-emulsion, and Transesterification.

2.3.1) Micro-emulsification

Microemulsions optically transparent, thermodynamically stable isotropic solutions are made from water and oil that have been successfully formulated by a blend of surfactant and cosurfactant (Sapra et al., 2013). A surfactant is a compound that decreases the surface tension of the liquid (Aga, 2018). The process revolves around a mixture of two immiscible liquids such as water and oil, which is stabilised by an emulsifier (Kapadia et al., 2019). Biodiesel micro-emulsions consist of components that include vegetable oil, diesel fuel, alcohol, a surfactant and potentially a cetane improver in appropriate proportions. Short chained alcohols are used frequently as additives to reduce the viscosity. Longer chained alcohols are used frequently as surfactants (Gashaw and Teshita, 2014). Disadvantages of microemulsion are greater viscosity, lower volatility, and lower stability. Due to these disadvantages, treatment methods are needed to decrease the viscosity and free fatty acid content before the biodiesel production process (Neupane, 2022).

2.3.2) Pyrolysis

Converting pure vegetable oils by pyrolysis reactions are a favourable substitute to create biodiesel. Pyrolysis is a process that transforms biomass into solid charcoal (biochar), biodiesel and gaseous products such as syngas. The thermal-decomposition process is completed without oxygen present (Callegari, Hlavinek and Capodaglio, 2018). Numerous vegetable oils can be used in this process and each oil produces considerable variations in the oil due to its compositions. High temperatures result in more breaking reactions to occur, which cause liquid and char to turn into gas. Therefore, the temperatures for biomass pyrolysis should be between

400-550 °C for optimal liquid yield (Junsittiwate, Srinophakun and Sukpancharoen, 2022). Pyrolysis could also take place utilising a catalyst, as this will cause bonds to break and produce multiple types of small molecules. The char is dependent on the rate of pyrolysis (Gebremariam and Marchetti, 2017). As a fuel, bio-oil has various unfavourable properties including corrosive organic acids, poor heating value due to water content, thermally unstable components that can form gum, and phase instability (Virginia Tech Intellectual Properties Inc, 2015). Besides the solid char being fuel, it can also be utilized as a filter medium, activated carbon, oil adsorbent, and fertilizer. The gas by-product created can be useful for crops, water pumps and boilers (Mohammad, Shaibu-Imodagbe and Okuofu, 2012). Pyrolysis has several advantages over transesterification, such as reduced processing cost, lower fuel and engine standards, and a wider range of choices for feedstock (Taufiqurrahmi and Bhatia, 2011). Pyrolysis requires the use of costly equipment for distillation, and this makes the overall cost quite high (Gebremariam and Marchetti, 2017). Other disadvantages of pyrolysis are high temperatures and low purity caused by the intolerable amounts of clinker and carbon residue (Neupane, 2022).

2.3.3) Transesterification Process

The overall transesterification reaction, alternatively identified as Alcoholysis, is displayed in Figure *4-1*. This is a process where triglycerides undergo a reaction alongside an alcohol in order to form glycerol and biodiesel as the final product. This reaction takes place with a catalyst and consists of three reversible and consecutive reactions. The initial reaction results in triglycerides converting into diglycerides and an ester, followed by a second reaction where diglycerides convert into monoglycerides and an ester. Finally, it is followed by the third reaction, where monoglycerides are converted into an ester and glycerol. An ester molecule is produced from the three reactions compared to a single glycerol molecule from the final reaction (Demirbas et al., 2016).

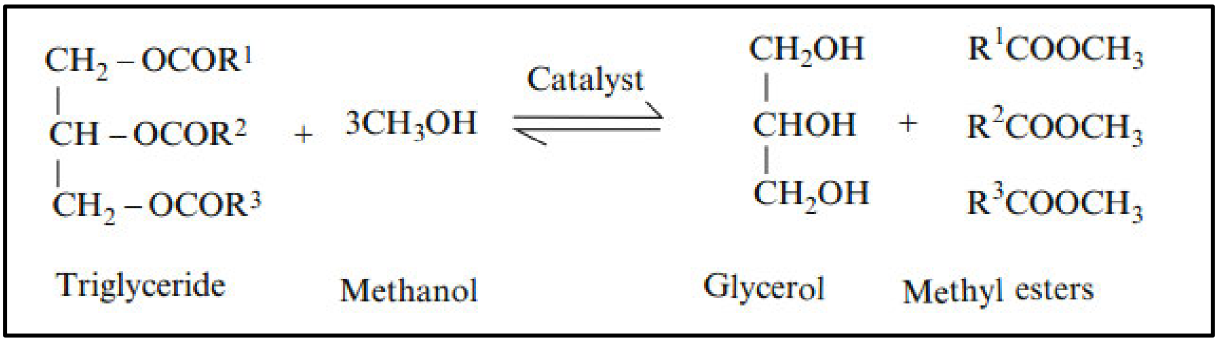


Figure 4-1: Overall chemical reaction for transesterification of triglycerides. (Gebremariam and Marchetti, 2017).

Short Chained alcohols are used frequently in the transesterification process such as ethanol and methanol but other alcohols in particular butanol, propanol, and amyl alcohol have also been used (Narwal and Gupta, 2012). Methanol/Ethanol and oil are immiscible, and therefore the reaction would contain two separate liquid phases (Demirbas et al., 2016). Due to the reversibility of the reaction and the immiscibility existing between alcohol and oil, catalysts namely Potassium Hydroxide (KOH) or Sodium Hydroxide (NaOH) and greater alcohol-to-oil molar ratios are employed in order to maximise biodiesel production. Reaction time for biodiesel production varies from 30-120 minutes and the catalyst concentration varies from 0.1-2%. The variations are caused by the level of free fatty acid (FFA) content of the oil and the degree of unsaturation present in the fatty acid molecules. Catalysts for this process are classified as alkaline homogenous, acid homogenous, enzymatic, alkaline heterogeneous and acid heterogeneous (Rabu, Janajreh and Ghenai, 2012).

Transesterification is the most used and is considered the most convenient method of the four discussed biodiesel production processes. Transesterification is seen as the most promising method as it greatly decreases the viscosity of triglycerides without adversely impacting the volumetric heating value while also producing high cetane numbers and flash points. This widely used process produces fatty acid methyl ethers that can be viewed as a potential replacement for diesel engines if the need arises (Fukuda, Kondo and Noda, 2001).

2.3.3.1) Transesterification from homogeneous acid catalysts

Specific feedstock such as low-quality oils contain triglycerides with relatively high free fatty acid content (FFA). Alkaline based catalysts are not suited for these feedstocks, as during the transesterification reaction process, saponification reactions also occur and lead to the formation of soap. Therefore, acid-based catalysts are more appropriate for these feedstocks as saponification can be avoided (Dalai, Issariyakul and Baroi, 2012). Acids frequently used in this process are phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and hydrochloric acid (HCL). During this process, two types of reactions take place: Transesterification reaction and esterification reaction. The esterification reaction is where free fatty acids (FFA) react with an alcohol such as methanol to create methyl ester products. Unlike the transesterification process, 1 mol of FFA reacts with 1 mol of methanol in order to create 1 mol of methyl ester. An important consideration for this process is that hydrolysis is the reverse reaction, where water and methyl ester react to create free fatty acids (FFA) (Dalai, Issariyakul and Baroi, 2012).

Homogeneous acid catalysts are not used in the industry as often as alkaline catalysts. This is due to the harsher reaction process conditions such as high pressure and temperature, catalyst corrosion, greater alcohol to oil molar ratio, and longer duration of reaction times (Linganiso et al., 2022). An area for concern when using acid-based catalysts is that it is crucial to maintain a water content below 0.5 weight %. Acid based catalysts are sensitive to water and become deactivated if large amounts of water exist in the oil. The effect water has on acid catalysed transesterification is far more severe than when compared with alkaline catalysed transesterification, as excess amounts of water result in the reverse reaction becoming favoured (Dalai, Issariyakul and Baroi, 2012).

Figure *4-2* below shows the homogeneous acid catalysed reaction for the transesterification of triglycerides. Step 1 shows the protonation in the carbonyl group caused by the acid catalyst. Step 2 shows the nucleophilic attack of the alcohol, thus forming a tetrahedral intermediate. Step 3 occurs twice; this step is the proton migration and breakage of the intermediate (Bohlouli and Mahdavian, 2019).

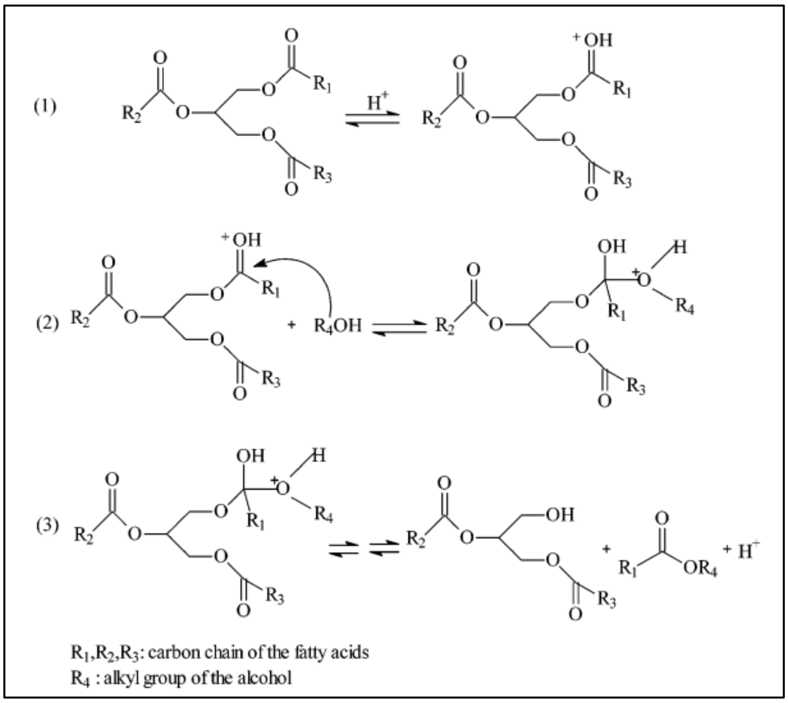


Figure 4-2: The Reaction Mechanism for Homogeneous Acid Catalysed Transesterification Reaction (Bohlouli and Mahdavian, 2019).

2.3.3.2) Transesterification from homogeneous alkaline catalyst

The most common type of catalyst used to produce biodiesel is homogeneous alkaline catalysts. This is because a transesterification reaction utilising an acid catalyst is significantly more sluggish than the base catalysed reactions. The majority of alkaline catalysts utilised are sodium hydroxide (NaOH), potassium hydroxide (KOH), and sodium methoxide ($NaOCH_3$). Despite the fact that homogeneous alkaline catalysed biodiesel production processes are relatively fast and display good conversions with limited side reactions, this process is not cost competitive with conventional diesel. One major disadvantage of this process is that the used catalyst is unable to be recovered and therefore needs to be neutralized once the process is complete. The alkaline catalysts used during this process, usually KOH and NaOH, are neutralized with phosphoric acid, and the salts produced form large amounts of unwanted waste chemicals (Narasimharao, Lee and Wilson, 2007).

For this process, alkaline metal alkoxides have been determined as the better catalyst when compared to hydroxides, as these catalysts do not produce any water. If water is produced, it results in hydrolysis where free fatty acids (FFA) are formed, thereby increasing the acid value (Dalai, Issariyakul and Baroi, 2012). The effect free fatty acid (FFA) content has on the homogeneous base catalysed transesterification reaction is a major disadvantage. If the vegetable oil chosen has a high level of FFA content, a side reaction takes place with the catalyst and FFA to produce soap. This results in contamination decreasing the yield of biodiesel produced. When refined vegetable oil is utilised, which has extremely low free fatty acids (FFA), to create biodiesel, homogeneous alkaline catalysts are favoured because of their higher reaction rate and shorter duration of reaction time (Zulqarnain et al., 2021).

Figure *4-3* below shows the homogeneous alkaline catalysed reaction mechanism for transesterification of triglycerides. Step 1 shows the creation of active species, RO^-. Step 2 shows the nucleophilic attack of the RO^- on a carbonyl group of triglycerides, forming a tetrahedral intermediate. Step 3 displays the breakage of the intermediate. Step 4 occurs twice, this step deals with the restoration of the RO^- active species (Bohlouli and Mahdavian, 2019).

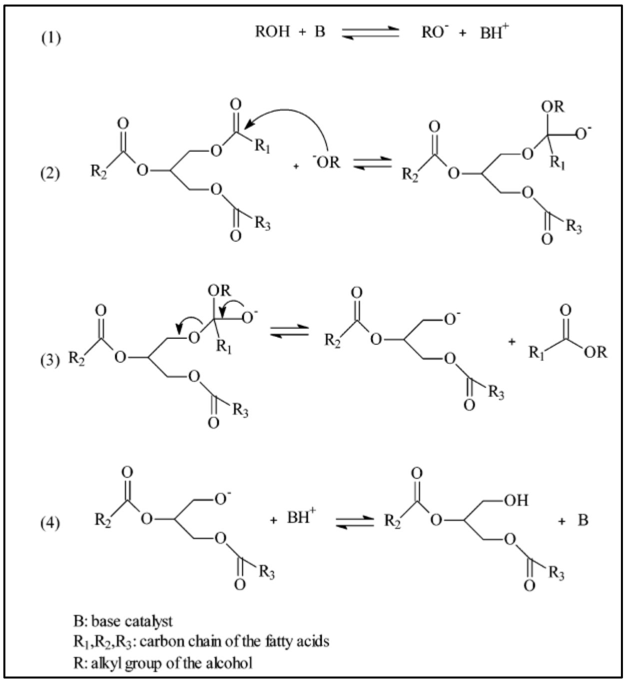


Figure 4-3: Reaction Mechanism for homogeneous base catalysed transesterification reaction (Bohlouli and Mahdavian, 2019).

2.3.3.3) Transesterification from heterogeneous alkaline catalyst

During heterogeneous transesterification, a reaction takes place with glyceride and an alcohol with a heterogeneous catalyst present producing fatty acid alkyl esters and glycerol. Common heterogeneous catalysts are magnesium oxide (MgO) and calcium oxide (CaO). Heterogeneous catalyst transesterification can be viewed as more cost-effective since the catalyst is recycled and used again; the reaction time required is short; no side reaction such as hydrolysis can occur; and washing with distilled water is not needed (Elgharbawy et al., 2021). From a previous study by Dalai, Issariyakul and Baroi (2012), it was discovered that the active species of many of the heterogeneous alkaline catalysts present, seep out into the reaction, thereby reducing the selectivity for the transesterification process, and forming soap with any free fatty acids (FFA) present. It was also concluded that the heterogeneous base alkaline catalysts lose the ability to be reusable (Dalai, Issariyakul and Baroi, 2012).

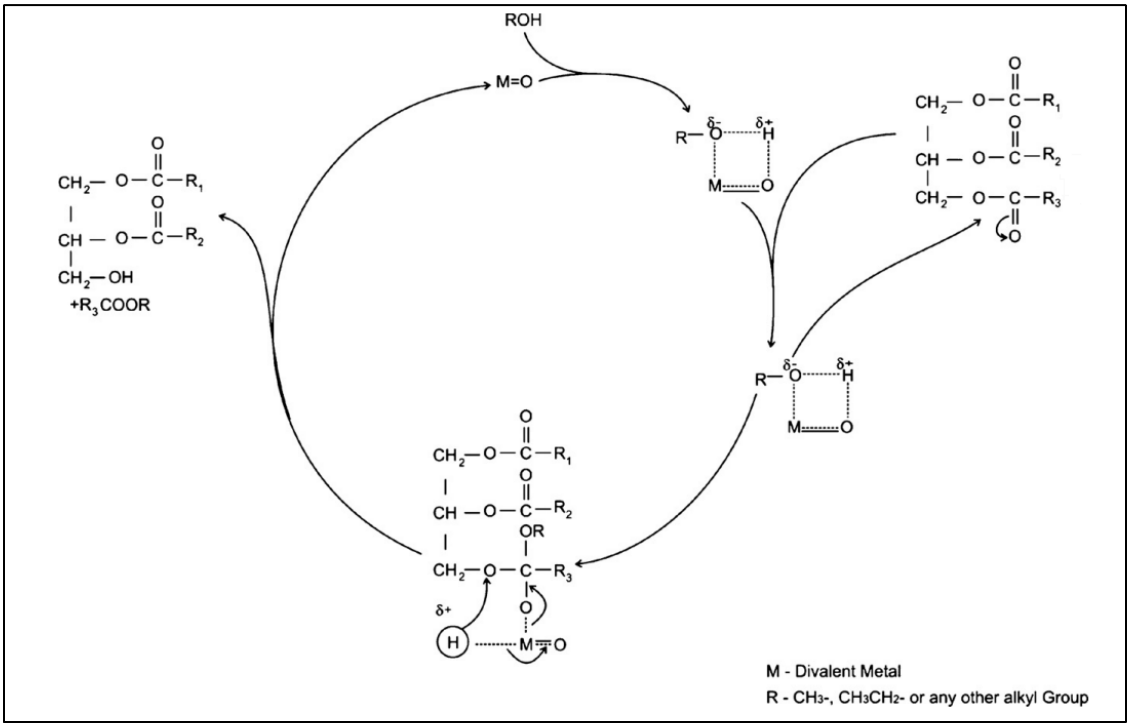


Figure 4-4: Reaction Mechanism for heterogeneously base catalysed transesterification reaction (Bohlouli and Mahdavian, 2019).

2.3.3.4) Transesterification from heterogeneous acid catalyst

Some common examples of heterogeneous acid catalysts are zeolite, pure oxide, or altered transition metals. Heterogeneous acid catalysts are much more environmentally friendly and stable when compared with homogeneous acid catalysts. These catalysts should have moderate acidity, numerous active sites, and porosity to reduce diffusional issues. These catalysts are used for their reusability, conversion, and easy separation. The disadvantages of using heterogeneous acid catalysts are the greater temperatures and longer duration of reaction times. Figure *4-5* below displays the transesterification reaction of soybean oil (Bohlouli and Mahdavian, 2019). Heterogeneous acid catalysts are unaffected by high free fatty acid content and the presence of water. This allows for cheaper, low-quality feedstock that does not require pre-treatment processes for biodiesel production. These catalysts help improve the biodiesel process’s economic feasibility by allowing production with feedstock such as animal fats and used cooking oils (Mandari and Devarai, 2021).

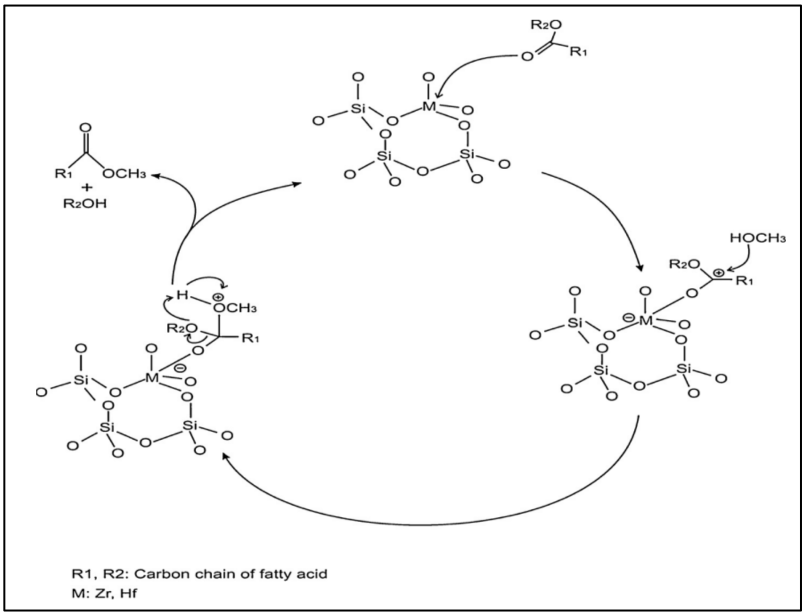


Figure 4-5: Reaction Mechanism for heterogeneously acid catalysed transesterification reaction (Bohlouli and Mahdavian, 2019).

2.3.3.5) Saponification and Hydrolysis Reaction

Homogeneous catalysts such as alkaline hydroxides (KOH and NaOH) can potentially generate soap (Chanakaewsomboon et al., 2020). The saponification reaction will take place during transesterification, where the feedstock has elevated levels of free fatty acid content. This reaction leads to the production of soap and a reduction in biodiesel quality (Reda, 2014). Equation 2.1 below shows the reaction with sodium hydroxide catalyst.

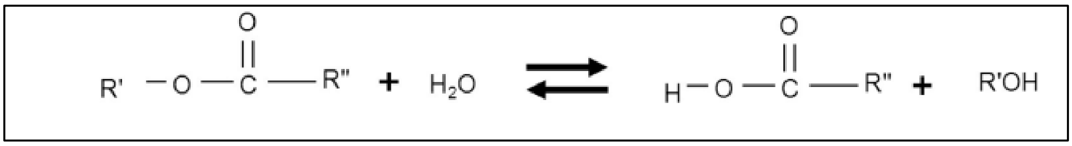
Saponification Reaction (Pullen and Saeed, 2015)

$$R'' - COOH + NaOH \leftrightarrow R'' - COONa + H_2O \tag{2.1}$$

$$\text{where R}'' = \text{ fatty acid chain}$$

The definition of saponification value (SV) is, “the number of saponifiable units (acyl groups) per unit weight of oil.” Low saponification value demonstrates a lower proportion of low molecular weight fatty acids. This value is used to estimate the average molecular weight of an oil (Ismail and Ali, 2015). The saponification value is calculated using ASTM Standards D5558. The SV is determined by adding 2 grams of vegetable oil to a potassium hydroxide solution with a phenolphthalein indicator. This prepared solution is now titrated against 0.5 N hydrochloric acid. Endpoint is reached when the pink colour disappears. A blank solution is also prepared and titrated (Aworanti et al., 2019).

It can be noted that the existence of high traces of moisture in the feedstock can give rise to a high rate of hydrolysis of triglycerides and Fatty Acid Methyl Esters (FAME). These feedstocks include lower quality feedstocks namely animal fats and used cooking oils (Chanakaewsomboon et al., 2020). Figure *4-6* below shows that if moisture is present in the system during the transesterification process, the water undergoes a reaction with triglyceride to produce diglyceride and fatty acid. The new fatty acid will undergo a reaction with the homogenous alkaline catalyst (KOH or NaOH) to produce more soap and water. The existence of saponification and hydrolysis reactions cannot be ignored as these reactions are essential to optimising the biodiesel experimental procedure.



$$R'-O-\overset{\overset{\displaystyle O}{||}}{C}-R'' + H_2O \rightleftharpoons H-O-\overset{\overset{\displaystyle O}{||}}{C}-R'' + R'OH$$

$$\text{where } \mathrm{R}'' = \text{fatty acid chain}, \mathrm{R}' = \text{short alkyl group}$$

Figure 4-6: Hydrolysis Reaction of Triglyceride with water (Pullen and Saeed, 2015).

2.4) Kinetic Study

The development of kinetic models are power tools for reactor design as these models enable the production of higher value products. The kinetic model is vital for optimisation of the design process including the heating and separation phase. Kinetic models aid in determining the most desirable reaction process conditions (reaction temperature, mixing speed, alcohol to oil ratio) to maximise the desired products and use of resources (Trejo-Zárraga et al., 2018). Multiple kinetic models have been studied and predictions have been made on feedstock, such as work for waste-based resources by Hazrat et al. (2022b), a study of zanthoxylum bungeanum seed oil (ZSO) by Zhang et al. (2020), a study of palm oil by Darnoko and Cheryan (2000), and a study of sunflower oil by Berrios et al. (2007). After conducting research, it was noted that there was an inability to find research on the kinetic study of producing biodiesel with the feedstocks chosen from this thesis. Kinetic Studies that utilised other vegetable oils as a feedstock generated kinetic models that were not applicable to this process.

The transesterification process displays a sigmoidal curve for the production of glycerol and methyl esters versus reaction time. The sigmoidal curve can be broken into three regions (Noureddini and Zhu, 1997). Figure *4-7* shows an example of this curve (Chowdhury et al., 2017). The three regions are as follows:

1. The early stages of the reaction are slow, and this is known as the mass transfer controlled region.
2. After the early period, a fast kinetically controlled region follows.
3. Completion of the reaction is slow, which is the equilibrium region.

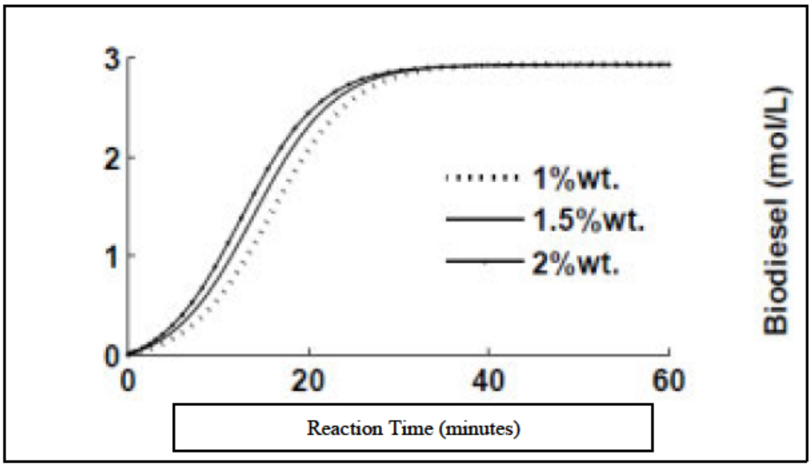


Figure 4-7: Sigmoidal curve displayed by the Transesterification Reaction at varying catalyst concentrations (%wt.) (Chowdhury et al., 2017).

Understanding the reaction mechanism of the transesterification reaction is very important as this helps estimate the kinetics of the chemical process. An important consideration to a kinetic model is the formation of glycerine, even though this complicates the kinetics (Pal, 2011). During the transesterification reaction high amounts of alcohol are consumed resulting in the rate of reaction being pseudo-forward (Hazrat et al., 2022a). According to a study by Andreo-Martinez et al. (2018), it was determined that the reaction rate could be pseudo-second order, pseudo-first order or pseudo-zero order.

For homogeneously catalysed transesterification reactions, the biodiesel production industry has developed methods to reduce the formation of soap such as utilising refined oils and methoxides. Therefore, the consideration of saponification reactions when developing the kinetic model can be ignored. A large majority of kinetic studies ignore the mass transfer controlling region. This is done to simplify the kinetic model in order to avoid complex computation of kinetic constants (Pal, 2011).

2.4.1) Process variables and their effect on the kinetic model

2.4.1.1) Stirrer Speed

According to Zheng et al. (2008), mixing speed has a significant contribution in determining the most desirable completion of the transesterification process. It is noted this process is mass transfer limited in the early stages of the reaction since both feedstocks are immiscible and at the separation phase when the glycerol combines with the catalyst. An investigation performed by Kafuku et al. (2010) noted the biodiesel production increased with every increase in stirrer speed till the highest level where production stabilized.

A comparative investigation performed by Roy et al. (2014) looked into the three stirring speeds, e.g., 300, 600 and 900 rpm for the reaction system while keeping the temperature of the reaction and alcohol to oil molar ratio constant to find the optimal stirrer speed. It was noted that at a stirrer speed set at 300 rpm, the concentration of biodiesel was low within the chosen reaction duration because of mass transfer limitations. Increasing the stirrer speed to 900 rpm initially increased biodiesel production, however, after 20.56 minutes, the concentration of biodiesel started to decline and dropped with time. This effect was caused by the stirrer speed affecting the volatility of the alcohol leading to the vaporisation of alcohol from the system. This not only reduced the amount of reactant in the system but also affected the correct alcohol to oil ratio. The investigation concluded that the 300 rpm and 900 rpm stirrer speeds led to undesirable outcomes. The stirrer speed set at 600 rpm led to the discovery of the highest yield of biodiesel produced at 24.73 minutes and increasing reaction time after led to a decrease in yield. It was concluded that the suitable stirrer speed was 600 rpm, and the reaction process required a controlled approach to reach optimum completion in the transesterification process (Roy et al., 2014).

A variation of stirrer speed in the transesterification reaction can change the kinetics. A good understanding of how the mixing intensity affects the kinetics is extremely useful for scale up designs. The intensity of mixing can be found with the Reynold’s number. The dimensionless number N_{Re} is defined in fluid dynamics as “the ratio of inertial forces to viscous forces.”

$$N_{Re} = \frac{ns \times Da^2}{\mu} \rho \qquad (2.2)$$

$$Where\ ns = Rotational\ speed\ of\ impeller\ (s^{-1})\ ; D_a = impeller\ diameter\ (m)$$

$$Where\ \rho = Fluid\ Density\ \left(\frac{kg}{m^3}\right)\ ;\ \mu = viscosity\ (Pa.s)$$

According to a study by Noureddini and Zhu (1997), the Reynold’s Number was investigated on transesterification reactions. The chosen rotational speeds for this study were 150, 300 and 600 rpm. The study concluded that for higher mixing intensities, the mass transfer regime was shorter. It also concluded that a reduction in viscosity was found when the Reynold’s number was increased (Noureddini and Zhu, 1997).

2.4.1.2) Temperature of Reaction

The temperature of the reaction is a very crucial process parameter in the production of biodiesel and in developing the kinetic model for the transesterification reaction. An investigation performed by Darnoko and Cheryan (2000) investigated how temperature affected palm oil transesterification with a KOH catalyst concentration set at 1% and alcohol to oil molar ratio chosen to be 6:1. Palm oil has a semisolid nature at room temperature, therefore the lowest temperature used in this study was 50 ^{o}C. The maximum temperature investigated in this study was 65 ^{o}C due to methanol having a boiling point of 68 ^{o}C. The rise of biodiesel concentration with raising the reaction temperature was small. The rate of transesterification increased up to 60 ^{o}C. Higher temperatures did not decrease the time it took for maximum conversion (Darnoko and Cheryan, 2000).

The temperature of a reaction can reduce the viscosity of the reactants and products and can increase mass transfer. At elevated reaction temperatures, the saponification rate is greater, resulting in a decrease in the yield of biodiesel produced (Trejo-Zárraga et al., 2018). Depending on the choice of alcohol, the temperature of the reaction is commonly chosen to be lower than the boiling point of that alcohol (Leung et al., 2010). A study by Krishnan and Dass (2012) investigated transesterification reactions with varying temperatures of 50 ^{o}C to 65 ^{o}C. The optimum temperature of biodiesel production was 60 ^{o}C. Increasing the temperature after 60 ^{o}C decreased the concentration of triglyceride, diglyceride and monoglyceride and increased the concentration of glycerol. Therefore, the rise in temperature above the optimal temperature of the reaction decreased the yield of biodiesel (Krishnan and Dass, 2012).

An investigation performed by Chowdhury et al. (2017), observed how reaction temperature affected the process. Again, a rise in reaction temperature resulted in the rate of production to increase as well. However, when the reaction temperature reached 50 ^{o}C or higher, even though the initial reaction conversion rate was higher, the overall biodiesel production was lower when compared to lower temperatures. This could have been caused by saponification due to the alkali catalyst since saponification is enhanced at temperatures of 50 ^{o}C or above (Chowdhury et al., 2017).

An investigation performed by Kadi et al. (2019), observed how reaction temperature affected the transesterification reaction of rapeseed oil with KOH homogeneous catalyst. The temperatures investigated were chosen to be 25 ^{o}C, 35 ^{o}C, 45 ^{o}C, 55 ^{o}C, and 65 ^{o}C, stirring speed of 600 rpm and 1 wt% KOH. The optimal yield was found to be 99.9% at a temperature of reaction of 65 ^{o}C. Temperature had a direct impact on the Arrhenius law rate constants. It was concluded that as the reaction temperature increased, the rate of biodiesel production increased (Kadi et al., 2019).

An investigation conducted by Stamenković et al. (2008) investigated low temperatures (10 ^{o}C, 20 ^{o}C and 30 ^{o}C) during the transesterification of sunflower oil using KOH catalyst. The alcohol to oil molar ratio was chosen to be 6:1 and the catalyst concentration was set to be 1% wt. During this study, lower temperatures had a slow reaction during the start of the reaction, and this was caused by poor mass transfer between the reactants due to the poor interfacial area. The initial size of the drop of methanol decreased massively during the reaction process. It was noted that increasing the temperature of the reaction resulted in a rise in the rate of reduction for the drop size. It could be possible that the reduction in drop size could be caused by the formation of monoglycerides, diglycerides or soap which are produced faster at higher temperatures. It is shown the kinetic behaviour of these various systems have different reaction temperatures; therefore, each case should be considered individually. Thus concluding that the temperature of the reaction has an important impact on the reaction kinetics.

An investigation performed by Lukić et al. (2013), discussed the transesterification of sunflower and waste cooking oil using heterogeneous catalyst CaOZnO. It was found that at low temperatures of 60-70 ^{o}C, there was a resistance to mass transfer during the start of the reaction, however the resistance to mass transfer reduces as the presence of methyl esters increases. Triglyceride places a mass transfer limitation on the rate process but increasing biodiesel concentration changes the rate limiting step to the chemical reaction. At higher temperatures of 84-96 ^{o}C, it was concluded the effects of mass transfer were almost negligible, therefore the chemical reaction controlled the conversion rate. The study showed the kinetic model as pseudo-first order (Lukić et al., 2013). It can therefore be concluded that the reaction temperature greatly affects the kinetics and equilibrium of the transesterification reaction.

2.4.1.3) Alcohol to Oil Molar Ratio

The alcohol to oil molar ratio is one of the most significant variables which massively affects the triglyceride conversion efficiency, the yield of final biodiesel produced, and the overall production costs. Referring to Figure *4-1*, the stoichiometric ratio of 3:1 can be seen for alcohol to oil for the transesterification process, however greater ratios are required to reach optimal biodiesel yield. The higher molar ratios allow for improved miscibility and increased contact time between the alcohol molecule and triglyceride. The reaction is reversible, and excess alcohol would cause a shift towards the forward reaction, following Le Chatelier’s Principle (Musa, 2016).

Under certain circumstances, a greater alcohol to oil molar ratio results in better alkyl ester conversion in a reduced period, thus increasing the amount of biodiesel. That statement is only correct until the optimum alcohol to oil molar ratio is reached, after which further increase pass this optimum ratio, decreases the alkyl ester conversion, and decreases the yield of biodiesel. A review by Paul and Adewale (2018) found that the optimal methanol to oil ratio to produce biodiesel from avocado oil is 6:1. A review by Musa (2016) concluded that the presence of alcohol influences the quality of fuel produced. Properties that are affected by the amount of alcohol present in the system are density, viscosity, and flash point (Musa, 2016).

