AN INVESTIGATION INTO THE SYNTHESIS OF BIODIESEL FROM CANOLA OIL VIA HETEROGENEOUSLY CATALYZED TRANSESTERIFICATION REACTION

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Abstract

Biodiesel has gained a great deal of attention worldwide due to its reduced toxicity, biodegradability, and renewable characteristics. Biodiesel fuel seems to be a promising alternative to petroleum diesel as it is derived from renewable feedstocks. The more conventional production of biodiesel is synthesized in the presence of homogeneous catalysts. However, heterogeneous catalysts have recently gained tremendous importance because of the current climate e.g., increased competition, stringent pollution regulations, etc.

Biodiesel is manufactured ideally through catalyzed transesterification reactions whereby the triglycerides (animal fats or vegetable oils) are reacted with an alcohol (with low molecular weight) to produce alkyl esters (biodiesel) and glycerol as a by-product. This study focused on the transesterification reaction of triglycerides to synthesize fatty acid ethyl esters in the presence of heterogeneous catalysts respectively. Canola oil was investigated in this study along with ethanol, and heterogeneous catalysts calcium oxide and magnesium oxide respectively. Canola oil had a free fatty acid content of 0.042 wt.% which was significantly lower than the recommended 0.5 wt.%, indicating no pretreatment step was necessary and only a single-step transesterification was required. The process variables taken into consideration included reaction temperature, catalyst loading, alcohol to oil molar ratio, and reaction time, and the response variable was the biodiesel yield attained. Box-Behnken design along with response surface methodology (RSM) was used to obtain the optimum process variable conditions which resulted in attaining a maximized biodiesel yield.

Biodiesel produced in the presence of calcium oxide achieved an optimum yield of 93.80%, while biodiesel produced in the presence of magnesium oxide achieved an optimum yield of 96.90%. The biodiesel yields obtained at the optimum conditions were subjected to being blended with kerosene to produce bio-jet fuel. Both biodiesel and bio-jet fuel were subjected to property testing in accordance with ASTM standard fuel requirements. The biodiesel yields produced from canola only in the presence of both calcium oxide and magnesium oxide respectively met all ASTM standard requirements except for the kinematic viscosities which were higher than the stipulated limit, however, biodiesel produced with magnesium oxide was closer to the specified limit. Nevertheless, biodiesel produced from canola oil reacting with ethanol in the presence of the aforementioned heterogeneous catalysts respectively is not recommended to be used in a diesel engine without further modification. The jet fuel samples met all the ASTM standard requirements, except for the kinematic viscosity and acid value properties, thus these are not recommended for use in an engine without further modification.

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Chapter 1 Introduction

1.1 Background

Sustainably manufacturing biofuels is a valuable tool in mitigating global warming, improving local economies, and enhancing energy security worldwide. Biodiesel is one such candidate seen as a promising biofuel to replace a significant percentage of petroleum diesel. Biodiesel can be prepared from any fatty acid source. Hence, it can be produced from renewable sources like vegetable oils or animal fats. Vegetable oils are commonly used for biodiesel production, there are more than 350 oil-bearing crops identified as prospective sources (Bart, et al., 2010). Biodiesel emissions mostly consist of carbon dioxide. Biodiesel is known as a carbon-neutral fuel as it has a closed carbon cycle, the carbon dioxide it releases is easily absorbed by crops producing oxygen (DeCicco, 2013). Direct use of vegetable oil in conventional diesel engines is not possible due to oil having high viscosity and low volatility, however, blending of biodiesel with petroleum diesel may be more effective. In order to make vegetable oil operational as a fuel it is required to go through blending, microemulsions, pyrolysis, or a transesterification process (Demirbas, 2003).

Transesterification and blending are the more common methods used to lower vegetable oil viscosity and increase its volatility. Blending does not require chemical modification of vegetable oil. However, blending is undesired, as it requires the vegetable oil to be purified before the blending process. Transesterification is most commonly used worldwide due to the quality of the biodiesel obtained through this method, and due to its simplicity and low cost (Fukuda, et al., 2001). There are two different transesterification processes; a non-catalytic and a catalytic method. Since alcohol is only slightly soluble in vegetable oils, the use of a catalyst is employed to enhance the solubility of alcohol, and therefore increase the reaction rate. Generally, the types of catalysts employed are either homogeneous or heterogeneous (Shahid & Jamal, 2011; Balat & Balat, 2010).

During the catalyzed transesterification process, the triglycerides (vegetable oil) are reacted with alcohol of low molecular weight (usually methanol or ethanol) to produce alkyl esters (biodiesel) and glycerol as a by-product (Schuchardt , et al., 1998). The advantages of biodiesel include being non-toxic, biodegradable and one of the most renewable resources currently available. Biodiesel has very small amounts of polycyclic aromatic hydrocarbons (such as naphthalene, acenaphthylene, fluorene), sulfur, and metals (like calcium and magnesium metals). Petrochemically produced diesel (petro-diesel) contains approximately 20% polycyclic aromatic hydrocarbons. These compounds tend to bioaccumulate, as they do not readily biodegrade and are reported to be mutagenic. Biodiesel is a safe alternative for transportation and storage since it does not contain polycyclic aromatic hydrocarbons. Similar to petro-diesel, biodiesel operates in compression-ignition engines. Biodiesel can be used as 100% pure biodiesel (B100), but it is generally blended with petro-diesel in ratios of 2% (B2), 5% (B5), or 20% (B20). Biodiesel compared to petro-diesel is a better lubricant in regular diesel engines, as it is oxygenated, thus increasing the engine's life. A lot of countries are implementing biodiesel blends to increase the lubricity of low-sulfur diesel fuels (Anastopoulos, et al., 2001). Biodiesel is the perfect fuel for sensitive environments, such as extremely polluted cities, as it has a relatively low emission profile, and it has lower greenhouse gas (GHG) emissions in comparison to petro-diesel (Salis, et al., 2005).

1.2 Motivation and significance

Energy security has become a major concern for the. Since the last century, the amount of energy consumed has exponentially increased due to population and economic growth. Globally there is a growing demand for energy while there is only a finite amount of fossil resources available. This results in increased fuel prices while the ability to supply fossil fuels decreases. It is anticipated by the year 2030, the world will require 50% more energy (Shahid & Jamal, 2011). Fossil fuels are used in pivotal roles such as running power plants, vehicles, and motor engines in the industrial, agricultural, and transport sectors, respectively.

Currently, the most pressing environmental impacts from burning fossil fuels include global warming (enhancing the greenhouse effect), acid rain, and smog. Fossil fuels are the main contributors to carbon dioxide (CO_2) and other greenhouse gases (GHG). It is predicted that carbon dioxide will boost up to forty thousand billion kilograms by 2030. Thus, it is extremely important to conduct research on potential renewable sources that minimize the effects of global warming, which will also simultaneously reduce the strain on non-renewable fossil fuels and ensure energy security for the future. However, one of the main challenges in large-scale production of biodiesel is its high cost (Arumugam & Ponnusami, 2014). Therefore, to reduce high expenses it is vital to optimize biodiesel process conditions in order to achieve maximized yields. Competition for land for feedstocks that are utilized in biodiesel production is problematic thus, the need to maximize biodiesel yields from a given feedstock is extremely necessary (Diamantopoulos, et al., 2015).

The most commonly used catalysts in biodiesel production are homogeneous base catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). However, heterogeneous catalysts are promising candidates for biodiesel production as they provide high reaction rates, high biodiesel yields, makes separation easy thus promoting recycling and reusability of the catalyst, they are also inexpensive, non-corrosive, and environmentally friendly (Endalew, et al., 2011).

1.3 The main aim and objectives of this study

The main aim of this study is to determine the optimum process conditions for the synthesis of biodiesel from canola oil by using two different heterogeneous catalysts respectively in order to obtain a maximized biodiesel yield to serve as an appropriate petro-diesel alternative, and therefore the biodiesel produced will be blended with kerosene to produce bio-jet fuel.

The aim will be achieved through the following objectives:

- Collection of necessary information through a comprehensive literature review to propose an efficient experimental method for biodiesel production.
- Feedstock property testing to assess its quality.
- Conducting experiments to determine optimum conditions for producing high quality and maximized biodiesel yields.
- Physical property tests to be done on the optimized biodiesel yields produced in accordance with American Society for Testing and Materials (ASTM) standards to assess its quality
- Blending biodiesel with kerosene to produce bio-jet fuel.
- Physical property testing on bio-jet fuel according to ASTM standards.

1.4 Dissertation outline

Chapter 1 is the introduction of the topic. It entails the background of the study, current issues faced, and the significance as to why such a study is required. The main research aim and objectives on how the aim will be achieved are explained and the dissertation outline is presented.

Chapter 2 provides a comprehensive literature review that presents various biodiesel production methods, the process variables that affect the yield of biodiesel, biodiesel properties as well as typical feedstocks and common catalysts utilized in biodiesel production.

Chapter 3 shows a detailed outline of all the experimental equipment and materials utilized in this study. The raw materials are presented with their purity and supplier and a detailed description of the experimental apparatus is given. Chapter 3 also focuses on the research methodology, the experimental procedure, and the design of experiment used to optimize the biodiesel yield.

Chapter 4 presents the results and discussion of canola oil transesterification in the presence of calcium oxide heterogeneous catalyst. The effects of the process variables on the yield of biodiesel are analyzed and the optimized process conditions to attain a maximized yield of biodiesel within the range of this study are proposed.

Chapter 5 presents the results and discussion of canola oil transesterification in the presence of magnesium oxide heterogeneous catalyst. This chapter entails comprehensive details of the findings and results obtained. The effects of the process variables on the yield of biodiesel are analyzed and the optimized process conditions to attain a maximized yield of biodiesel within the range of this study are proposed.

Chapter 6 focuses on biodiesel and bio-jet fuel property testing in accordance with ASTM fuel standards. The properties measured included acid value, kinematic viscosity, and density. GC-MS analysis of the biodiesel produced is also presented.

Chapter 7 is the final chapter in this dissertation which provides the conclusions drawn from this study and suggests recommendations for future studies.

Chapter 2 Theoretical Background

Due to the rapid development of the ever-growing number of vehicles and the global economy, fossil resources are being widely exploited. Since the industrial revolution in the 1800s, there has been an increasing demand for energy with an increase in awareness of hazardous environmental pollution. Thus, it is extremely necessary to find alternative resources of renewable energy (Noshadi, et al., 2012). The synthesis of biodiesel is aimed at the urgent need to drastically slow down the use of finite fossil resources, and reduce greenhouse gas emissions into the atmosphere. Biodiesel is considered a technologically feasible alternative to conventional petro-diesel due to its beneficial characteristics. Biodiesel has unique advantages, it reduces the strain on fossil fuels, it is biodegradable, eco-friendly, non-toxic to nature, and in comparison to petroleum diesel, it has a low emissions profile (Srilantha, et al., 2012). The quantity of carbon dioxide released by burning biodiesel is equivalent to the quantity absorbed during the formation of the raw material. Biodiesel is produced from renewable resources such as vegetable oils and animal fats, it is defined as a mono-alkyl ester of long-chain fatty acids (Schonborn, et al., 2009). Biodiesel is commonly produced via a simple, low-cost transesterification process, whereby vegetable oil reacts with alcohol, usually methanol or ethanol, in the presence of a catalyst. The properties of biodiesel are very similar to petro-diesel, therefore, it is possible to use biodiesel in a diesel engine without further modifications.

The history of biodiesel began in 1900 when Rudolph Diesel used peanut oil as a fuel to run a diesel engine (Sharma & Singh, 2009). The conclusion drawn by Dr. Diesel was that vegetable oils could be used to run diesel engines, however, there are numerous issues that are associated with the direct use of neat vegetable oils as fuel in diesel engines. The use of neat vegetable oils directly in diesel engines is not entirely practical due to their high viscosity, low oxidation stability, and low volatility which results in huge amounts of ash formation due to incomplete combustion. The high viscosities of vegetable oils ranging between 28 to 40 mm^2/s result in operational issues in diesel engines, these issues include injector coking due to poor atomization upon injection into the combustion chamber and formation of deposits (Demirbas, 2003). Therefore, the viscosity of vegetable oil needs to be reduced to eliminate the aforementioned issues and to attain fuel properties inline with petroleum-derived diesel.

2.1 Biodiesel production methods

There are namely four methods used for producing biodiesel. These methods can be divided into the "chemical" and "physical" methods in accordance with their biodiesel production characteristics. The chemical methods include transesterification and pyrolysis, while the physical methods include microemulsion and blending. The physical methods involve the mixing of biodiesel with petro-diesel, or other admixtures, in specified amounts to achieve high volatility and low viscosity biodiesel fuel. Biodiesel chemical properties are not altered by these methods (Ge & Choi, 2017).

2.1.1 Direct use and blending

Vegetative oils and animal fats can be utilized in direct injection engines (Rajalingam, et al., 2016). It has a good heating value and may provide sufficient power, however, studies have shown that many problems are experienced with the direct use of vegetable oil, such as carbon deposition on the injector, poor atomization of fuel, a build-up of fuel in lubricant oils, and incomplete combustion due to unsatisfactory properties such as high viscosity (Demirbas, 2008). Even though animal fats and vegetable oils have recognized biodiesel fuel properties, it requires chemical modification before implementing the use of it in engines; as the use of 100% pure vegetable oil in diesel engines is considered impractical (Balat & Balat , 2008; Singh & Singh, 2010). Vegetable oils are blended with conventional petro-diesel to combat the aforementioned issues with direct use. Vegetable oil has been blended successfully with petro-diesel in an oil to petro-diesel ratio of 20% to 80% (Mujeeb, et al., 2016). However, blending with oil percentage higher than 20% may lead to gelling of engine lubricant, fuel injector blockages, and increased carbon deposition on pistons due to increased reactivity of unsaturated bonds and higher viscosity presented by vegetable oil (Demirbas, 2008).

Table 2-1: Issues, possible causes, and possible solutions associated with the direct use of neat vegetable oil in diesel engines (Harwood, 1984)

Issue	**Possible cause**	**Possible solution**
Short term		
i. Engine knocking.	• Extremely low cetane number. • Inopportune injection timing.	• Injection time to be adjusted. • Chemically alter fuel to an ester.
ii. Cold weather starting.	• Vegetable oils with a low flash point, low cetane, and high viscosity.	• Chemically alter fuel to an ester. • Prior to injection the fuel should be preheated.
iii. Plugging and gumming of injectors, filters, and lines.	• Natural gums (phosphatides). • Other ash.	• Refine oil partially for the removal of gums. • Filter to four microns.
Long term		
iv. Excessive engine wear.	• Combustion of fuel is incomplete. • High viscosity of vegetable oil. • Possibly free fatty acid present in vegetable oil. • Dilution of engine lubricating oil due to blow-by of vegetable oil.	• Motor oil additives for the inhibition of oxidation. • Motor oil changes are to be done frequently.
v. Coking of injectors on piston and head of engine.	• High viscosity of vegetable oil. • Combustion of fuel incomplete. • Poor combustion at part load with vegetable oils.	• Prior to injection the fuel is required to be heated. • When operated at part load, switch to diesel fuel in the engine.
vi. Failure of engine lubricating oil due to polymerization.	• Collection of polyunsaturated vegetable oil blow-by the crankcase to the point where polymerization starts.	• Motor oil additives for the inhibition of oxidation. • Motor oil changes are to be done frequently.
vii. Carbon deposits on piston and head of the engine.	• High viscosity of vegetable oil. • Combustion of fuel incomplete. • Poor combustion at part load with vegetable oils.	• Chemically alter fuel to an ester.

2.1.2 Microemulsion

According to Ma & Hanna (1999), the microemulsion process is defined as “a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles”. The microemulsion process solves the issue with high viscosity by lowering it and it also helps with some other atomization oil properties. This method comprises of blending vegetable oils or animal fats with solvents or surfactants to create micro-emulsified biodiesel fuel (Ge & Choi, 2017). According to Ma & Hanna (1999), solvents such as methanol, ethanol, and 1-butanol have been previously studied. Typically, the alcohol utilized in this process is meant to reduce smoke and increase the volatile property of oil. Generally, the cetane number improver is the alkyl nitrate. The microemulsion method is characterized by reducing the biodiesel fuel viscosity, the process is also used to achieve excellent spry property when it is injected by a nozzle into an engine by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984). However, when engines utilize fuel produced from this method for a long period, many issues may arise; such as incomplete combustion, large amounts of carbon deposition, increased viscosity of lubricating oils, and nozzle failure (Kurnia, et al., 2016).

2.1.3 Pyrolysis (Thermal cracking)

Pyrolysis, also known as thermal cracking, is defined as the conversion of pyrolyzed materials into alkanes, dienes, aromatics, olefins, and carboxylic acids (Ge & Choi, 2017). Pyrolyzed materials include natural fatty acids, animal fats, vegetable oils, and methyl esters of fatty acids. This process is conducted by using heat, with or without the aid of a catalyst in the absence of oxygen or air (Ge & Choi, 2017; Ma & Hanna, 1999). It is conducted in the absence of oxygen in order to prevent the oxidization of oil at high temperatures. Pyrolysis is known for reducing the viscosity and density of oil, these two properties impact the atomization of an engine (Rajalingam, et al., 2016). The reaction conditions include rapid heating and short reaction time at atmospheric pressure, these conditions are harsh and rapidly breaks down the organic polymers in biomass into short-chain molecules. For the separation of the different fractions, the process requires separate distillation columns which adds to the process high cost, also the equipment for heating is expensive (Ge & Choi, 2017). The removal of oxygen in the process reduces the ecological advantage of using an oxygenated fuel. Also, the fuel produced contains sulfur, making it less eco-friendly for utilization (Jaiswali, 2018). Thus, the pyrolysis process has not been valued by researchers due to its high energy consumption and low conversion rate (Ito, et al., 2012; Santos, et al., 2010).