A study conducted by Krishnan and Dass (2012), investigated the impact molar ratio had on waste palm oil transesterification. According to stoichiometric coefficients, the molar ratio required was 3:1. This experiment investigated the effects of molar ratios from 4:1 to 9:1. It was found that 4:1 was the optimal molar ratio for alcohol to oil and any increase in ratio (5:1 to 9:1) caused a decrease in biodiesel production and a further increase in the cost of methanol feedstock. An increase in molar ratio did cause a change in the concentration of monoglycerides, diglycerides and triglycerides (Krishnan and Dass, 2012). According to a study by Kadi et al. (2019), an investigation was carried out on the impact of molar ratio on transesterification. It concluded that by raising the alcohol to oil ratio higher than a ratio set at 6:1, the increase in yield is insignificant. Doubling the ratio to 12:1 only increases the yield by 0.14%. Increasing the molar ratio also makes the separation of methyl ester and glycerine difficult (Kadi et al., 2019).

An investigation performed by Freedman et al. (1986), studied the effect alcohol to oil molar ratio on the transesterification of soy oil using a molar ratio of 6:1 and 30:1. The alcohols of choice were butanol and methanol. It was concluded that a 6:1 alcohol to oil ratio obtained a second order rate of reaction while a 6:1 butanol to oil ratio obtained a fourth order rate of reaction. For alcohol to oil ratios 10:1 and greater, it was concluded that a pseudo first order reaction rate would be seen. Therefore, molar ratios of 30:1 for both methanol and butanol observed a pseudo first order rate of reaction (Freedman et al., 1986). According to the study by Hazrat et al. (2022a), the kinetic conversion of triglyceride into FAME for a pseudo-first order reaction rate is shown in equation 2.3.

$$\ln(1-x) = -k_1 t \tag{2.3}$$

Where x is the fractional conversion entity of FAME and k_1 is the reaction rate constant. Using experimental data, a graphical representation can be used to estimate the reaction constant k_1 (Hazrat et al., 2022a). It can be concluded that alcohol to oil molar ratios higher than the stoichiometric ratio of 3:1 is required to drive the forward reaction. Increasing the alcohol to oil molar ratio above the optimal ratio favours the reverse reaction and causes separation problems. Therefore, careful consideration will be placed determining the range for this process variable in the experimental procedure.

2.4.1.4) Reaction Time

An investigation performed by Efavi et al. (2018), investigated the effect of reaction time on the yield and properties of Citrullus vulgaris seed oil. The study examined three different reaction times of 90, 120 and 150 minutes. The highest yield in this study was achieved at 120 minutes, with a gradual decline in yield with increasing reaction time after 120 minutes. After the optimal reaction time, any increasing reaction time decreases biodiesel yield due to the reverse reaction becoming favoured. This led to a reduction in esters and the formation of soap. (Efayi et al., 2018)

As the duration of the reaction is increased, the conversion of triglycerides increases. Due to the immiscibility of the reactants, the reaction starts very slowly. If the reactants are mixed well, the reaction rate is faster. The optimisation of reaction time is dependent on the type of catalyst chosen and the vegetable oil (Trejo-Zárraga et al., 2018). An investigation performed by Aworanti et al. (2019), stated the maximum yield of biodiesel produced from used vegetable oil and used palm oil reached optimum biodiesel yield at 90 minutes, and any increase in time after the optimum point decreased the yield. The study concluded that the biodiesel yields deteriorated due to the hydrolysis of esters which resulted in the production of soap. The reverse reaction of transesterification was also favoured after the reaction reached equilibrium further decreasing the yield of biodiesel (Aworanti et al., 2019). It can be concluded that too long reaction times lower biodiesel yield, this will be an important consideration in the experimental phase of this research paper.

2.4.1.5) Catalyst Loading

An investigation performed by Efavi et al. (2018), investigated the effect of NaOH catalyst concentration on the yield and properties of Citrullus vulgaris seed oil. The maximum yield of biodiesel produced was approximately 70% obtained at the lowest quantity of catalyst of 0.13g. It was discovered that increasing the amount of catalyst led to a steady decline in biodiesel yield, reaching approximately 49% biodiesel yield at a 0.18g catalyst concentration. This decline in biodiesel yield was caused by increasing quantities of excess catalyst, which led to soap formation (Efayi et al., 2018).

A study by Nahadi and Atadashi (2018), investigated the effects of various catalyst concentrations (NaOH) on biodiesel production using coconut oil and methanol. The catalyst loading ranged between 0.2-1.2 % w/w oil. The lowest biodiesel yield was found at the lowest catalyst concentration due to insufficient catalyst. The maximum yield was found at a 1% w/w oil catalyst concentration. Any increase in catalyst concentration after 1% w/w oil decreased biodiesel yield, potentially due to the saponification side reaction being favoured.

An investigation performed by Yunsari, Husaini and Rusdianasari (2019), investigated the effects of variations in catalyst concentrations when producing biodiesel from crude palm oil using sodium hydroxide as the catalyst. The catalyst concentration ranged from 0.6-1.4%. It was discovered that an increase in catalyst concentration leads to an increase in biodiesel yield. Any excess catalyst in the system could cause side reactions such as saponification, which reduce the biodiesel yield and cause difficulties in the separation process. These studies show that it is essential to limit the amount of excess catalyst in the system without directly affecting biodiesel production. This was taken into account during the planning of the experiments.

Type of Oil or Animal Fat	Type of Alcohol	Alcohol to Oil Molar Ratio	Reaction Time	Reaction Temperature	Catalyst	Catalyst Concentration (%)	Biodiesel Yield (%)
Canola Oil	Methanol with terahydrofuran	24:1	1080	110	AlCl3	5	98
Canola oil (20 % FFA)	Methanol	9:1	200	-	12-Tungstophosphoric Acid	3 wt.	90 wt.
Kusum	Methanol	8:1	60	50	KOH	0.7	95
Jatropha	Methanol	5.6:1	60	60	NaOH	1	98
Neem	Methanol	6:1	60	60	KOH	2	83.4

Corn Oil	Methanol	6:1	120	200	p-toluenesulfonic acid	4 wt.	100

Table 4-1 displays various types and feedstock with their respective biodiesel yields. Each process variable has varying conditions dependent on the choice of oil, catalyst and alcohol. Therefore, the choice of feedstock and their interactions need to be carefully considered before finalising the experimental procedure to ensure an optimal biodiesel production process.

Table 4-1: Effect of process variables on biodiesel yield (Gebremariam and Marchetti, 2017) (Banković-Ilić et al., 2012)

Type of Oil or Animal Fat	**Type of Alcohol**	**Alcohol to Oil Molar Ratio**	**Reaction Time**	**Reaction Temperature**	**Catalyst**	**Catalyst Concentration (%)**	**Biodiesel Yield (%)**
Canola Oil	Methanol with terahydrofuran	24:1	1080	110	$AlCl_3$	5	98
Canola oil (20 % FFA)	Methanol	9:1	200	-	12-Tungstophosphoric Acid	3 wt.	90 wt.
Kusum	Methanol	8:1	60	50	KOH	0.7	95
Jatropha	Methanol	5.6:1	60	60	NaOH	1	98
Neem	Methanol	6:1	60	60	KOH	2	83.4
Corn Oil	Methanol	6:1	120	200	p-toluenesulfonic acid	4 wt.	100

2.5) Biodiesel Feedstock Types and Properties

2.5.1) Vegetable Oil

Due to the increase in biodiesel production over the years, the consumption of their chosen feedstocks has grown rapidly worldwide. Palm oil, soybean oil and rapeseed oil are frequently used feedstock sources. Rapeseed oil has a significant advantage over other vegetable oils as it possesses higher winter quality because of its fatty acid structure. During the winter period, rapeseed oil is the feedstock commonly chosen (UFOP, 2020). The choice of which vegetable oil to use as a feedstock is heavily dependent on the regional climate. Due to this fact, rapeseed oil is mostly used in colder climates, soybean oil in the US, and palm or coconut oil in equatorial countries. All fats and oils have unique ranges of fatty acid concentrations therefore, biodiesel production costs depend, to a large extent, on the feedstock choice. The expense of animal fat or vegetable oil utilised as the feedstock to produce biodiesel undoubtedly impacts the overall final cost for biodiesel, making up 60 – 75% of the overall production cost. Due to this reason, less expensive feedstocks are favoured. An important consideration when selecting the best feedstock is its ability to produce a high-quality final biodiesel product. Therefore, to obtain a cost-effective process, a production plant must have available, a low-value feedstock and be able to develop quality, high-yielding biodiesel (Narasimharao, Lee and Wilson, 2007). Referring to Figure *4-8*, Used cooking oil contributed to 10% of the feedstock used worldwide in 2018. The most used feedstock worldwide was palm oil making up 35% of the total feedstock. Table *4-2* shows that different feedstocks have varying percentages of oil content. This variation in composition is due to the climate, soil, and other natural factors (Oldring, 2003).

Table *4-3* shows a comparison of the advantages and disadvantages of various biodiesel feedstocks. It shows waste cooking oil has disadvantages that have a drastic effect on biodiesel yield and that virgin oils have low processing costs but high feedstock expenditure.

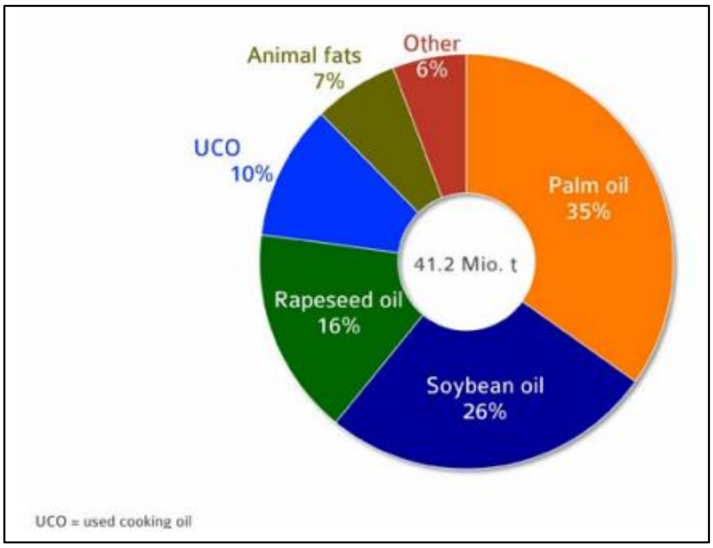


Figure 4-8: Feedstock used in biodiesel production worldwide in 2018 (UFOP, 2020)

Table 4-2: Percentage of oil content from different feedstocks (Singh et al., 2019) (Aransiola et al., 2019) (Patel and Sankhavara, 2017) (Lestari, 2012) (Morshed et al., 2011)

Edible Vegetable Oil	**Percentage of Oil content (%)**	**Nonedible oil**	**Percentage of Oil content (%)**	**Animal Fat or other sources**	**Percentage of Oil content (%)**
Soybean	15-20	Neem	20-30	Algae	30-70
Sunflower	25-35	Karanja	27-39	Micro algae	
Rapeseed	38-46	Jatropha	30-40	Pine and kapok	
Palm	30-60	Castor	45-50		
Canola	40-45	Rubber Seed	53.74 – 68.35		
Coconut	63-65				

Table 4-3: Comparison of Various Feedstocks (Gude et al., 2012).

Feedstock	**Advantages**	**Disadvantages**
Waste Cooking Oil	Very low Cost (Feedstock cost is low or free) High net energy ratio	High free fatty acid content Processing costs are high due to the restrictions present during mass transfer
Virgin Oils	Reduced free fatty acid content Processing costs are low	Approximately 80% of the total expense is due to the feedstock. Environmental concerns such as pollution and food security Low Net Energy Ratio
Algae	Growth is high. Oil yield is high. Recycling of used water and nutrients are possible. Removes carbon dioxide Environmentally friendly Wastewater cultivation	The process requires complex techniques
Other Terrestrial Plants	The process requires simple techniques	Growth is very slow. Oil yield is low. Large amounts of water are required. Requires high nutrients.

		Cultivation may cause environmental pollution

2.5.2) Waste Vegetable Oil

The main issue concerning biodiesel production becoming commercially viable is the large production cost. This is caused by the demand from human consumption of edible vegetable oils. Therefore, lowering the cost of biodiesel feedstock is essential, and this can be achieved using waste cooking oils (Patil et al., 2012). Vegetable oil which has repetitively been utilised for meal preparation is not adequate for human consumption because of the high free fatty acid content (Raqeeb and Bhargavi, 2015).

Waste cooking oil can create major environmental concerns. If the waste oil reaches water sources, it can lead to organic pollution forming layers in the water body which can prevent the exchange of oxygen and negatively affect its ecosystem. Oil dumping can clog pipes, create odours and lead to increased wastewater treatment costs. It is therefore vital to recover, treat and reuse waste cooking oil (Guerrero, Guerrero-Romero and Sierra, 2011). The amount of cooking oil created and used per year is extensive, approximately over 15 million tons. If this cooking oil is processed, it can greatly satisfy a large portion of the world's demand for biodiesel.

Cooking oil undergoes changes during frying. These include colour and tension alterations as well as increases in specific heat and viscosity. During food preparation, a thermolytic reaction occurs due to no oxygen being present at elevated temperatures. This leads to the creation of alkanes, carbon monoxide, carbon dioxide, free fatty acids, and alkenes. An oxidative reaction takes place where atmospheric oxygen, dissolved into the oil, reacts with unsaturated acylglycerol to create free fatty acids and free radicals which in turn increase the viscosity of the cooking oil. The process of cooking/frying produces steam. This dissolves into the oil creating more free fatty acids (Fragkou and Martin, 2014).

Therefore, the common issue experienced when utilising waste cooking oil is the existence of solid food particles, elevated water content and high free fatty acid content. Moisture in oil can result in hydrolysis where triglycerides in the oil form FFA. The FFA then undergoes another reaction with base catalyst to produce soap formations (Linganiso et al., 2022). Both chemical reactions are shown in Equation 2.1 and Figure *4-6*.

Waste cooking oil must undergo treatment before starting the biodiesel production process. The solid impurities can be removed using filtration, washing and centrifugation. Waste cooking oil can also be treated using acid catalysed esterification, passed through an acid ion-exchange resin, or treated with an adsorbent (Linganiso et al., 2022). Therefore, developing an efficient and effective pre-treatment process is pivotal to the success of this research paper.

Figure *4-9* shows the crop yields in the US in litres/m^2. It can be noted that palm oil produces the highest yield of crops. Food security is a real concern in third world countries like South Africa, therefore utilizing waste cooking oil to produce biodiesel could avoid this concern.

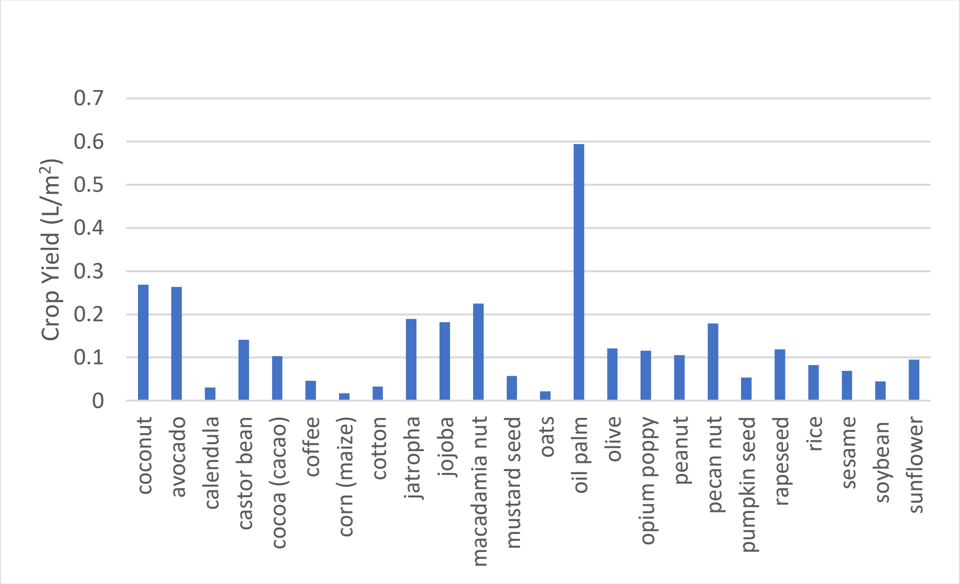


Figure 4-9: The yields of crops in litres/m^2 of the common crops used as feedstocks for biodiesel production adapted from (Addison, 2001)

2.5.3) Canola Oil

Canola oil has a high oil yield, approximately 40 – 50 %. Canola oil is used as a winter cover crop, allowing for double cultivation and additional crop rotation. Canola oil is considered as one of the most suitable cooking oils as it helps to reduce blood cholesterol levels (Romano and Sorichetti, 2011). Biodiesel produced from canola oil is seen as a suitable substitute for diesel engines. Biodiesel produced from canola oil displays excellent lubricity and does not contain sulphur. Canola oil biodiesel produces more nitrogen oxide when compared to conventional diesel. This is caused by canola oil biodiesel’s higher bulk modulus and higher boiling point.

2.5.4) Type of Alcohol

The choice of the type of alcohol for the transesterification process is extremely important. Many alcohols were investigated for biodiesel production, with the frequently used alcohols being ethanol and methanol. Other alcohols that are used are short-chain alcohols namely butanol, propanol, and isopropanol. These are rarely used as they are quite expensive. The choice of alcohol relies on the alcohol cost and the transesterification reaction performance (Aga, 2018). A very important note is that methanol is non-renewable, as it is mostly derived from fossil fuel resources like natural gas, therefore biodiesel produced with methanol as the alcohol cannot be termed as a renewable process. Therefore, a renewable alcohol would be more environmentally friendly. The use of ethanol is favourable as ethanol is created from agricultural wastes, for example biomass via fermentation methods. Ethanol is more environmentally friendly. Methanol is less soluble in oil when compared to ethanol therefore increases mass transfer limitations taking place during the transesterification reactions (Verma, Sharma and Dwivedi, 2016).

Methanol is however more commonly utilised because its cheaper when compared to other alcohols and the chemical and physical advantages it possesses. These advantages are that methanol is polar in nature and the shortest chain alcohol (Demirbas et al., 2016). Methanol is usually favoured due to its good reactivity with triglycerides, allows for greater conversions under the same reaction time compared to longer chain alcohols, and is readily accessible. Additionally, certain catalysts such as NaOH, can be easily dissolved in methanol. Figure *4-10* shows that biodiesel yield varies according to the choice of alcohol, displaying how important the decision of choosing the best alcohol for the chosen feedstock and process is.

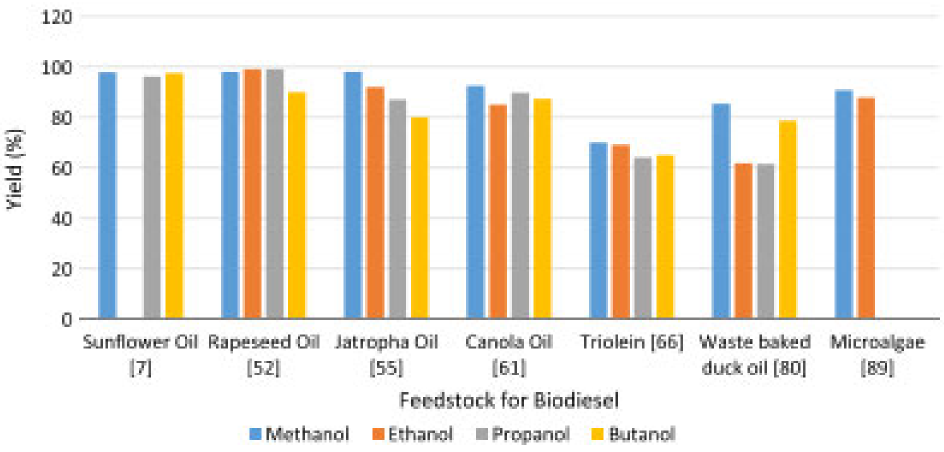


Figure 4-10: The comparison of yields obtained for biodiesel produced with different types of alcohols (Verma, Sharma and Dwivedi, 2016).

2.5.5) The Acid Value and free fatty acids

The acid value is an extremely crucial indication of the quality of oil chosen and produced. Acid value is defined as “the amount of catalyst KOH (in milligrams) required to neutralize free fatty acids (FFA) contained in 1 g of vegetable oil” (Kardash and Tur’yan, 2004). According to European Committee for Standardisation, the maximum acid value expressed in mg KOH/g is 0.5. Therefore, before the process can proceed any further, the acid value must be lower than 0.5 (Rutz and Janssen, 2006). Previous studies have shown that water or free fatty acids (FFA) function as poison for homogeneous catalysts (Javidialesaadi and Raeissi, 2013). High levels of free fatty acid (FFA) content can lead to major processing issues in biodiesel manufacturing, since free fatty acid (FFA) can be readily saponified with homogeneous base catalysts leading to form soap. Used cooking oil is a problematic feedstock to use to produce biodiesel since the oils contain moisture and high levels of free fatty acids. A high concentration of free fatty acids results in a negative impact on FAME conversion and favours side reactions such as saponification and hydrolysis of triglycerides. These side reactions lead to the available catalyst becoming neutralised and lead to increased purification costs as well (Sheikh et al., 2013). For this reason, it is pivotal to limit the maximum acid value.

2.6) Biodiesel Properties

2.6.1) Density

Density has a direct impact on the efficiency of fuel for combustion in diesel engines. According to the quality standards, density should be recorded at 15 ^{o}C (Aga, 2018). Since the fuel injection pump gauges fuel by volume instead of mass, the amount of fuel injected is solely dependent upon its density (Hoekman et al., 2012). Due to this reason, the energy content and the air fuel ratio in the chamber are also affected by density. If the density of fuel is too high, the usage could cause incomplete combustion or particulate matter emissions (Ismail and Ali, 2015). Biodiesel density is greatly reliant on the raw materials chosen and the biodiesel ester profile (Pratas et al., 2011). When comparing biodiesel to petroleum diesel, biodiesel always has a higher density (Hoekman et al., 2012).

2.6.2) Viscosity

Viscosity is deemed as a crucial property since viscosity affects the way fuel flows, i.e., its fluidity (Ayetor et al., 2015). Viscosity impacts the manner in which fuel is injected. Greater viscosity results in issues such as poor fuel atomization. High viscosity could result in poorer combustion, more emissions released, and greater oil dilution. When comparing biodiesel to petroleum diesel, biodiesel has a viscosity that is usually much greater. Viscosity is strongly influenced by temperature. A common problem with biodiesel is the great viscosity at low ambient temperatures which leads to engine problems at these lower temperatures (Hoekman et al., 2012).

2.6.3) Cetane number

The cetane number of fuels describes the quality and ignition behaviour. Improved performances and cleaner burning fuel have been noted with larger cetane numbers. The lowest possible cetane number for ultra-low sulphur diesel (ULSD) is 40. It is noted that the majority of the feedstocks for biodiesel production have higher cetane values than ULSD. (Neupane, 2022). Biodiesel exhibits a larger cetane number between 46 to 60 (Nolte, 2007). Biodiesel cetane number is dependent on the degree of saturation and length of fatty acid chains. An increase in the chain of fatty acid chains results in an increase in cetane number. A higher cetane number results in greater oxygen concentration and higher combustion efficiency (Neupane, 2022).

2.6.4) Sulphur Content

Sulphur influences engine emissions and performance significantly. Sulphur increases the particulate matter emissions causing more pollution to exit the exhaust. Excess sulphur can cause corrosion inside engine cylinders and can be oxidized into creating sulphuric acid when reacting with water. This sulphuric acid can cause damage, corrosion, and failure of engine parts (Al-Mashhadani and Fernando, 2017). According to SAPIA (2021), the draft Clean Fuels 2 regulations discussed the mandatory implementation of 10 ppm (w/w) sulphur petrol and diesel in SA. According to an investigation by He et al. (2009), the majority of biodiesel produced during the investigations were 15 ppm or less sulphur. Waste cooking oil was also investigated where the feedstock contained 21.4 ppm sulphur and was reduced by 66.3% during pre-treatment, biodiesel production and post treatment to 7.2 ppm sulphur (He et al., 2009).

2.6.5) Heat of Combustion

The definition for heat of combustion is, “the amount of heat generated when 1 mole of biodiesel is burnt” (Owolabi et al., 2011). In an investigation performed by Andrade et al. (2011), the heat of combustion for soya biodiesel and its blends were investigated. The study concluded that mixing biodiesel with diesel in blends decreased the heat of combustion. This was caused by the presence of an organic chain. These bonds act as resistance to heat flow. The study concluded that the heat of combustion for biodiesel was approximately 17% less than diesel. (Andrade et al., 2011).

2.6.6) Biodiesel Flash Point

The flash point is defined as, “the minimum temperature where vapours of the fuel form an inflammable mixture with air.” Vegetable oil biodiesel produces a flash point between 160 - 170 ^{o}C, however extremely small traces of alcohol still found in the fuel can massively reduce the flash point of the biodiesel. Therefore, the flash point of each batch of biodiesel produced should be measured (Boog et al., 2011). The flash point of a fuel is an extremely significant characteristic as it is vital for safety storage and handling parameters, however the flash point does not affect the performance of an engine. The recorded flash point of vegetable oils is relatively high usually over 220 ^{o}C, however the flash point for certain diesel oils reaches over 66 ^{o}C (Blin et al., 2013).

2.6.7) Petro-Diesel and Biodiesel Standards

Table *4-4* shows the quality testing methods used on diesel and biodiesel. The ranges for every property test mentioned are shown, biodiesel must comply with these standards in order to be sold commercially.

Table 4-4: Standards of Petro-Diesel and Biodiesel (Siraj et al., 2017) (Naureen et al., 2015) (Sakthivel et al., 2018)

Properties	Methods of Testing	Diesel	Biodiesel
Flash Point Temperature (^{o}C)	D93	60-80	100-170
Kinematic Viscosity (40 ^{o}C, mm^{2}/s)	D445	1.3 – 4.1	1.9-6.0
Sulphur (% wt.)	D5453	0.05 maximum	
Sulphur (% wt.)	D2622/129		0.05 maximum
Cetane Number	D613	40 minimum	47 minimum
Distillation Temperature (^{o}C)	D1160	282 to 338	-
Pour Point (^{o}C)	D97	-35 - -15	-15 – 16
Cloud Point (^{o}C)	D2500	-15 – 5	-3 – 12
Acid Number (mg KOH/g)	D664	0.5	0.5
Boiling Point (^{o}C)	D7398	-	100 – 615

Saponification Value (mg KOH/g)	D5558	-	370 maximum

2.6.8) The advantages and disadvantages of biodiesel

Table *4-5* discusses the advantages and disadvantages of biodiesel. The main disadvantages of biodiesel are its high viscosity and corrosive nature.

Table 4-5: The advantages and disadvantages of biodiesel (Hassan and Kalam, 2013)

Advantages of Biodiesel	Disadvantages of Biodiesel
Biodiesel feedstock is from renewable sources and are readily available.	Biodiesel in engines emit higher amounts of Nitrogen Oxide (NO) than petroleum diesel.
Biodiesel releases far fewer harmful emissions when compared to standard petro-diesel.	Biodiesel is corrosive in nature. Materials such as copper and brass must be avoided or regularly changed.
Biodiesel Production process is far simpler and requires less time to complete.	The viscosity of biodiesel is significantly higher than petroleum diesel, which can lead to pumping and combustion problems.
Biodiesel has the ability to prolong an engine's lifespan and minimize the need for servicing because of its superior lubricating qualities.	Biodiesel lowers the engine's power and speed.
Biodiesel does not require any mining or drilling, therefore more environmentally friendly.	A degradation of the biodiesel product can occur if stored for an extended period.
Biodiesel possesses a greater combustion efficiency and flash point when compared to conventional diesel.	Biodiesel causes carbon deposits to form with an engine.
Biodiesel provides an excellent opportunity for rural development and can potentially solve the energy crisis.	Biodiesel is more expensive than gasoline and petroleum diesel.

2.7) Cold Flow Property Tests

These properties depend on multiple factors namely impurities present, alcohol types, presence of free and bound glycerine and moisture content. The degree of variation in unsaturation in oil's fatty acids is caused by the choice of feedstock and the quality of biodiesel produced (Pradhan and Shrestha, 2007). Feedstocks, such as palm oil and tallow containing highly saturated fatty acid structures produce biodiesel fuels that display very unsatisfactory cold flow properties. Rapeseed, which contains high unsaturated fatty acid structures, produces biodiesel fuels with better cold flow properties (Hoekman et al., 2012).

2.7.1) Cloud Point

The cloud point of a fuel is defined as, "the measure of the temperature at which the liquid fatty material starts to precipitate due to the formation of crystals and the solidification of saturates." The cloud point of biodiesel is usually a higher temperature than the pour point of biodiesel. Formation of solidified material leads to fuel starvation and operability problems as these materials clog the fuel lines and filters. As the temperature further decreases pass this point, these crystals get larger. The cloud point of a fuel is frequently used to determine the low-temperature operability of a fuel (Veríssimo and Gomes, 2011).

2.7.2) Pour Point

The pour point is a property that involves the fatty acid composition and the degree of double bonds directly correlating to the temperature of crystallization due to their disruptive impact on packing capacity. It is extremely important to observe this parameter as biodiesel displays a much higher pour point than conventional diesel. The definition of pour point is, "the lowest possible temperature at which the biodiesel conglomerates and shows resistance." Gravitational force has no impact on biodiesel flow (Ortiz Lechuga et al., 2020).

2.8) Economic Analysis

2.8.1) South Africa and Biodiesel Production

2.8.1.1) South Africa's Energy Crisis

Data collected by Global Carbon Atlas (2021), showed South Africa as the highest emitter of CO_2 emissions on the continent and ranked fourteenth in CO_2 emissions in the world in 2021. South Africa used roughly 12.946 billion litres of diesel in 2021 (SAPIA, 2021). Figure *4-11* and Table *4-6* display the production and consumption of petroleum products and diesel during 2009-2021. The cost of diesel was R 20.16/litre at the coast (5 April 2023). A big contributing factor to the higher selling prices of diesel was the ongoing political conflicts between Russia and Ukraine. The selling prices of diesel drastically declined during the COVID-19 pandemic however as the lockdown restrictions were eased up until no restrictions were present, the price of petrol and diesel kept increasing. Another contributing factor to higher diesel selling prices in South Africa is the ever-fluctuating Rand to Dollar exchange and the rand weakening to the dollar, R 18.50 to the dollar (10 April 2023). With an ever-increasing fuel price, renewable alternatives need to be considered.

Table 4-6: Petrol and Diesel Consumption 2021 in millions of litres (SAPIA, 2021).

Year	Petrol	Diesel	Paraffin	Jet Fuels	Fuel Oils	LPGs
2009	11 321	9 437	551	2 349	724	554
2010	11 455	10 170	545	2 308	468	612
2011	11 963	11 225	581	2 434	477	717
2012	11 714	11 262	470	2 367	568	656
2013	11 153	11 890	530	2 223	523	485
2014	11 344	13 169	558	2 197	487	398
2015	12 072	14 178	573	2 441	591	588
2016	10 160	10 846	558	2 121	562	557
2017	11 174	12 147	648	2 713	523	551
2018	11 142	12 539	702	2 346	552	504
2019	10 773	12 909	620	2 439	410	495
2020	8761	11 690	702	1 091	486	448
2021	9302	12946	1 078	1 048	491	308

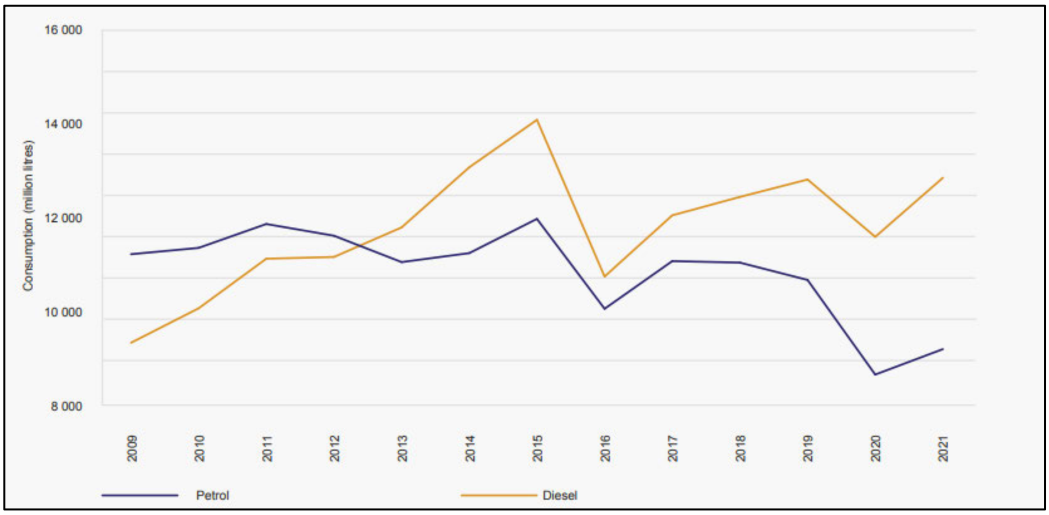


Figure 4-11: Petrol and Diesel Consumption (SAPIA, 2021).

2.8.1.2) The Main Motivation behind biodiesel in South Africa

South Africa and countries around the world are dealing with the repercussions of rising crude oil prices and high CO_2 emissions, and alternative sources of fuel/energy, such as biodiesel could be the solution to many of these problems:

1. The application of pressure leading to a reduction in the global crude oil costs and the imperative to enhance energy security (DMRE, 2007).
2. Support cleaner, environmentally friendly renewable energy (DMRE, 2007).
3. As Africa's number one CO_2 emission emitter, South Africa needs to lower its greenhouse effect and decrease the country's pollution rate.
4. Uplifting the agricultural sector by attracting investment to rural areas and promoting the development of agriculture (DMRE, 2007).
5. In 2014, the South African government launched the bio-economy strategy as a presidential initiative. This strategy aims to significantly contribute to the South African GDP by 2030 by prioritising and supporting research, development and innovation in biological processes (DST, 2013).

2.8.2) Biodiesel Feasibility Study

According to Murugesan et al. (2009), diesel fuel has had a significant effect on developing countries' economies. According to the Government Gazette (2020), the mandatory blending regulations for petroleum products started in October 2015, where local bioethanol and biodiesel are required to be blended at a minimum of 2% to petrol and 5% to diesel. Since the cost of producing first-generation biodiesel is more expensive than conventional fuel, there is no financial incentive for transport fuel manufacturers to purchase and blend biodiesel with conventional fuel. The biodiesel regulatory framework of South Africa acknowledges that biodiesel created using third-generation and second-generation feedstocks removes the food versus fuel debate (Government Gazette, 2020). In 2021, South Africa used approximately 9302 million litres of petrol and 12946 million litres of diesel (SAPIA, 2021). Table 4-7 below shows the overall biodiesel production potential for the top eight nations per volume. It can be noted from this table, that no country in Africa has made the top 8 nations list because biodiesel development is still in its early phases in Africa. South Africa has the third lowest production costs out of every country it is compared to. According to Greenthermo (2023), pure biodiesel sells for R12.24 but blended biodiesel (B10) costs R13.14, showing that biodiesel is cheaper than conventional fuel in South Africa.

Table 4-7: Overall Biodiesel Production in the top eight biodiesel producing nations.