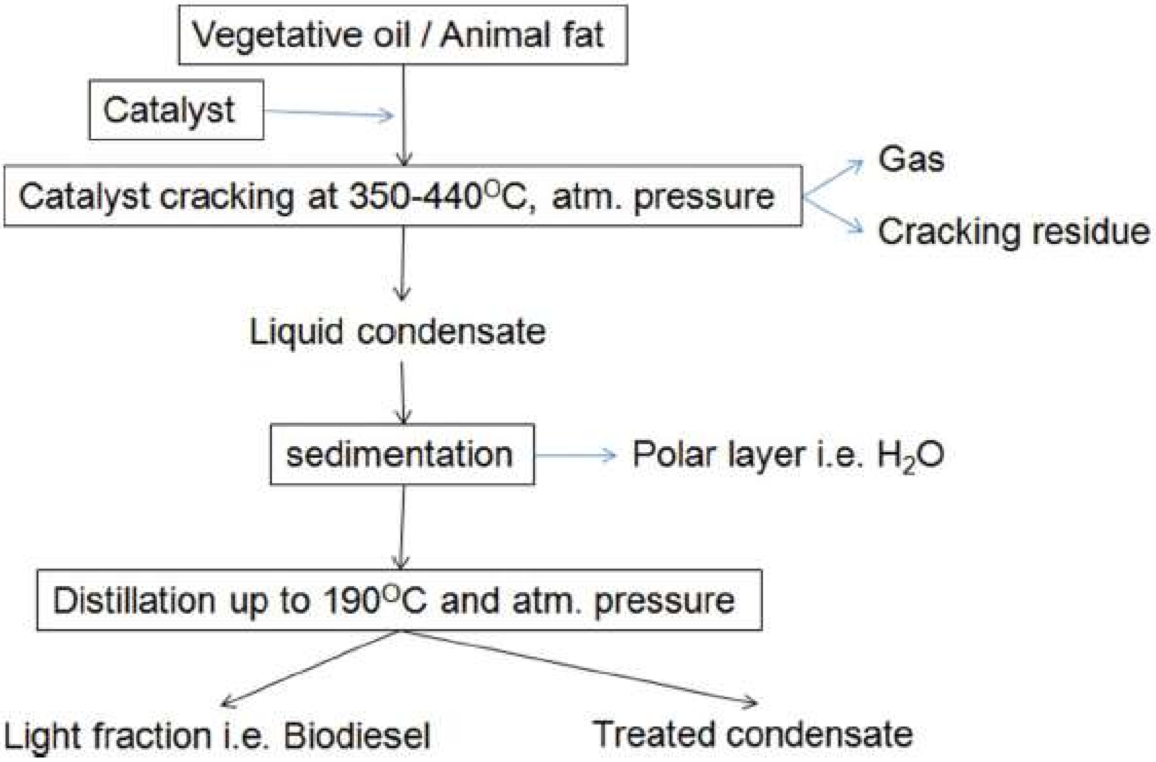


Figure 2-1: Pyrolysis process for the production of biodiesel (Mishra & Goswami, 2017)

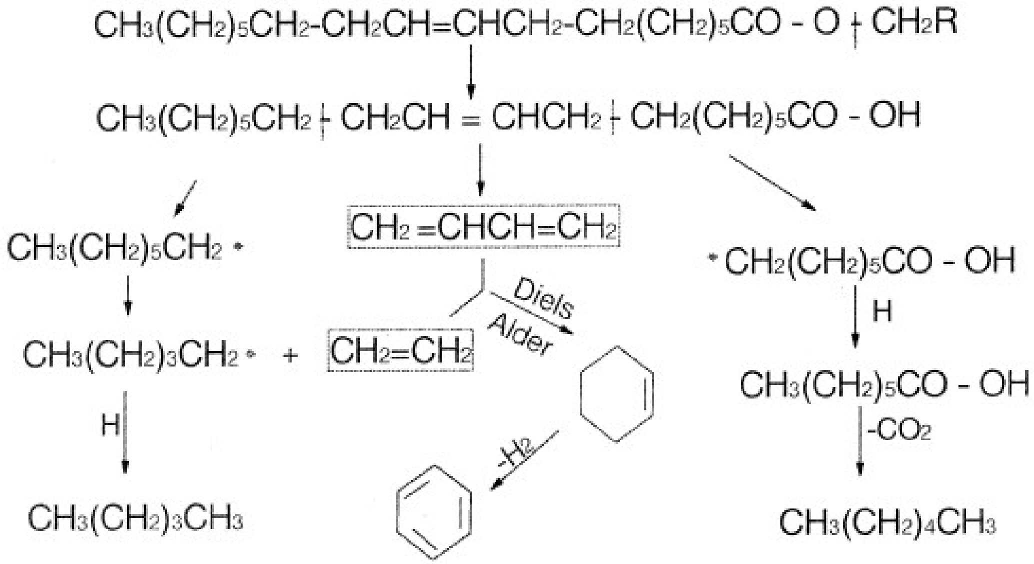


Figure 2-2: Mechanism for pyrolysis of triglycerides (Schwab, et al., 1988)

2.1.4 Transesterification (Alcoholysis)

The transesterification process (also known as alcoholysis), is a process which produces esters (biodiesel) and glycerol (by-product) from vegetable oils or animal fats (triglycerides) when reacted with alcohol at specified reaction conditions (Friedrich , 2003; Raghuvanshi & Singh, 2014). Transesterification reduces the viscosity of the feedstock by removing glycerol; the high viscosity component of the feedstock (Gashaw & Teshita, 2014). There are three steps in the transesterification reaction. The first step converts triglycerides to diglycerides, the second step converts diglycerides to monoglycerides, and the last step converts monoglycerides to glycerol (Soltani, et al., 2015). Stoichiometrically, a molar ratio of 3 moles of alcohol to 1 mole of triglyceride is required to produce 3 moles of biodiesel and 1 mole of glycerol, however, the reaction is reversible, thus a higher alcohol ratio is required to drive the reaction forward and produce a maximum ester yield (Mishra & Goswami, 2017; Ma & Hanna, 1999). A catalyst may also be employed in this reaction to improve the quality of the product as well as increase the reaction's speed. The type and quantity of catalyst used will depend on the free fatty acid (FFA) content present in the feedstock. Feedstocks with high FFA content are considered unfavorable for the production of biodiesel as saponification occurs and produces soap, thus, reducing the yield efficiency of biodiesel (Ramaraju & Ashok Kumar, 2011). The transesterification reaction occurs at a lower pressure and temperature, thus, it has lower operating costs (Nas & Berktay, 2007).

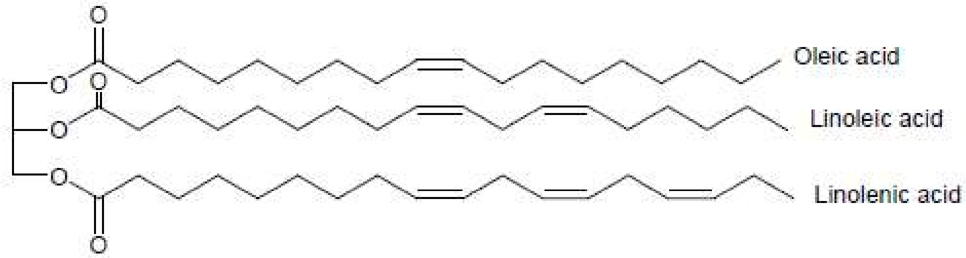


Figure 2-3: Edible vegetable oil triglyceride general structure (Karmakar, et al., 2017)

Table 2-2: Summary of the different biodiesel production methods (Zahan & Kano, 2018)

Process	Description	Advantages	Drawbacks
Blending (dilution)	Animal fats/vegetable oils were preheated and blended with petroleum diesel within 10-40% (w/w) ratio. The resulting mixture of oil-diesel was utilized in a diesel engine.	No technical modifications present and easy to implement.	Low volatility, high viscosity, unstable, incomplete fuel combustion, difficulty in handling by conventional engines.
Microemulsion	Animal fats/vegetable oils were solubilized in surfactant and alcohol until the desired viscosity was achieved.	Free of pollution. Simple process.	Low stability, high viscosity, incomplete combustion.
Pyrolysis (thermal cracking)	Preheated animal fats and vegetable oils are decomposed at a temperature greater than 350°C with or without the presence of a catalyst. Different products (liquid and gas) were analyzed based on their boiling temperature range to determine the exact product.	The process is simple, effective (filtering, drying. or washing is not needed), pollution-free, and reduces waste.	Requires expensive equipment and high temperatures to produce biodiesel of low purity (contain heterogeneous molecules including carbon residues and ash).
Transesterification (alcoholysis)	Animal fat or vegetable oil was reacted with an alcohol in the presence of a catalyst (basic or acid) to produce a biodiesel and glycerol (by-product) mixture which will therefore require separation and purification before utilization.	Relatively high conversions achieved with low cost, product properties close to petroleum diesel, mild reaction conditions, and is applicable for industrial-scale production.	The raw material must have a low water content as well as low FFA content. There are extensive purification steps, generation of large quantities of wastewater, and possibilities of side reactions may occur.

2.2 Transesterification

Transesterification is the most common method utilized for reducing vegetable oil viscosity. Due to its simplicity, low cost, and relatively high conversions. Transesterification has been regarded worldwide to be the best process among the other approaches. Common animal fats and vegetable oils are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters also known as triglycerides, reacts with alcohol in the presence of a catalyst.

$$1.\ \text{Triglyceride (TG)} + \text{R'OH} \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride (DG)} + \text{R'COOR}_1$$

$$2.\ \text{Diglyceride (DG)} + \text{R'OH} \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{Monoglyceride (MG)} + \text{R'COOR}_2$$

$$3.\ \text{Monoglyceride (MG)} + \text{R'OH} \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{Glycerol (GL)} + \text{R'COOR}_3$$

Figure 2-4: The three steps in the transesterification of vegetable oil with an alcohol to esters and glycerol (Freedman, et al., 1986)

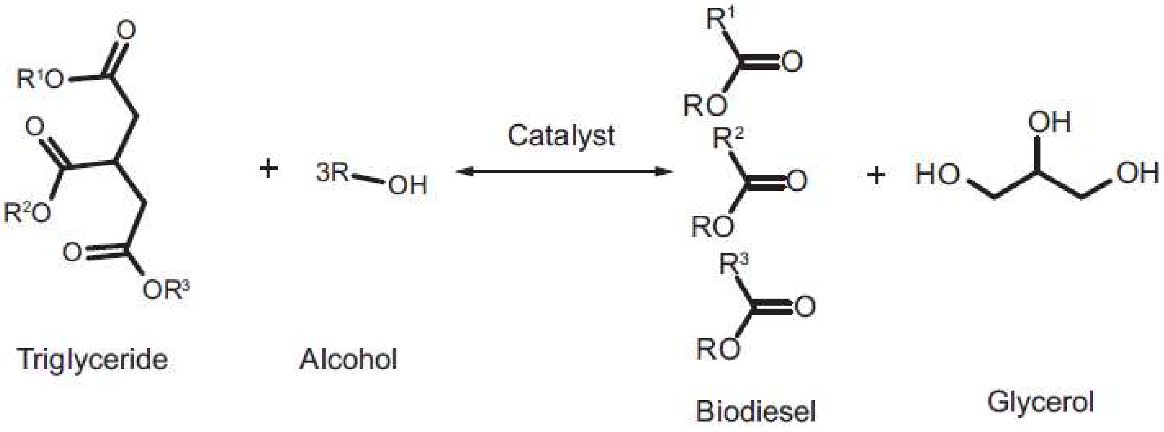


Figure 2-5: Overall transesterification reaction (Gaurav, et al., 2019)

In figures 2-4 and 2-5; R1, R2, R3 represent long-chain hydrocarbons also known as fatty acid chains.

2.3 Factors that affect the transesterification reaction for biodiesel production

Transesterification of vegetable oil/ animal fats undergoes intense chemical modification, whereby the more viscous component (glycerol) is removed, thus, producing biodiesel with a consistency similar to petroleum derivatives. The biodiesel produced is miscible in mineral diesel to a certain extent (Jaiswali, 2018). The quality and yield of biodiesel produced from the process are affected by some parameters which include feedstock, reaction temperature, alcohol to oil molar ratio, reaction time, and catalyst loading.

2.3.1 Feedstock

Biodiesel can be synthesized from animal fats, vegetable oils, waste cooking oil (WCO), microalgae, algae, and fungi. However, biodiesel is generally produced from oil-bearing plants. Globally, potential sources for biodiesel production include more than 350 recognized oil-bearing crops (Atabani, et al., 2012). Biodiesel feedstocks are categorized into four groups; edible vegetable oils, non-edible vegetable oils, animal fats, and waste recycled oil. Edible oils are classified as a first-generation biodiesel feedstock as it were the initial feedstocks used for biodiesel production. Oils considered to be first-generation include palm, soybean, safflower, sunflower, coconut, rapeseed, peanut, etc. (Mishra & Goswami, 2017). Globally, greater than 95% of biodiesel is synthesized from first-generation feedstocks. Non-edible oils are classified as second-generation biodiesel feedstock. Commonly used second-generation oil feedstocks include jatropha, karanja, castor, neem, etc. (Singh & Singh, 2010). Since the consumption of edible feedstocks has increased drastically, the price of these oils has also dramatically increased over the past 15 years.

Biodiesel feedstocks should fulfill the requirements of low production cost and large-scale production. If edible feedstocks keep being used for biodiesel production; Antabani, et al. (2012) predicts environmental issues such as deforestation, vital soil destruction, and usage of the available arable land. The utilization of non-edible feedstocks or waste cooking oils serves as a solution for the food vs. fuel crisis; as it eliminates competition for food, it is more environmentally friendly, reduces deforestation, produces useful by-products, and are more economical in comparison to edible feedstocks (Sarin, et al., 2009). The production and availability of biodiesel feedstocks depend on climatic conditions, geographical locations, local soil conditions, and agricultural practices.

Third generation biodiesel feedstock includes microalgae. These are photosynthetic microbes capable to convert sunlight, carbon dioxide, and water to algal biomass more efficiently as compared to conventional crops. Compared to edible and non-edible feedstocks, microalgae have better growth rates, high oil content, and better productivity which makes it a promising feedstock (Arshad, et al., 2018).

However, first, second, and third-generation has been reported to sometimes be misleading and should not be used to imply that biodiesel produced from feedstocks from the second and third generations to have superior fuel properties in comparison to first-generation feedstocks. For instance, second-generation jatropha oil has poorer cold flow properties in comparison to biodiesel synthesized from first-generation palm, soybean, and rapeseed oils (Konthe, et al., 2010).

Looking at figure 2-5, it can be seen that the two main requirements for biodiesel production are oil and alcohol. The most frequently used alcohols are methanol and ethanol. However, methanol is preferred over ethanol due to methanol being more reactive (Ilgen, et al., 2009), low in cost, as well as it has better physical and chemical advantages such as it being polar and the shortest chain alcohol (Musa, 2015).

The type of oil selected for the transesterification reaction greatly influences the quality and properties of the biodiesel produced. The greater the straight-chain length of fatty acid, the higher some property values will be; such as its cetane number (Dunn, 2009) and heat capacity (Konthe, et al., 2010). Pinto, et al. (2005) stated that esters produced from a saturated or long-chain fatty acid results in higher cloud point and cetane number which causes nozzle clogging. Biodiesel prepared from unsaturated fatty acid displays a low cetane value and it suffers oxidation easily. Typically, the heat of combustion, cetane number, viscosity, and the melting point of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation (Pinto, et al., 2005). The free fatty acid (FFA) and water content in the oil should be very low because these are unfavorable and can lead to saponification which is the formation of soap; along with unwanted side reactions (Ma & Hanna, 1999) which reduces the biodiesel yield. Cheaper feedstocks are of lower quality as they have higher FFA content. In order to prevent soap formation and biodiesel yield loss, the oil and alcohol should not contain moisture and there should be a low amount of FFAs in the oil. The repeated washing of biodiesel removes any glycerol or alcohol present and improves the quality of the fuel (Mishra & Goswami, 2017). Oils comprising of high quantities of saturated fatty acids can block fuel lines during the winter season due to solidification (Demirbas, 2008; Pinto, et al., 2005). Knothe (2005) reported; oils with higher amounts of oleic acid have characteristics that are most similar to conventional biodiesel.

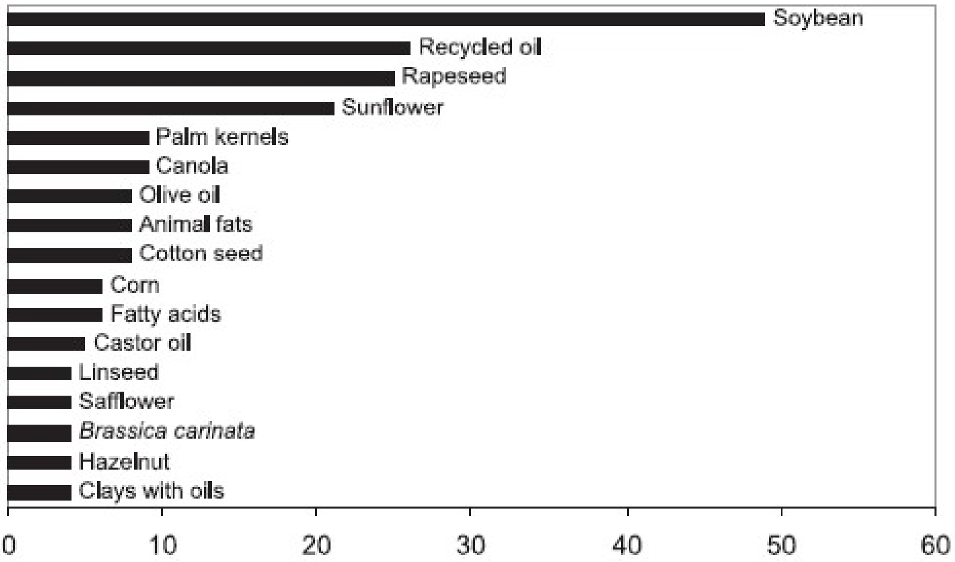


Figure 2-6: Leading feedstocks for biodiesel production cited in scientific articles (Pinto, et al., 2005)

The fuel properties of vegetable oils as listed in table 2-3 on page 16, indicate that the cetane number (CN) of vegetable oils vary in the range of 34.6 – 44.6 which indicates that the cetane number of the vegetable oils presented here don't vary much. The kinematic viscosities vary between 27.2 – 53.6 mm^2/s. The high viscosities of these oils are due to their large molecular masses ranging between 600 – 900 g/mol, which is approximately 20 times higher than that of diesel fuel. The flash point values are very high, ranging between 150-277 °C. The volumetric heating values range from 39.5 to 40.5 MJ/kg which is close to the heating value of diesel at 43 MJ/kg. The presence of chemically bound oxygen in vegetable oils lowers their heating values by 10%, however, the presence of oxygen also aids the combustion process (Misra & Murthy, 2010). It can be seen from table 2-3, Crambe oil has the highest heating value of 53.6 MJ/kg amongst all the vegetable oils mentioned. This is influenced by the long-chain ester C22:0 which is behenic fatty acid (chemical name docosanoic fatty acid and chemical formula $C_{22}H_{44}O_2$) that composes 57.2% Crambe oil (Oliveira & Da Silva, 2011). According to Singh & Singh, (2010), since Crambe oil is generally synthesized from older varieties of Rapeseed, it can be utilized as a possible replacement for Rapeseed oil.