Rank	Country	Biodiesel Production (per billion Litres) (Azizan, 2020) (Government Gazette, 2020)	Production costs ($/L) (Sharma and Singh, 2009) (Greenthermo, 2023)
1	USA	6.0	0.70
2	Brazil	4.3	0.62
3	Germany	3.5	0.79
4	Argentina	3.3	0.62
5	Indonesia	2.5	0.49
6	France	2.3	0.85
7	Thailand	1.4	0.38
8	Spain	1.3	1.71
-	**South Africa**	**0.46**	**0.62**

2.8.2.1) Choice of Biodiesel Production Process

A very important economic factor to consider in biodiesel production is the choice of production, as there are variations in operating costs and capital costs exist with different processes (Amigun et al., 2008b). Biodiesel can be produced through three primary methods: microemulsion, pyrolysis, and transesterification reactions. Transesterification is a frequently used process. This reaction occurs with oil and alcohol with a catalyst producing glycerine and biodiesel (Aktaş et al., 2020). This choice of production can vary from the catalyst type, alcohol type and vegetable oil used. Scale of production and conversion technology chosen, both impact the operating and capital costs. According to a study by Karmee et al. (2015), a techno-economic analysis was performed on Biodiesel production with WCO as the feedstock in Hong Kong. Table *4-8* shows the comparative analysis of the different catalyst productions. Three different types of catalysts were evaluated. Due to variation in production designs, the capital investment cost in base and acid catalysts were significantly higher than the lipase catalyst. However, the lipase catalyst had a significantly higher production cost than the other two catalysts. Acid and base catalysts created biodiesel at a lower price than the average biodiesel price in Hong Kong of $1.01. Biodiesel production from lipase catalyst was found to be more expensive at $1.15. Biodiesel production via acid catalysed method was found to be the most cost-effective process (Karmee et al., 2015).

Table 4-8: Comparative Analysis of Different Catalyst Productions in Hong Kong (Karmee et al., 2015).

Component	Base Catalyst Component Cost ($)	Acid Catalyst Component Cost ($)	Lipase Catalyst Component Cost ($)
Capital Investment	6 782 505.50	5 759 338.38	2 689 144.63
Production Cost	6 948 835.57	6 003 071.75	8 383 729.46
Average Biodiesel Cost per Litre	0.90	0.80	1.15

In this study, homogeneous base catalyst KOH and heterogeneous base catalyst MgO were utilised. Base homogeneous catalysts have large activation energy and are frequently used as the catalyst is cheaper than alternatives. The rate of reaction for base catalysts is significantly faster when compared to acid-based catalysts (De Lima et al., 2016). Homogeneous base catalysts cannot create high yields of product when the oil contains large amounts of free fatty acids. It is recommended that the FFA content should be lower than 1% for biodiesel production (Helwani et al., 2009). Used vegetable oil has significant amounts of free fatty acids (Fragkou and Martin, 2014). Due to this setback, biodiesel production processes involving a homogeneous base catalyst must include pre-treatment processes which increase the capital and operating costs. Heterogeneous catalysts require high temperatures for catalysis which is a disadvantage as this results in higher operating costs. However, the simplicity of separation, purification, and reusability of the catalyst are advantages of this process (Fattah et al., 2020).

A study by Amigun et al., (2008a) found a major problem for the production of biodiesel is determining whether the process should be continuous flow or batch. A study by Peterson et al., (2002) stated that the production time and cost for producing small amounts of biodiesel are high using a batch reactor. A continuous flow process allows for larger scale operations and compared to a batch process more fuel is produced per unit of labour thereby reducing costs (Peterson et al., 2002). According to a study by Eidman (2007), continuous flow processes have a larger capital cost however this will be minimised by advantages like cheaper processing costs and more consistent output. Continuous flow processes have the ability to reuse catalysts and recovered chemicals that are often unfeasible for batch processes, leading to a greater reduction in processing costs (Amigun et al., 2008b).

Batch processes have an advantage of being feasible on smaller scales and benefit from the established design. These benefits will have a better application in less well-established regions in the African continent, where lower financial costs will attract local investors. In countries with unpredictable and uncertain energy supplies, investors may want to mitigate risk and favour a process that produces discrete runs of products and has lower capital investments. The advantages of a batch process are more favourable to be used in Africa (Amigun et al., 2008b).

2.8.2.2) Biodiesel Production Cost

According to a study by Ianda et al. (2020), Sub-Saharan Africa has been characterized by extreme poverty, very common energy deficits and a large dependence on oil imports. During the 20th century, developing infrastructure and transportation relied on oil products. Due to Sub-Saharan Africa’s reliance on oil, these countries became vulnerable during oil crises due to the lack of energy alternatives and dependence on imports. The production of biodiesel aims to strengthen the economy, reduce oil imports, and contribute to socio-economic development in this region. Due to the intense involvement of the agricultural systems in producing raw materials, these agricultural activities generate jobs and income for the people in the region. Labour costs for biodiesel production are heavily reliant on the feedstock chosen; the type of process (continuous or batch flow); the degree of automation; and production capacity (Amigun et al., 2018b). In sub–Saharan Africa, land ownership is established with small hectares per family which could result in competition for land use for food production versus biodiesel (Ianda et al., 2020). A good consideration in this region would be to use non-edible oilseeds or waste cooking oil. According to a study by Mulugetta (2008), from a South African perspective, there is little research regarding the feasibility and the possible effects of the growth of a worldwide biofuel sector. Due to this, local studies utilise production data from North America or Europe.

After reviewing multiple research papers, the conclusion is that the effect feedstock has on the production cost changes significantly by feedstock choice and design process. According to a study by Acevedo et al. (2015), an investigation predicted the palm oil cost as the feedstock was roughly 73% of the total production costs. According to a study by Liu et al. (2022), an investigation predicted Jatropha oil cost as the feedstock to be roughly 54.58% of the total production cost. An investigation by Huang et al. (2016) estimated the Soybean cost as the feedstock to be roughly between 80-90 % of the total production cost. A study by Doddabasawa and Patil (2014), estimated the cost of Pongamia as the feedstock to be roughly 60 % of the total production cost. It can be concluded that feedstock costs play an important factor in influencing the economic feasibility of the production process. The daily operational efficiency of a biodiesel production plant is a more crucial factor for its long-term success than the initial capital investment (Amigun et al., 2008b).

Table 4-9: Popular oil feedstocks and their respective pricing (Liu et al., 2022).

Feedstocks	Sunflower seed	Cotton seed	Rapeseed	Soybean	Palm	Jatropha Oil	Waste Cooking Oil
Cost (ZAR/ton)	25567,00	15854,50	15762,00	12635,50	11766,00	6108,89	4144,00

A study completed by Kenkel and Holcomb (2006) discussed the important considerations that influence the location and operations of biodiesel plants such as the availability of feedstock; the location of distribution centres for biodiesel; accessibility to the market for by-products; utility costs; local/state incentives. Table *4-9* displays the various cost prices of feedstock; it can be concluded that there is a great variation in prices for each feedstock. Table *4-9* shows the cheapest feedstock to be waste cooking oil (Liu et al., 2022). According to Amigun et al. (2008b), industries should aim to reduce the cost of feedstock by creating new developments that can maximise the biodiesel yield from the chosen stock.Figure *4-12* displays the breakdown of costs for a biodiesel production process in Egypt. It can be noted that even though this process is using waste cooking oil, an estimated 65% of production cost is spent on waste cooking oil and methanol is estimated to be 14% of total production cost.

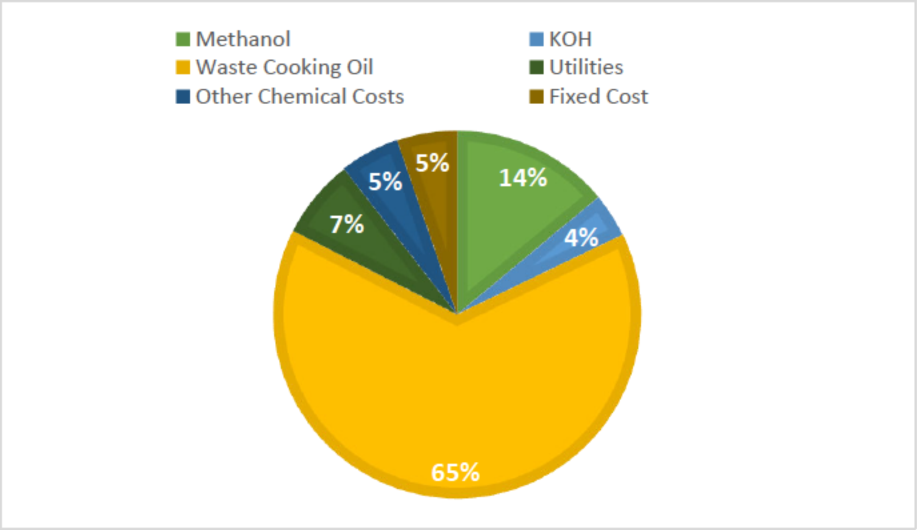


Figure 4-12: Estimation for Production of 1 Litre of Biodiesel in Egypt (El-Gharabawy. 2017).

2.8.2.3) Feasibility Study

A framework is extremely useful to evaluate the economic viability of a biodiesel production plant. Figure *4-13* is adapted from a study by Jacobs (2016) with some modifications.

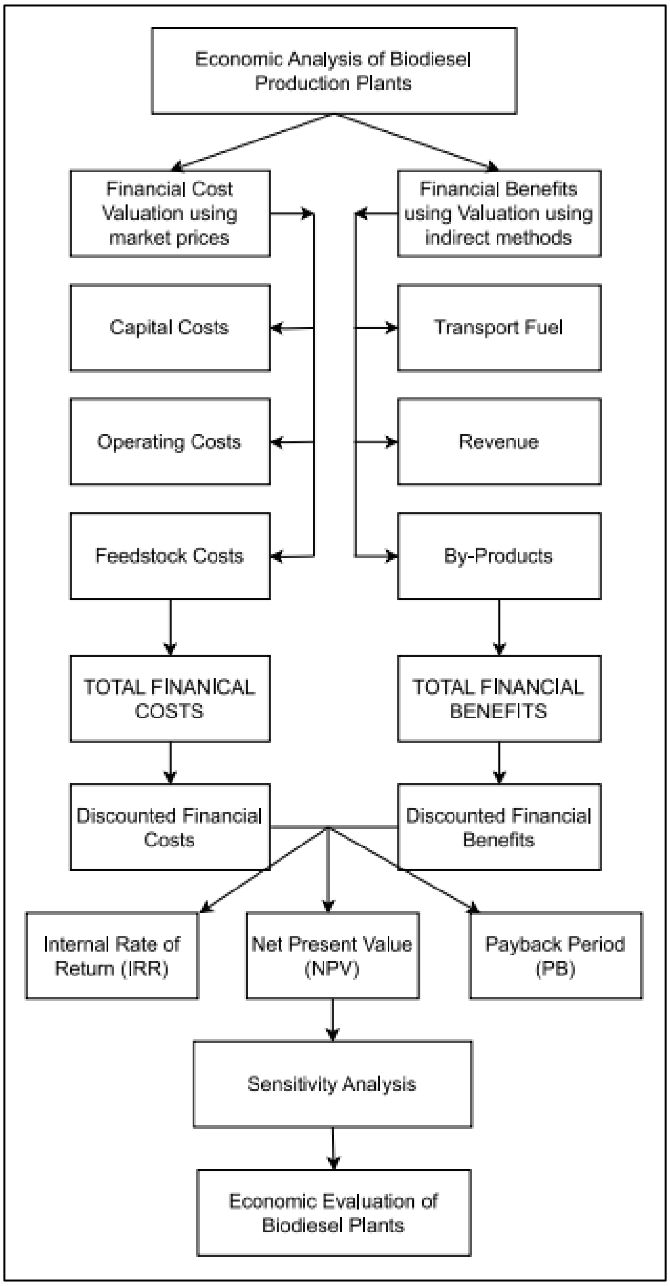


Figure 4-13: Framework for evaluation of economic viability of biodiesel plants (Jacobs, 2016)

Studies from South Africa and around the world which have assessed the economic viability of biofuels as a replacement for conventional fuel, have found that biodiesel production is only viable and profitable if there is sufficient government support. Without government support, higher feedstock and capital costs were found, making the procedure not commercially viable (Mvelase and Mustapha, 2018; Ndokwana and Fore, 2018). Other studies have found that the biofuel selling price was simply just not competitive with fuel prices. This was due to either high feedstock costs or high capital costs (Bechstrom et al., 2020; Pascheco-López et al., 2021).

A survey stated that the Department of Energy was strongly opinionated about the profitability of biofuels in South Africa. The department indicated that biofuel technologies are primarily capital-intensive and the majority of the machinery and equipment would need to be imported (Ndokwana and Fore, 2018). Companies from the private sector (Mabele Fuels, Greentech Biofuels and Green-Diesel) believe that importing biofuel plants will hike the fixed capital investment costs. These companies believe that poor government support, large capital costs and the inability of companies to develop profitable projects are the reasons for the slow progress of biofuel production in South Africa (Ndokwana and Fore, 2018).

Therefore, to ensure that biofuel prices are competitive with petroleum fuels in South Africa, this study recommends that financial support needs to be provided. This can come from government support or potential investors which would result in subsidized capital and production costs (Mvelase and Mustapha, 2018). South Africa is a dry country which experiences an average annual rainfall of 464 mm. Water availability is therefore an issue in South Africa and has contributed to the slow progression of biofuels in South Africa due to the increased irrigated requirements for biofuel feedstock. This study aimed to remove this concern by utilizing waste cooking oil eliminating the enormous water consumption thereby reducing the overall operating costs of the production process (Bonsch et al., 2014). The biodiesel production process produces the by-product glycerine. The production plant can potentially counteract the large production costs by selling glycerine, thereby lowering the costs (Jacobs, 2016). Figure *4-14* displays a general biodiesel production chain in South Africa that utilizes methanol and potassium hydroxide. The process displays how glycerol is sold as a by product and how biodiesel is used for diesel blending.

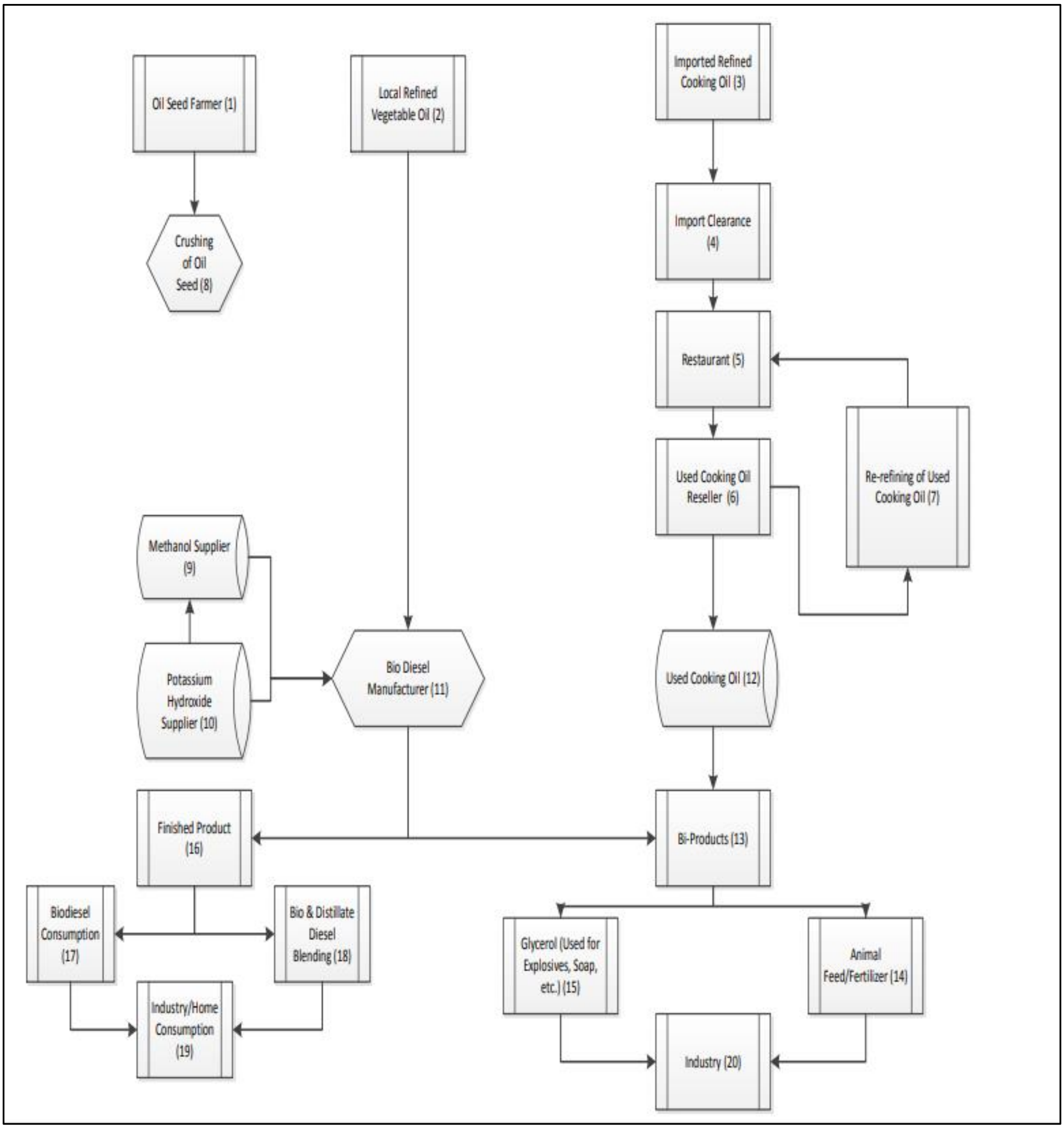


Figure 4-14: Biodiesel Production Chain in South Africa (SARS, 2019)

Several studies have drawn the conclusion that because of the high production costs of biodiesel caused by the raw materials, it is more economically feasible to use commercial diesel as it costs less (Amigun et al., 2008a). Due to the unavailability of data displaying the variation in the cost of biodiesel in South Africa, Figure *4-15* was utilised to show how the advancements in technology were able to reduce the selling price of biodiesel in USA below the selling price of conventional fuel. Figure *4-15* displays that the blends of biodiesel in the US were more expensive than pure commercial diesel until 2017, after that pure diesel became more expensive than the B20 biodiesel blend (U.S. Department of Energy, 2023). Therefore, the choice of feedstock should be region specific and cost specific, waste cooking oil would be a perfect feedstock as it is always readily available in the hospitality industry (Linganiso et al., 2022).

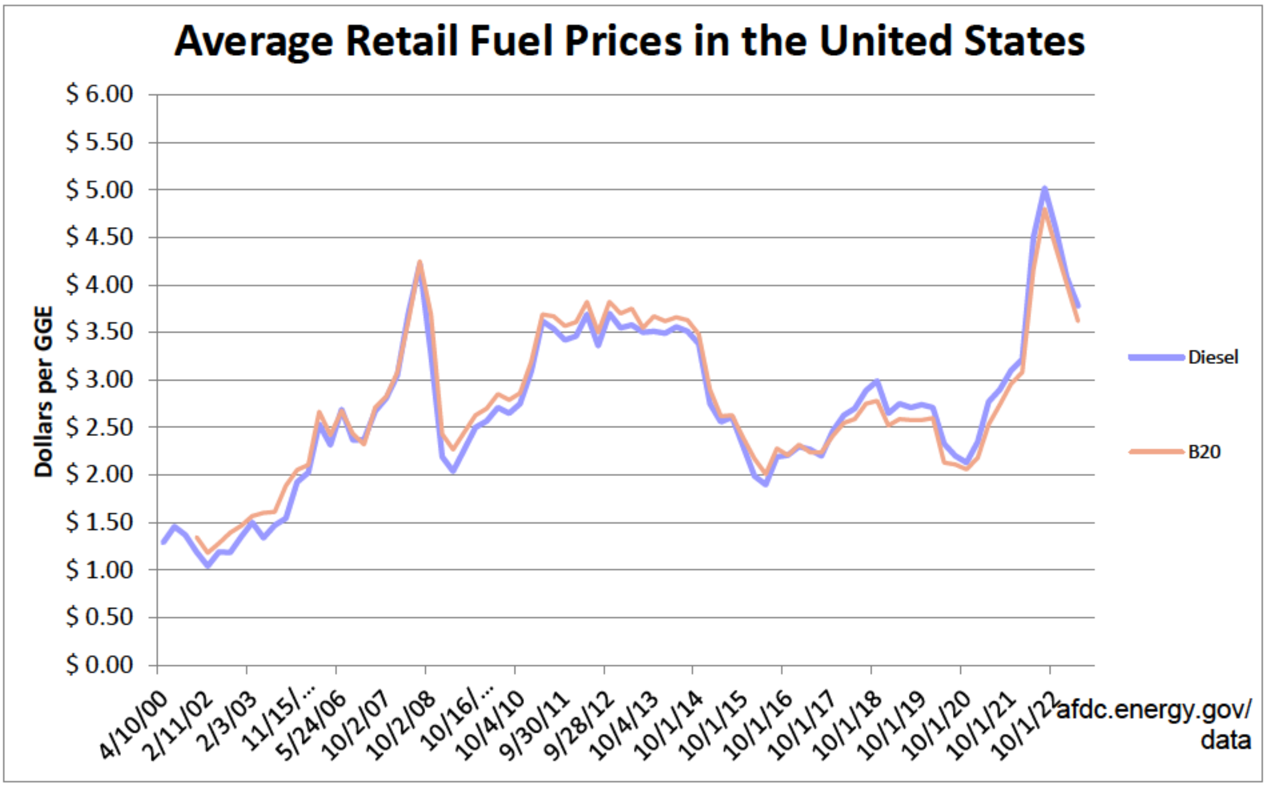


Figure 4-15: Average US price of pure diesel and B20 versus Time (U.S. Department of Energy, 2023)

According to Linganiso et al. (2022), in South Africa, the important factors in producing biodiesel are the expense of raw materials and the inadequate availability of feedstock. In the past few years, South Africa has experienced drought and therefore is unable to transition to producing biodiesel that utilises high amounts of vegetable oils. Due to the fact that roughly 75% of the production cost of biodiesel is the feedstock, commercial diesel is two-thirds of the price of biodiesel. Used cooking oil is roughly one-third of the price of vegetable oil and can therefore decrease the biodiesel production expense greatly. With the food security issues in Africa, and the fact that some waste cooking oil is carelessly dumped, utilising this waste oil could solve many problems. Since the hospitality industry produces large amounts of waste cooking oil and are legally responsible for disposing of the used oil, biodiesel plants could purchase this oil significantly cheaper than virgin vegetable oil (Linganiso et al., 2022).

Table *4-11* and Table *4-12* show the profitability of biodiesel production is highly reliant on the feedstock chosen (Nolte, 2007). These show that profitability is extremely unpredictable. Table *4-10* displays the manufacturing costs for the SERP Plant and the COBP Plant based in South

Africa utilising various feedstocks (Nolte, 2007). This study was chosen as it was the only study to be found in the South African Market. Since this study was completed in 2007, the price estimates are inaccurate to base assumptions on, in 2023 due to inflation; food security issues; and rising demand or shortage of resources. However, the point of including this sensitivity analysis conducted in Table *4-11* and Table *4-12* is to show how the profitability of biodiesel production varies while changing the price of the feedstock or biodiesel selling price. Table *4-10*, Table *4-11* and Table *4-12* show how important the choice of feedstock and biodiesel selling price are as they significantly impact the rate of return on investment and net profit.

Table 4-10: Manufacturing costs of various feedstock at SEBP Plant and COBP Plant (Nolte, 2007).

SEBP Plant		**COBP Plant**	
Feedstock from a local source	**Production Cost (ZAR/Litre)**	**Feedstock from an imported source**	**Production Cost (ZAR/Litre)**
Canola Oil	4.81	Palm Oil	6.62
Sunflower Oil	6.67	Soybean Oil	6.89
Soybean	6.70	Sunflower Oil	7.48
		Rapeseed Oil	9.28

Table 4-11: Sensitivity Analysis displaying the profitability of the canola SEBP plant at multiple biodiesel selling prices (Nolte, 2007).

Biodiesel Selling Price (ZAR/Litre)	**Profit per Litre before tax (ZAR/Litre)**	**Net Profit after 29% income tax (in 1000 Rand)**	**Rate of Return on Investment (%)**
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

Table 4-12: Sensitivity Analysis displaying profitability of the canola SEBP plant for multiple Canola Oilseed prices (Nolte, 2007).

Biodiesel Selling Price (ZAR/Litre)	**Canola Oilseed Price (ZAR/Litre)**	**Manufacturing Cost (ZAR/Litre)**	**Net Profit after 29% income tax (in 1000 Rand)**	**Rate of Return on Investment (%)**
6.50	**1520**	3.87	25606	23
	1615	4.10	21971	20
	1710	4.33	18335	17
	1805	4.57	14542	13
	1900	4.80	10906	10
	1995	5.04	7113	7
	2090	5.27	3477	3
	2185	5.50	-158	0
	2280	5.74	-3952	-4

The critical success factors of biodiesel production in South Africa are: (Takavarasha, Uppal and Hongo, 2005) (Nolte, 2007)

- Minimum rate of return
- Choice of biodiesel feedstock
- Selling price of biodiesel in SA and International Market
- Security of supply
- Mandatory blending requirements
- Legislation by the government which ensures a market
- Special incentives by the government for production, marketing and consumption of biofuels
- Job opportunities
- Foreign market opportunities

CHAPTER 3: Materials, Equipment and Experimental Method

3.1) Material and Equipment

This chapter of the study focuses on comprehensive descriptions of the equipment and materials used during the experiments. The feedstock for this process was waste canola oil and ethanol. The homogeneous catalyst chosen was potassium hydroxide and the heterogeneous catalyst chosen was magnesium oxide. The transesterification reaction incorporated waste canola oil with ethanol and a catalyst to create biodiesel. Table 3-1 and Table 3-2 display the equipment and chemicals that were used during the period of this study.

3.1.1) Materials

Table 3-1: Raw Materials, Suppliers and Purity.

Chemicals	Suppliers	Purity
Canola Oil	Suncat Catering Supplies	100 %
Potassium Hydroxide	Radchem	Analytical Reagent
Magnesium Oxide Light Powder	Radchem	Analytical Reagent
Ethanol	Lichro Chemical and Laboratory Supplies	99.9 %
Methanol	Lichro Chemical and Laboratory Supplies	Analytical Reagent (AR)
Phenolphthalein	Lichro Chemical and Laboratory Supplies	1% in 96% Ethanol
Hydrochloric Acid	Radchem	32 % Analytical Reagent

3.1.2) Equipment Description

The equipment below was chosen for either pre-treatment processes, transesterification process, or post-treatment.

Table 3-2: Equipment and Description.

Equipment	Description
Ahlstorm Filter Paper Ahlstrom NO 1 – 110 mm	110 mm Grade 597 filter paper to filter the waste cooking oil in the pre-treatment stage
Polyscience 7306A11B Standard Immersion Circulator	Provides constant heat for the reaction and displays the temperature of the water bath
Density Meter Easy D40	Measures specific gravity
Brookfield DC-II Pro Viscometer	Measures viscosity
Automatic Digital Refractometer RX-5000i	Measures refractive index
Hanna Instruments Hi 255 (pH meter)	Measures pH
Mechanical Stirrer	Provides intensive stirring of the reaction mixture at constant speeds (rpm)
Thermometer	Used to ensure a constant reaction temperature. The thermometer has a temperature range of -20 ^oC to 110 ^oC.
Separation Funnel (500 ml and 1000 ml)	Enable the separation phase
Rotary Evaporator	To eliminate any excess water and ethanol remaining from the product
Parafilm	To cover the glass beaker
Dropper	Used to add phenolphthalein indicator
Burette Stand	Hold the burette in place
Centrifuge	Remove the heterogeneous catalyst from the biodiesel samples.
Haier Ultra Low Temperature Freezer	Freezer was used to complete the pour point property test.
MajorTECH Type K/j Thermometer	Used to measure temperature in property test.
Furnace	Used to activate heterogeneous catalyst Magnesium Oxide

3.2) Design of Experiments

3.2.1) OVAT Approach

One variable at a time (OVAT) approach is a common method still used by various organizations when performing experiments to estimate the optimal conditions for the main factors. This method is performed by varying one variable while keeping the others constant until the optimal conditions for this variable are found. This process is repeated with another variable, finding the optimal condition (Wahid and Nadir, 2013).

Downfalls of OVAT approach: (Wahid and Nadir, 2013)

- The prediction of the variable's effects is less accurate due to the experimental conclusions being decided upon after data is collected from trial runs and compared to previous data.
- The optimum conditions for the process could be omitted if the independent variables have effects on one another and interactions are present.

From literature, it is known that the OVAT approach is one of the most basic forms of optimisation (Hernandez and Ochoa, 2022). This method allows for a simple investigation of the most desirable conditions to produce biodiesel. Due to other independent variables being fixed, the data can easily be plotted to display where the optimum reaction conditions display the maximum yield of biodiesel produced.

3.2.2) Factorial Design

The factorial design describes the most necessary experiments for simultaneously determining the influence of k factors on the response and whether the factors interact with one another. The experiments are designed to vary simultaneously but are always kept from changing in the same direction. This absence of corelated factors avoids redundant experiments. The 2k factorial approach reduces the number of simulations required, evaluates the relation between different factors and reduces the simulation time required. A set of interest factors are defined. This is determined by the two critical levels (- and +). These represent the extreme values of the chosen factors, i.e., best-case and worst-case scenarios (Mass-Sanchez et al., 2018). A zero-level known as a centre is also included. This zero-level is where all the variables are fixed at their respective median value. Every number combination is referred to as a treatment and is represented by a lowercase letter. Every treatment undergoes several test units, and this is called the number of replicates (Durakovic, 2017).

3.2.3) Box Behnken Design

The response surface methodology is an accumulation of mathematical and statistical procedures utilised for the analysis and modelling of experiments where the desired optimized response is affected by various variables and objectives (Ali et al., 2016). For process optimization, the response surface methodology utilising a design of experiments is extensively used. A multivariate analysis method is an experimental design that simultaneously determines the impact various independent parameters have on the response variable. Multivariate analysis can easily be done with the Box-Behnken design; therefore, it was chosen as an appropriate response surface methodology. Figure 3-1 shows the response design varies at three levels and all the design points lie within the operating range and the designs are rotatable or close to rotating (Kumari et al., 2021). This design method is considered to be the most powerful and more proficient than the other designs such as the three-level full factorial design, central composite design, and doehlert design. The Box-Behnken Design requires less experimental runs than the other design methods (Karmoker et al., 2019). The model equation created helps understand the relationship between the independent and dependent responses. This design is a quadratic design in which the combination is centred at the edges of the process area and in the centre (Kumari et al., 2021). Box-Behnken Design does not accommodate combinations where the variables are all at the lowest or highest values. This is done to avoid situations where the experiment would be performed under extreme conditions and potentially produce unsatisfactory results (Ferreira et al., 2007).

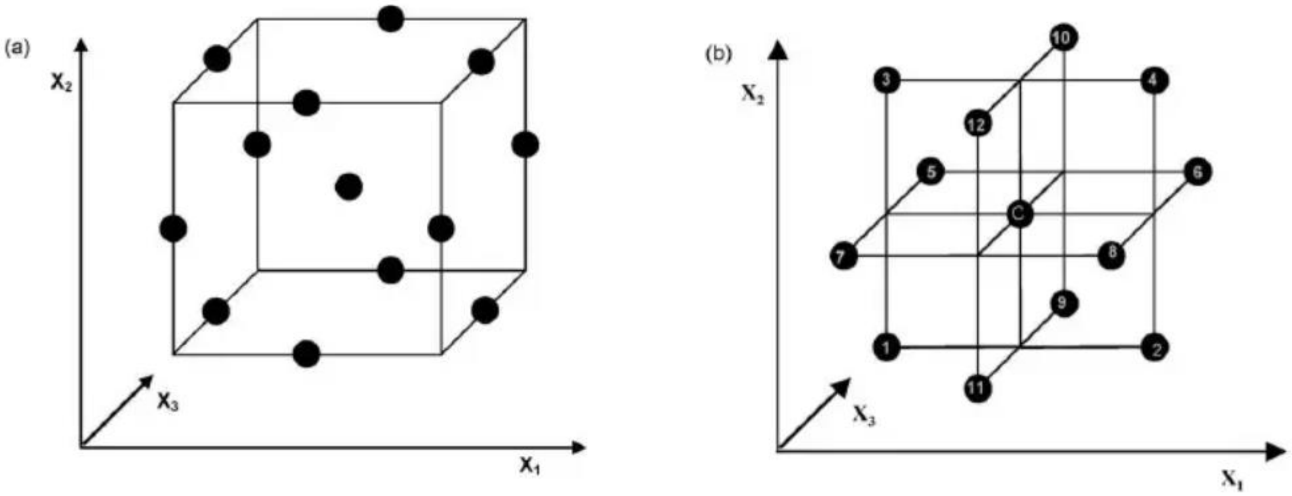


Figure 3-1: Cube showing the Box Behnken Design and three interlocking 22 factorial design (Ferreira et al., 2007)

3.3) Experimental Design

The most vital part of the Design of Experiment process is deciding on a suitable experimental design as this is very important for the success of the study. The decision of which experimental design depends on a variety of aspects such as the nature of the problem/study, Optimization or screening, the variables and interactions to be studied, and the resources available. A key part of the decision is also placed on the knowledge of past studies and identifying potential interactions between the process parameters (Gujral, Kapoor, and Jaimini, 2018).

The use of One Variable at a Time (OVAT) is deemed rigorous, costly, and poor when determining the optimal conditions when interactions are present between the independent variables (Oboh, Ackah and Owusu, 2018). Therefore, the alternative design of experiment (DOE) was chosen. Design of experiment (DOE) is an extremely powerful method used to determine which process variables are vital in the system and calculate the conditions the process variables need to be to maximise performance. This method is a relatively quick and cost-effective method that can be used to understand and optimize any process (Antony, 2002).

A multivariate analysis method is an experimental design that simultaneously determines the impact various independent parameters have on the response variability. Multivariate analysis can easily be done with the Box-Behnken design; therefore, it was chosen as an appropriate response surface methodology (Kamala Kumari, Yarraguntla, Sharmila and Harika, 2021). Box-Behnken Design does not accommodate combinations where the variables are all at the lowest or highest values. This is done to avoid situations where the experiment would perform under extreme conditions and potentially produce undesirable results (Ferreira et al., 2007). Therefore, it can reduce the required number of experiments to estimate the optimum process conditions to produce biodiesel. The equation below calculates the number of experiments required for the Box-Behnken Design (Ferreira et al., 2007).

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

$N = Experiments\ Required$; $C_0 = Central\ Points$; $k = factors\ chosen$

For the production of biodiesel, 4 independent factors and 3 central points.

$$N = 2\ x\ 4\ (4 - 1) + 3 = 27$$

The Box Behnken Design was completed on Minitab Statistical Software 2022. Four independent factors were varied: Reaction Temperature, Catalyst Loading, Reaction Time, and Alcohol to Oil Molar Ratio. The study contained 27 experiments for each catalyst type, including 3 replicates which ensured the reliability and accuracy of the findings. Minitab Statistical Software was used to estimate a regression equation using the recorded experimental results.

The following equations express the quadratic regression model in detail (Halder et al., 2015).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i X_i + \sum_{i=1}^{k} \beta_{ij} X_i X_j \tag{3.2}$$

Equation 3.3 below is the fully expanded version of Equation 3.2

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11}(X_1)^2 + +\beta_{22}(X_2)^2 + \beta_{33}(X_3)^2 \\ & + \beta_{44}(X_4)^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 \\ & + \beta_{34} X_3 X_4 \end{aligned} \tag{3.3}$$

The generated conditions of the independent factors in Table 3-3 *and* Table 3-4 were guided by the following literature data and preliminary experimental results. According to Sigma Aldrich (2023), ethanol has a boiling point of 78 ^{o}C. Therefore, the temperature of the reaction should not be higher than the boiling point of ethanol as this leads to the vaporisation of the alcohol and reduced contact between the reactants. This led to choosing the maximum temperature for homogeneous and heterogeneous transesterification at 74 ^{o}C and 70 ^{o}C, respectively. According to Marciniuk, Garcia, and Schuchardt (2014), alcohol to vegetable oil molar ratio commonly falls within the range from 6:1 to 30:1. Ethanol displays satisfactory results from 6:1 to 12:1 (Marciniuk, Garcia, and Schuchardt, 2014). Balat and Balat (2008) stated that acceptable ranges of molar ratios range from 6:1 to 30:1. Therefore, the decision to choose the homogeneous transesterification alcohol molar ratio range of 10:1 to 26:1 was made. A molar ratio of 8:1 to 20:1 was chosen for the heterogeneous transesterification process. According to a study by Ashok et al. (2018), a 93.3% yield of biodiesel was achieved with a 2% concentration loading of Magnesium Oxide (MgO). Similarly, a study by Rasouli and Esmaeili (2019), obtained their optimum biodiesel yield using 1 wt. % oil concentration loading of Magnesium Oxide (MgO). Therefore, this study will investigate the catalyst concentration loading of 1-2 wt. % oil. A study conducted by Malewska, Polaczek, and Kurańska (2022) investigated the various impacts catalyst have on the transesterification of used cooking oil utilizing a potassium catalyst concentration of 0.15 wt. % oil. Therefore, this study will investigate the catalyst concentration loading of 0.02-0.15 wt. % oil. Freedman, Kwolek, and Pryde (1986) stated that an increase in reaction time resulted in an increase in the conversion of triglycerides. However, the maximum conversion was achieved in under 90 minutes. According to a study by Anisah, Suwandi and Agustian (2019), the variation of time was studied by selecting reaction times of 30-150 minutes. These studies lead to an adapted range by utilizing a reaction time from 30-120 minutes.

Table 3-3: Experimental Design generated from Minitab Statistical Software for the transesterification of waste cooking oil with homogeneous catalyst KOH.

Experiment Number	**Reaction Temperature (ºC)**	**Potassium Hydroxide Catalyst Loading (wt. % oil)**	**Reaction Time (minutes)**	**Alcohol to Oil Molar Ratio**
1	30	0.020	75	18
2	74	0.020	75	18
3	30	0.150	75	18
4	74	0.150	75	18
5	52	0.085	30	10
6	52	0.085	120	10
7	52	0.085	30	26
8	52	0.085	120	26
9	30	0.085	75	10
10	74	0.085	75	10
11	30	0.085	75	26
12	74	0.085	75	26
13	52	0.020	30	18
14	52	0.150	30	18
15	52	0.020	120	18
16	52	0.150	120	18
17	30	0.085	30	18
18	74	0.085	30	18
19	30	0.085	120	18
20	74	0.085	120	18
21	52	0.020	75	10
22	52	0.150	75	10
23	52	0.020	75	26
24	52	0.150	75	26
25	52	0.085	75	18
26	52	0.085	75	18
27	52	0.085	75	18

Table 3-4: Experimental Design generated from Minitab Statistical Software for the transesterification of waste cooking oil with heterogeneous catalyst MgO.

Experiment Number	**Temperature (ºC)**	**Catalyst Loading (wt. % oil)**	**Reaction Time (minutes)**	**Alcohol/Oil Molar Ratio**
1	30	1.0	75	14
2	70	1.0	75	14
3	30	2.0	75	14
4	70	2.0	75	14
5	50	1.5	30	8
6	50	1.5	120	8
7	50	1.5	30	20
8	50	1.5	120	20
9	30	1.5	75	8
10	70	1.5	75	8
11	30	1.5	75	20
12	70	1.5	75	20
13	50	1.0	30	14
14	50	2.0	30	14
15	50	1.0	120	14
16	50	2.0	120	14
17	30	1.5	30	14
18	70	1.5	30	14
19	30	1.5	120	14
20	70	1.5	120	14
21	50	1.0	75	8
22	50	2.0	75	8
23	50	1.0	75	20
24	50	2.0	75	20
25	50	1.5	75	14
26	50	1.5	75	14
27	50	1.5	75	14

3.4) Experimental Procedure

All equipment used were thoroughly washed to ensure no impurities were present that may affect the reaction and final product produced. Two titrations were performed in order to calculate the free fatty acid (FFA) content and acid value of the used cooking oil.

3.4.1) Waste Canola Oil Preparation

1) The collected waste cooking oil was left to settle for 5 days at room pressure and temperature to prevent any dust accumulation.
2) Ahlstorm Filter Paper, Ahlstrom no. 1 (Equivalent to Grade 597), was used to filter the used canola oil.
3) The water removal process was completed by heating the filtered oil to 110 ^{o}C.
4) The free fatty acid (FFA) content was measured using the method in Section 3.4.2 and Section 3.4.3
5) If the FFA Content was higher than 0.5%, the next pre-treatment step followed, if the FFA was less than 0.5%, the pre-treatment process had stopped here.
6) 2.25 g methanol and 0.05 g sulfuric acid were added for each gram of FFA in the waste canola oil.
7) The methanol and sulfuric acid were first mixed together and then added to the treated oil.
8) The solution was agitated for 60 minutes at 60-65 ^{o}C.
9) The solution was placed into a separation funnel and allowed to settle. At the top of the funnel, a methanol-water layer formed. The top layer was removed (methanol, water, and sulfuric acid layer).
10) Using the biodiesel layer, the actual titration step was redone.
11) If the FFA content was still greater than 0.5%, return to step 6 using the new FFA content % for the proceedings. If FFA was lower than 0.5%, the Transesterification Reaction step followed.

3.4.2) Blank Titration

1) A 0.1 M standard solution of KOH was created. This was achieved by dissolving roughly 0.1 g of potassium hydroxide (KOH) pellets in 100 ml deionised water.
2) Four drops of phenolphthalein indicator were added to approximately 10 ml of methanol in a beaker.

3) Standard solution created was added to a burette, clamped onto the metal stand, and then titrated against the methanol-phenolphthalein mixture present in the beaker. The mixture was swirled continuously to make sure proper mixing occurred.
4) The solution reached endpoint when the indicator present turned the solution a light pink colour.

3.4.3) Actual Titration

1) Approximately 10 ml of methanol was added to a beaker containing 1 ml of the treated waste oil.
2) Four drops of phenolphthalein indicator were added to the mixture present in a glass beaker.
3) KOH standard solution created, already present in the burette, was titrated against the methanol-oil mixture present in the beaker.
4) The mixture reached endpoint when the indicator present turned the mixture a light pink colour.
5) With the volume of standard solution used to achieve endpoint along with the volume from the blank titration, the free fatty acid (FFA) content and acid number of the oil can now be calculated.

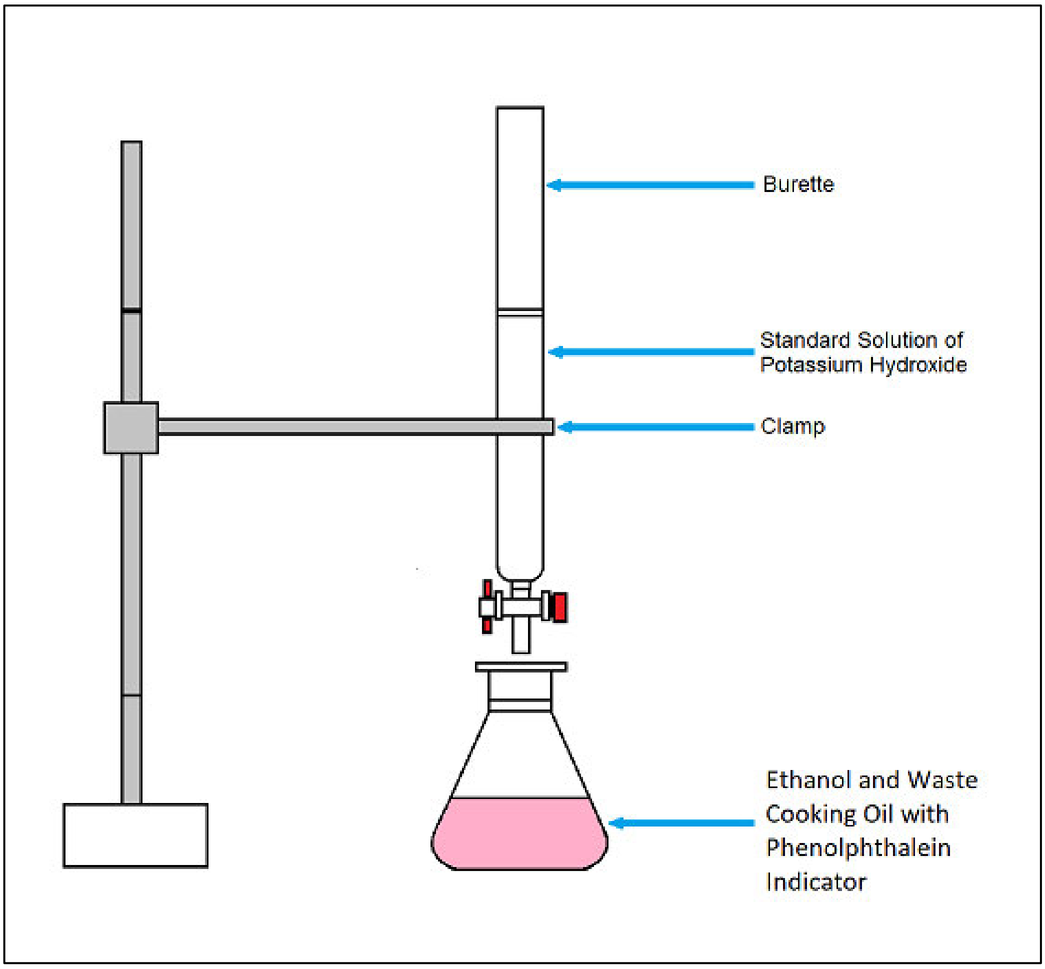


Figure 3-2: Actual Titration Process.

3.4.4) Catalyst Preparation for Heterogeneous Transesterification only

1) Magnesium oxide completed calcination at 800 ^{o}C for 120 minutes in a furnace.
2) The magnesium oxide is then put under vacuum conditions in a desiccator which has a desiccant present.

Note: The following steps are the steps followed to complete experiment 21 for Homogeneous Transesterification.

3.4.5) The Transesterification Reaction:

1) 200 ml of treated waste oil was measured out using a measuring cylinder and added to a 600 ml beaker.
2) A water bath was prepared and pre-heated to a temperature of 52 ^{o}C using the PolyScience 7306A11B Standard Immersion Circulator. The 600 ml beaker with the

treated waste oil was then clamped and positioned in the water bath to allow the oil to heat up. Mechanical stirrer was then switched on and set to 600 rpm, stirring the oil.

3) Whilst the temperature of the oil increased, the amount of ethanol was calculated using an alcohol ratio of 10:1. The volume of the ethanol needed was measured out in a beaker.
4) A catalyst loading of 0.02% wt. to waste canola oil was utilised. The calculated amount of potassium hydroxide pellets was weighed out on the analytical balance and then added to the ethanol in the beaker.
5) The ethanol and KOH pellets were then stirred continuously, and the mixture could only be added once the KOH pellets dissolved completely in the ethanol. The KOH catalyst pellets did not dissolve easily in ethanol and therefore had to be crushed with a glass rod and stirred until it completely dissolved.
6) The solution was added to the 600 ml beaker containing the treated oil. Parafilm was used to cover the opening of the beaker to prevent any ethanol vapour from escaping.
7) A thermometer was used to determine the temperature of the reaction, but the water bath kept the temperature relatively constant. This was removed as the reaction proceeded.
8) While the reaction continued, it was evident to see that two separate layers were forming, the upper layer was the biodiesel product, and the lower layer was the glycerol.
9) The reaction was allowed to proceed for 75 minutes before switching off the mechanical stirrer and being removed from the water bath.

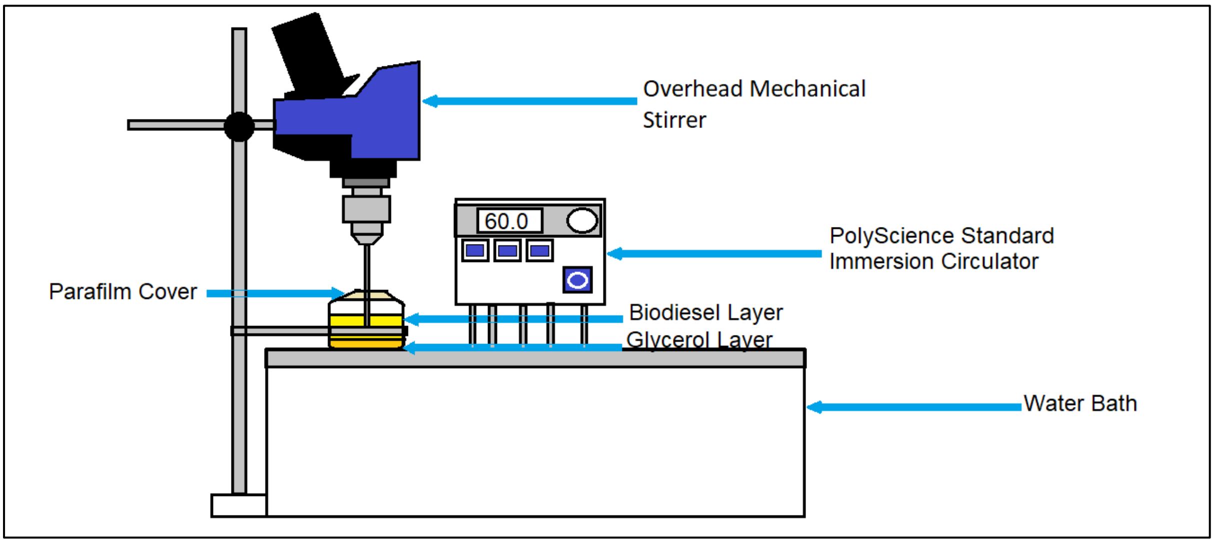


Figure 3-3: Transesterification Process.

3.4.6) Separation of Products:

1) The solution was left to cool in the beaker for 20 minutes after the reaction time had completed and then poured into the separation funnel.
2) To remove any impurities such as excess ethanol, glycerol and potassium hydroxide remaining in the biodiesel product, 3 drops of deionised water heated to 50 ^{o}C were added with a dropper to dissolve the impurities. The deionised water forms a white cloud when added and excess ethanol and impurities dissolve into the cloud and sink to the bottom.
3) The product was left to separate for 5 hours. This allowed the glycerol and biodiesel product to separate into 2 distinct layers.
4) The tap of the separating funnel was then opened, and the glycerol layer was removed and discarded into a waste container.
5) The biodiesel was then drained and added into a clean beaker.
6) Heterogeneous Catalyst Only: A centrifuge was utilised to remove any catalyst still present in the biodiesel product. The centrifuge was set to 6000 rpm for approximately 15 minutes.

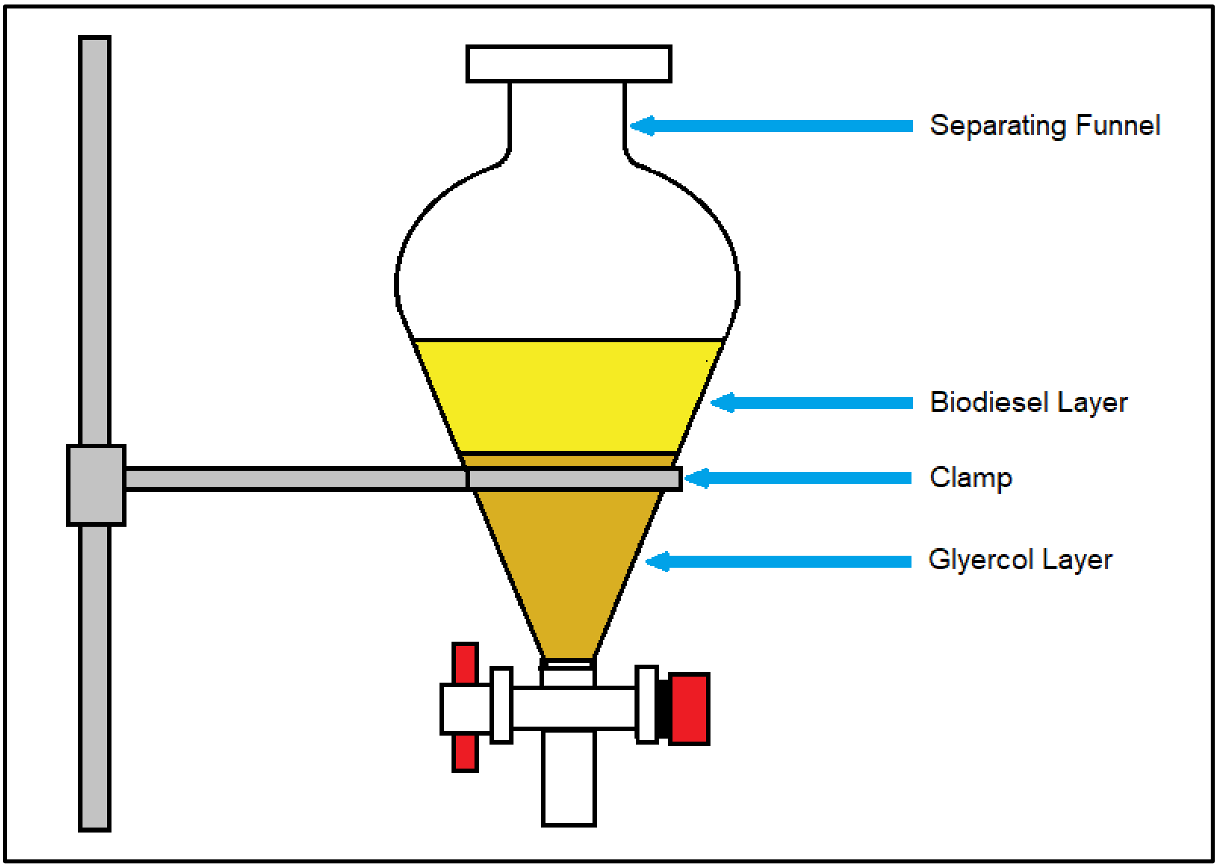


Figure 3-4: Separation Process.

3.4.7) Rotary Evaporator

1) The biodiesel was then added into the round bottom flask and attached to the rotary evaporator and the tap inlet for the cooling coils was opened.
2) The bath temperature was set to 90 ^oC (heterogeneous catalyst) and 70 ^oC (homogeneous catalyst) and the speed of rotation was chosen to be 35 rpm.
3) The round flask was immersed in the oil bath and the pressure was set to 150 mBar.
4) This process allowed for the removal of excess ethanol as well as the purification of the biodiesel product. The process continued until no more liquid was visibly entering the distillate connected to the condenser.

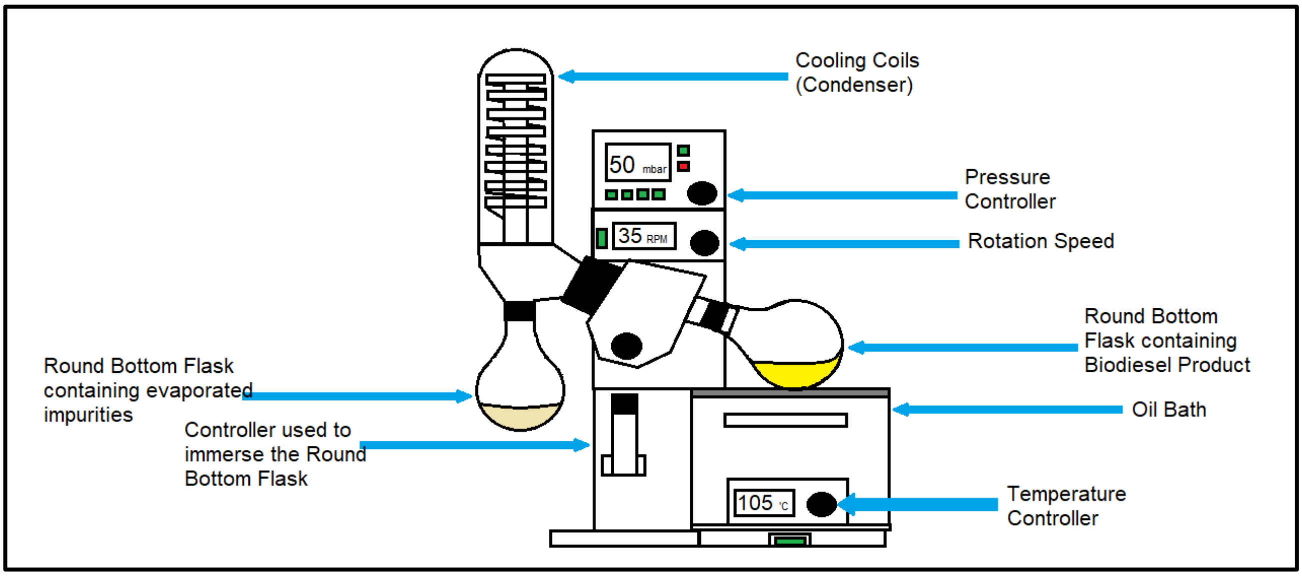


Figure 3-5: Rotary Evaporator.

3.4.8) Property testing

3.4.8.1) Density:

1) Roughly 8 ml of the final biodiesel sample was inserted into a syringe and inserted into the Density Meter Easy D40. This instrument is used to accurately record the density of the product at 15 ^oC.

2) Once the density was recorded, the instrument undergoes a drying process where a compressed air tube was connected, and the machine visibly displayed the density on the monitor. The tubes force all the samples out of the machine, and the sample leaves out the tubing without any contaminants present.

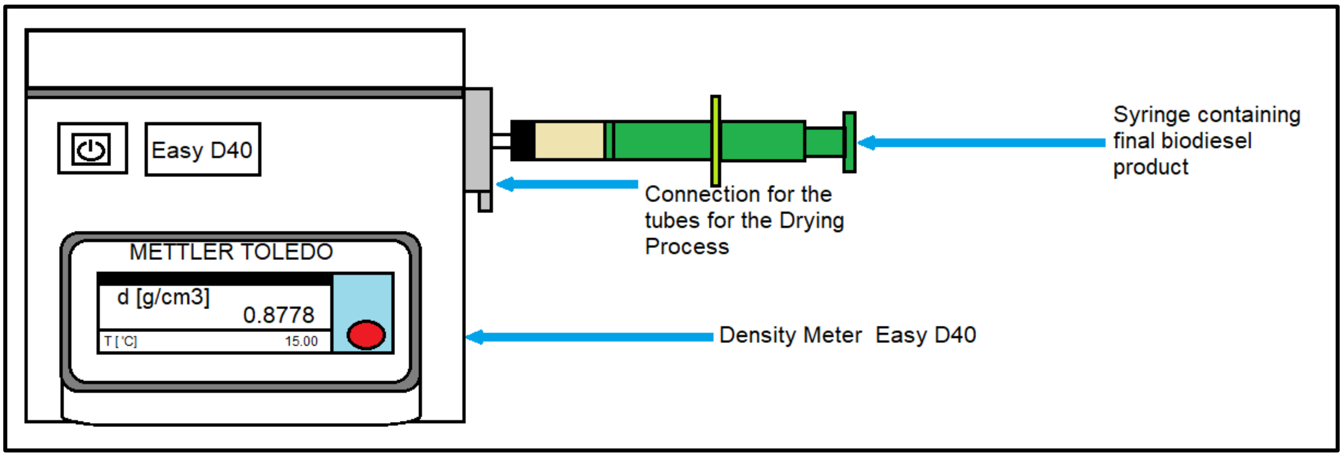


Figure 3-6: Density Meter Easy D40.

3.4.8.2) Viscosity:

1) Viscosity of the biodiesel product was estimated using the BROOKFIELD DV-II+Pro Viscometer, a beaker and various spindles were used in order to obtain an accurate viscosity reading.
2) The final biodiesel product was added to a 200 ml beaker.
3) The correct spindle chosen produced a torque under 10%. Therefore, in order to achieve this, various spindles were used until the correct spindle for the biodiesel product was found.

4) The viscometer was left to stabilise for 10 minutes. The final viscosity reading was then taken.

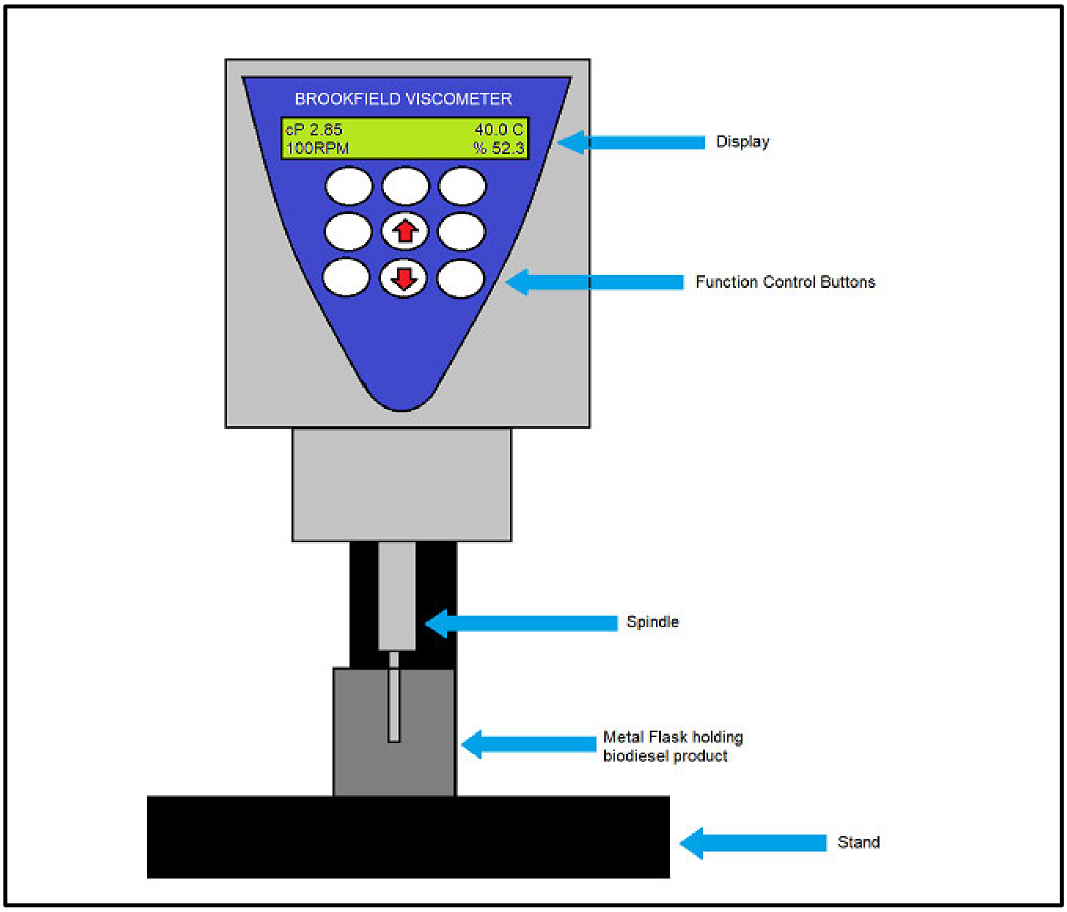


Figure 3-7: The Viscometer.

3.4.8.3) Refractive Index:

1) Before use, the refractometer was calibrated utilising deionised water.
2) After the calibration process, 3 drops of biodiesel were added onto the refractometer and covered.
3) Refractometer displayed the Refractive Index for the biodiesel product.

4) This was done three times and the average Refractive Index was calculated.

Figure 3-8: Photograph of Refractometer.

3.4.8.4) Percentage Hydrogen:

1) Before use, the pH meter had to be calibrated using a set of standard solutions of different pH: a 4.01 pH and a 7.01 pH.
2) The sample of the biodiesel product was placed in a thin, tall 100 ml beaker and the pH meter's probe was placed in the beaker in order to determine the pH.

Figure 3-9: Photograph of pH Meter.

3.4.8.5) Pour Point:

1) 30 ml sample of biodiesel was added to a 50 ml beaker.
2) Parafilm was used to cover the beaker and then the beaker was positioned in the Haier Ultra Low Temperature Freezer.
3) The samples were inspected every 30 seconds by tilting the beaker until the biodiesel product was unable to flow. The temperature at which the product solidifies and cannot flow was recorded with a MajorTech Type K/J Thermometer.

CHAPTER 4: Results and Discussion

4.1) Used Canola Oil Transesterification Utilising Potassium Hydroxide

This chapter discusses Potassium Hydroxide as the homogeneous alkaline catalyst in the transesterification for used canola oil and the alcohol chosen, ethanol. The Box-Behnken design method was chosen because of the ability to carry out multivariant analysis on the experiments easily. This design method is considered to be the most powerful and most proficient compared to the other designs such as the Doehlert design, three-level full factorial design and central composite design. This software generated 27 experiments with varying parameters in order to estimate the optimal reaction conditions for these parameters: Reaction Temperature, Catalyst Loading, Reaction Time and Alcohol to Oil molar ratio.

The acid value of canola oil was found to be relatively low at 0.1167 mg KOH/g. This indicates canola oil can undergo transesterification with a base catalyst in a single step reaction to produce Biodiesel (Rutz and Janssen, 2006). This study aimed to determine whether used canola oil could be used to produce biodiesel. To prevent any contamination and ensure the validity of the results, fresh canola oil underwent simulated cooking. The canola oil was cooked at 180 ^{o}C for 5 hours (Sarno and Iuliano, 2019). After cooking, the waste cooking oil was collected and allowed to settle for 5 days at room temperature and pressure to prevent any dust accumulation. Ahlstorm Filter Paper Ashlstrom No. 1, equivalent to grade 597, was utilised to filter the used canola oil. The filter oil was subjected to 110 ^{o}C to eliminate any moisture in the oil. The acid value for the cleaned oil was found to be low at 0.3535 mg KOH/g oil. Since the acid value was lower than 1%, the single step transesterification method could be used to produce biodiesel (Rutz and Janssen, 2006). A pre-treatment method was prepared to treat the cleaned oil if the acid value was found to be higher than 1%. This involved using methanol and sulfuric acid to decrease free fatty acid content in the oil. The low acid value found for the used oil was one of the contributing factors that led to the choice of utilising a catalyst loading range of 0.02-0.15 wt% of oil.

The yield of biodiesel produced using ethanol as the chosen alcohol over methanol is advantageous since ethanol and the chosen catalysts produce higher yields of biodiesel. A contributing deciding factor is that ethanol is produced from renewable resources and therefore ethyl esters are more environmentally friendly than methyl esters (Manurung, Bestari and Syabri, 2017). It can be noted that the transesterification chemical formula requires a 3:1

stoichiometric ratio for the production of biodiesel. However, since the reaction is reversible, the presence of excess alcohol in the reaction promotes the forward reaction by shifting the equilibrium to the right-side (Mandari and Devarai, 2021). Due to this reasoning, for this study, the alcohol ratio range was chosen to be 10:1 to 26:1. Freedman, Kwolek, and Pryde (1986) stated that an increase in reaction time resulted in an increase in the conversion of triglycerides. However, the maximum conversion was achieved in under 90 minutes. According to a study by Anisah, Suwandi and Agustian (2019), the variation of time was studied by selecting reaction times of 30-150 minutes. These studies lead to an adapted range by utilizing a reaction time from 30-120 minutes. An extended separation period was required as the solubility of glycerol increased due to higher alcohol concentrations. In the homogeneous separation phase for this study, the total separation time was approximately 5 hours.

Using Minitab Statistical Software and the Box-Behnken Design Model, 27 experiments were generated to complete this study on used canola oil. These experiments were conducted three times to ensure accurate and reliable results. After the experimental phase, Minitab Statistical Software was utilised to estimate a regression equation using recorded experimental results. Each parameter was assigned a letter for simplicity:

$$\boldsymbol{A = Temperature\ (^{o}C)}$$

$$\boldsymbol{B = Catalyst\ Loading}\ (\%)$$

$$\boldsymbol{C = Reaction\ Time\ (minutes)}$$

$$\boldsymbol{D = Alcohol\ to\ Oil\ Molar\ Ratio}$$

Table *5-1* shows the experimental yield and the calculated yield of the biodiesel results for the catalyst KOH. The experimental yield shown was the average of three experiments for each run. The calculated yield is the yield generated using the regression equation 4.1 obtained from Minitab Statistical Software. The ranges for each process variable interval are explained in Section 3.3.

Table 5-1: Biodiesel Results from KOH.

Run Number	**Temperature (^oC)**	**Catalyst Loading (%)**	**Time (min)**	**Alcohol To Oil Ratio**	**Experimental Yield**	**Calculated Yield**
1	30	0.020	75	18	0.8479	0.8592
2	74	0.020	75	18	0.8536	0.8636
3	30	0.150	75	18	0.7976	0.8061
4	74	0.150	75	18	0.8370	0.8442
5	52	0.085	30	10	0.7589	0.7538
6	52	0.085	120	10	0.7793	0.7915
7	52	0.085	30	26	0.8422	0.8503
8	52	0.085	120	26	0.8516	0.8765
9	30	0.085	75	10	0.7906	0.8061
10	74	0.085	75	10	0.8090	0.8218
11	30	0.085	75	26	0.8853	0.8912
12	74	0.085	75	26	0.9153	0.9181
13	52	0.020	30	18	0.8054	0.8061
14	52	0.150	30	18	0.7638	0.7658
15	52	0.020	120	18	0.8161	0.8340
16	52	0.150	120	18	0.7826	0.8019
17	30	0.085	30	18	0.8383	0.8350
18	74	0.085	30	18	0.8247	0.8345
19	30	0.085	120	18	0.8519	0.8452
20	74	0.085	120	18	0.8874	0.8883
21	52	0.020	75	10	0.7732	0.7717
22	52	0.150	75	10	0.7580	0.7586
23	52	0.020	75	26	0.8919	0.8856
24	52	0.150	75	26	0.8302	0.8262
25	52	0.085	75	18	0.8651	0.8824
26	52	0.085	75	18	0.8968	0.8824
27	52	0.085	75	18	0.8701	0.8824

Table *5-1* displays the highest yield of biodiesel of 0.9153 obtained at run twelve. This run took place at 74 ^{o}C, had a catalyst loading of 0.085%, 75-minute reaction time and 26:1 alcohol to oil molar ratio. The smallest biodiesel yield was found to be 0.7580, which was obtained from run 22. This run had a temperature of 52 ^{o}C, a catalyst loading of 0.15%, a 75-minute reaction time and a 10:1 alcohol to oil molar ratio. Contributions that could have resulted in the lower yield were the lowest possible alcohol ratio in the study and the highest possible amounts of catalyst in the study. The presence of a large quantity of excess catalyst may have resulted in saponification occurring in the reaction phase of the experiment.