Table 2-3: Physical properties of different vegetable oils (Misra & Murthy, 2010)

Vegetable oil	**Cetane no.**	**Kinematic viscosity at 38°C (mm^2/s)**	**Heating value (MJ/kg)**	**Flash point (°C)**	**Pour point (°C)**	**Cloud point (°C)**	**Density (kg/m^3)**	**Reference**
Babassu	38	30.3	-	150	-	20	946	(Misra & Murthy, 2010)
Canola	-	31.388 (40°C)	-	150	-13.6	-9.8	915	(Sahin & Aydin, 2018)
Corn	37.6	34.9	39.5	277	-40	-1.1	909.5	(Misra & Murthy, 2010)
Cottonseed	41.8	33.5	39.5	234	-15	1.7	914.8	(Misra & Murthy, 2010)
Crambe	44.6	53.6	40.5	274	-12.2	10	904.8	(Misra & Murthy, 2010)
Linseed	34.6	27.2	39.3	241	-15	1.7	923.6	(Misra & Murthy, 2010)
Olive	-	39	-	177	-14	-11	918	(Akhtar, et al., 2009)
Palm	42	39.6	-	267	-	31	918	(Misra & Murthy, 2010)
Peanut	41.8	39.6	39.8	271	-6.7	12.8	902.6	(Misra & Murthy, 2010)
Rapeseed	37.6	37	39.7	246	-31.7	-3.9	911.5	(Misra & Murthy, 2010)
Safflower	41.3	31.3	39.5	260	-6.7	18.3	914.4	(Misra & Murthy, 2010)
Sesame	40.2	35.5	39.3	260	-9.4	-3.9	913.3	(Misra & Murthy, 2010)
Soya bean	37.9	32.6	39.6	254	-12.2	-3.9	913.8	(Misra & Murthy, 2010)
Sunflower	37.1	33.9	39.6	274	-15	7.2	916.1	(Misra & Murthy, 2010)
Diesel	50	3.06	43.8	76	-16	-	855	(Misra & Murthy, 2010)

Table 2-4: Common feedstocks for biodiesel production (Mishra & Goswami, 2017; Singh & Singh, 2010)

Edible	Non-edible	Animal fats	Other
Soybeans (*Glycine max*)	Jatropha curcas	Pork lard	Bacteria
Rapeseed (*Brassica napus L.*)	Mahua (*Madhuca indica*)	Beef tallow	Algae (*Cyanobacteria*)
Safflower`	Pongamia (*Pongamia pinnata*)	Poultry	Microalgae (*Chlorellavulgaris*)
Rice bran oil (*Oryza sativum*)	Camelina (*Camelina sativa*)	Fish oil	Tarpenes
Barley	Cotton seed (*Gossypium hirsutum*)	Chicken fat	Poplar
Sesame (*Sesamum indicum L.*) Groundnut	Karanja or honge (*Pongamia pinnata*)		Switchgrass
Sorgum	Cumaru		Miscanthus
Wheat	*Abutilon muticum*		Fungi
Corn	*Cynara carduriculus*		Latexes
Coconut	Neem (*Azadirachta indica*)		Cooking oil (Yellow grease)
Canola	Jojoba (*Simmondsia chinensis*)		
Peanut	Passion seed (*Passiflora edulis*)		
Palm and palm kernel (*Elaeis guineesis*)	Moringa (*Moringa oleifera*)		
Sunflower (*Helianthus annuus*)	Tobacco seed		
Copra	Rubber seed tree (*Hevca brasiliensis*)		
Cotton seed	Salmon oil		
Oat	Tall (*Carnegiea gigantea*)		
Rice	Coffee ground (*Coffea arabica*)		
Winter rapeseed oil	Nagchampa (*Calophyllum inophyllum*)		
	Croton megalocarpus		
	Pachira glabra		
	Aleurites moluccana		
	Terminalia belerica		

Vegetable oils contain 98% triglycerides (also known as triacylglycerols) and a small amount of diglycerides, and monoglycerides. Triglycerides consist of a three-carbon backbone with a long hydrocarbon chain attached to each of the carbons. These chains are attached through an oxygen atom and a carbonyl carbon, which is a carbon atom that is double-bonded to a second oxygen. Along the length of the carbon chain, the fatty acids vary in the number of double bonds. Different kinds of vegetable oils have different types of fatty acids. The various vegetable oil fatty acids structures and empirical formulae can be seen in table 2-5.

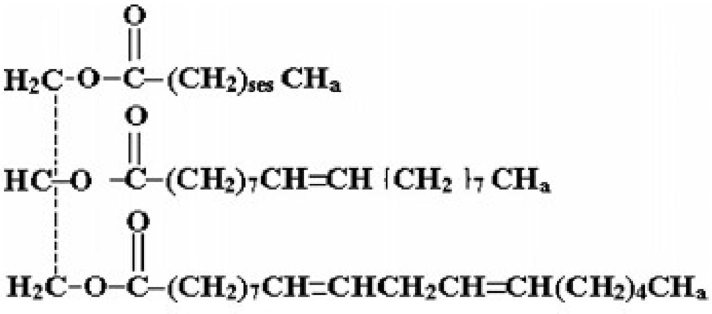


Figure 2-7: Triglyceride structure (Musa, 2015)

Table 2-5: Common fatty acids (Barnwal & Sharma, 2005)

Fatty acid name	**Fatty acid chemical name**	**Structure (xx:y)**	**Formula**
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9,cis-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucle	*cis*-13-Docosenoic	22:1	$C_{32}H_{42}O_2$

xx indicates the number of carbons and y indicates the number of double bonds in the fatty acid chain.

The majority of fatty acid chains from animal and plant-based oils are 18 carbons long, with between zero and three double bonds. If double bonds are not present in fatty acid chains, it is considered to be saturated, vice versa. Esters produced from fatty acid chains with double bonds has a dramatic effect on its properties (Misra & Murthy, 2010). The deformation of the molecule caused by the double bonds inhibits the growth of the crystals and this lowers the biodiesel's gel temperature. At higher temperatures, saturated fats tend to gel. Hydrogenated vegetable oils, animal fats, and some tropical oils such as coconut and palm oil consist of between 35-45% saturated fatty acids and may be solid at room temperature (Misra & Murthy, 2010).

At extremely high temperatures, biodiesel synthesized from these oils may gel. The carbon-carbon double bonds in unsaturated fats and oils are prone to oxidation by oxygen in the air. Bonds that are conjugated (two double bonds separated by two single bonds) magnifies this effect, as is the case for linoleic and linolenic acids. In comparison to oleic acid with an unconjugated double bond, linoleic and linolenic acids will oxidize 50 to 100 times quicker (Knothe, et al., 2005). Saturated acids are not subjected to this type of oxidative attack. Biodiesel produced from an extremely saturated feedstock will have better oxidative stability and higher cetane number, however, it will experience poor cold flow properties. Biodiesel produced from feedstocks with low saturated fat levels will have lower oxidative stability and lower cetane number, but it will have better cold flow properties (Knothe , et al., 2005).

Table 2-6: Different oils and their fatty acid composition ratios (Singh & Singh, 2010)

Oil	**Fatty acid composition (wt%)**															
	12:0	**14:0**	**14:1**	**16:0**	**16:1**	**18:0**	**20:0**	**20:1**	**22:0**	**24:0**	**18:1**	**22:1**	**18:2**	**18:3**	**18:4**	**Other**
Cotton seed	-	-	-	28.7	-	0.9	-	-	-	-	13	-	57.4	-	-	-
Tobacco	-	0.09	-	10.96	0.2	3.34	-	-	-	-	14.54	-	69.49	0.69	-	0.69
Rapeseed	-	-	-	3.5	-	0.9	-	-	-	-	64.1	-	22.3	8.2	-	-
Safflower	-	0	-	9	-	2	0	-	0	0	12	0	78	0	-	-
Sunflower	-	-	-	6.4	0.1	2.9	-	-	-	-	17.7	-	72.9	-	-	-
Sesame	-	-	-	13.1	-	3.9	-	-	-	-	52.8	-	30.2	-	-	-
Linseed	-	-	-	5.1	0.3	2.5	-	-	-	-	18.9	-	18.1	55.1	-	-
Palm	-	-	-	42.6	0.3	4.4	-	-	-	-	40.5	-	10.1	0.2	1.1	-
Corn	-	0	-	12	-	2	-	-	-	-	25	0	6	-	-	-
Tallow	-	-	-	23.3	0.1	19.3	-	-	-	-	42.4	-	2.9	0.9	2.9	-
Soybean	-	-	-	13.9	0.3	2.1	-	-	-	-	23.2	-	56.2	4.3	0	-
Peanut	-	0	-	11	-	2	1	-	2	1	48	0	32	1	-	-
Hazelnut kernel	-	-	-	4.9	0.2	2.6	-	-	-	-	83.6	-	8.5	0.2	0	-
Walnut kernel	-	-	-	7.2	0.2	1.9	-	-	-	-	18.5	-	56	16.2	0	-
Almond kernel	-	-	-	6.5	0.5	1.4	-	-	-	-	70.7	-	20	0	0.9	-
Olive kernel	-	-	-	5	0.3	1.6	-	-	-	-	74.7	-	17.6	0	0.8	-
Coconut	48.8	19.9	-	7.8	0.1	3	-	-	-	-	4.4	-	0.8	0	65.7	8.9
Poultry fat	-	0.57	0.26	22.76	8.37	5.36	0	0.45	-	-	42.07	-	17.14	1.07	0.22	-
Yellow grease	-	0.7	0	14.26	1.43	8.23	0.33	0.48	-	-	43.34	-	26.25	2.51	0.47	-
Castor	-	-	-	1.1	0	3.1	-	-	-	-	4.9	-	1.3	0	-	89.6
Poppy seed	-	-	-	12.6	0.1	4	-	-	-	-	22.3	-	60.2	0.5	-	-
Wheat grain	-	0.4	-	20.6	1	1.1	-	-	-	-	16.6	-	56	2.9	1.8	11.4
Crambe	-	0	-	2	-	1	2	-	1	1	19	59	9	7	-	-

(i) Canola oil

Canola oil is an edible first-generation feedstock oil that can be used for biodiesel production (Moser , 2009; Knothe, 2005). It is the third major vegetable oil produced worldwide after palm oil and soybean oil. Canola oil is extracted mainly from the seeds of genetically modified *Brassic napus L*., however, a small quantity of extracted canola oil is from *Brassica rapa L*. (Ghazani & Marangoni, 2016). Canola seed contains approximately more than 43% oil content, which is considered high in comparison to other oilseeds; including soybeans, which produce only 18% of oil (Anderson, 2008). Canola oil is more viscous than the regularly tested vegetable oils (Ma & Hanna, 1999), thus, esters synthesized from the transesterification reaction of canola oil increases the lubricity of the biodiesel produced (Lang, et al., 2001). According to Zakaria & Somchit (2004), canola oil is non-polar, therefore, it is less soluble in methanol than in ethanol due to the low polarity of ethanol. It has a sulfur atom in certain fatty acid structures which in turn are responsible for the oils sulfur flavor. The dominant fatty acid present in the oil is oleic acid which makes up approximately 61.4% of the oil and linolenic acid makes up 9.9 %. Makoure, et al. (2019) stated that standard oxidation shows that oils with high oleic acid content are much more stable to oxidation in comparison to oils with low oleic acid content. It was also found that during engine emission tests, this high stability of oils with high oleic acid content makes it possible to obtain a significant reduction in NOx emissions during combustion (Makoure, et al., 2019). Canola oil has a low saturated fatty acid content of less than 7.1% in comparison to all other major vegetable oils (Ghazani & Marangoni, 2016). Having low saturated fatty acid content benefits the performance of the biodiesel in cold weather. Anderson (2008) reported that in extremely cold weather conditions even petro-diesel will gel or crystallize. Biodiesel synthesized from pure canola oil has 10% oxygen by weight, thus, this oxygen contributes to the reduction of emissions like hydrocarbons, carbon monoxide, toxic compounds, and particular matter (Anderson, 2008).

Table 2-7: Canola seed analysis (Unger , 2011)

Component	**Analysis Result**
Oil, % at 8.5% moisture basis	43.4
Protein, % at 11% moisture and 2% oil	39.0
Chlorophyll, ppm	14.4
Total glucosinolates, µmol/g at 8.5% moisture basis	13.2
Erucic acid, % in oil	0.1
Linolenic acid, % in oil	9.9
Oleic acid, % in oil	61.4
Total saturated fatty acids, % in oil (C16:0, C18:0, C20:0, C22:0, C24:0)	7.1

Table 2-8: Fatty acid composition of main vegetable oils (Ghazani & Marangoni, 2016)

Fatty acids %	Soybean	Canola	Sunflower	Cottonseed	Corn	Peanut	Olive
12:0	-	-	-	-	-	-	-
14:0	0.1	-	-	0.5-1.3	<0.1	-	<0.1
16:0	11.0	4.3	5-7	17-31	8-13	8-13	7.5-20
16:1	0.1	0.2	<0.4	<1	<1	<0.3	0.3-3.5
18:0	4.0	1.8	4-6	1-3	1-4	3-4	0.5-5
18:1	23.4	62.3	15-25	13-21	24-32	48-66	55-83
18:2	53.2	19.4	62-70	34-60	55-62	14-28	3.5-21
18:3	7.8	9.2	<0.2	<1	<2	<0.3	<1
20:0	0.3	0.6	<1	0.2-0.5	<1	1-2	<0.8
20:1	-	1.2	<0.5	-	<0.5	1-2	-
20:2	-	0.1	-	-	-	-	-
22:0	0.1	-	<1	-	<0.5	2-4	<0.3
24:0	-	-	-	-	-	1-2	<1

2.3.2 Temperature

Temperature is one of the main factors that influences the yield of biodiesel produced via the transesterification reaction. Temperature affects the reaction rate and the percentage conversion (Ma & Hanna, 1999). Bouaid, et al. (2009) studied the effect of temperature in the production of biodiesel from *Brassica carinata*, he reported that the temperature presented a positive effect indicating that heating is required in order to enhance the alcohol solubility in the reacting mixture and increase the rate of the reaction. Noureddini and Zhu (1997) noted when a higher reaction temperature was utilized, the transesterification reaction sped up and the reaction time resulted to be shorter, this is due to the reduction of viscosity in the vegetable oil (Gashaw & Teshita, 2014). According to Kusdiana & Saka (2004), high-temperature conditions dramatically increased the yield of the esters synthesized from the reaction. The transesterification reaction is an endothermic process (Samart, et al., 2009), therefore, from Le Chatelier's principle; by increasing the temperature the equilibrium of the reaction is shifted to the forward direction which favors the production of esters (Ong, et al., 2011). However, the transesterification reaction temperature must be kept below the boiling point of the alcohol used to prevent vaporization, or else this will result in a lower biodiesel yield (Sharma, et al., 2008).

Although high reaction temperature sometimes has benefits, it can also negatively affect the transesterification reaction by favoring side reactions as well as saponification. Eevera, et al. (2009) found that temperatures above an optimum value favors side reactions along with other variables that may be taken into account. Depending on the source of literature, the transesterification reaction temperature value varies, however, the range between 50°C and 70°C is usually considered optimal temperatures depending on the type of oil used (Meng, et al., 2008). Other drawbacks associated with high reaction temperatures include the process becoming complex, the process will require larger quantities of energy along with a reactor which will be able to withstand high temperature conditions which drastically increases production costs. Wear and tear on reactors due to high reaction temperatures also contribute to increasing production cost.

2.3.3 Catalyst Loading

Catalyst loading is generally depicted as the quantity of catalyst utilized in the transesterification reaction typically by a mass percentage of oil. The use of a catalyst is imperative in a transesterification reaction as alcohol is only slightly soluble in oil or fat. The catalyst enhances the solubility of the alcohol and thus increases the reaction rate (Atabani, et al., 2012). A transesterification process under atmospheric conditions strongly requires the use of a catalyst. The catalyst loading influences the yield of the biodiesel product (Leung, et al., 2010). Catalyst loading is determined on the free fatty acid (FFA) content present in the oil feedstock (Rajalingam, et al., 2016).

In general, the types of catalysts used for biodiesel production are categorized into 3 types; alkalis, acids and enzymes (Shimada, et al., 1999). Recently, enzyme catalysts have become more popular; the lipase enzyme-based transesterification reaction can tolerate FFA and water without saponification, thus the purification of the end product is done easily (Semwal, et al., 2011). A saponification reaction occurs when small amounts of water and FFA found in vegetable oils and fats react with the catalyst to form soap and water (Leung, et al., 2010). However, enzyme catalysts are not used often because of their high cost, longer reaction times, and their deactivation due to feed impurities, which are a major hindrance to the commercial viability of this process (Leung, et al., 2010; Dizge, et al., 2009).

Homogeneous catalysts consist of alkali and acid catalysts. The most commonly used homogeneous alkali catalysts are potassium hydroxide (KOH), and sodium hydroxide (NaOH). These catalysts are widely used commercially because of their low cost, high activity (Rashid & Anwar, 2008), and they are also less corrosive in comparison to acidic compounds (Pinto, et al., 2005). These catalysts are the most economic because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment and the conversion rate is high with no intermediate steps (Leung, et al., 2010). However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from the air during storage. They also form water when dissolved in the alcohol reactant and affect the yield (Leung & Guo, 2006). Hence, they should be properly handled. Sodium methoxide (CH_3ONa) and potassium methoxide (CH_3OK) are homogeneous alkaline catalysts that produce better biodiesel yields compared to NaOH and KOH. However, they're too costly, thus are not frequently used (Atabani, et al., 2012).

The most commonly used homogeneous acid catalysts are hydrochloric (HCl), and sulphuric acid (H_2SO_4). Homogeneous acid catalysts are usually preferred for vegetable oils and fats with high FFA acid content (Pinto, et al., 2005). The acids catalyze the free fatty acids during esterification to produce fatty acid esters, therefore increasing the biodiesel yield. However, the acid-catalyzed transesterification reaction is much slower than the alkali catalyzed reaction and also requires more extreme temperature and pressure conditions (Pinto, et al., 2005).

In order to reduce the problems experienced with homogeneous catalysts, heterogeneous catalysts have emerged as a preferred route as it is environmentally friendly and simplifies the existing process (Ilgen, et al., 2009). Heterogeneous catalysts include titanium silicates, enzymes, anion exchange resins, and alkali earth metals (Arshad, et al., 2018). From previous studies, the most common metal oxide catalysts used are calcium oxide (CaO), magnesium oxide (MgO), strontium oxide (SrO), and barium oxide (BaO). Heterogeneous catalysts greatly simplifies the separation and purification process of the end product. In addition to being easily separated, the catalyst can also be recovered and reused. Furthermore, they are capable of withstanding aqueous treatment steps and are amenable to modification to attain high activity, selectivity, and longer catalyst life. Heterogeneous catalysts are known to improve the transesterification process by eliminating the extra process costs that are involved with homogeneous catalysts as well as reduce the generation of pollutants, therefore making it an overall cost-effective green process. Heterogeneous catalysts are considered essential in certain harsh reaction conditions such as high pressure and temperature (Thangaraj, et al., 2019).