The regression equation below was generated on Minitab Statistical Software via multivariable regression analysis. Each parameter of the experiment below was assigned a Letter.

$$\begin{aligned} Y = 0.505 - 0.00217A + 1.532B + 0.002568C + 0.02303D + 0.00001A^2 - 10.4B^2 \\ - 0.000018C^2 - 0.000436D^2 + 0.00589AB + 0.000011AC \\ + 0.000016AD + 0.0007BC - 0.0223BD - 0.000008CD \end{aligned} \tag{4.1}$$

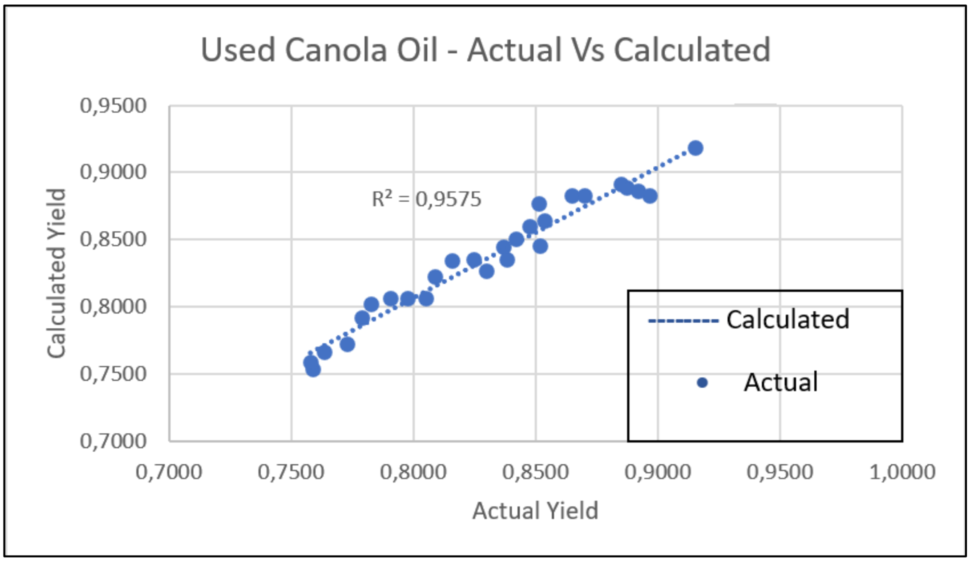


Figure 5-1: Used cooking oil biodiesel production: Actual vs Calculated.

Figure *5-1* shows the experimental yield (actual yield) obtained against the calculated (predicted model). The actual yield values were obtained as the average of three from each run. The calculated yield values were obtained using regression equation 4.1. Figure *5-1* displays a linear trendline with an R^2 value very close to 1, thus demonstrating a high degree of correlation between the predicted values and the experimental values. Table *5-2* shows the probability p-value for the regression model is 0 which suggests the model is very significant. For the 95%

confidence level, statistical significance is indicated by a p-value less than 0.05 (Zhang and Zheng, 2009).

4.1.1) Anova Analysis for Regression Model

Table *5-2* displays the ANOVA Analysis performed on the Full Quadratic regression model. The intent of completing the ANOVA Analysis was to establish whether any statistically significant differences exist between the four process variables.

Table 5-2: ANOVA Analysis for Regression Model and Results.

Analysis Source	**Degree of Freedom**	**Adjusted Sum of Squares**	**Adjusted Mean Squares**	**P-Value**	**Characteristics**
Model	14	5.145E-02	3.675E-03	0.000	Significant
Linear	4	3.165E-02	7.912E-03	0.000	Significant
Temperature	1	9.780E-04	9.780E-04	0.043	Significant
Catalyst Loading	1	3.992E-03	3.992E-03	0.001	Significant
Reaction Time	1	1.699E-03	1.699E-03	0.011	Significant
Molar Ratio	1	2.498E-02	2.498E-02	0.000	Significant
Square	4	1.846E-02	4.614E-03	0.000	Significant
Temperature*Temperature	1	1.140E-04	1.140E-04	0.455	Not Significant
Catalyst Loading*Catalyst Loading	1	1.031E-02	1.031E-02	0.000	Significant
Reaction Time*Reaction Time	1	7.470E-03	7.470E-03	0.000	Significant
Molar Ratio*Molar Ratio	1	4.158E-03	4.158E-03	0.001	Significant
2-Way Interaction	6	1.340E-03	2.230E-04	0.382	Not Significant
Temperature*Catalyst Loading	1	2.840E-04	2.840E-04	0.246	Not Significant
Temperature*Reaction Time	1	4.360E-04	4.360E-04	0.156	Not Significant
Temperature*Molar Ratio	1	3.300E-05	3.300E-05	0.683	Not Significant
Catalyst Loading*Reaction Time	1	1.700E-05	1.700E-05	0.773	Not Significant
Catalyst Loading*Molar Ratio	1	5.400E-04	5.400E-04	0.118	Not Significant
Reaction Time*Molar Ratio	1	3.100E-05	3.100E-05	0.695	Not Significant
Error	12	2.286E-03	1.900E-04		
Lack-of-Fit	10	1.706E-03	1.710E-04	0.768	Not Significant
Pure Error	2	5.800E-04	2.900E-04		
Total	26	5.373E-02			

This analysis technique generated p-values. These p-values were used to establish whether the relationship between the four process variables from the experiments are significant or not significant. The null hypothesis is that there is no association between the term and the response, i.e., Process Variable A and A or Process Variable A and B. Minitab Statistical Software utilises a significance level of 0.05. This indicates that there is a 5% risk of concluding that an association exists even though there is no actual association. Table *5-3* shows the interpretations of the model terms.

Table 5-3: Significant model terms and their interpretations

Model Term	Interpretation
If the process variable for a factor is significant, e.g., process variable A.	Conclude that not all level means are equal.
If the process variables for the interaction are significant, e.g., process variables A and B.	Conclude that the relationship between the process variables depends on other factors in the model. Suggesting that the model should include both the interaction effects and the main effects.

Table *5-2* indicates all four process variables are linearly significant. These four parameters have a great effect on the biodiesel yield obtained from the transesterification of ethanol and used canola oil with potassium hydroxide.

This full quadratic model included many insignificant coefficients which were found in the statistical analysis, these terms could have contributed to a lower calculated R^2 value at 0.7928. Potentially removing the not significant terms from the full quadratic model, may improve the model regression. This will be investigated in Section 4.1.2. This value is greater than the minimum limit for a great fit for a regression model (Joglekar and May, 1987). The aim of this thesis was to investigate the effect the chosen parameters had therefore, the current unmodified regression model developed is a great fit for the experimental results. Further experimentation would be required to determine whether modification of the model would result in the ability to predict biodiesel yield outside the range of the process parameters in this thesis.

4.1.2) Homogeneous Transesterification Regression Model

Table *5-4* displays the various reduced models estimated to generate a regression equation for the experimental results.

Table 5-4: Reduction of the Proposed Regression Model Summary.

Regression Model	Standard Deviation	R^2 Value	R^2 (adjusted) Value	R^2(calculated) Value
Linear	0.03168	0.5890	0.5143	0.4175
Linear + Square	0.02024	0.8551	0.8018	0.7240
Linear + 2-Way Interactive	0.03601	0.6139	0.3727	0.0056
Full Quadratic	0.01380	0.9575	0.9078	0.7928

Qiu et al. (2013) states the definition for the correlation (R^2) value is “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.” According to an investigation performed by Joglekar and May (1987), the minimum limit for R^2 required to represent a great fit for a regression model is 0.8. The results displayed in Table *5-4* show that the linear + square model and the full quadratic model obtained R^2 values above 0.8. The full Quadratic model obtained an R^2 value significantly higher than the linear + square model. This indicates that the full quadratic regression model estimated the best fit to the experimental results recorded. This indicates that this regression model would be the most accurate in estimating the yield of biodiesel for this study.

Table *5-4*, displayed a R^2 at 0.9575 and adjusted R^2 at 0.9078 with a confidence level of 95%. The calculated R^2 value was found to be 0.7928, this represents that the quadratic model for the study is 79,28 % accurate predicting the yield not within the range of the process parameter of this thesis. The calculated R^2 is significantly smaller when compared to the R^2 and adjusted R^2, and the value is less than 0.8 which is the minimum limit for R^2 to be a good representation of the regression model. Therefore, this quadratic model obtained through this study could only be utilised to accurately estimate the yield within the ranges of process variables chosen for this thesis.

Standard Deviation according to this study, “represents the standard deviation of the distance between the data values and the fitted values.” Standard deviation for each model is displayed as the S-value in Table *5-4*. The full quadratic model displayed a standard deviation of 0.01380. This extremely low value indicates a small deviation of the data points from the estimated values, signifying the regression model equation estimated from this thesis is a great fit for the experimental results.

4.1.3) Minitab Statistical Software: Response Optimiser

To reduce the cost of the overall biodiesel production process, it is necessary to determine the optimum reaction conditions to produce the highest possible yield of biodiesel. The function Response Optimiser was used on Minitab Statistical Software to accurately predict the optimum conditions to produce biodiesel within the chosen process parameters. The response optimizer tool calculates the optimal solution using the input process variables while producing an optimisation plot. This plot allows the ability to interact and change the process variables to investigate how to potentially improve upon the initially generated biodiesel yield and optimal conditions. Table *5-5* shows the optimum conditions.

Table 5-5: Optimal Reaction Conditions estimated from Minitab Statistical Software.

Reaction Temperature (ºC)	**Percentage of Catalyst Loading (%)**	**Molar Ratio**	**Reaction Time (Minutes)**	**Calculated Yield**
74	0.06727	26	84.55	0.9247

The maximum yield was estimated at 0.9247. An investigation was completed to produce biodiesel using these optimum conditions in the laboratory, the yield was found to be 0.9358. An experimental error of 1.2% was calculated, which is significantly small thereby supporting the conclusion that the full quadratic regression model will be a great fit for the thesis.

4.1.4) Three-Dimensional Surface Response Plots and Contour Plots

Surface Response Plots and Contour Plots are used to determine the effects the four parameters had on the optimum biodiesel yield. These plots were generated using MATLAB R2021B and the regression equation 4.1. These generated plots are displayed from Figure 4-2 to 4-17. An individual plot displays the impact two parameters have on biodiesel production within the chosen ranges. The remaining parameters were set at their respective median values. The surface response plots show how each parameter influences biodiesel production. The degree of curvature in the contour plots displays the nature and extent of the interaction for two parameters. Referring to Qiu et al. (2013), an elliptical contour plot displays a noticeable interaction, whereas a negligible interaction is displayed by a more circular contour plot.

4.1.4.1) Process Variables: Catalyst Loading (B) vs Reaction Temperature (A)

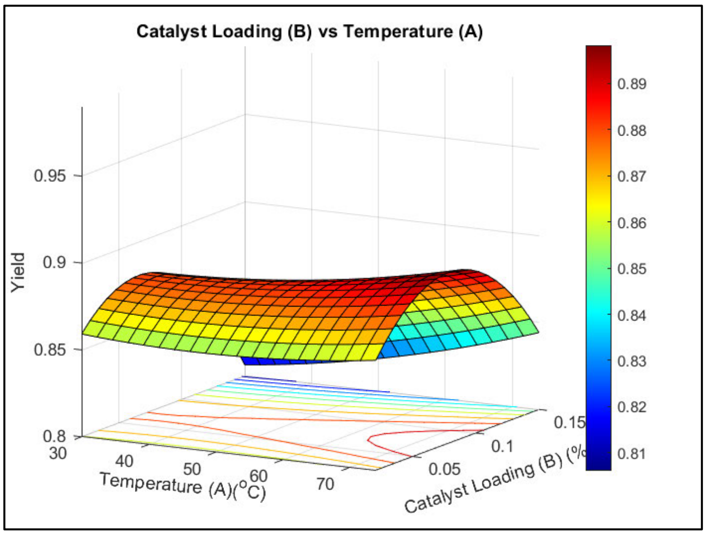


Figure 5-2: Influence Catalyst Loading and Reaction Temperature have on Biodiesel Yield.

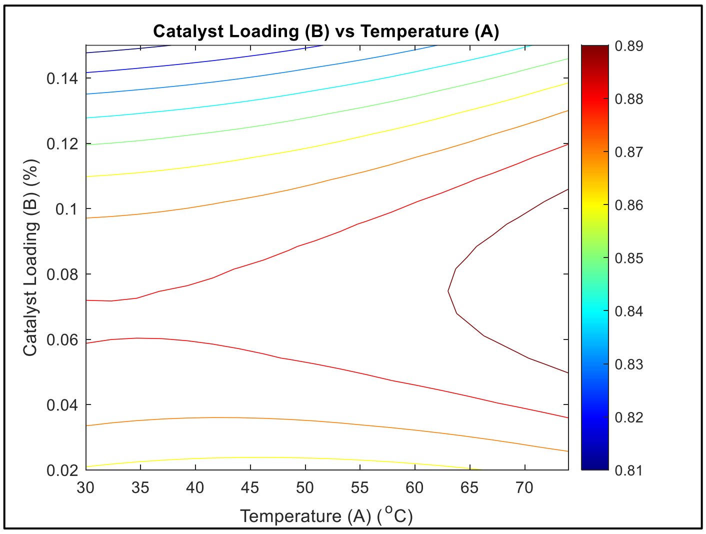


Figure 5-3: Nature and extent of interaction between catalyst loading and Reaction Temperature on biodiesel yield.

Figure *5-2* displays the three-dimensional Surface Response Plot showing the surface interaction between process variables (B) and (A). This plot shows an early increase in biodiesel yield with a rise in catalyst loading, however after the optimal alcohol to oil molar ratio of 0.0747 wt. %, growing amounts of excess catalyst present results in decreasing the yield. According to Rahimi et al. (2014), large quantities of base catalyst present in the system could lead to the production of soap and a decrease in the biodiesel yield produced. It can be noted that increasing the temperature resulted in improved yields of biodiesel due to the transesterification reaction being endothermic. Endothermic reactions absorb heat and higher temperatures favour the forward reaction (Antolin et al., 2002). The increase in catalyst concentration could have caused the parabolic nature of catalyst loading, as this exponentially increases the production of soap. As the reaction temperature increases, the rate of transesterification and saponification increases as well (Nisar et al., 2021). It is important to limit the amount of excess catalyst. Excess alkaline catalysts reduce biodiesel yield as more triglycerides partake in the saponification reaction producing more soap (Leung and Guo, 2006). The lowest biodiesel yield produced resulted from a high catalyst loading and low reaction temperature. Therefore, high temperatures and moderate catalyst loading result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.246 had been estimated indicating these two process variables are not statistically significant. Figure *5-3* further supports the statement as a circular plot is displayed on the right side of the plot indicating negligible interactions.

4.1.4.2) Process Variables: Reaction Time (C) vs Reaction Temperature (A)

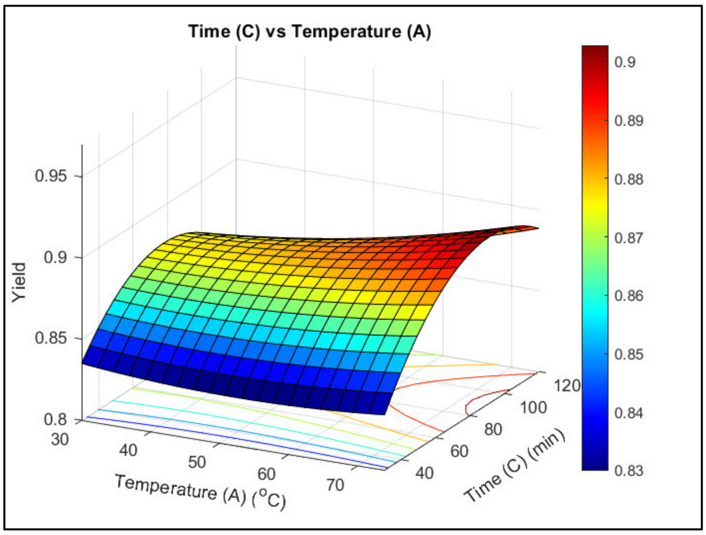


Figure 5-4: Influence Reaction Time and Reaction Temperature have on Biodiesel Yield.

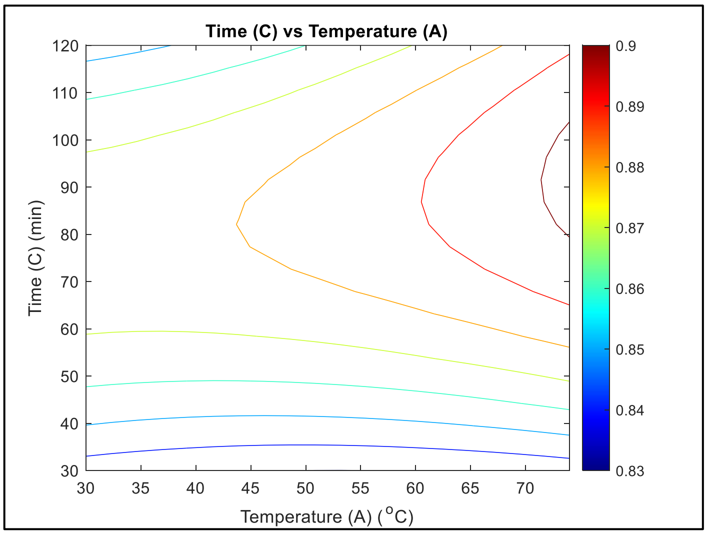


Figure 5-5: Nature and extent of interaction between Reaction Time and Reaction Temperature on Biodiesel Yield.

Figure *5-4* displays a three-dimensional Surface Response Plot showing the surface interaction between process variables (C) and (A). The transesterification of triglycerides are endothermic reactions. Therefore, an increase in temperature will favour the forward reaction (Daramola et al., 2016). The biodiesel yield increased with longer reaction times up till 91.57 minutes; any additional time after this period gradually decreased the biodiesel yield. This gradual decline could have been caused by the forward reaction completing as a result of one of the reactants being used up. This would have favoured the reverse reaction and resulted in reduced biodiesel yield and soap production. Regardless of the temperature, a lower yield was produced when there was insufficient time for the transesterification reaction to complete. It can therefore be noted that high temperatures and high reaction times result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.156 had been estimated indicating these two process variables are not statistically significant. Figure *5-5* further supports the statement as the interaction between reaction time and reaction temperature display curved figures above 45 ^{o}C and 60 minutes indicating negligible interactions.

4.1.4.3) Process Variables: Alcohol to Oil Molar Ratio (D) vs Reaction Temperature (A)

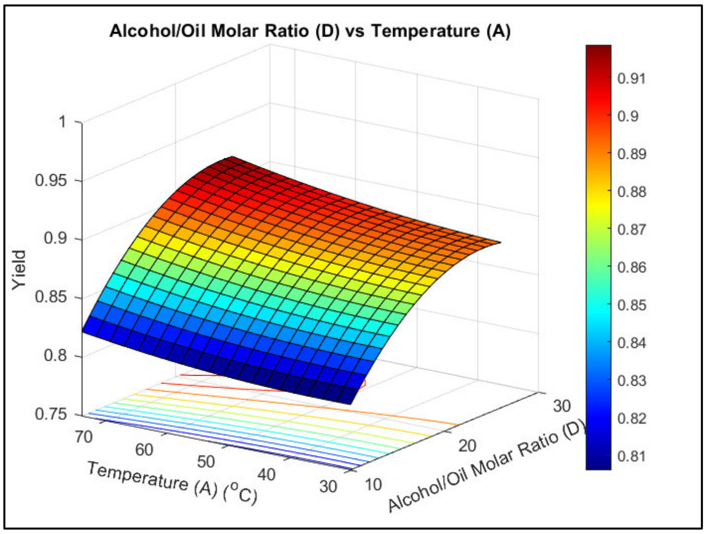


Figure 5-6: Influence of Alcohol/Oil Molar Ratio and Reaction Temperature on Biodiesel Yield.

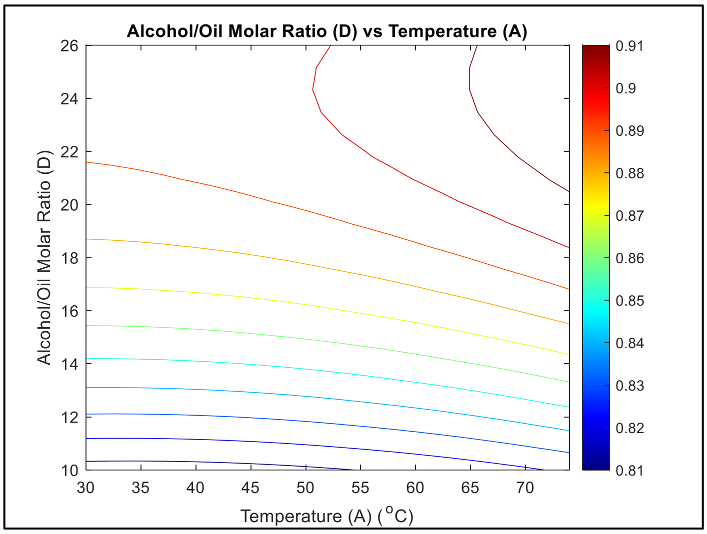


Figure 5-7: Nature and extent of interaction between Alcohol/Oil Molar Ratio and Temperature on Biodiesel Yield.

Figure *5-6* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (D) and (A). The surface response plot shows that a rise in reaction temperature resulted in improved biodiesel yields. Transesterification reactions are endothermic and elevated temperatures favour the forward reaction (Antolin et al., 2002). Increasing the alcohol to oil molar ratio leads to a rise in biodiesel production. The alcohol to oil molar ratio displays a directly proportional relationship with the yield of biodiesel. As Le Chatelier's Principle specified, increasing the volume of alcohol above the optimum volume would increase the solubility of glycerol in biodiesel. This glycerol interacts with biodiesel and causes equilibrium to shift back to the left-side. Thus, favouring the reverse reaction thereby reducing the yield produced. Therefore, the interactions with process variables A and D resulted in a 24.90:1 alcohol molar ratio was found to be the optimal molar ratio. The lowest regions of the surface response plot were found when the alcohol to oil ratio was 10:1, however increasing the reaction temperature from 30 °C to 70 °C caused a slight rise in biodiesel production. Therefore, high reaction temperatures and high Alcohol to Oil molar ratios result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.683 indicates that the two process variables are not statistically significant. Figure *5-7* also supports this statement, as the contour plot displays a circular shape in the upper regions of the plot indicating negligible interactions.

4.1.4.4) Process Variables: Reaction Time (C) vs Catalyst Loading (B)

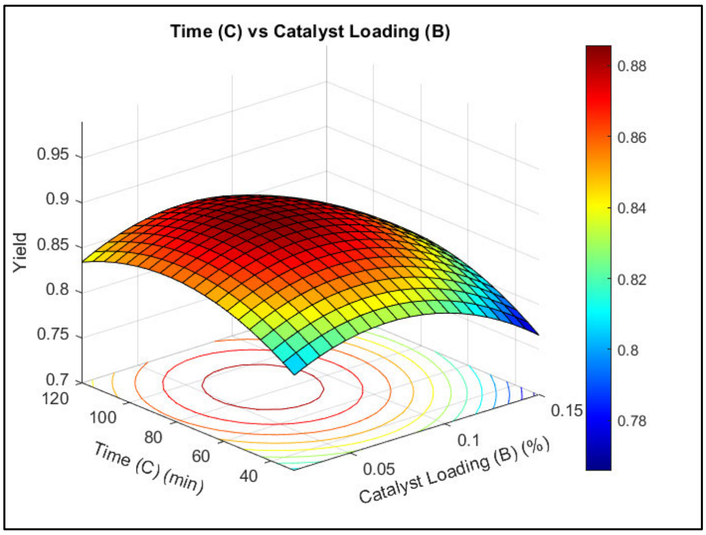


Figure 5-8: Influence of Reaction Time and Catalyst Loading on Biodiesel Yield.

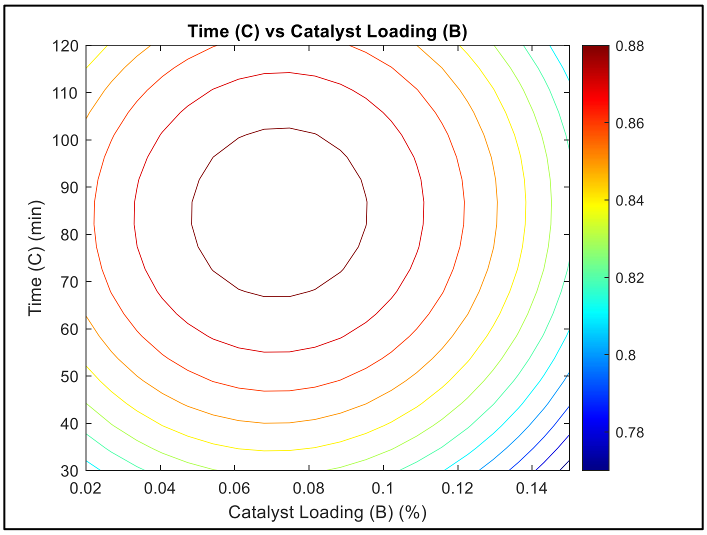


Figure 5-9 Nature and extent of interaction between Reaction Time and Catalyst Loading on Biodiesel Yield.

Figure *5-8* displays a three-dimensional Surface Response Plot showing the surface interaction between process variables (C) and (B). This figure shows a parabolic effect present between Catalyst loading and the biodiesel yield. Initially, increasing the amount of catalyst leads to the biodiesel yield increasing accordingly however after 0.075 wt. %, increasing amounts of excess catalyst result in a reduction in biodiesel production. High amounts of base catalyst may lead to soap production (Gashaw and Teshita, 2014). The saponification reaction simultaneously produces soap during the transesterification reaction when the feedstock has elevated levels of free fatty acid content (Reda, 2014). Soap can also form during the hydrolysis reaction of a triglyceride if there is moisture present in the reaction (Pullen and Saeed, 2015). Therefore, ensuring all equipment used was clean and dry was essential. According to Thanh et al. (2012), soap creation negatively affects the glycerol separation from the biodiesel layer and inhibits the purification process of fatty acid esters with water. Reaction Time displays a similar effect as catalyst loading, a parabolic effect is present between reaction time and the biodiesel yield. The steady decline in yield after 86.84 minutes is reached could be due to the fact that adequate time was provided for the reaction to complete and as more product was forming, equilibrium shifted to favour the reverse reaction thereby reducing the biodiesel yield. The lowest amount of biodiesel produced was found in the region with a low reaction time and a high catalyst concentration. Therefore, moderate Catalyst Loading and moderate reaction time result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.773 had been estimated indicating these two process variables are not statistically significant. Figure *5-9* further supports this statement, as the contour plot displays circular contour lines throughout the plot indicating negligible interactions.

4.1.4.5) Process Variables: Alcohol to Oil Molar Ratio (D) vs Catalyst Loading (B)

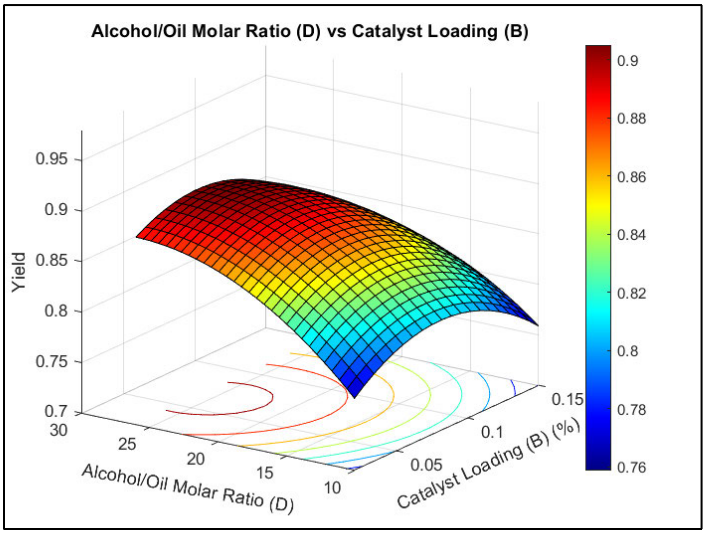


Figure 5-10: Influence of Alcohol/Oil Molar Ratio and Catalyst Loading on Biodiesel Yield.

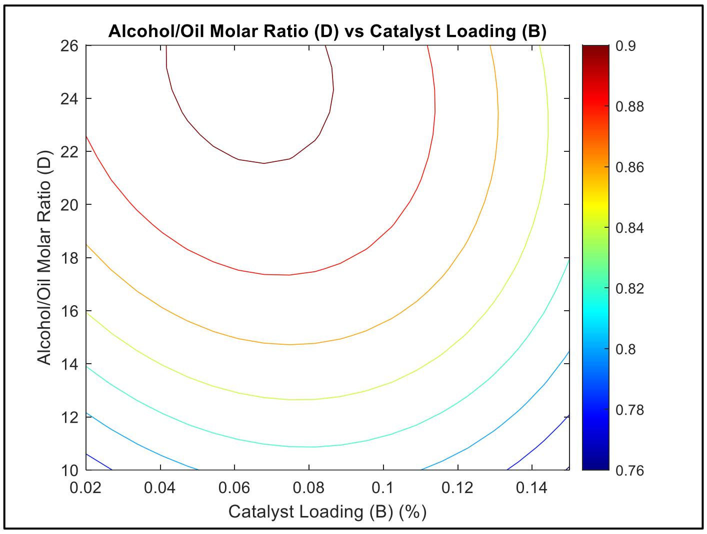


Figure 5-11: Nature and extent of interaction between Alcohol/Oil Molar Ratio and Catalyst Loading on Biodiesel Yield.

Figure *5-10* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (D) and (B). A parabolic effect is displayed between Catalyst loading and biodiesel yield. It can be seen that increasing the quantity of catalyst results in the biodiesel yield rises accordingly however after 0.061 wt. %, increasing amounts of excess catalyst result in a decrease in biodiesel production. A directly proportional relationship exists between Process Variables B and D, however after passing the optimal alcohol molar ratio of 24.90:1, any increase in the volume of alcohol results in a reduction in biodiesel yield. A large excess amount of ethanol and moderate catalyst amounts are required to drive the reaction forward. According to an investigation by Fereidooni et al. (2017), biodiesel with high viscosity was produced when large amounts of base catalyst were used. This not only complicates the separation phase of removing the glycerol but also leads to biodiesel that cannot be utilised in diesel engines. The lowest yield of biodiesel production was found in the regions of low alcohol to oil ratio and low catalyst loading; and low alcohol to oil ratio and high catalyst loading. It can therefore be noted that moderate Catalyst Loading and high alcohol/oil molar ratio result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.118 had been estimated indicating these two process variables are not statistically significant. Figure *5-11* displays circular contour lines throughout the plot indicating negligible interactions.

4.1.4.6) Process Variables: Alcohol to Oil Molar Ratio (D) vs Reaction Temperature (A)

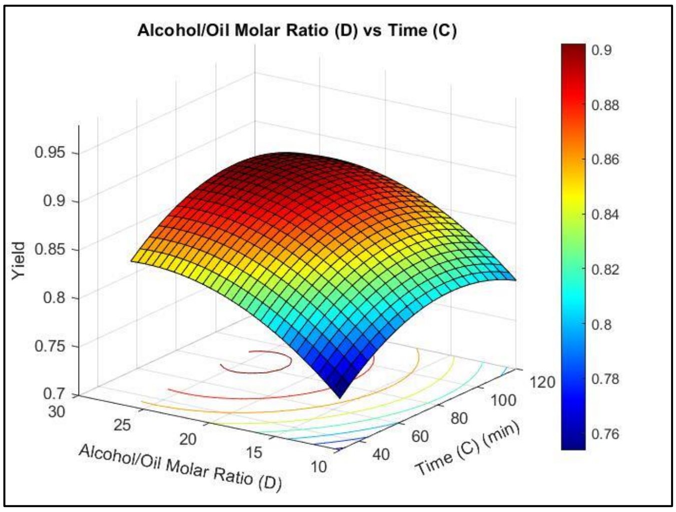


Figure 5-12: Influence of Alcohol/Oil Molar Ratio and Reaction Time on Biodiesel Yield.

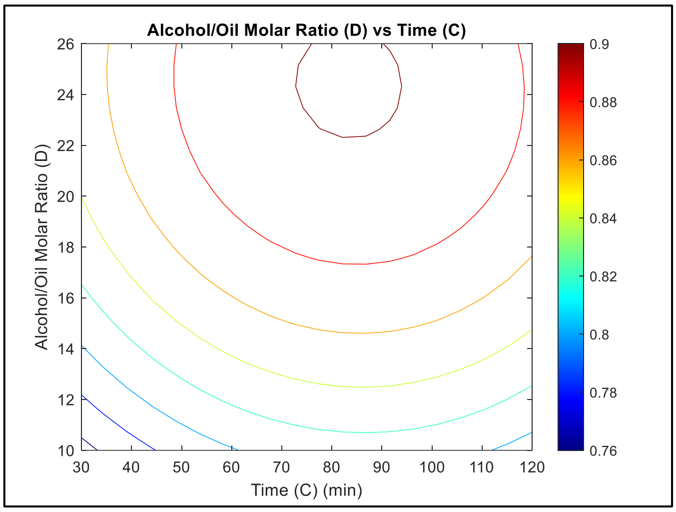


Figure 5-13: Nature and extent of interaction between Alcohol/Oil Molar Ratio and Reaction Time on Biodiesel Yield.

Figure *5-12* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (D) and (C). Increasing the alcohol to oil molar ratio leads to a rise in biodiesel production. The alcohol to oil molar ratio displays a directly proportional relationship with the yield of biodiesel. According to Munoz et al. (2012), high alcohol to oil molar ratios negatively affects the separation of glycerol as it causes the solubility of glycerol to increase. This favours the reverse reaction producing reactants, thus reducing the yield of biodiesel. The plot indicates a directly proportional effect between the Alcohol to Oil Molar Ratio and biodiesel yield is exhibited until a 24.34 alcohol to oil molar ratio, after which a reduction in yield in found with an increase in alcohol to oil molar ratio. Reaction Time displays a parabolic effect is present between reaction time and biodiesel yield. The gradual decrease in yield after 82.10 minutes is reached could mean adequate time was provided for the completion of the reaction. As more product was forming, equilibrium shifted to favour the reverse reaction thereby reducing biodiesel yield. The lowest amount of biodiesel produced can be seen in the region of low reaction time and low alcohol to oil molar ratio. High alcohol to oil molar ratio and moderate reaction time result in high biodiesel yields. Referring to Table *5-2*, a p-value of 0.695 had been estimated indicating these two process variables are not statistically significant. Figure *5-13* further supports this statement, as the contour plot displays circular contour lines throughout the plot.