Research has also been conducted using microwaves and ultrasonic reactors. Microwaves are used in conjunction with a catalyst; however, the use of microwaves results in reaction times that are shorter in comparison to conventional heating methods (Mazzocchia, et al., 2004)

The supercritical method has also been investigated. This method does not require the utilization of a catalyst, it requires high pressures and temperatures (Sharma, et al., 2008).

Table 2-9: Benefits and drawbacks of the various types of catalysts utilized in a transesterification reaction (Lam, et al., 2010)

Type of catalyst	**Benefits**	**Drawbacks**
Homogeneous base catalyst	• Includes catalysts like KOH and NaOH which are cheap and easy to obtain. • Reaction rate is very fast in comparison to acid-catalyzed transesterification (4000 times faster). • Low energy consumption and mild reaction conditions.	• Sensitive to free fatty acid (FFA) in oil. • Side products are produced If the oil feedstock has FFA content greater than 2 wt. %. • Large quantity of water is required for product purification if there is excessive soap formation which lowers the biodiesel yield and conversion rate.
Homogeneous acid catalyst	• High FFA low-grade oils are suitable because it is insensitive to the water and FFA content in the feedstock. • Low energy consumption and mild reaction conditions. • Esterification and transesterification occur simultaneously.	• The rate of reaction is extremely slow. • Catalysts such as sulphuric acid is used, which is corrosive and causes corrosion issues on the pipelines and reactor. • Separation of catalyst from the final product is difficult.
Heterogeneous base catalyst	• The rate of reaction is faster in comparison to acid-catalyzed transesterification. • Low energy utilization and the reaction may occur at mild conditions. • Catalyst easily separated from the end product. • Simple catalyst recovery and catalyst reusability.	• Sensitive to FFA in oil. • Catalyst poisoning; when in contact with moist or ambient air. • Soap formation occurs if the FFA content in the feedstock is greater than 2 wt. %. • Biodiesel yield and conversion rate will decrease when there is excessive soap formation. This will result in product purification issues. • Leaching of catalyst active sites may result in product contamination.

Heterogeneous acid catalyst	• High FFA low-grade oils are suitable because it is insensitive to the water and FFA content in the feedstock. • Separation of catalyst from the end product is done easily. • Esterification and transesterification occur simultaneously. • Simple catalyst recovery and catalyst reusability.	• Energy-intensive. • High reaction temperatures, higher alcohol to oil molar ratios, and longer reaction times are required. • Complicated catalyst synthesis procedures lead to longer processing time and higher cost. • Leaching of catalyst active sites may result in product contamination.
Enzyme	• Low temperatures may be utilized for transesterification. • High FFA low-grade oils are suitable because it is insensitive to the water and FFA content in the feedstock. • Simple product purification step is needed.	• High cost. • The rate of the reaction is the slowest. • Sensitive to alcohol, especially methanol that can deactivate the lipase catalyst.

2.3.4 Alcohol to oil molar ratio

The alcohol to oil molar ratio is one of the major parameters influencing conversion efficiency and the cost of biodiesel production. As seen in figure 2-8 below, the transesterification reaction stoichiometry suggests 3 moles of alcohol per mole of vegetable oil is required to synthesize 3 moles of biodiesel (fatty acid esters) and 1 mole of glycerol. However, since the reaction is reversible; an excess amount of alcohol (higher alcohol to oil molar ratio) is generally used to shift the reaction forward to completion in accordance with Le Chateliers principle (Barnwal & Sharma, 2005). Higher molar ratios enhance the miscibility as well as increases the contact between the alcohol and oil molecules (Mishra & Goswami, 2017). Furthermore, excess alcohol breaks the glycerin-fatty acid linkages during transesterification to form biodiesel (Miao & Wu, 2006), thus resulting in more biodiesel being produced with higher purity over a shorter reaction time (Fukuda, et al., 2001). However, according to Leung and Guo (2006), the increase in the alcohol to oil molar ratio only favors biodiesel production to a certain point, thereafter, further increase in alcohol concentration past a certain point will not increase biodiesel yield but will increase the alcohol recovery cost. Common alcohols utilized in the transesterification reaction are methanol, ethanol, propanol, and butanol (Jaiswali, 2018). Methanol is the most commonly used alcohol due to it being the shortest chain of alcohol and because of its low cost. Higher chain molecular alcohols are generally not selected for the transesterification reaction due to the steric hindrance effect. Ethanol is also commonly considered for the transesterification reaction; however, it is more expensive in comparison to methanol. Ethanol is completely bio-based, hence the renewability of ethanol has suggested advantages due to it being carbon neutral, less toxic, and environmentally friendly, thus making ethanol the most suitable substitute to methanol (Hameed, et al., 2009). In practice, the alcohol to oil molar ratio for alkali-catalyzed transesterification is 6:1, which attains a yield of approximately 98% biodiesel (Fukuda, et al., 2001). Oils with high free fatty acid content, such as waste cooking oil (WCO), is where acid-catalyzed transesterification is employed with molar ratios as high as 15:1 (Leung & Guo, 2006). Balat and Balat (2008) noted that the universally accepted alcohol to oil molar ratios ranges from 6:1 to 30:1. However, the optimum molar ratio for a specified transesterification reaction is dependent on a variety of variables like the type of alcohol, catalyst selected, etc.

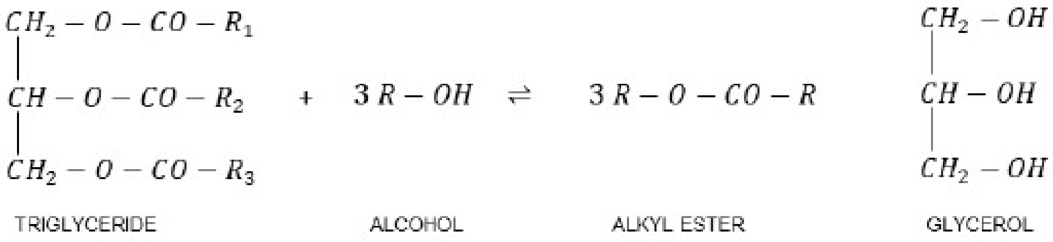


Figure 2-8: Stoichiometric transesterification reaction (Leung, et al., 2010)

2.3.5 Reaction time

Reaction time is a vital parameter that plays an important role in the production of biodiesel. The beginning of a transesterification reaction starts off slow due to the dispersion and mixing of alcohol into triglycerides and after some time the reaction proceeds relatively quickly (Freedman, et al., 1986). According to Freedman, et al. (1986) the fatty acid ester conversion rate increases with reaction time. Generally, at a reaction time of less than 90 minutes a maximum yield is reached, which remains fairly constant with a further increase in reaction time (Leung & Guo, 2006). However, excess reaction time will lead to a reduction in the product yield due to the backward transesterification reaction being favored, resulting in a loss of esters as well as causing more fatty acids to form soaps (Eevera, et al., 2009).

2.3.6 Free fatty acid and moisture content

Free fatty acid (FFA) and moisture content are key variables in the transesterification process. It is used in order to determine the feasibility of the triglyceride feedstock (Meher, et al., 2006). Water and free fatty acids always cause a negative effect on catalyzed transesterification reaction. The presence of high FFAs and water lead to saponification which produces soap (Wright, et al., 1944). This process results in the consumption of the catalyst and thus, there is a reduction in catalytic efficiency, which in turn produces a low biodiesel conversion (Demirbas & Karslioglu, 2007). According to Demirbas (2009), the presence of water gives a greater negative effect than that of free fatty acids, this is due to water causing frothing and soap formation by promoting hydrolysis of the alkyl esters to FFAs, which leads to an increase in viscosity. The formation of foam and gel creates difficulty in the separation of glycerol from the biodiesel product (Demirbas , 2009).

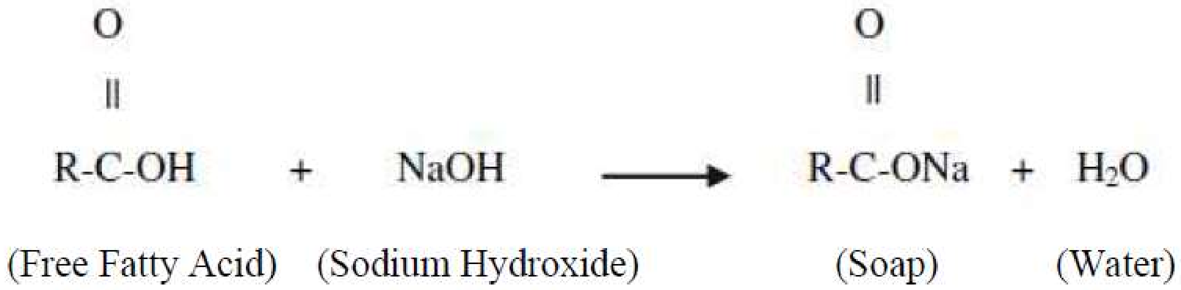


Figure 2-9: Saponification reaction (Canakci & Sanli, 2008)

Figure 2-9 above represents a typical saponification reaction in the presence of sodium hydroxide catalyst. The reaction is unfavorable as it results in the deactivation of the catalyst and therefore prevents it from accelerating the transesterification reaction (Lam, et al., 2010). The presence of high FFA and moisture in the feedstock can easily react with an alkali catalyst which in turn produces soap and water. The resulting soap causes viscosity to increase, gel formation, and thus, makes the separation of glycerol difficult. In addition, from figure 2-10, it can be seen the presence of water and an alkali catalyst; particularly at high temperatures, triglycerides will hydrolyze into diglycerides and FFAs. Consequently, the downstream recovery and purification of the biodiesel product are made more complicated by the formation of soaps.

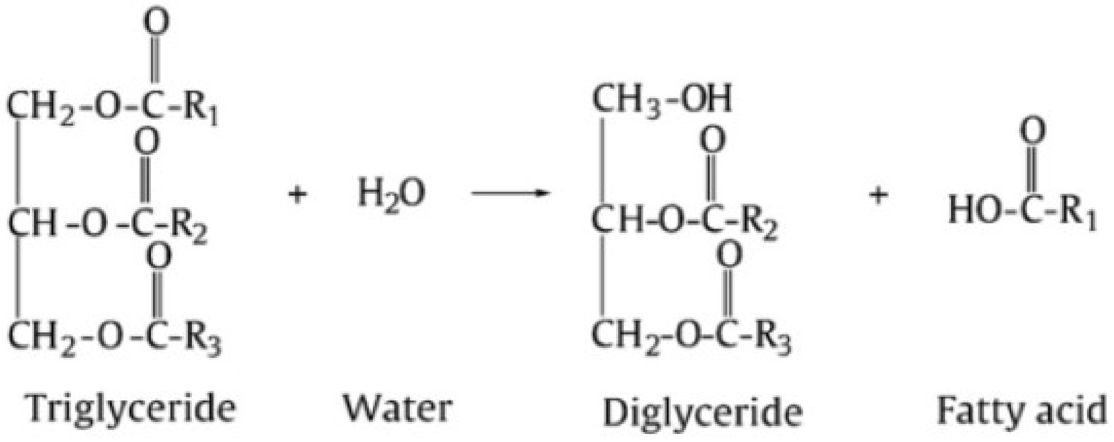


Figure 2-10: Hydrolysis of triglyceride reaction (Lam, et al., 2010)

Table 2-10: FFA content recommendations

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

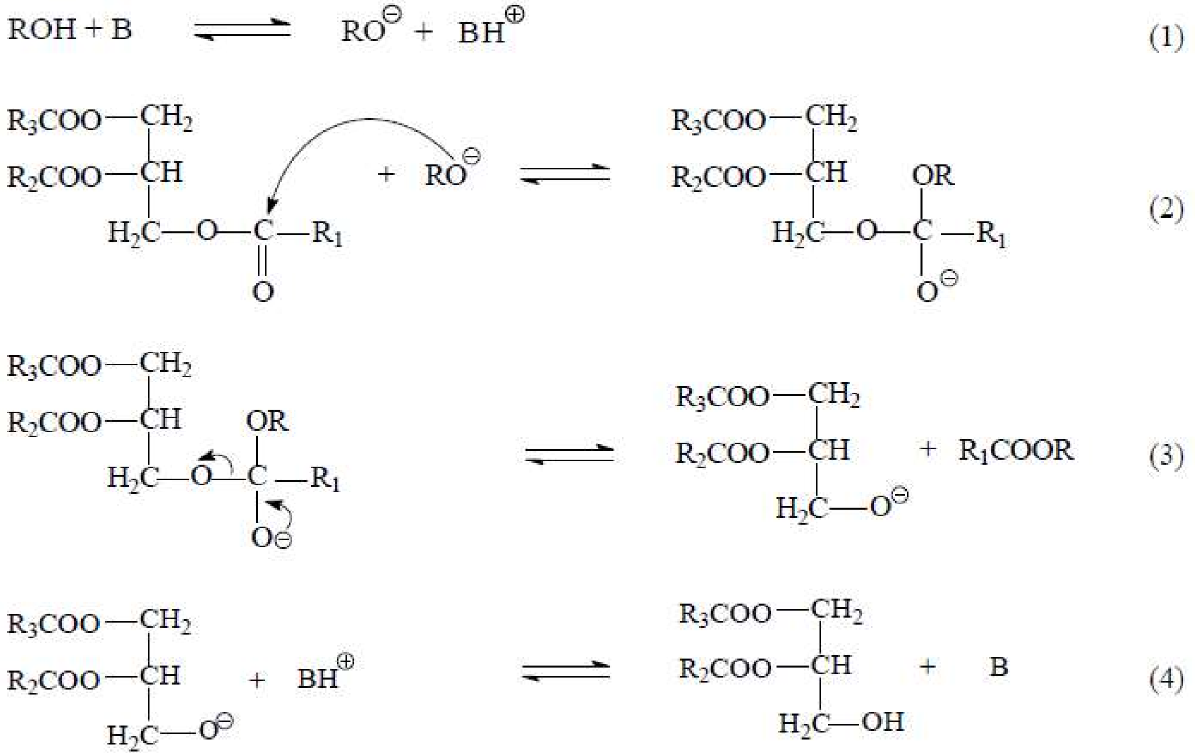
2.4 Transesterification reaction mechanisms

2.4.1 Homogeneous base-catalyzed transesterification

Common homogeneous base-catalysts utilized in the transesterification process include potassium hydroxide (KOH), sodium hydroxide (NaOH), carbonates, and alkoxides such as sodium methoxide, sodium ethoxide, etc. Alkaline catalysts give good performance provided that the vegetable oil used has a moisture content of < 0.5 wt.% and FFA content of < 1% (Helwani, et al., 2009). A major disadvantage for a base-catalyst is that it cannot be used with feedstocks containing FFA content > 1 wt.%. However, with regards to table 2-10, some researchers have suggested FFA content of up to 2 wt. %. Base-catalysts neutralizes the FFA to produce water and soap, which in turn decreases the catalyst activity. In addition, soap formation inhibits glycerol separation from the reaction mixture and the purification of esters with water (Canakci & Gerpen, 2003). Removal of saponified catalysts is difficult and it adds extra to the cost of biodiesel production. Furthermore, since homogeneous catalysts mainly dissolve in the glycerol and alcohol phase after the reaction is completed, they cannot be recycled for use in the following batches (Thanh, et al., 2012).

Lotero, et al. (2005) stated that the main reasons why homogenous catalysts are widely used include the fact that they are cost-effective, able to catalyze the reaction at low temperatures, and atmospheric pressure, as well as achieve high conversions and high yields in short durations. According to Rajalingam, et al. (2016) sodium methoxide is one of the most efficient base catalysts for the transesterification process, however, it is not economically feasible to use. The most widely used alkaline catalyst is NaOH because it is easy to prepare and it is inexpensive (Meka, et al., 2007). Fukuda, et al. (2001) reported that base-catalyzed transesterification proceeds 4000 times faster than acid-catalyzed reactions. Due to this reason, and alkali catalysts being less corrosive than acidic catalysts, alkali catalysts are favored for commercial use in the production of biodiesel.

The mechanism of base-catalyzed transesterification is comprised of four steps. In the first step, the alkali-catalyst reacts with the alcohol resulting in an alkoxide and the protonated catalyst. The second and third steps include the nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride, producing the alkyl ester and the corresponding anion of the diglyceride and in the last step, the diglyceride deprotonates the catalyst, making it active and able to react with another alcohol, starting a new transesterification cycle. Monoglycerides and diglycerides are equally converted to a mixture of glycerol and alkyl esters by the mechanism (Encinar, et al., 2012).



B: Base catalyst

R_1, R_2, R_3: Carbon chain of fatty acid

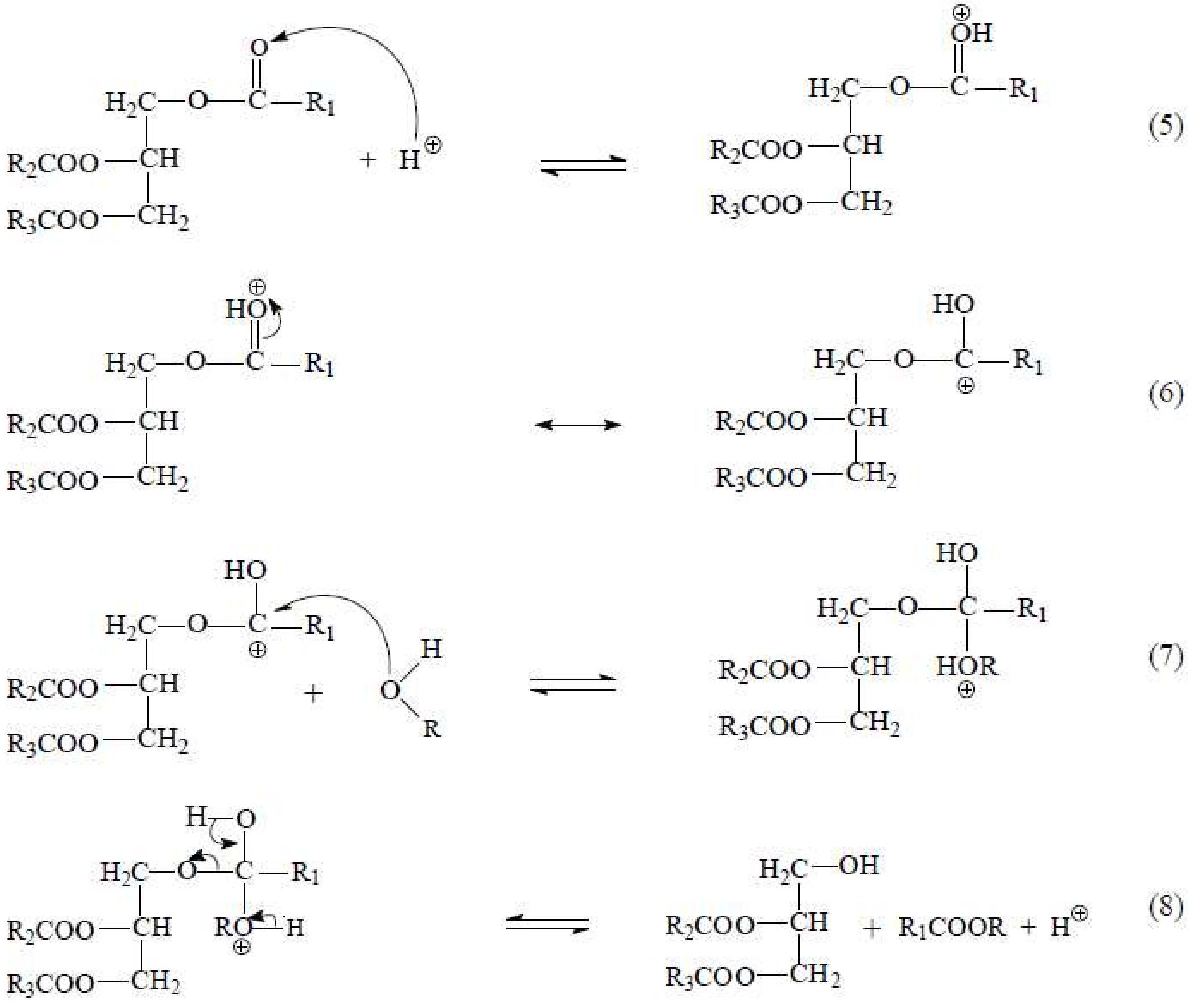
Figure 2-11: Reaction mechanism of the transesterification of triglyceride with alcohol in the presence of a homogeneous base-catalyst: (1) producing RO^-, the active species, (2) nucleophilic attack of RO^- to carbonyl group on triglyceride forming a tetrahedral intermediate, (3) breakdown of the intermediate, (4) active species RO^- regeneration (Thanh, et al., 2012)

2.4.2 Homogeneous acid-catalyzed transesterification

Acid-catalyzed transesterification is a recommended method by most researchers to be used for less-expensive feedstocks that contain relatively high FFA content greater than 1 wt.% (Freedman, et al., 1984). Acid-catalysts are claimed to be FFA tolerant and would reduce production cost when dealing with unrefined feedstocks (Hou, et al., 2007). Acid-catalysts are able to catalyze esterification as well as transesterification simultaneously (Jacobson, et al., 2008).

The most commonly used acid catalysts used are hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and sulfuric acid (H_2SO_4). An advantage of using an acid-catalyst over a base-catalyst is that the acid-catalyzed reaction will not produce soap (Thanh, et al., 2012). However, the acid-catalyst is very sensitive to the water content of the raw materials. The reaction is completely inhibited if the water concentration is 5 wt.% (Thanh, et al., 2012). Other drawbacks of the acid-catalyst include longer reaction times (low rate of reaction), higher reaction temperatures, and large quantities of alcohol to increase triglyceride conversion. In addition, acid-catalysts also cause corrosion of the equipment used (Freedman, et al., 1984).

Generally, a two-step process is utilized in order to reduce the long reaction time, the first step (esterification) employs the use of an acid catalyst which is adapted as a pretreatment step, and in this step, the FFA content is converted to esters. The second step (transesterification) employs the use of an alkaline catalyst to convert triglycerides to esters (Thanh, et al., 2012).



R_1, R_2, R_3: Carbon chain of fatty acid

R: Alkyl group of the alcohol

Figure 2-12: Reaction mechanism of the transesterification of triglyceride with alcohol in the presence of a homogeneous acid-catalyst: (5) and (6) protonation of carbonyl group by acid catalyst, (7) tetrahedral intermediate formation by nucleophilic attraction of the alcohol, (8) migration of proton and intermediate breakdown (Thanh, et al., 2012)

2.4.3 Heterogeneous base-catalyzed transesterification

Heterogeneous catalytic transesterification is a process where the catalyst remains in a different phase of the reactants. Due to the many shortcomings associated with homogeneous catalyst transesterification, such as high energy consumption, costly separation of the catalyst from the reaction mixture, and purification of biodiesel fuel (Thanh, et al., 2012), heterogeneous solid base catalysts have recently received great attention and has surfaced as a preferred production method for biodiesel. Heterogeneous base-catalysts are proposed with an advantageous form of replacing the use of alkaline and acidic homogeneous catalysts (Sani, et al., 2014). Some of the advantages associated with heterogeneous base-catalysts are that they are non-corrosive (Fadhil, et al., 2018), they can be reused, regenerated, applied in continuous processes, and can be separated from the reaction mixture easily because they're usually in powder or solid form (Shibasaki-Kitakawa, et al., 2011). Colombo, et al. (2017) found that in comparison to homogeneous catalysts, heterogeneous base-catalysts provides higher conversion efficiency. Recent heterogeneous catalysts that have been studied include metal oxides, hydrotalcites, zeolites, and ion exchange resins.

In this study, calcium oxide (CaO) and magnesium oxide (MgO) alkaline earth oxide catalysts will be used in the transesterification reaction. They are non-toxic, inexpensive, and insoluble in alcohol (Baskar, et al., 2017). The activity of the solid catalyst is dependent on the active sites on the surface of CaO or MgO. Since the surface of these metal oxides is easily poisoned by absorption of carbon dioxide and water in the air to form carbonates and hydroxides, respectively. The activity of these catalysts decreases with time. However, the catalytic activity of these metal oxides can be recovered by calcination of the catalysts to remove carbon dioxide and water at high temperatures (Thanh, et al., 2012).

CaO is usually synthesized from cheap sources by thermal decomposition of minerals such as calcite and limestone or from natural sources such as eggshells and seashells which comprises of calcium carbonate ($CaCO_3$). This is attained by the calcination of $CaCO_3$-containing raw materials at high temperatures in order to liberate a molecule of carbon dioxide (CO_2) leaving quicklime. Different raw materials require different calcination temperatures to obtain CaO (Marinković, et al., 2016).

According to Refaat (2011), CaO heterogeneous catalysts can synthesize biodiesel with exceptionally high yield and purity that are close to the theoretical value. Veljkovic, et al. (2009) found that approximately 98% of biodiesel yield was achievable during CaO-catalyzed transesterification reaction. However, the major drawback of heterogeneous catalysts is deactivation, which occurs over time due to coking, poisoning, leaching, and sintering.

It is necessary to calcinate calcium oxide as it readily deactivates when exposed to air. Moisture and carbon dioxide in the air acts as poisons for the catalyst because when it reacts with air the outermost surface of the catalyst gets covered with a layer of calcium carbonate which deactivates the catalyst. da Silva Castro, et al. (2018) reported as calcination temperature increases, the kinematic viscosity of biodiesel simultaneously increases. This is not desired as the fuel specifications are not be met.

As seen in figure 2-13 below, as the temperature increases the absorbance peaks decrease. From observation, it can be noted that there is a negligible effect between calcination temperatures between 600 ℃ and 900 ℃. Thus, CaO catalyst may be calcinated at a temperature of 600 ℃ for 3hours (Esipovich, et al., 2014).

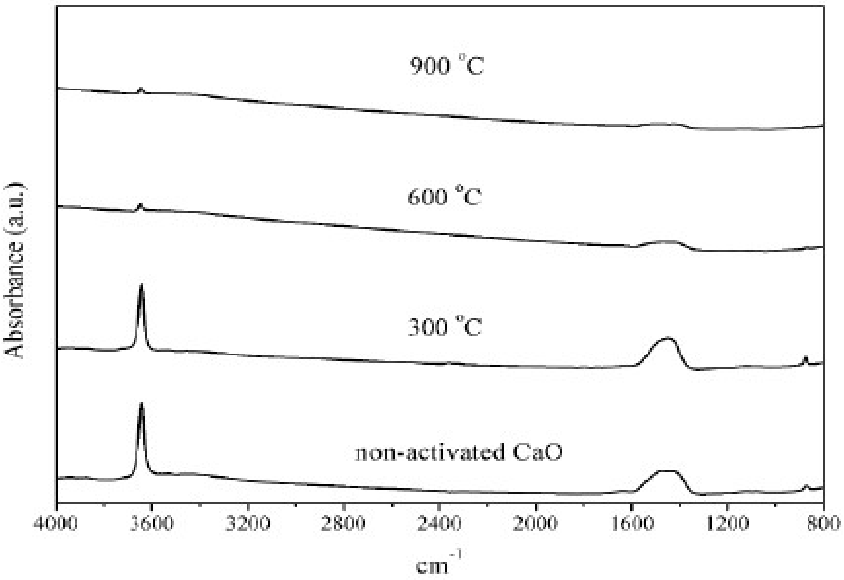


Figure 2-13: IR spectrum of calcium oxide at different temperatures (Esipovich, et al., 2014)

MgO is a naturally occurring compound found in metamorphic rocks and it is known as magnesia. MgO can be attained from magnesium carbonate ($MgCO_3$), magnesium hydroxide ($Mg(OH)_2$), and dolomite ($CaCO_3 \cdot MgCO_3$) (Pekguleryuz, et al., 2013). MgO is a hygroscopic substance, thus it spontaneously absorbs water when exposed to air. MgO is less soluble in alcohol and has an overall weak basic strength (Baskar, et al., 2017).

Calcination temperature of magnesium oxide has been reported to be an important parameter affecting the basicity of the catalyst, i.e., concentration and site strength (Yoosuk B, et al., 2010). Thermal treatment of magnesium oxide leads to defect migration from the bulk of crystallites to their surfaces (Pandey & Kumar, 2007). However, calcination not only affects the basicity but also the surface area of the active material. High calcination temperatures stimulate sintering of the metal oxide and therefore there is a reduced surface area, leading to a loss in catalytic activity in the reaction. MgO catalyst may be calcinated at a temperature of 800 ℃ for 2 hours (Thanh, et al., 2012).

Dossin, et al. (2006) investigated the transesterification activity of magnesium oxide by utilizing methanol and rapeseed oil as a feedstock for industrial biodiesel production. Their findings displayed that magnesium oxide had exceptional potential and could be used as a heterogenous base-catalyst at ambient temperature conditions for the production of biodiesel. Similarly, Di Serio, et al. (2007) produced a 92% biodiesel yield via MgO catalyzed transesterification, where soybean oil was used as the feedstock with an oil to methanol molar ratio of 1:12, catalyst loading of 5 wt. %, and a reaction time of 1 hour.

Heterogeneous-catalyzed transesterification mechanism follows a similar principle to that of homogeneous-catalyzed transesterification. In heterogeneous-catalyzed transesterification, adsorption of reactants and desorption of products occurs on the solid catalyst surface. There are two basic mechanisms that signify the basis of today's heterogeneous transesterification mechanisms. The first one is known as the Eley-Rideal (ER) mechanism and the second is known as Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism. In accordance to the ER mechanism, the reaction is performed by direct pick up of species from the surface by a liquid phase molecule, whereby the LHHW mechanism assumes the reactants are first adsorbed on the surface of the catalyst and therefore react, followed by the desorption of the product (Marinković, et al., 2016).

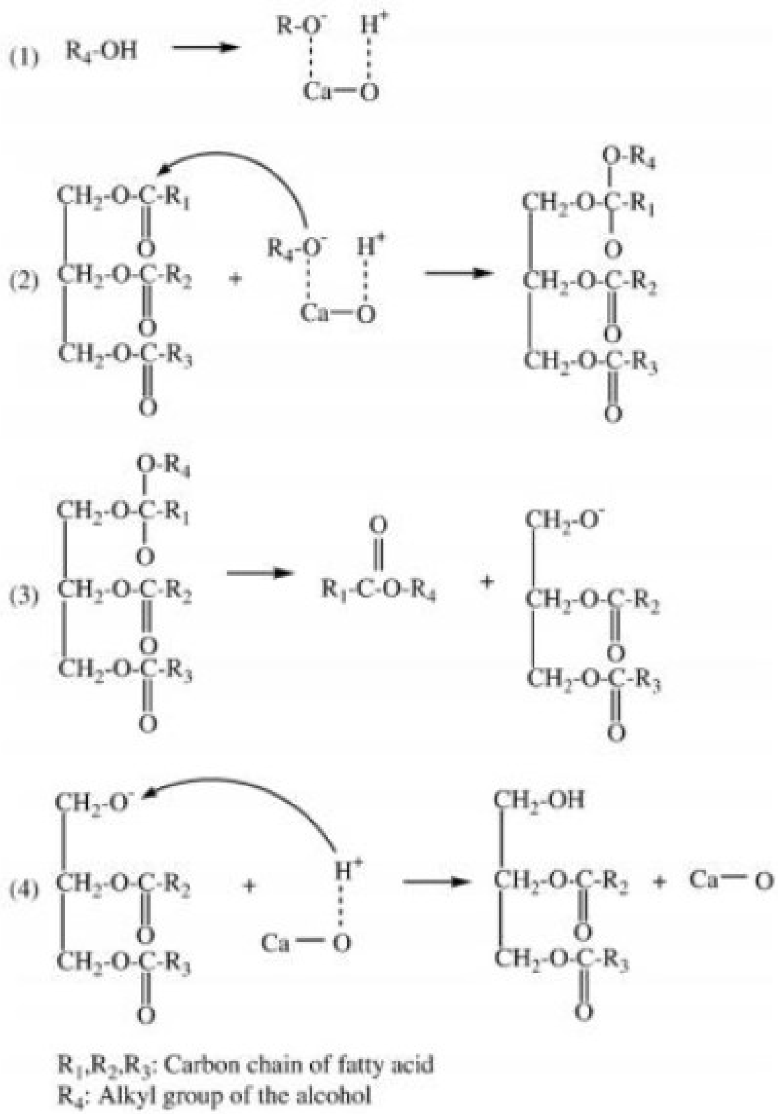
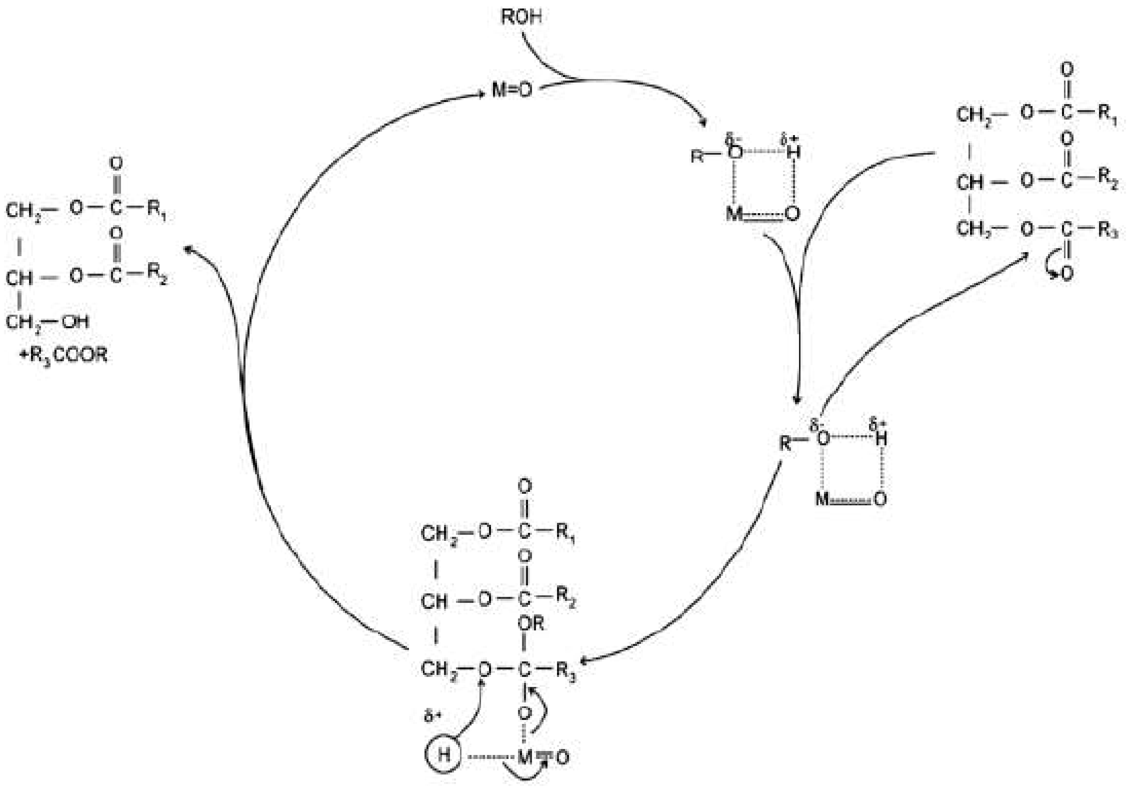


Figure 2-14: Reaction mechanism of the transesterification of triglyceride with alcohol in the presence of a heterogeneous base-catalyst: (1) proton abstraction from alcohol to form methoxide anion, (2) carbonyl carbon attacked by methoxide anion in a molecule of the triglyceride resulting in alkoxycarbonyl intermediate formation, (3) transformation of alkoxycarbonyl into more stable form, (4) methoxide attracts the anion of diglyceride resulting in diglyceride formation (Lotero, et al., 2005)



$M = Metal\ (Divalent)$

$R = CH_3 -, CH_3CH_2 - or\ any\ other\ alkyl\ group$

Figure 2-15: General heterogeneous base-catalyzed transesterification mechanism (Chouhan & Sarma, 2011)

2.4.4 Heterogeneous acid-catalyzed transesterification

Heterogeneous acid-catalyst is an ecologically significant area in catalysis for the production of biodiesel. They have exceptionally high potential to simultaneously carry out esterification of free fatty acids and transesterification of triglycerides, while utilizing feedstocks of low grade usually with high free fatty acid concentration, thus reducing the overall biodiesel production cost.

Some of the many advantages heterogeneous solid acid catalyst includes:

- Elimination of biodiesel washing step therefore making the purification process simple and cheap (Jitputti, et al., 2006).
- Toleration of high FFAs and it is not affected by water during the transesterification reaction (Lotero, et al., 2005).

- Easy separation process from the reaction mixture as the catalyst is not dissolved or consumed during the reaction (Zabeti, et al., 2009).
- Corrosion problems are reduced even in the presence of acid species (Lam, et al., 2010).
- Regeneration and reusing of catalyst without affecting the activity of the transesterification reaction (Lam, et al., 2010).
- Has the potential to simultaneously proceed with esterification and transesterification (Di Serio, et al., 2007).
- Since the separation step doesn't require acid or water treatment, the process is seen as more environmentally benign (Zabeti, et al., 2009).

As mentioned by Chouhan and Sarma (2011) an ideal heterogeneous solid acid-catalyst should consist of a moderate to high concentration of strong acid sites, an interconnected system of large pores, and a hydrophobic surface.