4.1.4.7) Interaction Summary Table

Table *5-6* shows the Interaction Summary Table. This table summarizes the results obtained from the generated three-dimensional surface plots and contour plots from Regression Equation 4.1.

Table 5-6: Interaction Summary Table

Process Variables	**Significant or not Significant**	**Regions producing the lowest biodiesel yield**	**Regions producing the highest biodiesel yield**
Reaction Temperature and Catalyst Loading	Not Significant	High Catalyst Loading (%) and Low Reaction Temperature	High Reaction Temperature and Moderate Catalyst Loading (%)
Reaction Temperature and Reaction Time	Not Significant	Low Temperature and Low Reaction Time; High Temperature and Low Reaction Time	High Temperature and High Reaction Time
Reaction Temperature and Alcohol to Oil Molar Ratio	Not Significant	High Reaction Temperature and Low Alcohol to Oil Molar Ratio	High Reaction Temperature and High Alcohol to Oil Molar Ratio
Catalyst Loading and Reaction Time	Not Significant	Low Reaction Time and High Catalyst Loading (%)	Moderate Reaction Time and Moderate Catalyst Loading (%)
Catalyst Loading and Alcohol to Oil Molar Ratio	Not Significant	Low Catalyst Loading (%) and Low Alcohol to Oil Molar Ratio	Moderate Catalyst Loading (%) and High Alcohol to Oil Molar Ratio

Process Variables	**Significant or not Significant**	**Regions producing the lowest biodiesel yield**	**Regions producing the highest biodiesel yield**
Reaction Time and Alcohol to Oil Molar Ratio	Not Significant	Low Reaction Time and Low Alcohol to Oil Molar Ratio	High Alcohol to Oil Molar Ratio and Moderate Reaction Time

Table *5-6* shows that the optimum biodiesel yield can be obtained from a High Reaction Temperature; High Alcohol to Oil Molar Ratio; Moderate Reaction Time; and Moderate Catalyst Loading (%). This investigation supports the optimum conditions estimated in Table *5-5*.

4.1.5) One Variable at a Time (OVAT) Approach

Figures 4-14 to 4-17 display the impact each process parameter has on biodiesel yield. The plots were generated utilising the one variable at a time approach. When one parameter was investigated, the remaining process parameters were kept at their median values:

$$Temperature = 52\ °C \quad ; \quad Catalyst\ Loading = 0.085\%$$

$$Reaction\ Time = 75\ minutes \quad ; \quad \frac{Alcohol}{Oil} Molar\ Ratio = 18$$

4.1.5.1) Process Variables: Impact of Reaction Temperature on Biodiesel Yield

Figure *5-14* displays the impact reaction temperature has on biodiesel yield. As the reaction temperature increases so does the production of biodiesel. It is very crucial to ensure that the reaction temperature does not exceed 78 ^{o}C, as this is the boiling point temperature for ethanol. Exceeding the boiling point temperature will drastically reduce the yield of biodiesel as ethanol would escape from the system as a vapour.

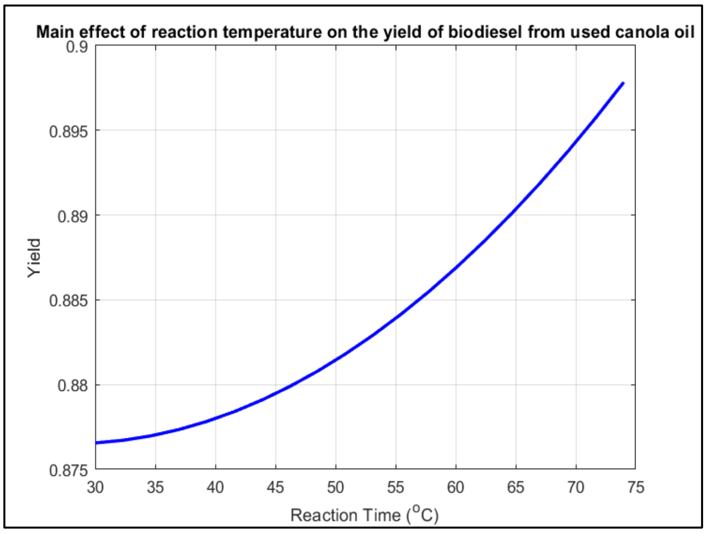


Figure 5-14: Impact Reaction Temperature has on the yield of Biodiesel.

At low temperatures the yield of biodiesel was still high, indicating that extremely high temperatures would not be required for this process. The effect reaction temperature has on the system is caused by the endothermic nature of transesterification reactions. This means higher temperatures favour endothermic reactions (Rahimi et al., 2014). The optimum reaction temperature for producing biodiesel using this process is 74 °C. The yield for biodiesel was still increasing, indicating that reaction temperature has a significant impact on the biodiesel yield using potassium hydroxide catalyst.

4.1.5.2) Process Variables: Impact of Catalyst Loading (%) on Biodiesel Yield

Optimizing the biodiesel production process is extremely important to minimise the production cost. An essential factor to consider is the catalyst loading percentage, as a high catalyst loading percentage could increase the complexity of product separation with extra catalyst present (Rahimi et al., 2014). Figure *5-15* displays the impact catalyst loading has on production.

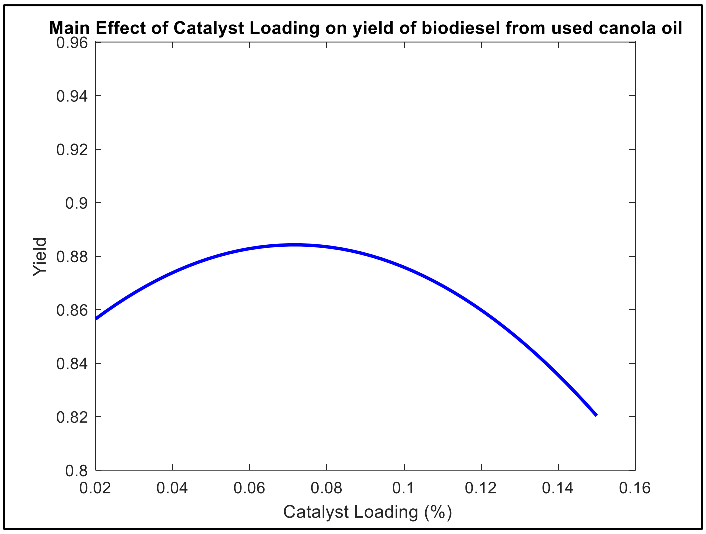


Figure 5-15: Impact Catalyst Loading has on the yield of Biodiesel.

Catalyst loading has a parabolic effect with biodiesel yield. After 0.07 wt. %, the yield of biodiesel heavily starts to decrease as the weight of excess catalyst increases. Large quantities of extra catalyst led to soap formation reducing the biodiesel yield. High amounts of catalyst also affect the separation phase as it becomes difficult for the glycerol layer to separate from the biodiesel layer due to its higher viscosity and increased solubility. This in turn promotes the reverse reaction and the yield decreases. The difference between the highest and lowest yield is below 0.07, however the yield of biodiesel would continue to decline as the catalyst loading increases. This indicates the impact that catalyst loading has on biodiesel yield obtained from used canola oil using Potassium Hydroxide is significant.

4.1.5.3) Process Variables: Impact of Reaction Time on Biodiesel Yield

Figure *5-16* displays the impact reaction time has on the production of biodiesel.

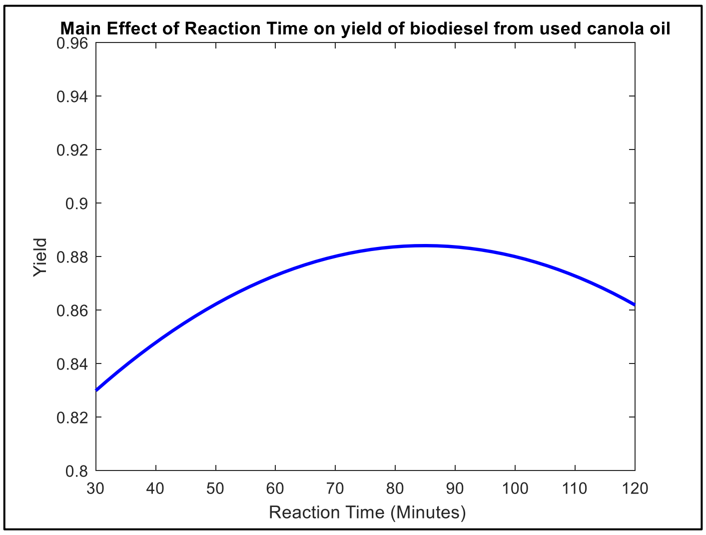


Figure 5-16: Impact Reaction Time has on the yield of Biodiesel.

The biodiesel yields increased as reaction time increased up until 85.38 minutes, any additional time after this period decreased the biodiesel yield. The gradual decrease in yield after the optimal reaction time is reached could be because adequate time was provided for the reaction to complete and as more products were produced, the equilibrium shifted to favour the reverse reaction thereby reducing the yield of biodiesel. The difference between the highest and lowest yield is below 0.06, indicating the impact reaction temperature has on biodiesel yield obtained from used canola oil using Potassium Hydroxide is significant.

4.1.5.4) Process Variables: Impact of Alcohol to Oil Molar Ratio on Biodiesel Yield

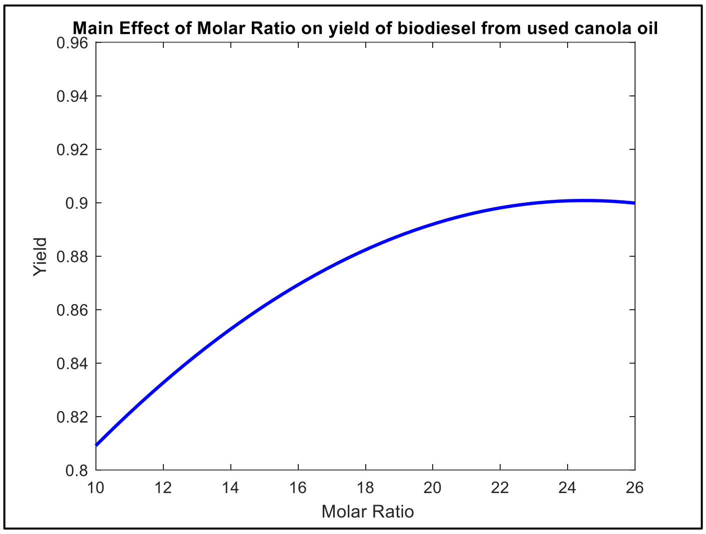


Figure 5-17: Impact Alcohol/Oil Molar Ratio has on the yield of biodiesel.

Increasing the alcohol to oil molar ratio led to a rise in biodiesel yield. The alcohol to oil molar ratio displays a directly proportional relationship with the yield of biodiesel. The one variable at a time approach from the regression model estimated 24.36:1 to be the optimal ratio while the other 3 process variables were kept at their median values. The slow reduction in biodiesel yield caused after the alcohol to oil ratio increased passed 24.36:1 is due to the increased solubility of glycerol caused by high alcohol to oil molar ratios. The glycerol present lowered the conversion of triglycerides by favouring the reverse reaction (Ahmed, 2023). This increase in solubility also impeded the separation of glycerol further reducing the final biodiesel yield (Ahmed, 2023). However, within this study and taking into account the interactions between all 4 process variables, a 26:1 alcohol molar ratio was found to be the optimal molar ratio.

4.2) Used Canola Oil Transesterification Utilising Magnesium Oxide

This part of the study aims to use Magnesium Oxide as the heterogeneous alkaline catalyst in the transesterification of used canola oil and the alcohol chosen, ethanol. Minitab Statistical software generated 27 experiments with varying parameters in order to estimate the optimal reaction conditions for these parameters: Reaction temperature, catalyst loading, reaction time and alcohol to oil molar ratio. According to Sigma Aldrich (2023), ethanol has a boiling point of 78 ^{o}C. Therefore, the temperature of the reaction should not be higher than the boiling point of ethanol as this leads to the vaporisation of the alcohol and reduced contact between the reactants. Before selecting the catalyst for each process, an evaluation of the reusability over the feasibility was completed. The expense and effect on the environment when compared to the preparation of a new batch of catalyst. Heterogenous catalysts are found in natural sources. The interactions are strong for MgO preventing lixiviation and creating stability to the catalyst during the reactions (Oueda, Bonzi-Coulibaly and Ouédraogo, 2017). After the reaction process, a centrifuge was utilised to remove the catalyst and the catalyst can be reused. However, the number of recycles that a catalyst can experience is greatly reduced when comparing waste cooking oil to fresh oil; this can be explained by the higher free fatty acid content found in used cooking oil. Used Cooking Oil destroys the catalytic activity of heterogeneous catalysts (CaO and MgO) much faster than fresh cooking oil (Oueda, Bonzi-Coulibaly and Ouédraogo, 2017). Due to this reasoning, the extracted catalyst will not be reused after each reaction.

The ranges for each process variable interval are explained in Section 3.3. The Low Acid Value found for the used oil led to the choice of utilising a catalyst loading range of 1-2 wt% of oil. It can be noted that the transesterification chemical formula requires a 3:1 stoichiometric ratio for the production of biodiesel. However, it was discovered that excess alcohol present in the reaction promotes the forward reaction by shifting the equilibrium to the right-side. Due to this reasoning, for this study, the alcohol ratio range was chosen to be 8:1 to 20:1. The reaction time for this process was chosen to be between 30-120 minutes. It was noted that the catalyst would solidify at the bottom of the separating funnel, making it impossible to separate the layers unless scraped and cleaned. To prevent this, the centrifuge was utilised before the use of the separation funnel. An extended separation period was required as the solubility of glycerol increased due to higher alcohol concentrations. In the heterogeneous separation phase for this study, the total separation time was roughly 24 hours.

The quality testing of used canola oil signified this oil displayed desirable properties, resulting in used canola oil becoming an ideal feedstock for biodiesel production. An investigation performed by Hoekman et al. (2012), indicated that the biggest problem when utilising vegetable oils directly in diesel engines were its high viscosity. Canola Oil has a comparably low viscosities for a vegetable oil, making this oil a desirable feedstock for producing biodiesel. Table *5-7* shows that used canola oil has a significantly higher viscosity than canola oil.

Table 5-7: Quality Testing for Canola Oil and Used Canola Oil.

Property	**Canola Oil**	**Used Canola Oil**
Density (kg/m^3)	*917*	917.3
Refractive Index	1.4660	1.4729
Viscosity (mm^2/s) (Fasina and Colley, 2008)	46.3359	72.5680
Acid Value (mg KOH/g)	0.1167	0.3535
FFA (%)	0.0584	0.1767

Using Minitab Statistical Software and the Box-Behnken Design Model, 27 experiments were generated to complete this study on used canola oil. These experiments were completed three times to ensure accurate and reliable results. After the experimental phase, Minitab Statistical Software was utilised to estimate a regression equation using the experimental results recorded. Each parameter was assigned a letter for simplicity:

$$\boldsymbol{A = Temperature\ (^oC)}$$

$$\boldsymbol{B = Catalyst\ Loading}\ (\%)$$

$$\boldsymbol{C = Reaction\,Time\ (minutes)}$$

$$\boldsymbol{D = Alcohol/Oil\ Molar\ Ratio}$$

Table 5-8 shows the experimental yield and the calculated yield of the biodiesel results for the catalyst MgO. The experimental yield shown was the average of three experiments for each run. The calculated yield is the yield generated using the regression equation 4.2 obtained from Minitab Statistical Software.

Table 5-8: Biodiesel Results from MgO.

Run Number	**Temperature (^oC)**	**Catalyst Loading (%)**	**Time (min)**	**Alcohol to Oil Ratio**	**Experimental Yield**	**Calculated Yield**
1	30	1.0	75	14	0.8593	0.8578
2	70	1.0	75	14	0.8428	0.8566
3	30	2.0	75	14	0.8327	0.8304
4	70	2.0	75	14	0.8378	0.8507
5	50	1.5	30	8	0.7936	0.8048
6	50	1.5	120	8	0.8344	0.8477
7	50	1.5	30	20	0.9442	0.9411
8	50	1.5	120	20	0.9602	0.9592
9	30	1.5	75	10	0.7946	0.8352
10	70	1.5	75	10	0.8056	0.8363
11	30	1.5	75	20	0.9001	0.9058
12	70	1.5	75	20	0.9364	0.9280
13	50	1.0	30	14	0.8617	0.8697
14	50	2.0	30	14	0.8575	0.8640
15	50	1.0	120	14	0.9273	0.9111
16	50	2.0	120	14	0.9012	0.8836
17	30	1.5	30	14	0.8867	0.8751
18	70	1.5	30	14	0.9056	0.8919
19	30	1.5	120	14	0.9114	0.9129
20	70	1.5	120	14	0.9142	0.9152
21	50	1.0	75	8	0.7988	0.7883
22	50	2.0	75	8	0.7724	0.7643
23	50	1.0	75	20	0.9064	0.9049
24	50	2.0	75	20	0.8946	0.8956
25	50	1.5	75	14	0.9298	0.9239
26	50	1.5	75	14	0.9250	0.9239
27	50	1.5	75	14	0.9200	0.9239

Table 5-8 shows the largest biodiesel yield was found to be 0.7724, obtained from run 8. This run had a temperature of 70 ^{o}C, a catalyst loading of 1.5 wt. % of oil, a 120-minute reaction time and a 20:1 alcohol to oil molar ratio. The smallest biodiesel yield was found to be 0.7724, obtained from run 22. This run had a temperature of 50 ^{o}C, a catalyst loading of 2 wt. % of oil, a 75-minute reaction time and an 8:1 alcohol to oil molar ratio. Contributions that could have resulted in the lower yield were the lowest possible alcohol ratio in the study as well as the highest possible amounts of catalyst in the study. The presence of a large quantity of excess catalyst may have resulted in saponification occurring in the reaction phase of the experiment.

$$\begin{aligned} Y = 0.003 + 0.00629A + 0.508B + 0.000924C + 0.03851D - 0.000073A^2 - 0.1835B^2 \\ + 0.000028C^2 - 0.001105D^2 + 0.000538AB - 0.000004AC \\ + 0.000053AD - 0.000242BC + 0.00122BD - 0.000023CD \qquad (4.2) \end{aligned}$$

Figure *5-18* displays the experimental yield (actual yield) obtained against the calculated (predicted model). The actual yield values were calculated as the average of three from each run. The calculated yield values were obtained using regression equation 4.2. Figure *5-18* displays a linear trendline with an R^2 value very close to 1, thus demonstrating a high degree of correlation between the predicted values and the experimental values. Table *5-9* shows the probability p-value for the regression model is 0 which suggests the model is very significant. For the 95% confidence level, statistical significance is indicated by a p-value less than 0.05 (Zhang and Zheng, 2009).

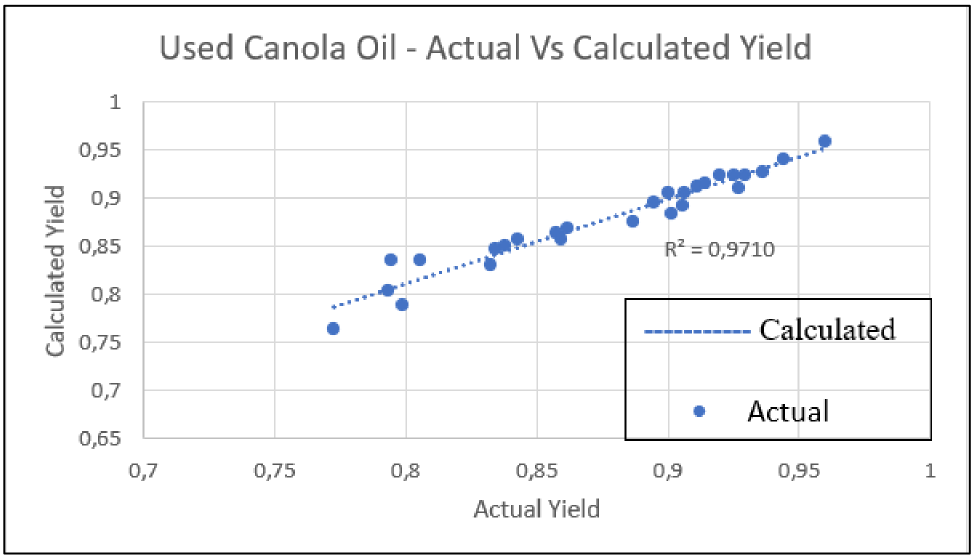


Figure 5-18: Used cooking oil biodiesel production: Actual vs Calculated (MgO).

4.2.1) Anova Analysis for Regression Model

Table 5-9 displays the ANOVA Analysis which was performed on the Full Quadratic regression model. The intent of completing the ANOVA Analysis was to establish whether any statistically significant differences exist between the four process variables. This analysis technique generated p-values. These p-values were used to establish whether the relationship between the four process variables from the experiments are significant or not significant.

Table 5-9: ANOVA Analysis for Regression Model and Results.

ANOVA Analysis for Used Canola Oil with MgO					
Source	**Degree of freedom**	**Adjusted Sum of Squares**	**Adjusted Mean Squares**	**P-Value**	**Characteristics**
Model	14	7.137E-02	5.098E-03	0.000	Significant
Linear	4	5.037E-02	1.259E-02	0.000	Significant
Temperature (A)	1	2.760E-04	2.760E-04	0.236	Not Significant
Catalyst Loading (B)	1	8.350E-04	8.350E-04	0.051	Not Significant
Time (C)	1	3.312E-03	3.312E-03	0.001	Significant
Molar Ratio (D)	1	4.595E-02	4.595E-02	0.000	Significant
Square	4	2.033E-02	5.081E-03	0.000	Significant
Temperature*Temperature (A^2)	1	4.501E-03	4.501E-03	0.000	Significant
Catalyst Loading*Catalyst Loading (B^2)	1	1.122E-02	1.122E-02	0.000	Significant
Time*Time (C^2)	1	1.230E-04	1.230E-04	0.422	Not Significant
Molar Ratio*Molar Ratio (D^2)	1	8.441E-03	8.441E-03	0.000	Significant
2-Way Interaction	6	6.690E-04	1.110E-04	0.706	Not Significant
Temperature*Catalyst Loading (AB)	1	1.160E-04	1.160E-04	0.435	Not Significant
Temperature*Time (AC)	1	6.500E-05	6.500E-05	0.555	Not Significant
Temperature*Molar Ratio (AD)	1	1.610E-04	1.610E-04	0.360	Not Significant
Catalyst Loading*Time (BC)	1	1.190E-04	1.190E-04	0.430	Not Significant
Catalyst Loading*Molar Ratio (BD)	1	5.300E-05	5.300E-05	0.593	Not Significant
Time*Molar Ratio (CD)	1	1.540E-04	1.540E-04	0.369	Not Significant
Error	12	2.129E-03	1.770E-04		
Lack-of-Fit	10	2.081E-03	2.080E-04	0.108	Not Significant

Pure Error	2	4.800E-05	2.400E-05		
Total	26	7.350E-02			

The null hypothesis is that there is no association between the term and the response, i.e., Process Variable A and A or Process Variable A and B. Minitab Statistical Software utilises a significance level of 0.05. This indicates that there is a 5% risk of concluding that an association exists even though there is no actual association. Table *5-10* shows the interpretations of the model terms.

Table 5-10: Significant model terms and their interpretations

Model Term	Interpretation
If the process variable for a factor is significant, e.g., process variable A.	Conclude that not all level means are equal.
If the process variables for the interaction are significant, e.g., process variables A and B.	Conclude that the relationship between the process variables depend on other factors in the model. Suggesting that the model should include both the interaction effects and the main effects.

Table *5-9* indicates that the two process variables are not linearly significant. The terms Reaction Temperature and Catalyst Loading were not significant. This means that these two parameters do not have a great effect on the biodiesel yield obtained from the transesterification of ethanol and used canola oil with magnesium oxide. The other parameters Reaction Time and Alcohol to Oil Molar Ratio are linearly significant and have a great effect on the biodiesel yield obtained from the transesterification of ethanol and used canola oil with magnesium oxide. Table *5-9* displays the coefficients for quadratic behaviour. This full quadratic model included many insignificant coefficients which were found in the statistical analysis, these terms could have contributed to a lower calculated R^2 value at 0.8354. Potentially removing the insignificant terms from the full quadratic model, may improve the model regression. This will be discussed in section 4.2.2. This value is greater than the minimum limit indicating the polynomial models used were a good choice for describing the effect of the process variables on the response (biodiesel yield) (Joglekar and May, 1987). The coefficient of determination (R^2) of 0.8354 suggests that approximately 16.46 % of the total variation is unaccounted for by the model predicting outside the field range of the study. The R^2 value of the regression model of 0.9710 suggests that approximately 2.90% of the total variation is unaccounted for by the model predicting within the field range of the study. Therefore, it can be noted that the model generated would give an accurate and reliable estimation for the impact the process variables have within this study and outside the range of parameters. However, this statement does not mean the model could be used for ranges outside this thesis, further experimentation would be required.

4.2.2) Heterogeneous Transesterification Regression Model

Table *5-11* displays the various reduced models used to generate a regression equation for the experimental results.

Table 5-11: Various Regression Model Summary.

Regression Model	**S-Value**	**R^2 Value**	**R^2 (adjusted) Value**	**R^2(calculated) Value**
Linear	0.03242	0.6854	0.6282	0.5527
Linear + Square	0.02716	0.8092	0.7390	0.6438
Linear + Interactive	0.03746	0.6945	0.5035	0.1991
Full Quadratic	0.01332	0.9710	0.9372	0.8354

According to an investigation performed by Joglekar and May (1987), the minimum limit for R^2 required to represent a great fit for a regression model is 0.8. Table *5-11* shows that the linear + square and full quadratic models obtained R^2 values above 0.8. The full Quadratic model obtained an R^2 value significantly higher than the linear + square model. This indicates that the full quadratic regression model estimated the best fit to the experimental results recorded. This suggests that this regression model would be the most accurate in estimating the yield of biodiesel for this study. Table *5-11* displayed a R^2 value of 0.9710 and an adjusted R^2 value of 0.9375 with a confidence level of 95%. The calculated R^2 value was found to be 0.8354. This represents that the quadratic model for the study is potentially 83.54 % accurate in predicting the yield not within the range of the process parameters of this thesis. Even though the calculated R^2 is significantly smaller when compared to the R^2 and adjusted R^2, the value is still greater than 0.8 and therefore the quadratic model obtained through this study, could potentially be utilised for accurately predicting the biodiesel yield not within the range of this thesis. Further investigation would be required to prove that statement.

The standard deviation for each model is displayed as the S-value in Table *5-11*. The full quadratic model displayed a standard deviation of 0.01332. This extremely low value indicates a small deviation of the data points from the estimated values. Signifying the regression model equation estimated from this thesis is a great fit for the experimental results. Table *5-9* indicates that the probability p-value for the regression model is 0 which suggests the model is very significant. For the 95% confidence level, statistical significance is characterised by a p-value less than 0.05 (Zhang and Zheng, 2009).

4.2.3) Minitab Statistical Software: Response Optimiser

Minitab Statistical Software was utilised to obtain the optimal reaction conditions for biodiesel yield produced using used Canola oil. Table *5-12* shows the optimum conditions.

Table 5-12: Optimum Reaction Conditions obtained from Minitab Statistical Software.

Temperature (^oC)	**Catalyst Loading (%)**	**Molar Ratio**	**Time (Minutes)**	**Calculated Yield**
51.41	1.44	18.18	120	0.97

The maximum yield was estimated at 0.9667. An investigation was completed to produce biodiesel using these optimum conditions in the laboratory, the yield was found to be 0.9742. An experimental error of 0.78% was calculated, which is significantly small thereby providing more evidence that the full quadratic regression model will be a great fit for the thesis.

4.2.4) Three-Dimensional Surface Response Plots and Contour Plots

Surface Response Plots and Contour Plots are used to determine the effects the four parameters had on the optimum biodiesel yield. These plots were generated using Matlab R2021B and Regression Equation 4.2. These generated plots are displayed in Figures 4-19 to 4-34. An individual plot displays the impact two parameters have on biodiesel production within the chosen ranges. The remaining parameters were set at their respective median values. The surface response plots show how each parameter influences of biodiesel production. The degree of curvature in the contour plots displays the nature and extent of the interaction for two parameters. Referring to Qiu et al. (2013), an elliptical contour plot displays a noticeable interaction whereas a negligible interaction is displayed by a more circular contour plot.

4.2.4.1) Process Variables: Catalyst Loading (B) vs Reaction Temperature (A)

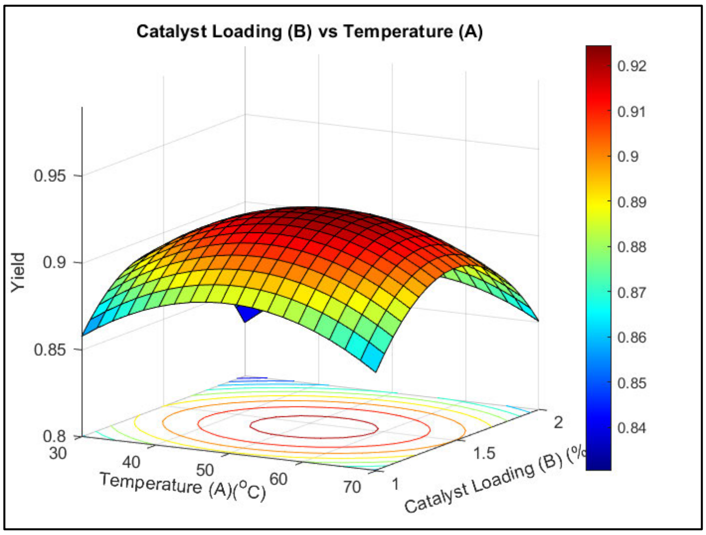


Figure 5-19: Influence Catalyst Loading and Reaction Temperature have on biodiesel yield.

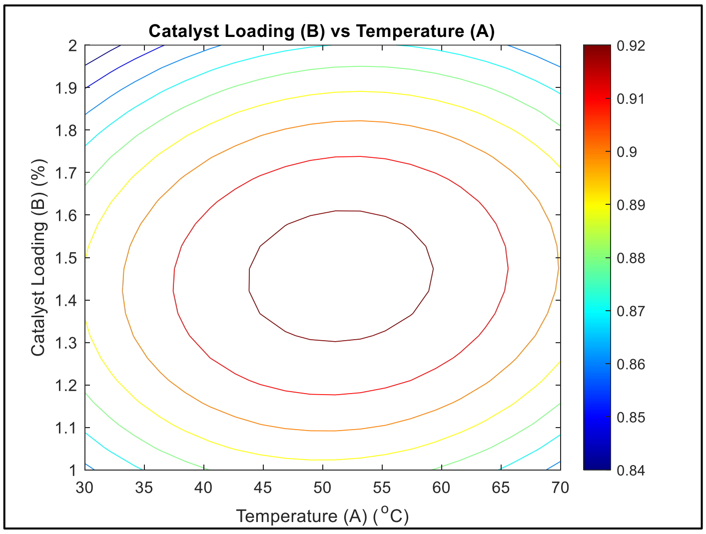


Figure 5-20: Nature and extent of interaction between catalyst loading and Reaction Temperature on Biodiesel Yield.

Figure *5-19* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (B) and (A). This plot shows an early increase in biodiesel yield with a rise in catalyst loading however, after a 1.47 wt% of catalyst loading, growing amounts of excess catalyst present results in decreasing the yield. According to Rahimi et al. (2014), high amounts of base catalyst present in the system could lead to the production of soap and lead to a decrease in the biodiesel yield produced. A gradual rise in biodiesel yield is seen with an increase in temperature, and this is due to transesterification reactions being endothermic where higher reaction temperatures favour the production of biodiesel (Moyo et al., 2020). However, reaction temperatures higher than the optimal temperature of 53.16 °C would result in the saponification of triglycerides as high temperatures accelerate saponification (Chozhavendhan et al., 2020). The reaction temperature and catalyst loading display a parabolic nature with regards to biodiesel production. Low biodiesel yield is found in the following combinations: low temperature and low catalyst loading; high temperature and low catalyst loading; high temperature and high catalyst loading; and low temperature and high catalyst loading. It can therefore be noted that moderate temperatures and moderate catalyst loading result in high biodiesel yields. Referring to Table *5-9*, a p-value of 0.435 was estimated indicating these two process variables are not statistically significant. Figure *5-20* further supports this statement, as the contour plot displays circular contour lines throughout the plot indicating negligible interactions.

4.2.4.2) Process Variables: Reaction Time (C) vs Reaction Temperature (A)

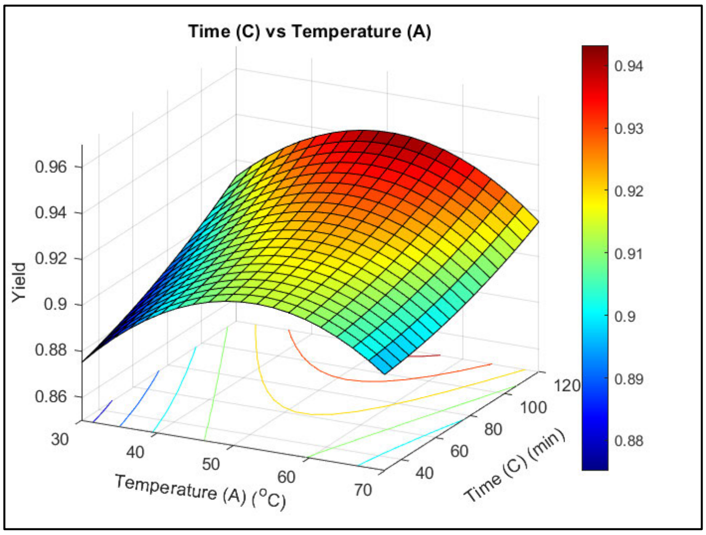


Figure 5-21: Influence Reaction Time and Reaction Temperature have on Biodiesel Yield.

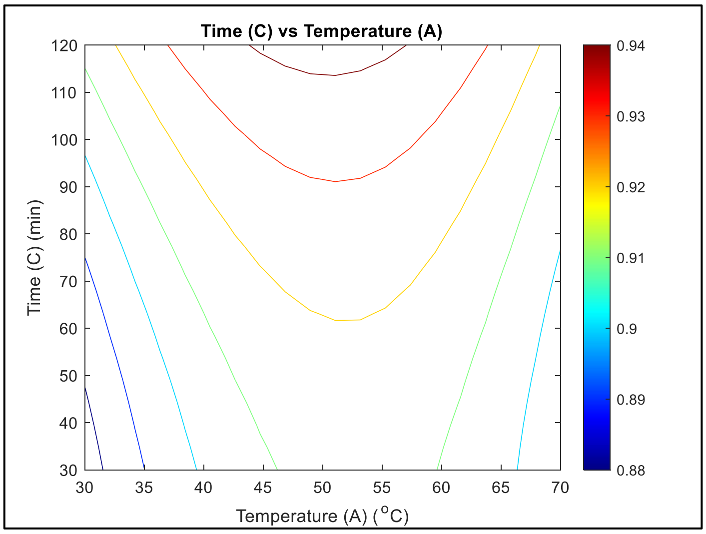


Figure 5-22: Nature and extent of interaction between Reaction Time and Reaction Temperature on Biodiesel Yield.