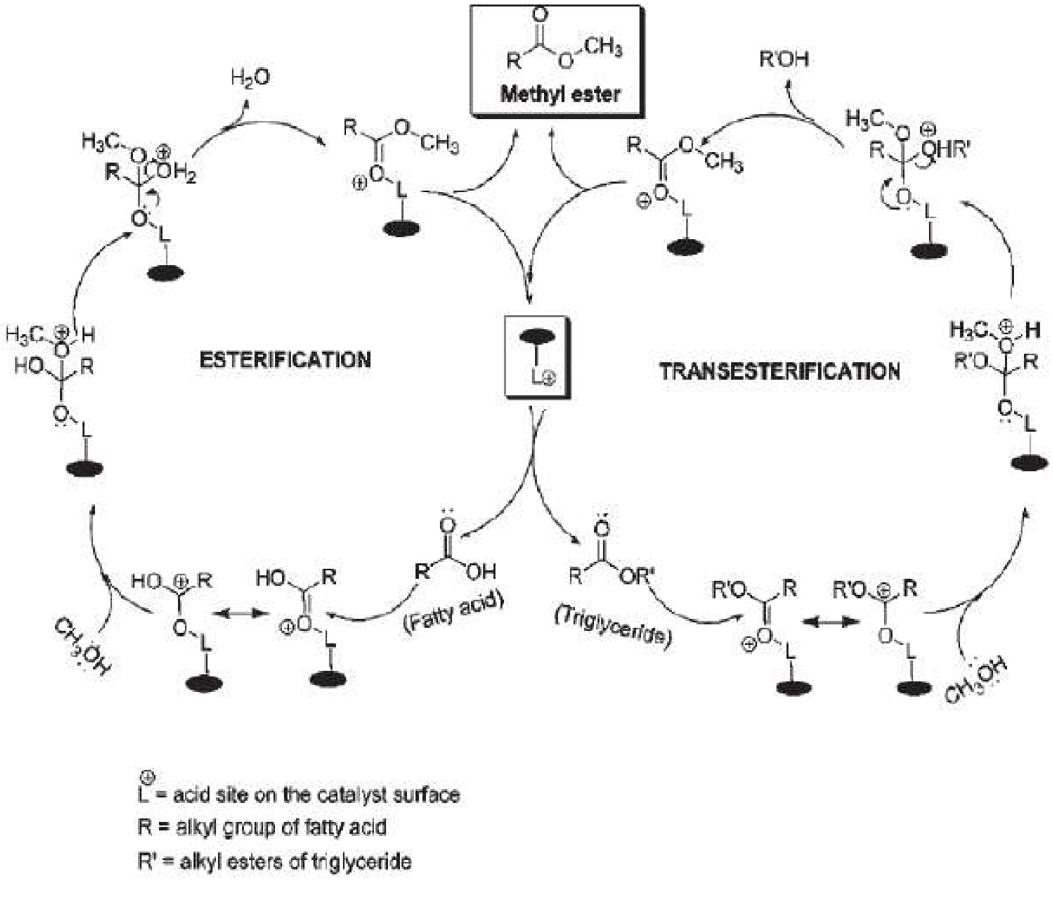


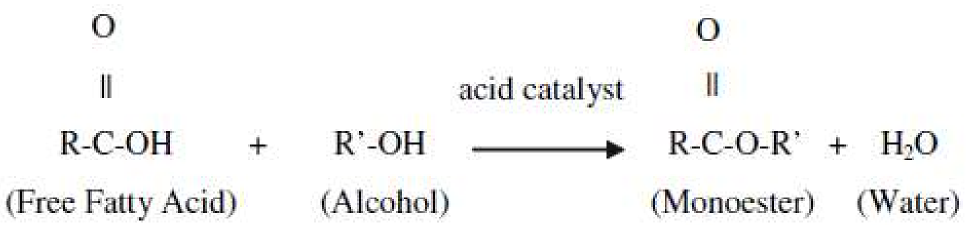
Figure 2-16: General heterogeneous acid-catalyzed transesterification mechanism (Di Serio, et al., 2007)

Table 2-11: Comparison between homogeneous and heterogeneous catalysts (Baskar, et al., 2017)

Homogeneous Catalysts	**Heterogeneous Catalysts**
Same phase as reaction medium. Insensitive to fatty acid and water content.	Usually distinct solid phase.
Often difficult to separate.	Readily separated.
Expensive and difficult to recycle.	Readily regenerated and recycled.
Often very high rates. Base catalysis highly favors kinetics.	Rates not usually as fast as homogeneous.
Not diffusion controlled.	May be diffusion controlled.
High selectivity	Lower selectivity.
Short life and requires extensive purification.	Long life and requires less purification.

2.5 Esterification

The esterification reaction is an organic reaction that involves two reactants, namely a free fatty acid source and alcohol reacting together in the presence of an acid catalyst to synthesize an ester. According to Zhang, et al. (2003) esterification is generally performed when the FFA content in the feedstock is greater than 1 wt.%. Generally, esterification is used as a pretreatment to convert FFAs to monoesters, the pretreatment reaction can be seen in figure 2-17. Acid catalysts are used because they are able to tolerate high FFA content in comparison to alkali catalysts. Acid catalysts are too slow for converting triglycerides into biodiesel, but they’re fast enough to convert FFAs to esters. A major concern with pretreatment is the production of water which is produced when FFAs react with alcohol, water inhibits FFA to ester conversion. In addition, drawbacks when producing biodiesel from these feedstocks is the slow reaction rate and higher alcohol quantity is required (Canakci & Sanli, 2008).



$$\underset{\text{(Free Fatty Acid)}}{\mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH}} + \underset{\text{(Alcohol)}}{\mathrm{R'\text{-}OH}} \xrightarrow{\text{acid catalyst}} \underset{\text{(Monoester)}}{\mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R'}} + \underset{\text{(Water)}}{\mathrm{H_2O}}$$

Figure 2-17: Pretreatment reaction (Canakci & Sanli, 2008)

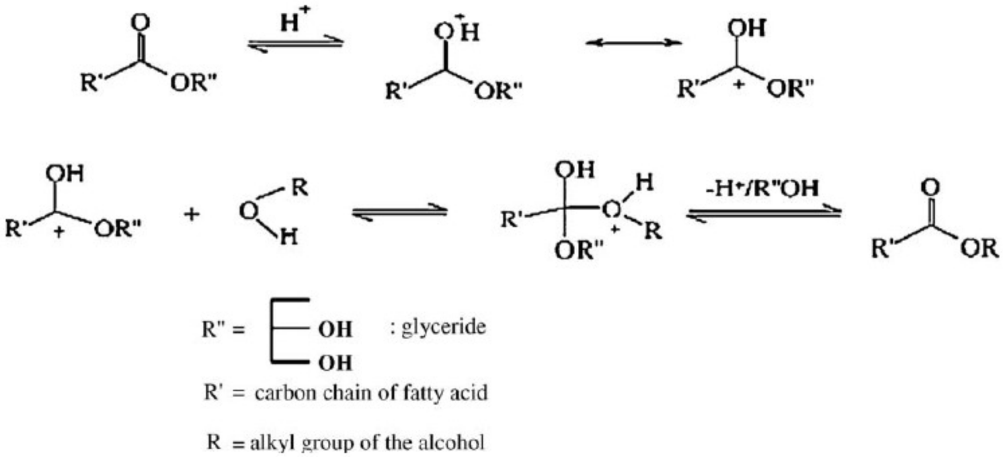


Figure 2-18: Acid-catalyzed esterification mechanism (Singh & Singh, 2010)

2.6 Biodiesel properties

2.6.1 Kinematic viscosity

The degree of a fluid's resistance to flow overtime is defined as viscosity. Less viscous fluids flow with ease, while highly viscous fluids flow with difficulty (Linus , et al., 2011). Biodiesels kinematic viscosity decreases with an increase in temperature. Highly viscous fuels in engines cause the formation of deposits as it affects the atomization of fuel upon injection into the combustion chamber. The more viscous the fuel, the greater the tendency for the engine to encounter such problems (Knothe, 2005). According to ASTM D6751, the acceptable kinematic viscosity range falls between 1.9 and 6 mm^2/s. The kinematic viscosity of biodiesel fuel is an imperative element that plays a vital role in the fuel's performance in the engine; as both high and low viscosities can have negative impacts on the performance of an engine. Highly viscous fuels lead to the formation of large droplets on injection into the combustion chamber, which results in raised exhaust smoke, poor combustion, and more emissions. Biodiesels high viscosity and its blends alter the pattern of injector spray in engines, thus, carbon deposits are formed in the engine which ultimately ends up in engine failures and piston rings stuck in the cylinder. This is caused due to fuel impingement on the piston and other combustion surfaces, however, it would rarely occur with the use of petro-diesel (Samuel, et al., 2011; Seung, et al., 2008). If the viscosity of the fuel is high, the pumping chamber will not receive a sufficient fuel supply through the injection pump and will result in power loss. If the viscosity of the fuel is low, the outflow will correspond to a power loss for the engine. Biodiesel's viscosity range typically overlaps the range for petro-diesel. If the viscosity is high as in the case of vegetable oils; there will be black smoke production, contamination of the lubricating oil, and degradation of the spray in the cylinder causing poor atomization (Gerpen, 2005).

Researchers have found ways to improve the kinematic viscosity of biodiesel. In the viscometric and thermodynamic evaluation of biodiesel blends and biodiesel (B100) from vegetable oils like cashew nut oil and olive oil. Linus, et al. (2011) found that blending petrodiesel with biodiesel can be done to favor utilization in the engine system as it corrects viscosity values.

2.6.2 Density

Density is related to viscosity, heat value, and the cetane number of fuels (Ge & Choi, 2017). Biodiesel produced from fats and vegetable oils normally has a higher density in comparison to petro-diesel. This is evident by the work of Anastopoulos, et al. (2009) who used sunflower, rapeseed, olive, and waste cooking oil at densities of 921.7, 918.6, 908.2, and 926 kg/m^3 to produce biodiesel at densities of 882.7, 881.2, 881.5 and 888.5 kg/m^3, respectively. A fuel with lower viscosity and density is better for engines; as when the fuel is injected, enhanced mixture formation and better atomization can be achieved. Denser fuels will have increased fuel diameter droplets. Thus, the inertia of the increased fuel diameter droplets are big and their penetrations in the combustion chamber will also be greater (Choi & Reitz, 1999). The density of biodiesel at 40 °C as specified in ASTM D6751 must range between 0.82-0.9 g/cm^3.

2.6.3 Cetane number (CN)

Cetane number (CN) is an indicator of a fuel's ignition and combustion quality. It is influenced by the chemical and physical properties of the fuel; such as surface tension, density, and viscosity. Majority of biodiesel fuels CN generally ranges between 40 – 60 (Ramadhas , et al., 2004), while petro-diesel lies between 35 – 60 (Giakousmis & Srakatsanis, 2019). The CN is linked to the ignition delay time which is the time between the beginning of injection and the commencement of combustion. Ignition delay decreases when CN increases, thus, the combustion phase increases. Ignition delay is unacceptable as diesel knock occurs (Canakci & Sanli, 2008). From previous studies, it was found that the ideal CN in fuels is obtained when long straight-chain hydrocarbons are used as there is minimum branching and it possesses CN values which are high (Knothe, 2014; Hoekman, et al., 2012).

2.6.4 Flash point

Flash point is defined as the lowest temperature at which vapor above the liquid fuel will experience a momentary flash when exposed to an ignition source (Muhammad, et al., 2019). It is a vital parameter to consider in terms of safety, handling, and storing of the fuel, as well as transporting the fuel. Biodiesel generally has a higher flash point than petro-diesel, indicating it is safer for transporting. The flash point of a fuel is correlated to the fuel's volatility; which is a significant feature for the warming and starting of an engine. According to Canakci & Sanli (2008), fuels with high flash points can result in carbon deposits in the combustion chamber.

2.6.5 Cloud point (CP) and pour point (PP)

Anguebes-Franseschi, et al. (2019) stated that the cloud point is defined as “the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under controlled conditions during the standard test”. The ASTM defines pour point as the minimum temperature at which biodiesel fuel is able to move (be poured) after being removed from the freezer (ASTM, 2003). Biodiesel fuels generally has higher pour point and cloud point temperatures compared to diesel fuels (Copeland, et al., 2006).

2.6.6 Acid value (AV)

Acid value is an indicator of the amount of free fatty acids (FFA) present in oils or animal fats. It is defined as the weight of potassium hydroxide (KOH) required in milligrams to neutralize organic acids present in 1g of oil/fat (Muhammad, et al., 2019). AV is also used to determine the degree of decomposition of a fuel during storage (Anguebes-Franseschi, et al., 2019). Fuels with high AV have a high likelihood to decompose. Base catalyzed transesterification is not suitable for oils/fats with an excess or high AV (FFA greater than 5% excess) (Remesh , 2004). The maximum AV specified by the ASTM is 2 mg KOH/g oil. Cheap feedstocks such as waste cooking oil has to go through acid esterification in order to lower acid value before proceeding with transesterification.

2.6.7 Heating value

Heating value is considered an important parameter of fuel. The heating value indicates the amount of heat transferred to the chamber during combustion and specifies how much energy is available in the fuel (Demirbas, 2008). The higher the heating value the greater the energy contained in the fuel. The heating value of biodiesel ranges between 39-41 MJ/kg which is much higher in comparison to other liquid fuels, however, it is lower than oil (42 MJ/kg), diesel fuel (43 MJ/kg), and petrol (46 MJ/kg), but higher than coal (32-37 MJ/kg) (Oliveira & Da Silva, 2013). For a constant level of unsaturation as the chain length increases, the quantity of oxygen decreases thus, resulting in an increase in the heating value (Ismail & Ali, 2015).

2.6.8 Saponification value (SV)

According to Muhammad, et al. (2019) saponification value is the measure of the total free and combined acid in the oil expressed as the number of milligrams of KOH required for the complete saponification on 1g of the oil, it is a measure of acyl groups (saponifiable units) per unit weight of oil (Ismail & Ali, 2015). SV has an inversely proportional relationship with the average molecular weight of a sample. High SV is an indication of low molecular weight fatty acids in fats/oils. Oils/fats with high SV would result in the increased formation of soap during base-catalyzed transesterification, therefore this will hinder the formation of biodiesel and affect the biodiesel quality (Lam, et al., 2010). Nakarmi & Joshi (2014) reported, after refining castor oil the SV dropped from 79.159 to 76.258 mg KOH/g oil. Thus, oils with lower SV are preferred for biodiesel production.

2.6.9 Iodine value

The definition of iodine value (also known as iodine number, iodine index, and iodine adsorption value) is the absorption quantity of iodine in grams per 100 grams of oil. It is used to measure the quantity of unsaturation in fatty acids (Ge & Choi, 2017). Due to the existence of double bonds; there will be a reaction between the unsaturation and iodine compounds. By determination of the iodine number, the average double bond number of fatty acids can be calculated. The amount of unsaturated double bonds is in relation to the kinematic viscosity, cold filter point, and combustion performance of biodiesel fuel (Ge & Choi, 2017). Thus, biodiesel fuel properties can be determined by the iodine number. Biodiesel fuels with a low degree of unsaturation have high CN, a low iodine value, and low-temperature performance, vice versa. Biodiesel iodine values have been limited in many parts of the world. For example; in Japan and Europe it is 120 g I_2/100g, in Europe it is 130 g I_2/100 g for biodiesel as heating oil, in South Africa it is 140 g I_2/100 g (Hernandez, et al., 2010; Barabas & Todorut, 2011).

The economic, social, environmental and energy security impacts of biodiesel can be seen in table 2-12 below.

Table 2-12: Impacts of biodiesel (Sani, et al., 2013)

Economic and social impact	**Environmental impact**	**Energy security**
Sustainability; made from agricultural or waste resources.	Reduced 78% greenhouse gas emissions.	Reduced dependence on fossil fuels.
Fuel diversity and improved fuel efficiency and economy.	Reduced air pollution.	Domestic targets.
Improved rural economy.	Biodegradability.	Supply reliability.
Increased income tax and trade balances.	Improved land and water use.	Readily available.
International competitiveness.	Carbon sequestration.	Renewability.
Increased investments in feedstocks and equipment.	Lower sulfur content.	Domestic distribution.
Technological developments.	Lower aromatic content.	Improved fuel economy.
Higher cetane number, lubricity, and flash point.	Lower toxicity.	Comparable energy content.
Knowledge development and diffusion.	Safer handling and storage.	Strict quality requirements are met.
Strong growth in demand and market formation.		
Improved engine performance.		
Reduces the need for maintenance and prolongs engine life.		
Compatible with all conventional diesel engines.		
Offers the same engine durability and performance.		
Has the potential of displacing petroleum diesel fuel.		
Comparable start-up, torque range, and haulage rates.		

2.7 Advantages and disadvantages of biodiesel

(i) Advantages

- Biodiesel is less toxic and safer to use in comparison to petroleum diesel (Romano & Sorichetti, 2011).
- Biodiesel is synthesized from renewable sources; thus, it is a renewable source of energy.
- Burning biodiesel produces less sulfur dioxide, carbon monoxide, and unburned hydrocarbons (Datta , et al., 2019).
- In comparison to diesel, biodiesel degrades rapidly. Thus, minimizing environmental consequences of biodiesel spills.
- Burning biodiesel produces less carbon dioxide which doesn't largely contribute to global warming, thus, lowering health risks (Datta , et al., 2019).
- Using B100 can reduce carbon dioxide (CO_2) emissions by 78% and lower the carcinogenic properties of diesel fuel by 94% (Azad, et al., 2013).
- Biodiesel has a flash point of greater than 100°C, therefore it is less combustible which makes it safe to transport, store, and handle (Romano & Sorichetti, 2011).
- Biodiesel can be utilized in existing engines and oil systems directly without making further modifications.
- Biodiesel may increase the life span of engines due to its lubricating property (Hoekman, et al., 2012).

(ii) Disadvantages

- The production of biodiesel can lead to a food crisis in many countries since it is synthesized using vegetable oils and animal fats. This may also lead to an increase in the price of food (Datta , et al., 2019).
- The cost of biodiesel is currently higher than petroleum diesel.
- Higher fuel consumption due to biodiesels lower calorific value.
- Biodiesel may be difficult to use in cold climates as it gels in cold weather. It has a higher freezing point in comparison to petroleum diesel fuel.
- The nitrous oxides (NOx) emissions are slightly higher in biodiesel than in diesel fuel. In the case of dissolving of NOx in the atmosphere, it can cause acid rain (Datta , et al., 2019).
- Biodiesel cleans the dirtiness from the engine. Although it is an advantage for biodiesel, this dirt can then collect in the fuel filter, thus clogging it. Hence, it damages filters and therefore filters have to be changed after the first several hours of biodiesel use (Hoekman, et al., 2012).

In this chapter, the many ways to produce biodiesel have been looked at and the transesterification method was seen as being the most ideal due to low production costs and high quality. Homogeneous base transesterification method is still commonly used to commercially produce biodiesel, however numerous environmental issues are associated with the high energy consumption and costly separation process required for it, thus heterogeneously base catalyzed transesterification was looked at to mitigate the issues such as costly separation, etc. The expected biodiesel properties have been studied along with the process variables such as reaction temperature, reaction time, alcohol to oil molar ratio and catalyst loading.

Chapter 3 Materials and Methods

This chapter concentrates on the feedstock, equipment, and other chemicals used to conduct numerous experiments. In this study canola oil was the selected vegetable oil. The oil was subjected to a transesterification reaction by reacting it with ethanol in the presence of a heterogeneous catalyst, which was either calcium oxide or magnesium oxide respectively; to synthesize biodiesel. The following chemicals were utilized throughout this study without any further purification.

Table 3-1: Materials used for the transesterification reaction and property testing

Material	**Supplier**	**Purity**
Ethanol	Lichro Chemical and Laboratory supplies	≥ 99.9%
Canola Oil	Suncat Catering Supplies	-
Calcium Oxide	Radchem laboratory supplies	Analytical Grade (AR)
Magnesium Oxide	Sigma-Aldrich	Analytical Grade (≥ 98%)
Isopropyl alcohol	Radchem (Pty) Ltd	Analytical Grade (AR)
Toluene	Merck	Analytical Grade (≥ 99%)
Phenolphthalein	Lichro Chemical and Laboratory supplies	1% in 96% ethanol
Kerosene	Lichro Chemical and Laboratory supplies	-
Potassium hydroxide	Radchem laboratory supplies	Analytical Grade (AR)
Hydrochloric acid	Sigma-Aldrich	Analytical Grade (AR)

Additional materials were required for property testing of the biodiesel synthesized in accordance with the American society for testing and materials (ASTM) standards. In order to determine the acid value of canola oil and biodiesel; a titration solvent made up of toluene, isopropyl alcohol and water was used in the ratio of 100:99:1 together with a 0.1 M potassium hydroxide titrant solution and phenolphthalein as the indicator. Hydrochloric acid and ethanol were used in conjunction with potassium hydroxide in order to determine canola oil saponification value. Lastly, in order to produce bio-jet fuel, the biodiesel produced was blended with kerosene.

The following equipment was used in the transesterification of canola oil and physical property testing of the biodiesel produced.

Table 3-2: Description of equipment used

Equipment/ material used	Key	Description
Beaker (600 mL)	3	Vessel used as a reactor to accommodate the transesterification reaction.
Magnetic stirrer bar		Provide mixing between the reactants and catalyst.
Thermometer	1	To measure the reaction temperature. To allow for the appropriate temperature adjustment in order to maintain isothermal conditions.
Hot plate	4	Provide heat to the reaction mixture.
Parafilm	2	Prevent ethanol vapor from leaving the reaction vessel.
Separation funnel (500 mL)		Facilitate separation between immiscible liquids. Lower-density biodiesel lies at the top while high-density glycerol settles at the bottom.
Rotary evaporator		To remove excess ethanol and water present in the biodiesel after washing it.
Gas chromatography/ mass spectrometry (GC/MS)		Identifies the different types of fatty acid ethyl esters produced in a specific biodiesel sample.
Burette (50 mL)		Used in titrations for the base oil and biodiesel samples to determine their respective acid values.
Scale		To weigh the quantity of biodiesel produced, catalyst loading, etc.
Volumetric cylinder (250 mL)		Measure the respective amount of canola oil required.
Dropper		Used to add phenolphthalein to samples during titrations.
Viscometer		Measure biodiesel viscosity.
Digital density meter		Measure biodiesel density.
Centrifuge		Facilitate the separation of any residual solid catalyst left behind in a biodiesel sample.
Muffle furnace		Facilitate the calcination of the heterogeneous catalysts.
Porcelain crucible		Used to hold the catalyst for calcination in the furnace.
Vacuum desiccator		To remove residual moisture from the catalyst and store away from moisture after calcination.

3.1 Property testing methods

3.1.1 Density

The density of the samples was measured using a syringe and a digital density meter. Approximately 10mL of the sample was injected into a clean and dried digital density meter, after some time the density of the sample was displayed on the screen and therefore recorded. In order to improve the precision of the results, this process was carried out in triplicate and the results were therefore averaged. The density of all samples was measured at a standard reference temperature of 15 °C as specified in ASTM D941

3.1.2 Kinematic viscosity

The dynamic viscosity of the samples was measured with the aid of a viscometer. A water bath was utilized to allow the samples to reach their desired temperatures (20 °C for bio-jet fuel, 25°C for canola oil, and 40°C for biodiesel). Once the respective sample reached its desired temperature a spindle was immersed into the sample. Spindle S21 was utilized and set at a rotation speed of 60 rpm. The dynamic viscosity was therefore recorded in centipoise (cP), which was then divided by the density of the respective sample to attain its kinematic viscosity. In order to improve the accuracy of the results, this process was carried out in triplicate and the results were therefore averaged.

3.1.3 Acid value

Acid tests were conducted in accordance with the method outlined in ASTM D974. The acid test required preparing a titration solvent which was a mixture consisting of isopropyl alcohol, water, and toluene at a ratio of 99:1:100. A solution of 0.1 M potassium hydroxide (KOH) was also prepared and added to a burette.

After preparing the required solutions, a blank titration was conducted with the titration solvent to determine the amount of reactive substances in the titration solvent. This allowed for a correction of errors in subsequent titrations using the titration solvent. The blank titration was conducted as follows:

- 100 mL of titration solvent and 5 drops of phenolphthalein were added into an Erlenmeyer flask; therefore the 0.1 M KOH solution was titrated into the solvent. The volume of KOH solution required to titrate the titration solvent was recorded.

The following procedure (as per ASTM standard D974) was used to determine the acid value of all samples:

- For samples expecting low acid values, 20 g of sample was weighed and poured into an Erlenmeyer flask.

- 100 mL of the titration solvent along with 5 drops of phenolphthalein was added to the 20 g sample, which was therefore swirled until it was completely dissolved by the titration solvent.
- Using the 0.1 M KOH solution, the sample was titrated until the endpoint was reached (when a pale pink solution was achieved).
- The titrated volume was noted and the acid number was determined by the following formula:

$$\text{Acid number}\left(\frac{\text{mg KOH}}{\text{g}}\right)=\frac{(A-B)M\times 56.1}{W} \qquad [3.1]$$

Where:

A = Volume of KOH solution required for titration of the sample (mL)

B = Volume of KOH solution required for the blank titration (mL)

M = Molarity of the KOH solution

W = Mass of the sample used (g)

3.1.4 Flash point (closed cup)

Flash point by the Abel apparatus was used to determine the flash point of the biodiesel and bio-jet fuel samples. Approximately 50 mL of sample was poured into the lidded cup of the apparatus. The apparatus was filled with water and turned on. The water within the apparatus heated the sample in the cup. The lid of the cup was opened at 1°C intervals; where the sample was exposed to an ignition source. A thermometer was placed inside the lidded cup and the lowest temperature at which the vapour above the fuel flashed was recorded as the flash point. The flash point test was conducted in triplicate for each sample. The flash point apparatus used provides results with an uncertainty of $\pm$ 0.01°C.

3.1.5 Pour point

The pour points of the biodiesel samples were determined by surrounding a sufficient quantity of ice around a beaker containing biodiesel. The pour point was measured using a thermometer and recorded at the lowest temperature at which the biodiesel mixture was able to be poured. As specified in ASTM D6751, the acceptable pour point values range between -15 °C to 10 °C.

3.1.6 Gas chromatography-mass spectrometry (GC-MS) analysis

Biodiesel samples obtained at the optimum conditions were subjected to gas chromatography–mass spectrometry analysis to attain the composition of free fatty ethyl esters present. A Shimadzu GC-MS machine equipped with an ultra-alloy column was utilized for the biodiesel analysis. The column specifications are shown in table 3-3 below.

Table 3-3: GC-MS Column specifications

Name	Ultra Alloy Capillary Column
Diameter	0.25 mm
Thickness	0.25 µm
Length	30 m

Table 3-4: Gas Chromatography conditions

Injection temperature	250 ℃
Column oven temperature	120 ℃
Carrier gas	Helium
Injection mode	Split
Pressure	80.6 kPa
Flow control mode	Linear Velocity
Column flow	1 $\frac{mL}{min}$
Total flow	34 $\frac{mL}{min}$
Purge flow	3 $\frac{mL}{min}$
Linear velocity	37.5 $\frac{cm}{s}$
Split ratio	30

Table 3-5: GC column oven temperate program

Rate $\left(\frac{℃}{min}\right)$	**Temperature** (℃)	**Hold time** (min)
-	120	0
10	180	1
1	215	0
2	260	0

The settings depicted in tables 3-3, 3-4, and 3-5 were employed in the GC-MS which resulted in a run-time of 64.50 minutes. The aforementioned settings were adapted from the work of Warra (2015), however, necessary modifications were made to the method according to the biodiesel product.

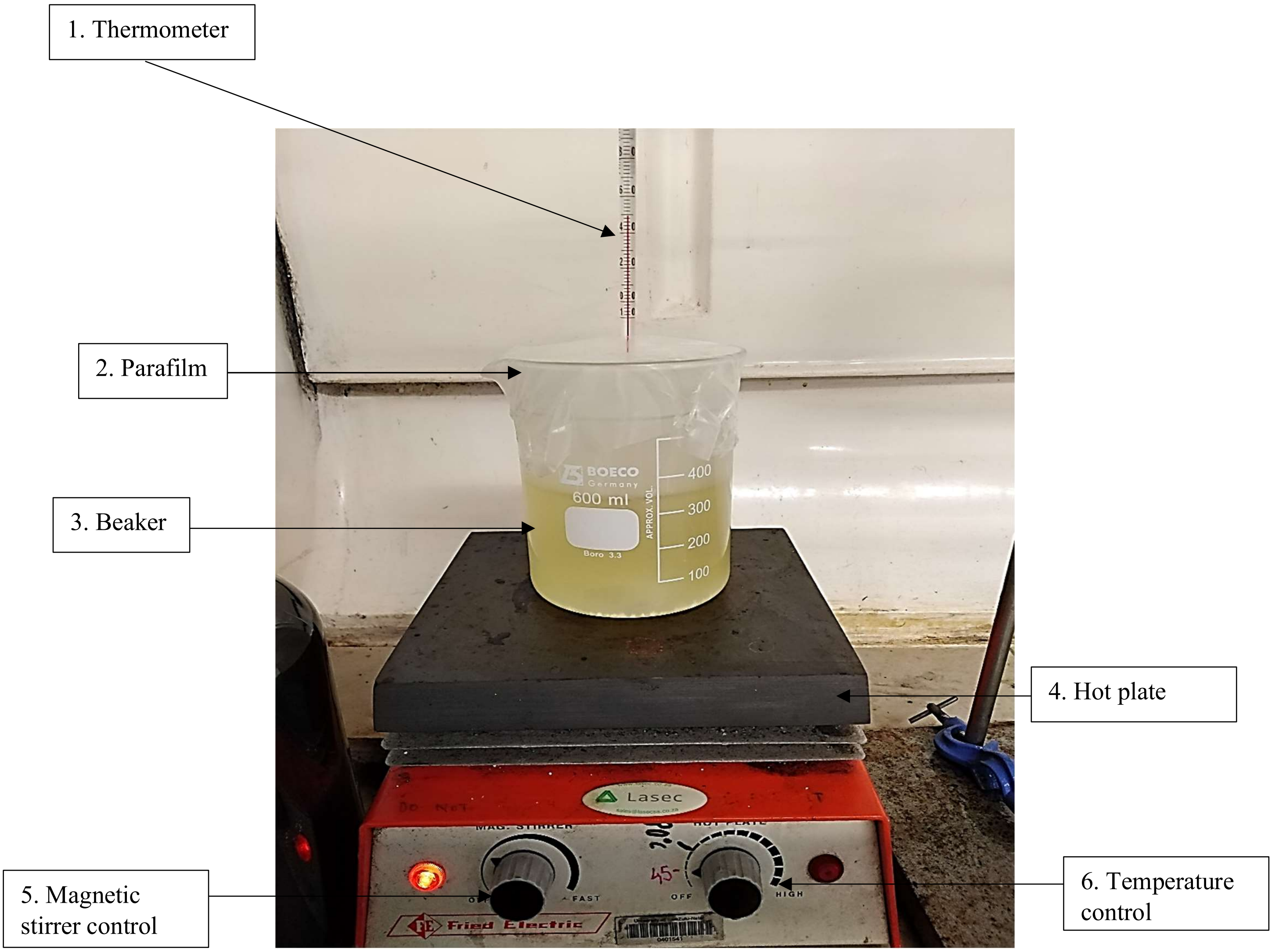


Figure 3-1: Experimental set-up

Figure 3-2: Canola oil biodiesel (top layer) and glycerol (bottom layer) synthesized in the presence of calcium oxide catalyst

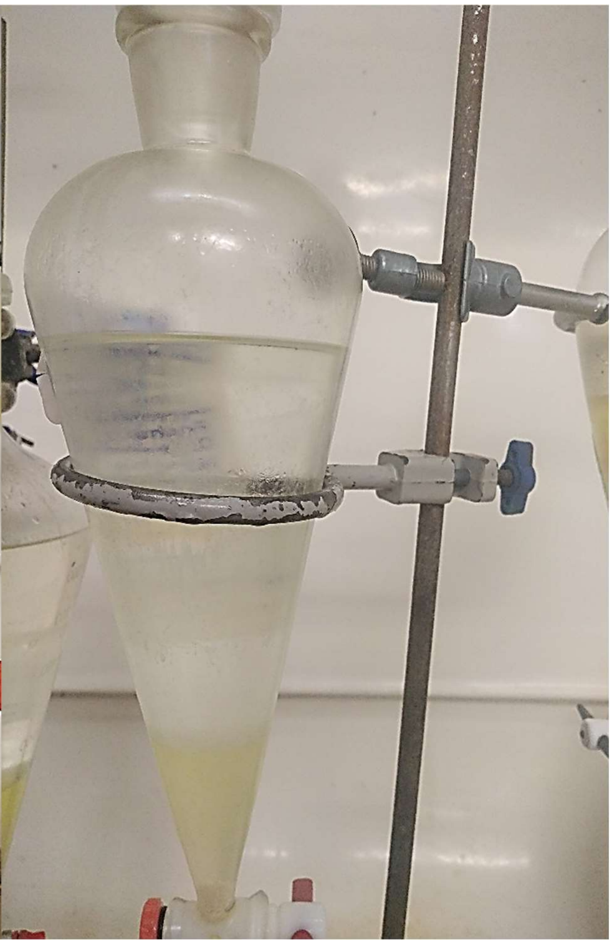


Figure 3-3: Canola oil biodiesel (top layer) and glycerol (bottom layer) synthesized in the presence of magnesium oxide catalyst

3.2 Experimental Design

A Box-Behnken design (BBD) was employed in this study. A Box-Behnken design with a response surface method (RSM) was used to analyze the influence of the process variables in the transesterification reaction and therefore used to optimize the process variables to attain a maximized biodiesel yield with good fuel characteristics. According to Ferreira, et al. (2007) the Box-Behnken design easily estimates regression parameters for a full quadratic model and permits the building of sequential designs by the use of multiple blocks. In addition, the design is able to determine the lack-of-fit of the model to the data set. A geometric view of the Box-Behnken design can be seen below in figure 3-4.

From literature, it was found that the most common approach for optimization of the process variables in a transesterification reaction was performed through the one-variable-at-a-time (OVAT) method. Since only one variable can be changed at a time while other variables are kept constant, a large number of experiments would be required to be performed, which is time-consuming and not economically feasible. Thus, in order to eliminate problems associated with the OVAT method, the Box-Behnken design was selected for this study. By adopting a statistical design of experiments such as the BBD, the number of experimental trials are reduced, the process variables can vary simultaneously, and the interaction between the process variables can systematically be studied, which is not possible with the OVAT method.

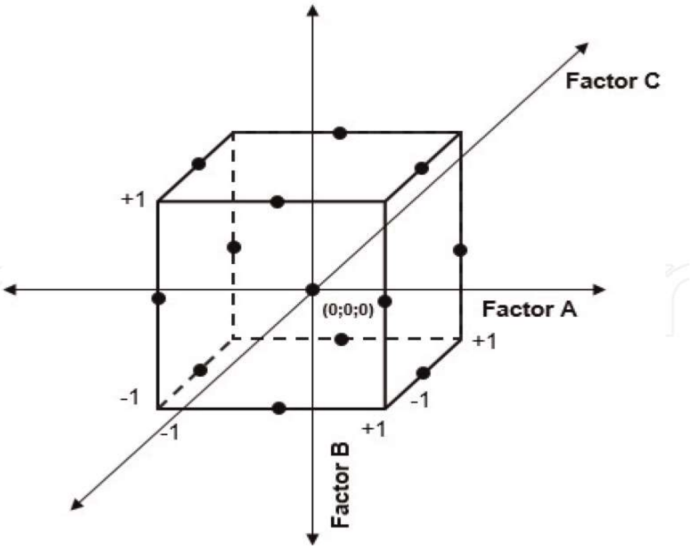


Figure 3-4: Geometric view of Box-Behnken design (Peixoto, et al., 2018)

The required number of experimental runs for the Box-Behnken design is determined as follows (Ferreira , et al., 2007)

$$\mathrm{N} = 2\mathrm{k}(\mathrm{k} - 1) + \mathrm{C_p} \qquad [3.2]$$

Where N represents the number of experiments, k the number of factors, and C_p the number of central points. Therefore, the number of experimental runs required for a BBD with 4 factors (process variables) and 3 central points is determined as:

$$\mathrm{N} = 2 \times 4(4 - 1) + 3 = 27 \text{ experimental runs}$$

Minitab software (version 17) was used to develop the experimental design and therefore used to optimize the results. Four independent factors were varied in the design, which included reaction temperature, reaction time, alcohol to oil molar ratio, and catalyst loading. Tables 3-6 and 3-7 show the experimental conditions for each of the 27 runs for calcium oxide and magnesium oxide, respectively. The 27 experimental runs which were also inclusive of 3 replicates (highlighted in bold) which helped increase the precision of the results. The experimental runs generated were randomized in order to reduce experimental error.