Figure *5-21* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (C) and (A). It can be noted that increasing the temperature resulted in improved yields of biodiesel however, the increase in biodiesel yield due to reaction temperature was up to 51.05 °C, after which any elevation in temperature reduced the yield. A contributing factor to the parabolic nature of reaction temperature could have been caused by saponification due to the alkali catalyst since saponification is enhanced at temperatures of 50 °C or above (Chowdhury et al., 2017). Improved biodiesel yield was discovered in longer reaction times. This shows a directly proportional effect of reaction time with biodiesel yield. The lowest biodiesel yield was found in regions with low reaction time and low reaction temperature. It can therefore be noted that moderate temperatures and high reaction time produce high biodiesel yields. Referring to Table *5-9*, a p-value of 0.555 had been estimated indicating these two process variables are not statistically significant. In support of this claim, Figure *5-22* displays circular contour lines in the centre of the plot indicating negligible interactions.

4.2.4.3) Process Variables: Alcohol to Oil Molar Ratio (D) vs Reaction Temperature (A)

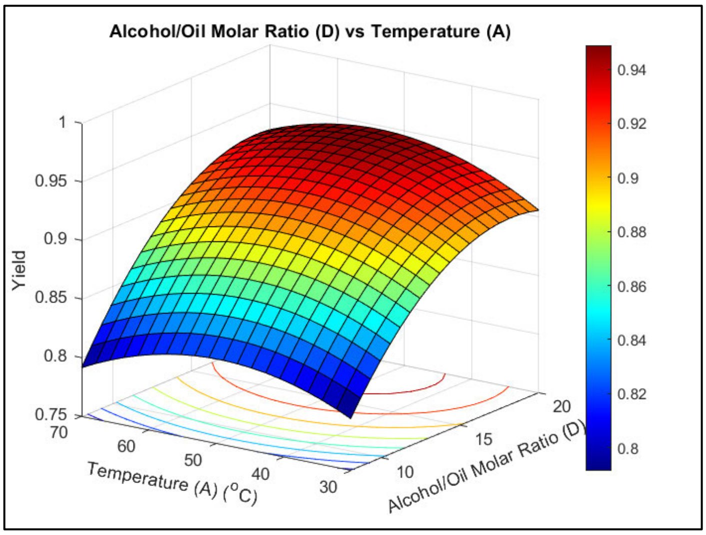


Figure 5-23: Influence Alcohol/Oil Molar Ratio and Reaction Temperature has on Biodiesel Yield.

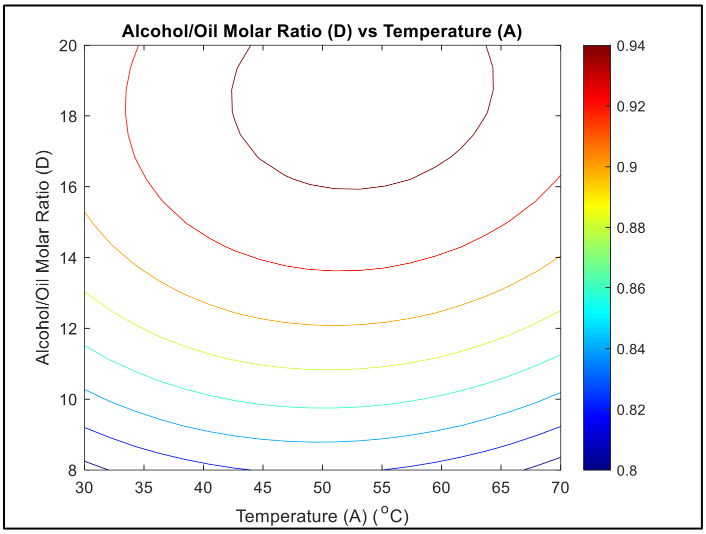


Figure 5-24 Nature and extent of interaction between Alcohol/Oil Molar Ratio and Temperature on Biodiesel Yield.

Figure *5-23* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (C) and (A). The transesterification of triglycerides are endothermic reactions. Therefore, an increase in temperature will favour the forward reaction (Daramola et al., 2016). However, the increase in yield due to reaction temperature was up until 53.16 °C, after which any elevation in temperature reduced the yield. This could be caused by the reverse reaction which would have resulted in the loss of desired products and soap production. It can be observed that increasing the alcohol to oil molar ratio led to a rise in biodiesel yield, however at an 18.76:1 molar ratio, the yield begins to decline slowly. This decline is related to high alcohol molar ratios affecting the separation of glycerol as the solubility of glycerol increases in the presence of excess methanol (Erchamo, 2021). The region where the poorest biodiesel production is found is a 10:1 alcohol to oil molar ratio. Moderate temperatures and high Alcohol to Oil molar ratios lead to high biodiesel yields. In reference with Table *5-9*, a p-value of 0.360 had been estimated indicating these two process variables are not statistically significant. Figure *5-24* also supports this statement, as the contour plot displays a circular shape in the upper regions of the plot indicating negligible interactions.

4.2.4.4) Process Variables: Reaction Time (C) vs Catalyst Loading (B)

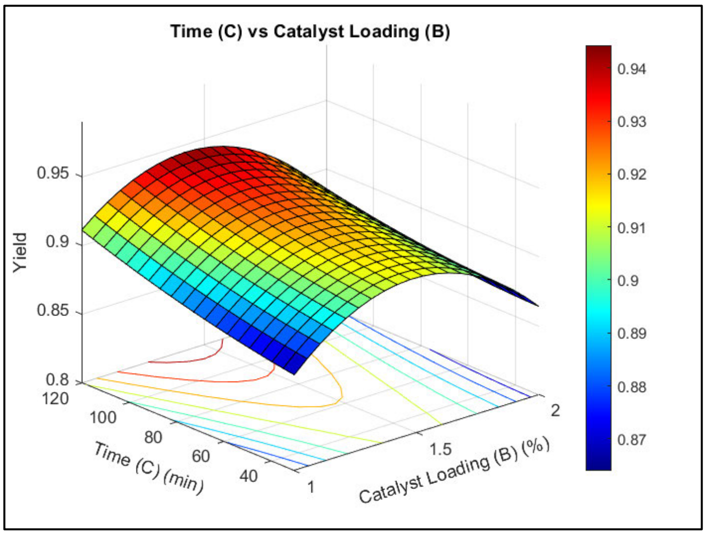


Figure 5-25: Influence Reaction Time and Catalyst Loading have on Biodiesel Yield.

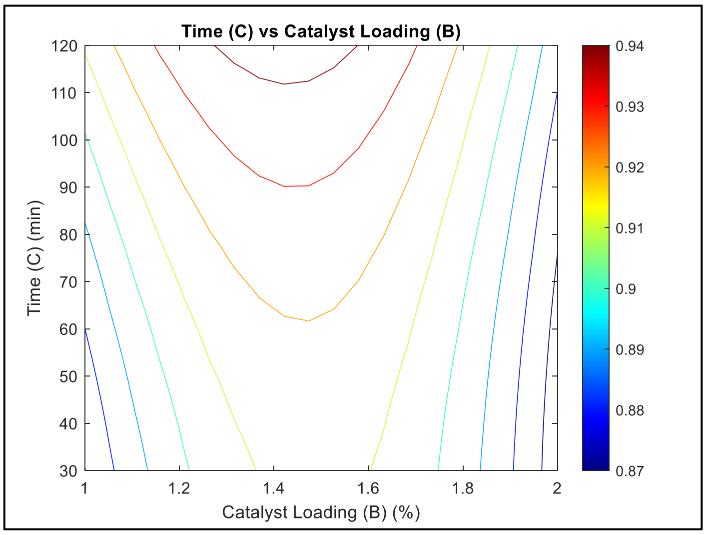


Figure 5-26: Nature and extent of interaction between Reaction Time and Catalyst Loading on Biodiesel Yield.

Figure *5-25* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (C) and (B). This figure shows a parabolic effect present between Catalyst loading and the biodiesel yield. As the amount of catalyst rises, the biodiesel yield rises accordingly however after 1.42 wt. % of oil catalyst loading, increasing the catalyst loading, lowers the rate of biodiesel production. High amounts of base catalyst may lead to soap production (Gashaw and Teshita, 2014). According to Hossain et al. (2010), high soap production could potentially cause gel formations that trap high amounts of esters in the glycerol layer, reducing the production of biodiesel. Soap can also dissolve into the glycerol layer thereby increasing the solubility of biodiesel leading to biodiesel loss in the post treatment process (Hossain et al., 2010). Evidently, increasing the length of the reaction resulted in improved yields of biodiesel. A directly proportional effect of reaction time with biodiesel yield can be observed. The lowest regions of biodiesel production are low reaction time and low catalyst loading; low reaction time and high catalyst loading. Moderate Catalyst Loading and high reaction time result in high biodiesel yields. Referring to Table *5-9*, a p-value of 0.430 had been estimated indicating these two process variables are not statistically significant. Figure *5-26* also provides support to this statement, as the contour plot displays a circular shape in the upper regions of the plot indicating negligible interactions.

4.2.4.5) Process Variables: Alcohol to Oil Molar Ratio (D) vs Catalyst Loading (B)

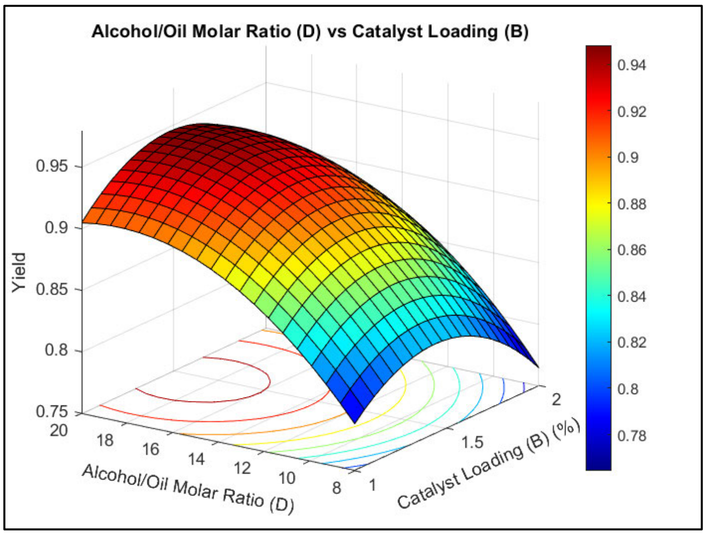


Figure 5-27: Influence Alcohol/Oil Molar Ratio and Catalyst Loading have on Biodiesel Yield.

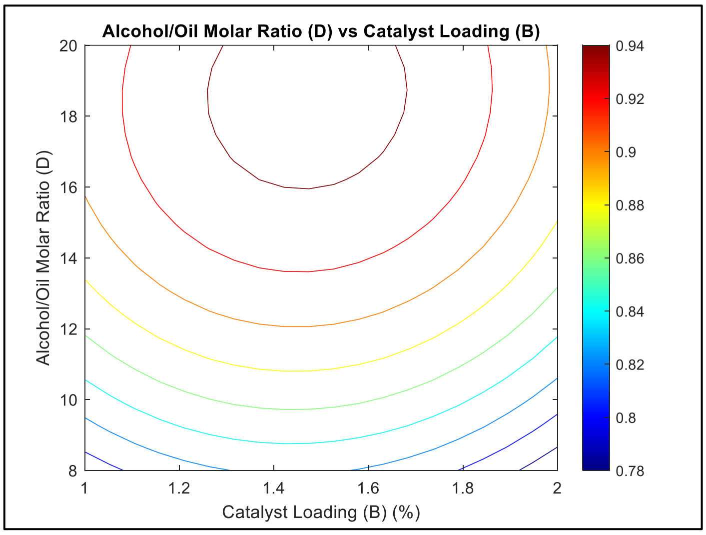


Figure 5-28: Nature and extent of interaction between Alcohol/Oil Molar Ratio and Catalyst Loading on Biodiesel Yield.

Figure *5-27* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (D) and (B). This figure shows a parabolic effect present between

Catalyst loading and biodiesel yield. The plot shows that as the percentage of catalyst loading increases, the biodiesel yield improves however after 1.47 wt. % of oil catalyst loading, increasing the catalyst loading leads to a reduction in yield. This figure also shows that a higher Alcohol to Oil Molar Ratio led to improved biodiesel yields up until the ratio of 18.76:1. Following this point, the yield gradually decreased. An excess amount of ethanol and a small amount of catalyst are needed to project the forward reaction. As specified by Le Chatelier's Principle, increasing parameters beyond the optimum points would favour the reverse reaction and potentially cause the formation of soap, which would decrease biodiesel yield. An investigation performed by Fereidooni et al. (2017), stated biodiesel with high viscosity was produced when large amounts of base catalyst were used. This not only complicates the separation phase of removing the glycerol but also leads to biodiesel that cannot be utilised in diesel engines. The region where the lowest biodiesel yield can be found in low catalyst loading and low alcohol to oil ratio; high catalyst loading and low alcohol to oil ratio. It can be concluded that moderate catalyst loading and high alcohol to oil molar ratio led to high biodiesel yields. Referring to Table *5-9*, a p-value of 0.593 was estimated indicating these two process variables are not statistically significant. Figure *5-28* supports this statement, as the contour plot displays circular contour lines throughout the plot indicating negligible interactions.

4.2.4.6) Process Variables: Alcohol to Oil Molar Ratio (D) vs Reaction Time (C)

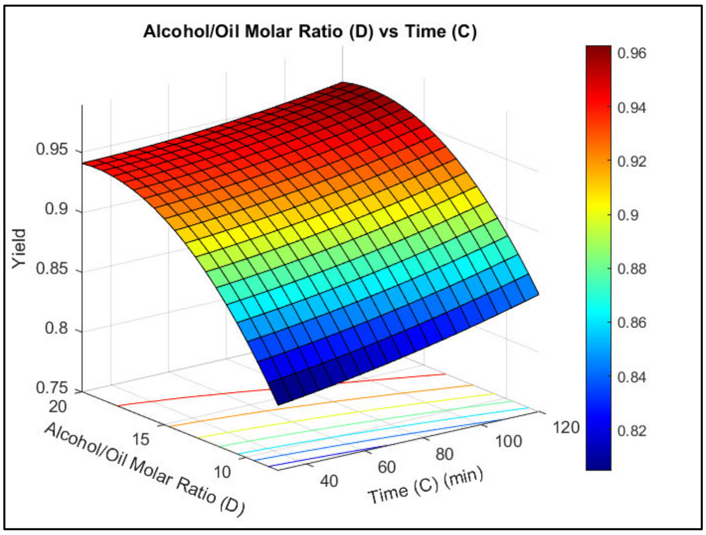


Figure 5-29: Influence Alcohol/Oil Molar Ratio and Reaction Time have on Biodiesel Yield.

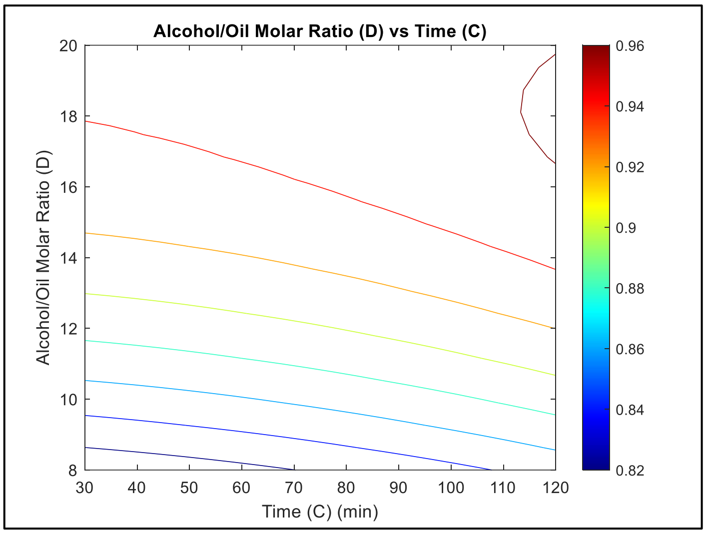


Figure 5-30 Nature and extent of interaction between Alcohol/Oil Molar Ratio and Reaction Time on Biodiesel Yield.

Figure *5-29* displays a three-dimensional Surface Response Plot showing the surface interaction between the process variables (C) and (B). It can be seen that increasing the alcohol to oil molar ratio resulted in the yield of biodiesel, however at 18.34:1 molar ratio, the yield starts to slowly decline. The slow reduction in biodiesel yield was caused by increased solubility of glycerol due to high alcohol to oil molar ratios. The dissolved glycerol in the solution reduced the conversion of triglycerides by favouring the reverse reaction (Ahmed, 2023). This increase in solubility also negatively affected the separation of glycerol further reducing the biodiesel yield (Ahmed, 2023). The smallest region of biodiesel production was found at low alcohol to oil molar ratios and short reaction times as there are insufficient amounts of alcohol to project the forward reaction and too short period of time to allow for reaction completion. Increasing the length of reaction time led to improved biodiesel yields, indicating a directly proportional effect of reaction time with biodiesel yield. In regard to Table *5-9*, a p-value of 0.369 had been estimated indicating these two process variables are not statistically significant. Figure *5-30* displays a circular contour line at the top right indicating negligible interactions.

4.2.4.7) Interaction Summary Table

Table *5-13* shows the Interaction Summary Table. This table summarizes the results obtained from the generated three-dimensional surface plots and contour plots from Regression Equation 4.2.

Table 5-13: Interaction Summary Table

Process Variables	**Significant or not Significant**	**Regions producing the lowest biodiesel yield**	**Regions producing the highest biodiesel yield**
Reaction Temperature and Catalyst Loading	Not Significant	Low Catalyst Loading (%) and Low Reaction Temperature; High Catalyst Loading (%) and Low Reaction Temperature; High Catalyst Loading (%) and High Reaction Temperature; Low Catalyst Loading (%) and Low Reaction Temperature	Moderate Reaction Temperature and Moderate Catalyst Loading (%)
Reaction Temperature and Reaction Time	Not Significant	Low Temperature and Low Reaction Time	Moderate Temperature and High Reaction Time
Reaction Temperature and Alcohol to Oil Molar Ratio	Not Significant	Low Reaction Temperature and Low Alcohol to Oil Molar Ratio; High Reaction Temperature and Low Alcohol to Oil Molar Ratio	Moderate Reaction Temperature and High Alcohol to Oil Molar Ratio
Catalyst Loading and Reaction Time	Not Significant	Low Reaction Time and High Catalyst Loading (%); Low Reaction Time and Low Catalyst Loading (%)	High Reaction Time and Moderate Catalyst Loading (%)
Catalyst Loading and Alcohol to Oil Molar Ratio	Not Significant	Low Catalyst Loading (%) and Low Alcohol to Oil Molar Ratio; Low Catalyst Loading (%) and High Alcohol to Oil Molar Ratio	Moderate Catalyst Loading (%) and High Alcohol to Oil Molar Ratio
Reaction Time and Alcohol to Oil Molar Ratio	Not Significant	Low Reaction Time and Low Alcohol to Oil Molar Ratio	High Alcohol to Oil Molar Ratio and High Reaction Time

Table *5-13* shows that the optimum biodiesel yield can be obtained from Moderate Reaction Temperature; High Alcohol to Oil Molar Ratio; High Reaction Time; and Moderate Catalyst Loading (%). This investigation supports the optimum conditions estimated in Table *5-12*.

4.2.5) One Variable at a Time (OVAT) Approach

Figures 4-31 to 4-34 displays the impact that every parameter has on biodiesel yield. The plots were generated utilising the one variable at a time approach. When one parameter was investigated, the remaining process parameters were kept at their median values:

$$Temperature = 50\ °C \quad ; \quad Catalyst\ Loading = 1.5\ wt.\%$$

$$Reaction\ Time = 75\ minutes \quad ; \quad \frac{Alcohol}{Oil} Molar\ Ratio = 14$$

4.2.5.1) Process Variable: Impact of Reaction Temperature on Biodiesel Yield

Figure *5-31* displays the impact reaction temperature has on the yield of biodiesel. The plot generated shows reaction temperature having a parabolic effect with biodiesel yield.

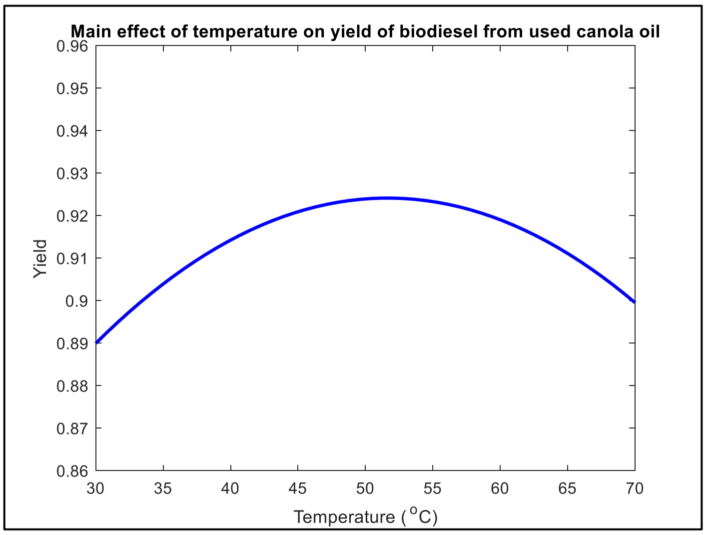


Figure 5-31: Impact Temperature has on Biodiesel Yield.

It is very crucial to ensure that the reaction temperature does not exceed 78 ^{o}C, as this is the boiling point temperature for ethanol. Exceeding the boiling point temperature will drastically reduce the yield of biodiesel as ethanol would escape from the system as a vapour. At low temperatures the yield of biodiesel was still high, indicating that extremely high temperatures would not be required for this process. The optimum reaction temperature for producing biodiesel using the generated OVAT approach was at 51.54 ^{o}C. Raising the reaction temperature higher than the optimum temperature would lead to a reduction in yield as saponification is favoured at higher temperatures. The difference between the highest and lowest yield is below 0.04. This indicates the impact that reaction temperature has on the biodiesel yield from waste canola oil using Magnesium Oxide is not significant within the range of this study.

4.2.5.2) Process Variable: Impact of Catalyst Loading on Biodiesel Yield

A crucial aspect to consider for the transesterification process is the cost of production, as the catalyst loading percentage could increase the complexity of product separation with extra catalyst present (Rahimi et al., 2014). Figure *5-32* displays the impact catalyst loading has on production.

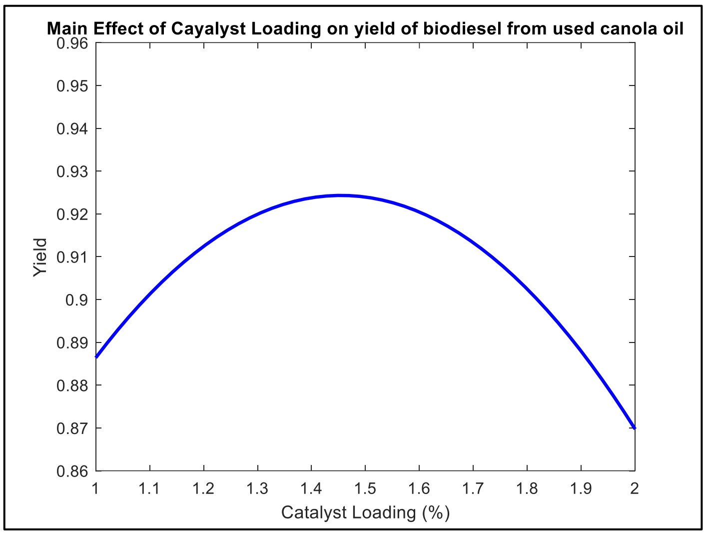


Figure 5-32: Impact Catalyst Loading has on Biodiesel Yield.

Catalyst loading has a parabolic effect with biodiesel yield. After 1.49 wt, % of oil catalyst loading, the yield of biodiesel heavily starts to decrease as the weight of excess catalyst increases. Large quantities of excess catalyst allows for the production of soap, which thereby reduces biodiesel yield. High amounts of catalyst also affect the separation phase as it becomes difficult for the glycerol layer to separate from the biodiesel layer due to its higher viscosity and increased solubility. This in turn promotes the reverse reaction and the yield decreases. The difference between the highest and lowest yield is below 0.06. This indicates the impact that catalyst loading has on biodiesel yield obtained from used canola oil using Magnesium Oxide is not significant within the range of this study.

4.2.5.3) Process Variable: Impact of Reaction Time on Biodiesel Yield

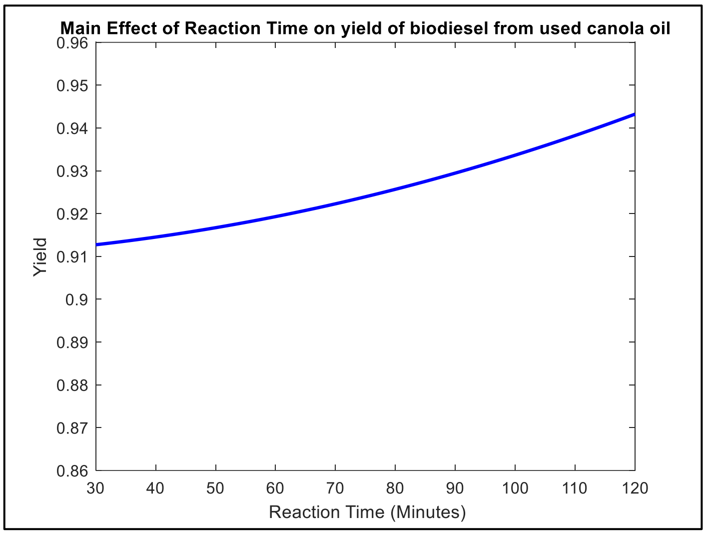


Figure 5-33: Impact Reaction Time has on Biodiesel Yield.

Figure *5-33* displays the impact reaction time has on the production of biodiesel. The biodiesel yield improved as the reaction time increased, indicating a directly proportional effect of reaction time with biodiesel yield. It can be noted that the reaction did not reach completion as the yield did not decrease at higher reaction times. A decrease in yield would have been noted as the reverse reaction would have been favoured once the forward reaction was completed.

4.2.5.4) Process Variable: Impact of Alcohol to Oil Molar Ratio on Biodiesel Yield

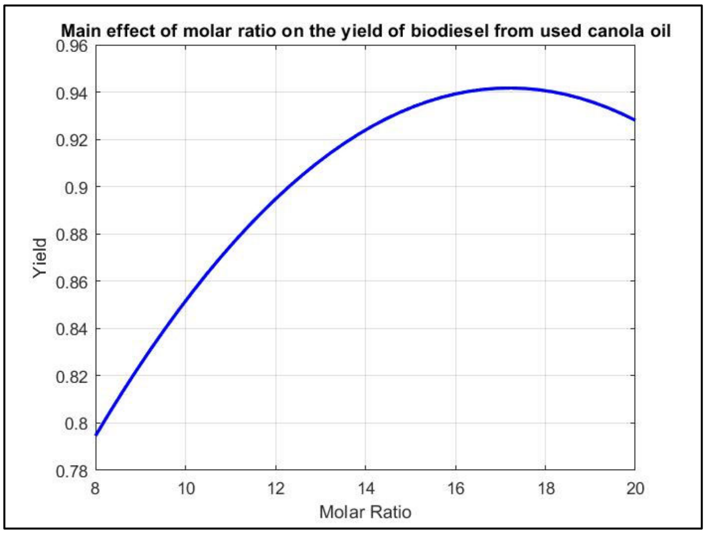


Figure 5-34:Impact Alcohol/Oil Molar Ratio has on Biodiesel Yield.

Increasing the alcohol to oil molar ratio led to a rise in biodiesel yield, however at a 17.23:1 molar ratio, the yield of biodiesel started to slowly decline. This decline is related to high alcohol molar ratios affecting the separation of glycerol as the solubility of glycerol increases in the presence of excess methanol. With glycerol still present in the solution, equilibrium is shifted back towards the reverse reaction, reducing the biodiesel yield. With glycerol still present in the solution, equilibrium is shifted back towards the reverse reaction, reducing the biodiesel yield (Erchamo, 2021).

Investigations performed by Rahimi et al. (2014) and Demirbas (2007) support the results and plots generated in Chapter 4. The individual process variable plots were generated to determine the effect a single variable had on the outcome while keeping the remaining process variables kept at their respective median values. The plots were not generated to help determine the optimal conditions for biodiesel production. Only a method such as Box-Behnken Design which incorporates multivariable analysis that varies all the variables and considers all the interactions between them could accurately predict optimised conditions. The response optimiser function on Minitab Statistical Software was utilised to estimate the optimum conditions. Since yields greater than 1 are not possible, the yields were fixed to lie between 0 and 1 on Minitab Statistical Software. All four parameters were fixed to stay between their respective ranges chosen and therefore, the regression model will only be able to predict trends inside the range of the study. Further investigation would be required to determine if the regression models generated could accurately predict biodiesel yields outside the range of study.

4.3) Pure and Blended Biodiesel Property Testing Discussion

This portion of the study discusses property testing completed on biodiesel produced using both KOH and NaOH from optimal conditions. Another focus of this chapter is the property results obtained from blends of biodiesel and kerosene, and the biodiesel feedstock. The first test completed on the samples was density. Referring to ASTM D941, biodiesel density has a maximum limit of 0.9 g/cm^3. Referring to ASTM D1655, biodiesel jet fuel blends have a density range of 0.775-0.840 g/cm^3. The average biodiesel tested for KOH and NaOH was 0.8924 g/cm^3 and 0.8987 g/cm^3, respectively. Referring to Table B-1, it can be concluded that the pure biodiesel samples fall below the maximum limit for density and the biodiesel blends fall within the specified range for biodiesel jet fuel blends.

According to ASTM D6751, the maximum limit for the acid value for biodiesel acid is 0.5 mg KOH/g (Alleman, Fouts and Chupka, 2013). The acid value of Jet fuel has a maximum limit of 0.015 mg KOH/g. Used canola oil in this thesis recorded an acid number of 0.3535 mg KOH/g, which justified the use of transesterification. Table B-2 showed the acid values of the samples were all below 0.5 mg KOH/g. With regards to jet fuel blends, the acid values obtained from these samples were over the allowable limit indicating that blending biodiesel made from used waste cooking oil may not be suitable for blends with jet fuels.

The aim of the transesterification reaction is to decrease the viscosity of vegetable oils to allow direct or indirect usage in diesel engines. Testing the biodiesel produced from used canola oil was pivotal in determining whether the biodiesel produced would be suitable for use. Referring to ASTM D445, the biodiesel maximum limit is 6 mm^2/s. According to ASTM D1665, the limit for jet fuels is 8 mm^2/s. The waste cooking oil had a viscosity of 72.57 mm^2/s. Even though the transesterification reaction greatly reduced the viscosity, biodiesel made from KOH and MgO did not fall below the maximum limit for biodiesel fuels. However, the jet fuel blends did in fact fall below the limit of 8 mm^2/s, as shown in Table B-5. It was noted that the viscosity of biodiesel produced by KOH had dropped considerably more than that of MgO biodiesel. The American Petroleum Index Gravity and heat of combustion were estimated utilising Equation B-2 and Equation B-3, respectively. Table B-6 and Table B-8 display the results, respectively. The refractive index relies on the concentration of unsaturated and saturated fatty acids; therefore, it is a commonly used method of standardisation. Referring to a study by Singh et al. (2008), the refractive index range for biodiesel according to ASTM standards is 1.447-1.48. Table B-4 shows all the biodiesel samples fall within this range.

According to Europe and the USA, biodiesel's pH value is 9 (Andualem and Gessess, 2012). Table B-3 displays the results, all pH values for the samples are below the accepted value specified. Referring to ASTM D1655, pure biodiesel has a pour point temperature range of -15 ^oC to 10 ^oC. Table B-7 displays the results, all values recorded fell within the specified range. The pour point for Jet fuels should be approximately -47 ^oC, all the jet fuel blends (B10 and B20) are higher than the maximum limit. Referring to ASTM 93, the flash point temperature range of biodiesel is 93^oC to 170 ^oC. Referring to ASTM D1655, the flash point for jet fuel has a minimum temperature limit of 38 ^oC.

Table B-9 displays the results, both biodiesel and kerosene blends were in accordance with ASTM standards.

The GC-Analysis testing incorporated an iterative process to determine the best conditions to generate the Chromatogram. First, undiluted KOH and MgO biodiesel was investigated and unfortunately, no peaks were displayed in various conditions chosen. Therefore, dilution had to be explored. Dilution tests using 10:1 and 5:1 still displayed no peaks on the chromatogram.

Dilution of 1:1 was chosen, and this displayed the best results with the chosen conditions in Table B-12 and Table B-13. Extremely small traces of compounds (less than 0.5%) were omitted.

Table B-14 shows the property testing summary table for the pure biodiesel products and blends. KOH was found to be the most suitable catalyst for the feedstock chosen. This conclusion is drawn from the pure KOH biodiesel having a much lower kinematic viscosity than MgO biodiesel, and KOH biodiesel had a higher flash point than pure MgO biodiesel.

CHAPTER 5: Conclusions and Recommendations

5.1) Conclusions

The conclusions below were reached after the study had been completed:

- Waste canola oil was selected as a feedstock for this thesis. Canola oil and waste cooking oil had low acid values of 0.1167 mg KOH/g oil and 0.3535 mg KOH/g oil, respectively. The low acid value indicated that the treatment step utilising methanol and sulphuric acid could be omitted.
- The acid value was less than 1 mg KOH/g oil, confirming that the one step transesterification reaction can used.
- A maximum yield of 0.9153 was obtained at run number twelve for transesterification of used canola oil with ethanol via potassium hydroxide. This experiment took place at 74 ^{o}C, had a catalyst loading of 0.085 wt % oil, a 75-minute reaction time and a 26:1 alcohol to oil molar ratio.
- From the four models investigated, the full quadratic model exhibited the best fit to the experimental data as this model obtained the highest coefficient of determination (R^2) in the study. This R^2 value was 0.9575.
- Minitab Statistical Analysis Software calculated a maximum yield of 0.9247 for the homogeneous transesterification of used cooking oil. This generated experiment had a reaction temperature of 74 ^{o}C, a catalyst loading of 0.06727%, an 84.55-minute reaction time and a 26:1 alcohol to oil molar ratio.
- An investigation was completed using the optimum generated conditions and resulted in a yield of 0.9358. An experimental error of 1.2% was calculated. Therefore, it can be concluded that the optimal yield for this study was found utilising Minitab Statistical Software.
- Used Cooking Oil destroys the catalytic activity of a heterogeneous catalyst like Magnesium Oxide much faster than fresh cooking oil. Due to this reasoning, the extracted catalyst will not be reused after each reaction.
- A maximum yield of 0.9602 was obtained at run number eight for the transesterification of used cooking oil with ethanol via Magnesium Oxide. This experiment occurred at 70 ^{o}C, had a catalyst loading of 1.5 wt. %, 120-minute reaction time and 20:1 alcohol to oil molar ratio.

- From the four models investigated for the heterogeneous transesterification of used cooking oil, the full quadratic model exhibited the best fit to the experimental data as this model obtained the highest coefficient of determination (R^2) in the study. This R^2 value was 0.9710.
- Minitab Statistical Analysis Software generated the maximum yield of 0.9667 for the heterogeneous transesterification of used cooking oil. This generated experiment had a temperature of 54.41 °C, a catalyst loading of 1.4444%, a 120-minute reaction time and an 18.18:1 alcohol to oil molar ratio.
- An investigation was completed using the optimal generated conditions, and a yield of 0.9742 was found. An experimental error of 0.78% was calculated. Therefore, it was concluded that Minitab Statistical Software could accurately predict the optimum yield using the regression model for the heterogeneous transesterification of used cooking oil.
- The acid value property testing concluded that the jet fuel blends (B10 and B20), were over the allowable limit of 0.015 mg KOH/g indicating blending biodiesel made from used waste cooking oil may not be suitable for blends with jet fuels.
- The kinematic viscosity property testing concluded that the pure KOH and MgO Biodiesel samples were over the maximum limit for kinematic viscosity. Further modification would be required for direct use in an engine.
- All the jet fuel blends (B10 and B20) are higher than the pour point maximum limit. However, the B20 blends of KOH and MgO were reasonably close with -45.27 °C and -44.53 °C, respectively.
- KOH was found to be the most suitable catalyst for the feedstock chosen. This conclusion is drawn from the pure KOH biodiesel having a much lower viscosity than MgO biodiesel, KOH biodiesel also had a higher flash point than pure MgO biodiesel.
- The feasibility study concluded that the critical success factors of biodiesel production in South Africa are: Minimum rate of return; Choice of biodiesel feedstock; Selling price of biodiesel in SA and International Market; Security of Supply; Mandatory Blending requirements; Legislation by the government which ensures a market; Special incentives by the government for production, marketing and consumption of biofuels; job opportunities and Foreign market opportunities.

- The feasibility study indicated used cooking oil was the cheapest feedstock to produce biodiesel from transesterification; eliminates the issue of food security; and provides additional income to businesses such as the hospitality sector.

5.2) Recommendations

- Different feedstocks with blends of waste cooking oil should be investigated.
- Longer chained alcohols should be investigated.
- Different catalysts should be investigated.
- Alternative methods of biodiesel production should be considered.
- A laboratory scaled reactor could be used to produce the most reliable and accurate results.
- The reusability of the heterogeneous catalyst should be investigated.
- Catalyst deactivation should be investigated.
- Biodiesel production should be investigated at various operating pressures.
- Investigate how various calcination temperatures affect the heterogeneous catalyst.
- Future studies should evaluate the accuracy of modifying and reducing the regression model to predict biodiesel yield outside the process parameter range of the field of their study.
- A preliminary investigation should be completed utilizing the OVAT approach before investigating the interactions of the process variables to accurately optimize the biodiesel production process.

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APPENDICES

APPENDIX A: Sample Calculations

Prepare 0.5 M HCL, commercial concentrated HCL is 12.1 M.

$$M_1V_1 = M_2V_2 \tag{A.1}$$

$$12.1\ M\ x\ V_1 = 0.5\ M\ x\ 0.1\ L$$

$$V_1 = 0.00146\ L\ or\ 4.16\ mL$$

Prepare 0.1 N Ethanolic KOH

Dissolve 6g of KOH in 5 ml of water. Add ethanol to produce 1000 ml. Allow the solution to stand in a tightly stopped bottle for 24 hours.

The saponification value was found utilising according to the method by Mohammed et al. (2019). 2 g of the treated waste cooking oil was mixed with 25 cm^3 of 0.1 N Ethanolic Potassium Hydroxide. Phenolphthalein indicator was dropped into the solution, and it turned a pink colour. The prepared solution was titrated against 0.5 M Hydrochloric acid solution. A blank titration was also completed by titrating the 0.1 N Ethanolic Potassium Hydroxide against 0.5 M Hydrochloric acid solution. The saponification value was determined using the formula below.

$$SV = \frac{56.1\ \times\ 0.5\ \times\ (V_b - V_t)}{m} \tag{A.2}$$

$$SV = \frac{56.1\ \times\ 0.5\ \times\ (20.20 - 5.46)}{2}$$

$$SV = 206.671\ \left(\frac{mgKOH}{g\ sample}\right)$$

m is the mass of the sample.

Acid Value:

The acid value was calculated using sections 3.4.2 and 3.4.3 and calculations from (Muhammad et al., 2019)

$$Acid\ Number\ \left(\frac{mgKOH}{g\ sample}\right) = \frac{V_{KOH}\ \times\ N_{KOH}\ \times\ 56.1}{sample\ weight} \tag{A.3}$$

where

V_{KOH} $is\ the\ difference\ between\ the\ volumes\ obtained\ from\ the\ actual\ titration\ and\ the\ blank\ titration$

$$N_{KOH}\ is\ the\ molarity\ of\ the\ prepared\ standard\ solution.$$

$$Acid\ Number\ \left(\frac{mgKOH}{g\ sample}\right) = \frac{(1.260 - 0.745)\ \times\ 0.1\ \times\ 56.1}{8.172}$$

$$Acid\ Number = 0.3535\ \left(\frac{mgKOH}{g\ sample}\right)$$

Free Fatty Acid:

$$Free\ Fatty\ Acid\ \left(\frac{mgKOH}{g\ sample}\right) = 0.5\ \times\ Acid\ Number \qquad (A.4)$$

$$Free\ Fatty\ Acid\ \left(\frac{mgKOH}{g\ sample}\right) = \ 0.3535\ \ \times\ 0.5$$

$$Free\ Fatty\ Acid = 0.1768\ \left(\frac{mgKOH}{g\ sample}\right)$$

Homogenous alkaline catalysts such as the provided catalyst KOH, are selectively suitable for producing biodiesel from vegetable oils with low content of free fatty acids (FFA) lower than 0.5% (Gebremariam and Marchetti, 2017). This now indicates that the homogenous alkaline KOH catalyst is a suitable catalyst to carry out the following investigations.

Molar Mass of Used Canola Oil:

$$MM_{Canola} = \ \frac{56.1\ \times\ 1000\ \times\ 3}{SV - AV} \qquad (A.5)$$

$$MM_{Canola} = \ 815.733\ g/mol$$

Using the Heterogeneous Study, experiment 21: 8:1 Ethanol to Oil Molar ratio, a 1% Catalyst Loading, 75-minute reaction time and temperature of 50 ^{o}C.

Number of Moles of Used Canola Oil:

$$n_{oil} = \frac{mass}{(Molar\ Mass_{canola\ oil})} \qquad (A.6)$$

$$n_{oil} = \frac{223.4}{815.733} = 0.2739\ mol$$

Moles of Alcohol Required:

$$n_{ethanol} = n_{oil} \times 8 \qquad (A.7)$$

$$n_{ethanol} = 0.2739 \times 8$$

$$n_{ethanol} = 2.1909\, mol$$

Volume of Alcohol Required:

$$V_{ethanol} = \frac{n_{ethanol} \times MM_{ethanol}}{\rho_{ethanol}} \qquad (A.8)$$

Molar Mass of ethanol = 46.07 g/mol (Sigma Aldrich, 2023)

Density of ethanol = 0.789 g/cm^3 (Sigma Aldrich, 2023)

$$V_{ethanol} = \frac{2.57443 \times 46.07}{0.789}$$

$$V_{ethanol} = 127.93\, cm^3$$

Catalyst Concentration:

The mass of the catalyst for 1% catalyst loading was calculated as follows:

$$\boldsymbol{m_{catalyst} = 0.01 \times 223.40 = 2.234\, g}$$

Biodiesel Yield:

$$Biodiesel\ yield\ (\%) = \frac{mass\ of\ product\ produced}{mass\ of\ oil} \times 100 \qquad (A.9)$$

$$Biodiesel\ yield\ (\%) = \frac{178.456}{223.40} \times 100 = 79.88\ \%$$

APPENDIX B: Property Tests

Appendix B discusses whether the biodiesel produced met international standards and determines whether the biodiesel without additional modifications can be utilised in diesel engines. Simple property testing was conducted, and the feedstock properties were also assessed. Property testing was completed on samples from the optimum reaction conditions while using both catalysts for their respective reactions. Blends of biodiesel of 10% and 20% were tested as well. 10% biodiesel blend (BK10) is split 90% Kerosene and 10% biodiesel. 20% biodiesel blend (BK20) is split 80% Kerosene and 20% biodiesel.

Density

Metler Toledo Density Meter Easy D40 was used in order to determine the density of the chosen samples. The meter had to be first cleaned and dried to ensure the reliability of the results, as residue could be present in the tubing from previous uses. The device was considered dry if the density recorded was 0.0016 g/cm^3 or lower after the drying process. A sample of 10 ml of biodiesel was inserted into the syringe. The syringe was inserted into the device and injected into the machine. The density property test was completed three times to ensure the reliability of the findings. Each sample was measured according to ASTM D941 and measured at the standard reference temperature of 15 ^{o}C. The limit for the density of biodiesel according to ASTM D941, is 900 kg/m^3. The Metler Toledo Density Meter Easy D40 has an accuracy of +/- 0.0005 g/cm^3.

Table B-1: Density Results.

Sample	**Density (g/cm^3)**			**Average Density (g/cm^3)**
	Run 1	**Run 2**	**Run 3**	
WCO	0.9173	0.9173	0.9173	0.9173
KOH	0.8924	0.8924	0.8924	0.8924
MgO	0.8987	0.8987	0.8987	0.8987
KOH BK 10%	0.8185	0.8188	0.8188	0.8187
KOH BK 20%	0.8272	0.8272	0.8272	0.8272
MgO BK 10%	0.8159	0.8163	0.8159	0.8160
MgO BK 20%	0.8327	0.8327	0.8327	0.8327

Acid Value

The method for the Acid Value tests were outlined in accordance with ASTM D974. A 0.1 M standard solution of Potassium Hydroxide (KOH) was created. First, a blank titration was completed where the standard solution was titrated against the methanol-phenolphthalein mixture. The endpoint was achieved when the colour of the solution changed to a light pink. This was completed by adding four drops of phenolphthalein indicator to 10 ml of methanol in a glass beaker. As outlined in the experimental method, approximately 10 ml of methanol was added to a beaker containing 1 ml of the treated waste oil and four drops of phenolphthalein indicator. The mixture reached endpoint when the indicator present turned the mixture a light pink colour. With the volume of standard solution used to achieve endpoint along with the volume from the blank titration, the free fatty acid (FFA) content and acid number of the oil can now be calculated.

$$Acid\ Value\ \left(\frac{mgKOH}{g\ sample}\right) = \frac{V_{KOH}\ x\ N_{KOH}\ x\ 56.1}{sample\ weight} \qquad (B.1)$$

where:

V_{KOH} $is\ the\ difference$ between $the\ volumes\ obtained\ from\ the\ actual\ titration\ and\ the\ blank\ titration$

N_{KOH} $is\ the\ molarity\ of\ the\ prepared\ standard\ solution.$

Table B-2: Test Results for Acid Value Titrations.

Sample	Acid Value (mg KOH/g)			Mean Acid Value (mg KOH/g)
	Run 1	Run 2	Run 3	
Canola Oil	0.1165	0.1168	0.1168	0.1167
Waste Cooking Oil	0.3715	0.3354	0.3537	0.3535
KOH	0.4930	0.5060	0.4930	0.4970
MgO	0.2270	0.5830	0.3760	0.3950
KOH BK 10%	0.2130	0.2200	0.1810	0.2050
KOH BK 20%	0.2570	0.3110	0.2850	0.2840
MgO BK 10%	0.2290	0.1940	0.1940	0.2060
MgO BK 20%	0.3040	0.2720	0.2460	0.2740

pH Test

The first step in determining the pH of each sample was to calibrate the pH meter. This calibration process exposed the probe to a set of standard solutions of different pH, a 4.01 pH and a 7.01 pH. After calibration, the biodiesel sample was added to a thin, tall 100ml glass beaker. The pH meter's probe was placed in the beaker in order to determine the pH. The uncertainty value of this equipment is +/- 0.01.

Table B-3: pH Test Results.

Sample	**pH**			**Average pH**
	Run 1	**Run 2**	**Run 3**	
WCO	7.39	7.20	7.18	7.26
KOH	8.38	8.57	8.48	8.48
MgO	7.48	8.16	7.67	7.77
KOH BK 10%	7.65	7.73	7.76	7.71
KOH BK 20%	8.22	8.22	8.12	8.19
MgO BK 10%	8.69	8.28	8.88	8.62
MgO BK 20%	7.67	8.11	7.65	7.81

Refractive Index

The first step in determining the refractive index of each sample was to calibrate the refractometer. This calibration process was completed by using deionized water. After the calibration process, 3 drops of biodiesel were added onto the refractometer and covered. The process was repeated three times to ensure the reliability of the results. The refractometer has a level of uncertainty of +/- 0.00002. According to Singh et al. (2008), the refractive index range for biodiesel according to ASTM standards is 1.447-1.48.

Table B-4: Test Results for Refractive Index.

Sample	**Refractive Index**			**Mean Refractive Index**
	Run 1	**Run 2**	**Run 3**	
WCO	1.4720	1.4733	1.4734	1.4729
KOH	1.4593	1.4595	1.4591	1.4593
MgO	1.4724	1.4724	1.4717	1.4722
KOH BK 10%	1.4497	1.4505	1.4510	1.4504
KOH BK 20%	1.4509	1.4525	1.4522	1.4518
MgO BK 10%	1.4518	1.4530	1.4536	1.4528
MgO BK 20%	1.4592	1.4605	1.4598	1.4599

Viscosity

The dynamic viscosity of the biodiesel product was estimated using the BROOKFIELD DV-II+Pro Viscometer. A water bath was utilised to ensure the desired temperature. The water bath temperature varied for each sample (40 ^{o}C for pure biodiesel samples, 25 ^{o}C for waste cooking oil and 20 ^{o}C for biodiesel jet fuel blends). Spindle 1 was utilised for the used canola oil and Spindles 1 or 2 were used for the remaining samples. The rotation speed was chosen to be 100 rpm. The values recorded were in centipoise (cP), in order to achieve the desired kinematic viscosity (mm^2/s), the recorded values had to be divided by the specific gravity for the respective sample. Ice was used in order to lower the temperature of the water bath. According to ASTM D445, the maximum limit for kinematic viscosity for biodiesel is 6 mm^2/s. According to ASTM D1665, the kinematic maximum limit for jet fuel is 8 mm^2/s. The viscometer has an uncertainty value of +/- 0.02 mm^2/s.

Table B-5: Viscosity Test Results.

Sample	**Kinematic Viscosity (mm^2/s)**			**Average Kinematic Viscosity (mm^2/s)**
	Run 1	**Run 2**	**Run 3**	**Viscosity**
WCO	74.89	71.95	70.86	72.57
KOH	8.18	8.07	7.96	8.07
MgO	14.94	15.04	14.83	14.94
KOH BK 10%	3.92	3.82	3.92	3.89
KOH BK 20%	5.12	5.01	4.69	4.94
MgO BK 10%	4.14	3.92	3.92	4.00
MgO BK 20%	6.10	6.10	6.21	6.14

American Petroleum Institute Gravity

The API gravity is utilised for expressing the relative density of fuels to water therefore, the API gravity was only calculated for blended biodiesel products. The API value was calculated using the specific gravity recordings and using the following equation used in Speight, 2002.

$$API\ value = \frac{141.5}{Specific\ Gravity} - 131.5 \qquad (B.2)$$

Table B-6: API Values for Biodiesel Blends.

Sample	API Values			Average API Values
	Run 1	Run 2	Run 3	
KOH BK 10%	41.38	41.31	41.31	41.33
KOH BK 20%	39.56	39.56	39.56	39.56
MgO BK 10%	41.93	41.84	41.93	41.90
MgO BK 20%	38.43	38.43	38.43	38.43

Pour Point

30 ml sample of biodiesel was added to a 50 ml beaker placed into a Haier Ultra Low Temperature (ULT) Freezer. A MajorTECH Type K/J Thermometer was used to gauge the temperature of the samples accurately. According to ASTM D1655, jet fuel has a pour point temperature of roughly -47 °C. According to ASTM D6571, biodiesel has a pour point temperature between the range of -15 °C to 10°C.

Table B-7: Test Results for Pour Point Testing.

Sample	Pour Point (°C)			Mean Pour Point (°C)
	Run 1	Run 2	Run 3	
KOH	-8.70	-8.60	-8.70	-8.67
MgO	-17.40	-17.00	-16.70	-17.03
KOH BK 10%	-44.60	-46.00	-45.20	-45.27
KOH BK 20%	-35.60	-36.10	-35.80	-35.83
MgO BK 10%	-44.20	-44.80	-44.60	-44.53
MgO BK 20%	-40.70	-41.50	-42.00	-41.40

Heat of Combustion

The definition for heat of combustion is, “the amount of heat generated when 1 mole of biodiesel is burnt” (Owolabi et al., 2011). The formula below was used to estimate the heat of combustion using the specific gravity for the biodiesel BK10 and BK20 blends (Speight, 2002).

$$Heat\ of\ combustion = 12400 - 2100\,(SG)^2 \qquad (B.3)$$

Table B-8: Test Results for Heat of Combustion.

Sample	Heat of Combustion (BTU/lb)			Average Heat of Combustion (BTU/lb)
	Run 1	Run 2	Run 3	
KOH BK 10%	10993.12	10992.09	10992.09	10992.43
KOH BK 20%	10963.05	10963.05	10963.05	10963.05
MgO BK 10%	11002.05	11000.67	11002.05	11001.59
MgO BK 20%	10943.88	10943.88	10943.88	10943.88

Flash Point

Due to unforeseen circumstances the flash point apparatus was badly damaged and even after repairs, unable to heat samples and reach high temperatures. An innovative approach was designed to obtain the results. A lasec hot plate was utilised to increase the temperature of the flash point apparatus. A small sample of biodiesel was added to the cup in the flash point apparatus. The lid was placed over the cup. In 1 ^{o}C intervals, while the biodiesel sample was heated, the lid was pushed up and the vapours above the cup were exposed to a flame. The temperature where the vapour flashed is known as the flash point.

Table B-9: Flash Point Test Results.

Sample	Flash Point (^{o}C)			Average Flash Point (^{o}C)
	Run 1	Run 2	Run 3	
KOH	103.00	105.00	103.00	103.67
MgO	98.90	98.00	98.00	98.30
KOH BK 10%	59.20	58.70	59.10	59.00
KOH BK 20%	72.20	74.00	73.50	73.23
MgO BK 10%	56.00	56.40	56.80	56.40
MgO BK 20%	62.00	59.80	60.20	60.67

GC Analysis

This section displays the conditions set on the Shimadzu Gas Chromatography-mass spectrometry (GC-MS) and the results generated from the optimal biodiesel experiment. Below are the results from the KOH and NaOH biodiesel products. Samples from the optimum KOH and MgO biodiesel experiments were used. The samples were diluted with Dichloromethane. Extremely small traces of compounds, i.e., less than 0.5%, were omitted from the GC-MS Results.

Table B-10: GC Conditions.

Injection Temperature (ºC)	250
Column Oven Temperature (ºC)	120
Injection Mode	Split
Carrier Gas	None
Flow Control Mode	Linear Velocity
Pressure (kPa)	80.6
Total flow (ml/min)	34
Linear velocity (cm/s)	37.5
Purge Flow (mL/min)	3
Split Ratio	30.0
Column Flow (mL/min)	1.00

Table B-11: GC Temperature Program.

Rate	Temperature (ºC)	Hold Time (minutes)
-	120	0.00
10	180	1.00
1	215	0.00
2	260	0.00

KOH Biodiesel Analysis

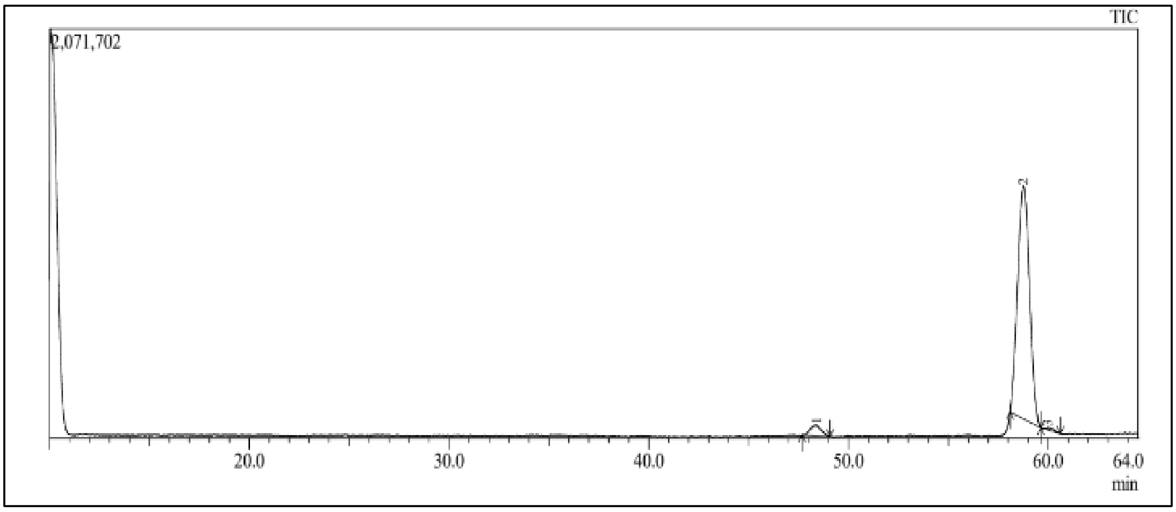

Figure B-1: 1:1 KOH Biodiesel: DCM Chromatogram.

Table B-12: 1:1 GC-MS Results for 1:1 KOH Biodiesel: DCM.

Peal Number	**Retention Time (Minutes)**	**Area (%)**	**Name of Compound**	**Chemical Formula**
1	48.402	3.83	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$
2	58.748	95.59	Ethyl Oleate	$C_{20}H_{38}O_2$
3	59.966	0.58	Octadecanoic Acid, ethyl ester	$C_{20}H_{40}O_2$

MgO Biodiesel Analysis

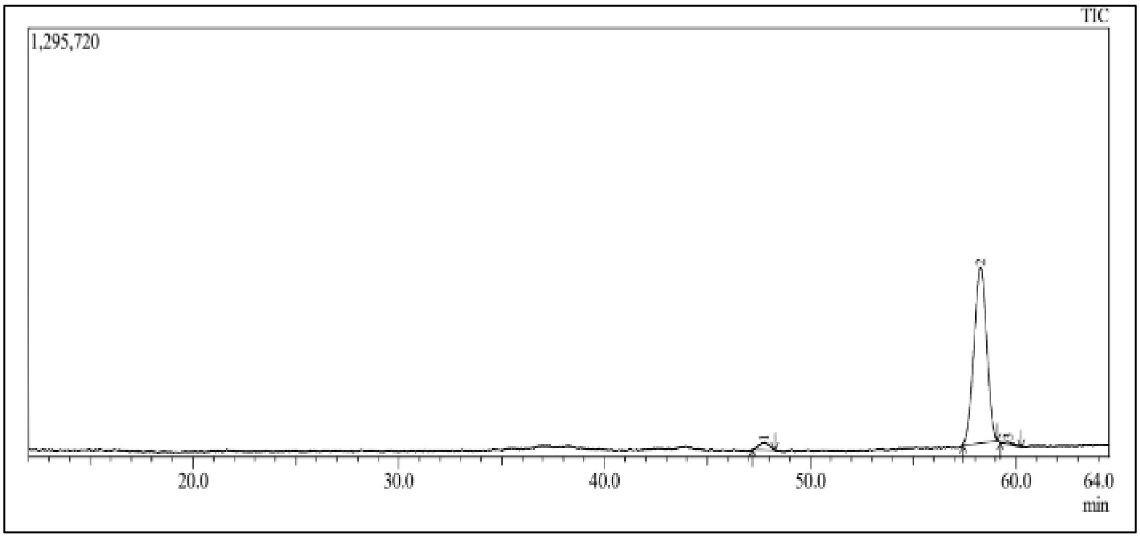

Figure B-2: 1:1 MgO Biodiesel: DCM Chromatogram.

Table B-13: GC-MS Results for 1:1 MgO Biodiesel: DCM Chromatogram.

Peal Number	**Retention Time (Minutes)**	**Area (%)**	**Name of Compound**	**Chemical Formula**
1	47.18	3.31	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$
2	57.43	95.59	Ethyl Oleate	$C_{20}H_{38}O_2$
3	59.23	0.89	Octadecanoic Acid, ethyl ester	$C_{20}H_{40}O_2$

Table B-14 below shows the property testing summary table for the pure biodiesel products and blends. KOH was found to be the most suitable catalyst for the feedstock chosen. This conclusion is drawn from the pure KOH biodiesel having a much lower viscosity than MgO biodiesel, and KOH biodiesel having a higher flash point than pure MgO biodiesel.

Table B-14: Property Testing Summary Table

Property Test	**KOH Biodiesel**	**MgO Biodiesel**	**KOH BK 10%**	**KOH BK 20%**	**MgO BK 10%**	**MgO BK 20%**
Density (g/cm^3)	0.08924	0.8987	0.8187	0.8272	0.8160	0.8327

pH	8.48	7.77	7.71	8.19	8.62	7.81
Refractive Index	1.4593	1.4722	1.4504	1.4518	1.4528	1.4599
Kinematic viscosity (mm^2/s)	8.07	14.94	3.89	4.94	4.00	6.14
API Value	-	-	41.33	39.56	41.90	38.43
Pour Point (°C)	-8.67	-17.03	-45.27	-35.83	-44.53	-41.40
Heat of Combustion (BTU/lb)	-	-	10992.43	10963.05	11001.59	10943.88
Flash Point (°C)	103.67	98.30	59.00	73.23	56.40	60.67

APPENDIX C: Raw Data

Table C-1: KOH Biodiesel Raw Data.

Experiment Number	Temperature (ºC)	Catalyst Loading (g)	Reaction Time (min)	Alcohol (g)	Run 1	Run 2	Run 3	Average Yield
1	30	0.0364	75	184.94	0.8421	0.8511	0.8504	0.8479
2	74	0.0364	75	184.94	0.8614	0.8501	0.8493	0.8536
3	30	0.2729	75	184.94	0.8052	0.7912	0.7963	0.7976
4	74	0.2729	75	184.94	0.8412	0.8289	0.8409	0.8370
5	52	0.1546	30	102.74	0.7595	0.7514	0.7657	0.7589
6	52	0.1546	120	102.74	0.7852	0.7761	0.7767	0.7793
7	52	0.1546	30	267.13	0.8410	0.8453	0.8404	0.8422
8	52	0.1546	120	267.13	0.8551	0.8487	0.8510	0.8516
9	30	0.1546	75	102.74	0.7947	0.7882	0.7888	0.7906
10	74	0.1546	75	102.74	0.7964	0.8115	0.8192	0.8090
11	30	0.1546	75	267.13	0.8889	0.8785	0.8885	0.8853
12	74	0.1546	75	267.13	0.9041	0.9211	0.9208	0.9153
13	52	0.0364	30	184.94	0.7997	0.8112	0.8053	0.8054
14	52	0.2729	30	184.94	0.7701	0.7611	0.7603	0.7638
15	52	0.0364	120	184.94	0.8110	0.8224	0.8148	0.8161
16	52	0.2729	120	184.94	0.7804	0.7888	0.7787	0.7826
17	30	0.1546	30	184.94	0.8314	0.8422	0.8413	0.8383
18	74	0.1546	30	184.94	0.8213	0.8284	0.8245	0.8247
19	30	0.1546	120	184.94	0.8539	0.8502	0.8516	0.8519
20	74	0.1546	120	184.94	0.8955	0.8826	0.8840	0.8874
21	52	0.0364	75	102.74	0.7780	0.7699	0.7718	0.7732
22	52	0.2729	75	102.74	0.7585	0.7570	0.7585	0.7580
23	52	0.0364	75	267.13	0.8901	0.8947	0.8909	0.8919
24	52	0.2729	75	267.13	0.8331	0.8271	0.8304	0.8302
25	52	0.1546	75	184.94	0.8687	0.8611	0.8654	0.8651
26	52	0.1546	75	184.94	0.9054	0.8905	0.7944	0.8968
27	52	0.1546	75	184.94	0.8769	0.8641	0.8693	0.8701

Table C-2: MgO Biodiesel Raw Data.

Experiment Number	**Temperature (ºC)**	**Catalyst Loading (g)**	**Reaction Time (min)**	**Alcohol (g)**	**Run 1**	**Run 2**	**Run 3**	**Average Yield**
1	30	2.234	75	176.64	0.8561	0.8647	0.8571	0.8593
2	70	2.234	75	176.64	0.8489	0.8378	0.8417	0.8428
3	30	4.468	75	176.64	0.8344	0.8301	0.8337	0.8327
4	70	4.468	75	176.64	0.8412	0.8322	0.8399	0.8378
5	50	3.351	30	100.94	0.7999	0.7865	0.7944	0.7936
6	50	3.351	120	100.94	0.8311	0.8364	0.8357	0.8344
7	50	3.351	30	252.34	0.9481	0.9411	0.9434	0.9442
8	50	3.351	120	252.34	0.9624	0.9582	0.9599	0.9602
9	30	3.351	75	100.94	0.7917	0.7991	0.7930	0.7946
10	70	3.351	75	100.94	0.8117	0.7989	0.8061	0.8056
11	30	3.351	75	252.34	0.9054	0.8974	0.8975	0.9001
12	70	3.351	75	252.34	0.9389	0.9351	0.9353	0.9364
13	50	2.234	30	176.64	0.8666	0.8541	0.8645	0.8617
14	50	4.468	30	176.64	0.8611	0,8650	0.8464	0.8575
15	50	2.234	120	176.64	0.9288	0.9261	0.9269	0.9273
16	50	4.468	120	176.64	0.9045	0.8925	0.9066	0.9012
17	30	3.351	30	176.64	0.8889	0.8779	0.8932	0.8867
18	70	3.351	30	176.64	0.9098	0.8977	0.9093	0.9056
19	30	3.351	120	176.64	0.9051	0.9187	0.9105	0.9114
20	70	3.351	120	176.64	0.9188	0.9089	0.9149	0.9142
21	50	2.234	75	100.94	0.8077	0.7936	0.7952	0.7988
22	50	4.468	75	100.94	0.7761	0.7699	0.7712	0.7724
23	50	2.234	75	252.34	0.9045	0.9098	0.9050	0.9064
24	50	4.468	75	252.34	0.8957	0.8966	0.8916	0.8946
25	50	3.351	75	176.64	0.9287	0.9304	0.9303	0.9298
26	50	3.351	75	176.64	0.9212	0.9287	0.9251	0.9250
27	50	3.351	75	176.64	0.9204	0.9256	0.9140	0.9200

Table C-3: Raw Data for Acid Value Titration.

Testing Sample	**Starting Value (mL)**			**End Value (mL)**			**Difference (mL)**			**Mean (mL)**
	Run 1	**Run 2**	**Run 3**	**Run 1**	**Run 2**	**Run 3**	**Run 1**	**Run 2**	**Run 3**	
Blank	2.22	5.86	9.44	5.80	9.04	12.94	3.58	3.54	3.50	3,54
Canola Oil	21.08	22.22	23.38	22.02	23.16	24.26	0.94	0.94	0.88	0.92
Waste Canola Oil	3.78	5.08	6.38	5.04	6.36	7.62	1.26	1.28	1.24	1.26
KOH	13.62	18.02	22.38	17.92	22.34	26.68	4.30	4.32	4.30	4.31
MgO	26.84	31.04	35.52	30.72	35.48	39.64	3.88	4.44	4.12	4.15
KOH BK 10%	40.04	2.84	6.80	43.90	6.72	10.62	3.86	3.88	3.82	3.85
KOH BK 20%	10.72	14.68	18.74	14.64	18.70	22.72	3.92	4.02	3.98	3.97
MgO BK 10%	22.82	26.74	30.64	26.70	30.58	34.48	3.88	3.84	3.84	3.85
MgO BK 20%	34.52	2.46	6.62	38.52	6.42	10.54	4.00	3.96	3.92	3.96

APPENDIX D: Phase Separation

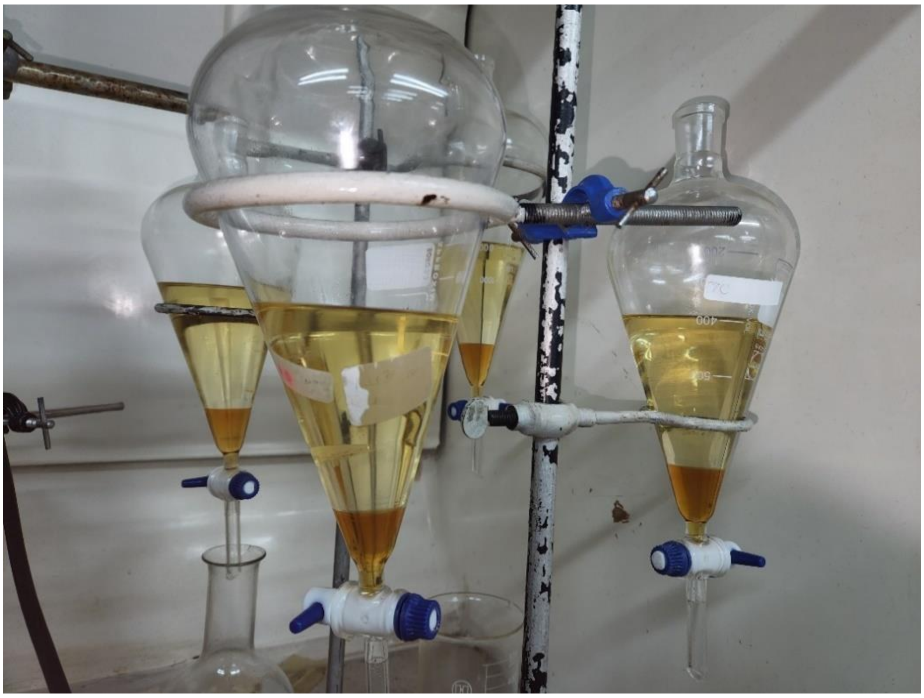

Figure D-1: Homogeneous Transesterification Separation Phase.

Figure D-2: Heterogeneous Separation Phase.

APPENDIX E: Property Testing Equipment

Figure E-1: Haier Ultra Low Temperature Freezer.

Figure E-2: Adapted Flash Point Property Set-Up.