Table 3-6: Box-Behnken experimental design for the transesterification of canola oil in the presence of CaO catalyst

Run Order	**Temperature (°C)**	**Catalyst Loading (wt%)**	**Alcohol/Oil Molar Ratio**	**Time (min)**
1	30	0.5	14	75
2	70	0.5	14	75
3	30	1.5	14	75
4	70	1.5	14	75
5	50	1	8	30
6	50	1	20	30
7	50	1	8	120
8	50	1	20	120
9	30	1	14	30
10	70	1	14	30
11	30	1	14	120
12	70	1	14	120
13	50	0.5	8	75
14	50	1.5	8	75
15	50	0.5	20	75
16	50	1.5	20	75
17	30	1	8	75
18	70	1	8	75
19	30	1	20	75
20	70	1	20	75
21	50	0.5	14	30
22	50	1.5	14	30
23	50	0.5	14	120
24	50	1.5	14	120
25	**50**	**1**	**14**	**75**
26	**50**	**1**	**14**	**75**
27	**50**	**1**	**14**	**75**

Table 3-7: Box-Behnken experimental design for the transesterification of canola oil in the presence of MgO catalyst

Run Order	Temperature (°C)	Catalyst Loading (wt.%)	Alcohol/Oil Molar Ratio	Time (min)
1	50	1.5	8	120
2	50	2	20	75
3	30	1.5	20	75
4	50	1	20	75
5	70	2	14	75
6	70	1.5	8	75
7	50	1	14	30
8	50	1.5	20	120
9	50	2	14	30
10	**50**	**1.5**	**14**	**75**
11	70	1.5	14	120
12	30	2	14	75
13	50	2	8	75
14	70	1	14	75
15	70	1.5	14	30
16	50	1.5	20	30
17	70	1.5	20	75
18	30	1	14	75
19	50	1	8	75
20	30	1.5	14	30
21	50	1	14	120
22	**50**	**1.5**	**14**	**75**
23	50	1.5	8	30
24	30	1.5	14	120
25	30	1.5	8	75
26	50	2	14	120
27	**50**	**1.5**	**14**	**75**

3.3 Experimental method

Firstly, the acid value of canola oil was determined via titrations in accordance with the ASTM standard methods. The titrations were performed in triplicate for precision in the results. The acid value was used to further calculate the weight percentage of free fatty acid present in the oil. Since the FFA wt.% of canola oil was found to be < 0.5 wt. % no pre-treatment (esterification) was required, only a single-step transesterification reaction.

It is important to note that 27 runs were generated for each catalyst using the Box-Behnken experimental design. These runs were conducted in triplicate and averaged for increased accuracy of the results. The following steps were performed for the transesterification of canola oil reacting with ethanol in the presence of either calcium oxide or magnesium oxide catalysts respectively:

- Using a volumetric cylinder and a scale, 224.17 g of canola oil was weighed. This mass corresponds to a volume of 250 mL.
- The number of moles of canola oil used was calculated and therefore multiplied by the selected alcohol to oil molar ratio in order to determine the number of moles of ethanol required. From the number of moles of ethanol, the mass of ethanol required was determined using its molar mass.
- The required masses of canola oil and ethanol were placed in separate 600 mL beakers.
- Prior to starting the respective experiment, the calcination of calcium oxide was done at 600 °C for 3 hours and calcination of magnesium oxide was done at 800 °C for 2 hours in a muffle furnace and thereafter placed in a desiccator under vacuum conditions with desiccant present.
- As per the reaction conditions shown from the Box-Behnken design generated, the necessary amount of catalyst was weighed out; added to the ethanol, and therefore mixed.
- The ethanol with catalyst mixture was placed on a hot plate and only added to the oil once the desired reaction temperature was reached. The temperature of the mixture was controlled by the hot plate and monitored with a thermometer.
- Once the heated ethanol and catalyst mixture was added to the heated oil, the beaker was sealed with parafilm.
- When the reaction time had elapsed, the mixture was poured into a separation funnel and was left to settle by gravity overnight.
- Upon observation of the mixture in the separation funnel presented two distinct layers. The less-dense biodiesel was the top layer and more dense glycerol settled at the bottom.
- Glycerol was decanted out of the separation funnel. The remaining biodiesel was washed with hot water to remove impurities. Washing was done until the bottom wash water layer was almost clear.

- In order to separate any catalyst still present in the biodiesel, centrifugation was conducted. Centrifugation was performed at 6000 rpm for 15 minutes.
- After water washing and centrifugation, the biodiesel was further purified using a rotary evaporator at a temperature of 90 °C and pressure of 150 mbar
- After removing excess ethanol and wash water in the rotary evaporator, the biodiesel was left to cool down and therefore weighed.
- The mass of biodiesel was therefore recorded and used to calculate the overall yield of biodiesel produced in accordance to Fereidooni, et al. (2017) equation as follows:

$$\text{Yield} = \frac{\text{Mass of biodiesel produced}}{\text{Mass of oil used}} \qquad [3.3]$$

- After all experimental runs were completed, the yields obtained were recorded and optimized to obtain the optimum process conditions.
- The maximized yield obtained at the optimum process conditions was subjected to GC-MS analysis to validate the production of biodiesel and check its composition.

Chapter 4 Calcium Oxide Catalyzed Transesterification Results and Discussion

This chapter focuses on the synthesis of biodiesel via heterogeneously-catalyzed transesterification. Canola oil was selected for this study. Canola seeds contain approximately between 40-45% oil which is relatively high in comparison to other oilseeds (Ge & Choi, 2017). Preliminary property testing conducted on canola oil showed that it is a suitable candidate for biodiesel production. Canola oil resulted in having a very low acid value of 0.084 $\frac{mg\ KOH}{g}$; which indicated that it can easily be transesterified by a base-catalyst and a pretreatment step such as esterification would not be necessary, thus reducing the cost of biodiesel production. Calcium oxide catalyst was chosen for this study because it is eco-friendly, cost-effective, promotes long catalyst life, has high activity and moderate reaction conditions. Furthermore, calcium oxide can be synthesized from natural calcium-rich waste materials, therefore promoting an effective green process (Thangaraj, et al., 2019). Response surface methodology (RSM) combined with Box-Behnken design was used to model the design of the experiment, perform statistical analysis, and optimize the biodiesel yield.

Table 4-1 below displays a summary of the measured physical properties of canola oil. Table 2-10 on page 29 exhibits the FFA % recommendations from previous research conducted using base-catalyzed transesterification. Canola oil had a low acid value and therefore a low free fatty acid content of 0.042% which falls below the limits displayed in table 2-10, therefore making it acceptable for base-catalyzed transesterification. In this study, canola oil was reacted with ethanol while calcium oxide catalyzed the transesterification reaction.

Table 4-1: Summary of canola oil properties

Property	
Acid value $\left(\frac{mg\ KOH}{g}\right)$	0.084
Density $\left(\frac{kg}{m^3}\right)$	916
Free fatty acid (%)	0.042
Dynamic (absolute) viscosity (cP)	54.5

As mentioned previously, the Box-Behnken design method was employed to determine the optimum reaction conditions which would produce a maximized biodiesel yield. The Box-Behnken design method was executed on Minitab statistical software (version 17). The parameters that were varied in the experimental design included reaction temperature, catalyst loading, alcohol to oil molar ratio, and reaction time. It is recommended that the reaction temperature should not exceed the boiling point of the alcohol during the transesterification reaction and since the boiling point of ethanol is 78.37°C, the reaction temperature was varied from 30°C to 70°C. If the reaction temperature exceeded the boiling point of ethanol; vaporization of ethanol would occur and consequently decrease the contact between the alcohol and oil (Sharma, et al., 2008). The catalyst loading was ranged between 0.5 wt. % of oil to 1.5 wt. % of oil. The transesterification reaction stoichiometry suggests 3 moles of alcohol per mole of vegetable oil would be required to synthesize 3 moles of biodiesel and 1 mole of glycero1. However, since the reaction is reversible, an excess amount of alcohol is generally required to shift its equilibrium to the right and drive the reaction forward. Therefore, the alcohol to oil molar ratio was varied from 8:1 to 20:1. An excess amount of alcohol aids the dissolution of water produced from the reaction (Fereidooni, et al., 2017). Moreover, higher molar ratios enhance the miscibility as well as increases the contact between the alcohol and oil molecules (Mishra & Goswami, 2017). The reaction time was varied between 30 minutes to 120 minutes. According to a study conducted by Freedman, et al. (1986), as time increased so did the conversion of triglycerides, the maximum conversion was reached in less than 90 minutes. However, the vegetable oils used in the study were different, therefore, in this study a maximum reaction time of 120 minutes was selected to cover a wider range.

The response surface Box-Behnken design generated 27 experimental runs in total, three of which were replicated. Upon completing all the required experiments, Minitab was utilized to fit a regression equation to the data. The results obtained from the 27 experimental runs are shown in table 4-2 using coded variables. The coded variables are as follows:

A: Reaction temperature (°C)

B: Catalyst loading (%)

C: Alcohol to oil molar ratio

D: Reaction time (min)

Table 4-2: Canola oil with calcium oxide transesterification results

Run Order	**A**	**B**	**C**	**D**	**Experimental Yield**	**Predicted Yield**
1	30	0.5	14	75	0.8560	0.8642
2	70	0.5	14	75	0.9156	0.9239
3	30	1.5	14	75	0.7978	0.7901
4	70	1.5	14	75	0.7358	0.7282
5	50	1	8	30	0.8160	0.7930
6	50	1	20	30	0.8624	0.8374
7	50	1	8	120	0.6092	0.6348
8	50	1	20	120	0.9019	0.9255
9	30	1	14	30	0.8694	0.8886
10	70	1	14	30	0.9272	0.9340
11	30	1	14	120	0.9139	0.9001
12	70	1	14	120	0.8787	0.8525
13	50	0.5	8	75	0.8585	0.8293
14	50	1.5	8	75	0.4203	0.4640
15	50	0.5	20	75	0.8170	0.7664
16	50	1.5	20	75	0.8397	0.8619
17	30	1	8	75	0.7733	0.7586
18	70	1	8	75	0.5990	0.5966
19	30	1	20	75	0.7565	0.7653
20	70	1	20	75	0.9040	0.9251
21	50	0.5	14	30	0.9234	0.9629
22	50	1.5	14	30	0.8153	0.7979
23	50	0.5	14	120	0.8740	0.8978
24	50	1.5	14	120	0.8260	0.7929
25	50	1	14	75	0.8621	0.8602
26	50	1	14	75	0.8311	0.8602
27	50	1	14	75	0.8875	0.8602

Table 4-2 on page 63 shows that the lowest experimental yield was obtained in run 14 which produced a yield of 0.4203 at a reaction temperature of 50 °C, a catalyst loading of 1.5 wt. % oil, an alcohol to oil molar ratio of 8:1, and a reaction time of 75 minutes, while the highest experimental yield was achieved in run 10 which synthesized a biodiesel yield of 0.9272 at a reaction temperature of 70 °C, a catalyst loading of 1 wt.% oil, an alcohol to oil molar ratio of 14:1, and a reaction time of 30 minutes. The low biodiesel yield obtained in run 14 can be attributed to the low alcohol to oil ratio in combination with the high amount of catalyst loading which promoted soap formation. The formation of soap was observed during the reaction, and this became more apparent during the water washing process. This increased the degree of difficulty during the separation of biodiesel from glycerol and even after decanting, therefore resulting in a reduced biodiesel yield. The high yield achieved in experimental run 10 can be attributed to the sufficient alcohol to oil molar ratio of 14:1, which was sufficient to shift the reactions equilibrium to the right and drive the reaction forward. The catalyst loading of 1 wt.% resulted in a negligible amount of soap formation, hence improving the yield without hindering the production and separation processes.

Table 4-3: Canola oil with calcium oxide transesterification model summary

Model	**R^2**	**R^2 (adjusted)**	**R^2 (predicted)**	**S**
Linear	0.4181	0.3123	0.0926	0.0950
Linear + squares	0.6582	0.5063	0.2310	0.0805
Linear + interactions	0.7141	0.5355	0.0894	0.0780
Full quadratic	0.9543	0.9009	0.7531	0.0360

The coefficient of determination (R^2) is an indication of the goodness-of-fit between the experimental data and the regression equation (Jiyane, et al., 2018). According to Joglekar & May (1987) an R^2 value of at least 0.8 is indicative of a good model fit. Table 4-3 exhibits that only the full quadratic model has an R^2 value greater than 0.8. Halder, et al. (2015) reported that if the difference between the R^2 and the adjusted R^2 is less than 0.1, this would signify the reliability of the model. The difference between the R^2 and the adjusted R^2 values for the full quadratic model is 0.0534, thus, indicating that the full quadratic model provides a good fit to the data attained. The full quadratic response model with an R^2 value of 0.9543 and an adjusted R^2 value of 0.9009 at a confidence level of 95% can sufficiently explain the calcium oxide catalyzed transesterification reaction. The predicted R^2 value of 0.7531 specifies that outside the range of this study the regression model may only be approximately 75% accurate in predicting the biodiesel yield.

Figure 4-1 on page 66 displays the experimental biodiesel yields obtained against the predicted model. The majority of the actual values lie close to the 45-degree line (predicted model), thus demonstrating a high degree of correlation between the experimental and predicted values. The coefficient of determination (R^2) of 0.9543 suggests that only approximately 4.57% of the total variation is unaccounted for by the model. The predicted R^2 value being lower than the R^2 and the adjusted R^2 values are indicative of the model being tailored specifically to the data attained in this study, therefore the model can be utilized to accurately predict the yield of biodiesel strictly in the range of this study. The standard deviation is represented by the S-value as depicted in table 4-3. The S-value indicates the distance between the experimental data values and the fitted values. The S-value of 0.0360 indicates that the data points deviation is low from the predicted response, further emphasizing that the regression equation fits the experimental data well. Table 4-4 on page 67 shows a very low probability (p-value) of 0 and a high F-value of 17.89 at a 95% confidence level, this indicates the full quadratic model is significant. According to Ye, et al (2017) for a confidence level of 95%, a p-value less than 0.05 indicates the developed models are statistically significant. The lower p-values imply that the variable plays a more important role in affecting the response and a p-value greater than 0.1 is indicative of an insignificant model.

The full quadratic regression equation is shown below using coded variables:

$$\begin{aligned}\text{Yield} = {} & 1.306 - 0.0041\text{A} - 0.312\text{B} + 0.0008\text{C} - 0.00555\text{D} - 0.000003\text{A}^2 - 0.1292\text{B}^2 \\ & - 0.002709C^2 + 0.000017D^2 - 0.00304\text{AB} + 0.00067\text{AC} - 0.000026\text{AD} \\ & + 0.03841\text{BC} + 0.000668\text{BD} + 0.000228\text{CD}\end{aligned} \quad [4.1]$$

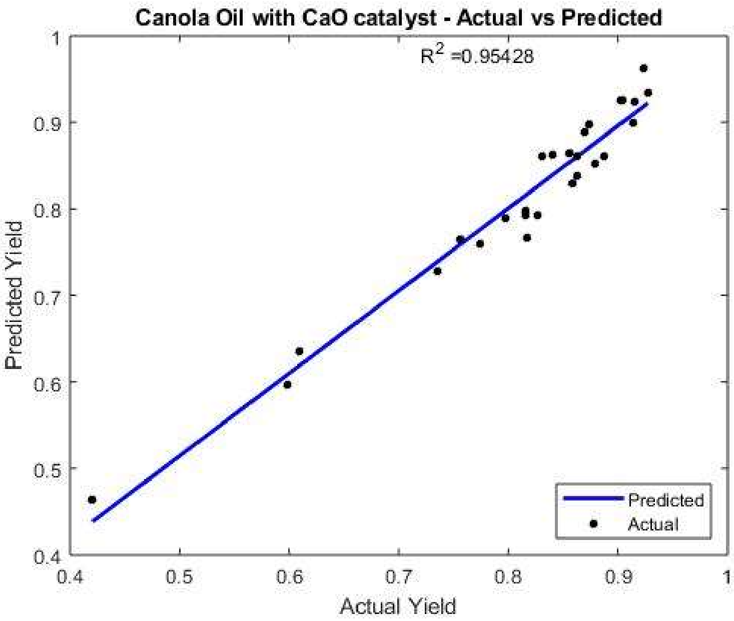


Figure 4-1: Model predicted yield vs actual yield for canola oil biodiesel produced in the presence of CaO catalyst

Table 4-4: Full quadratic model analysis of variance (ANOVA) for canola oil transesterification in the presence of CaO catalyst

Analysis of Variance						
Source	Degrees of freedom	Sum of squares	Mean squares	F-value	P-value	Significance
Model	14	0.325282	0.023234	17.89	0.000	Significant
Linear	4	0.142502	0.035625	27.43	0.000	Significant
A	1	0.000004	0.000004	0.00	0.959	Not significant
B	1	0.054621	0.054621	42.06	0.000	Significant
C	1	0.084202	0.084202	64.84	0.000	Significant
D	1	0.003675	0.003675	2.83	0.118	Not significant
Square	4	0.081856	0.020464	15.76	0.000	Significant
A^2	1	0.000010	0.000010	0.01	0.933	Not significant
B^2	1	0.005569	0.005569	4.29	0.061	Slightly significant
C^2	1	0.050713	0.050713	39.05	0.000	Significant
D^2	1	0.006510	0.006510	5.01	0.045	Slightly significant
2-way interaction	6	0.100924	0.016821	12.95	0.000	Significant
AB	1	0.003697	0.003697	2.85	0.117	Not significant
AC	1	0.025889	0.025889	19.94	0.001	Significant
AD	1	0.002162	0.002162	1.67	0.221	Not significant
BC	1	0.053107	0.053107	40.90	0.000	Significant
BD	1	0.000903	0.000903	0.70	0.421	Not significant
CD	1	0.015166	0.015166	11.68	0.005	Significant
Error	12	0.015583	0.001299			
Lack-of-fit	10	0.013987	0.001399	1.75	0.417	Not significant
Pure error	2	0.001596	0.000798			
Total	26	0.340865				

Analysis of variance (ANOVA) is a statistical tool used to detect the importance of a model and its parameters (Qiu, et al., 2014). ANOVA results are displayed in table 4-4 for the full quadratic model. By looking at the coefficients for the linear terms, it can be seen that the reaction temperature (A) and reaction time (D) are statistically insignificant, this indicates that these two process variables do not have a significant impact on the calcium oxide transesterification reaction as proposed by the regression model. It can be noted that the coefficients for the quadratic terms are either significant or slightly significant except for the reaction temperature (A) which has a probability of 0.933 indicating that the quadratic term for temperature (A) does not impact the yield predicted by the regression model significantly in comparison to the quadratic coefficients of the other variables. It can further be noted that the interactions between reaction temperature (A) and catalyst loading (B), reaction temperature (A) and reaction time (D), as well as catalyst loading (B) and reaction time (D), are all statistically insignificant as they have probabilities greater than 0.1. This suggests that the interactions between the aforementioned variables are not as significant in comparison to the three other interactions which are highly significant in predicting the biodiesel yield in the quadratic model. Further validation of the model is noted by the model's lack-of-fit which has an insignificant p-value of 0.417, which confirms the model fits the data well. The inclusion of the terms that were not significant in the model attributed to a lower predicted R^2 value of 0.7531. The predicted R^2 value could be improved by modification by the removal of the insignificant terms in the model, however, the predicted R^2 value is only slightly lower than the recommended value of 0.8, and the purpose of this study was aimed around understanding how the process variables within the range of this study affect the production of biodiesel, therefore the model obtained is still deemed a good fit for the data. Moreover, modification of the obtained model will not necessarily mean that the model can be used to predict biodiesel yields outside the range of this study, further experiments are required to validate this.

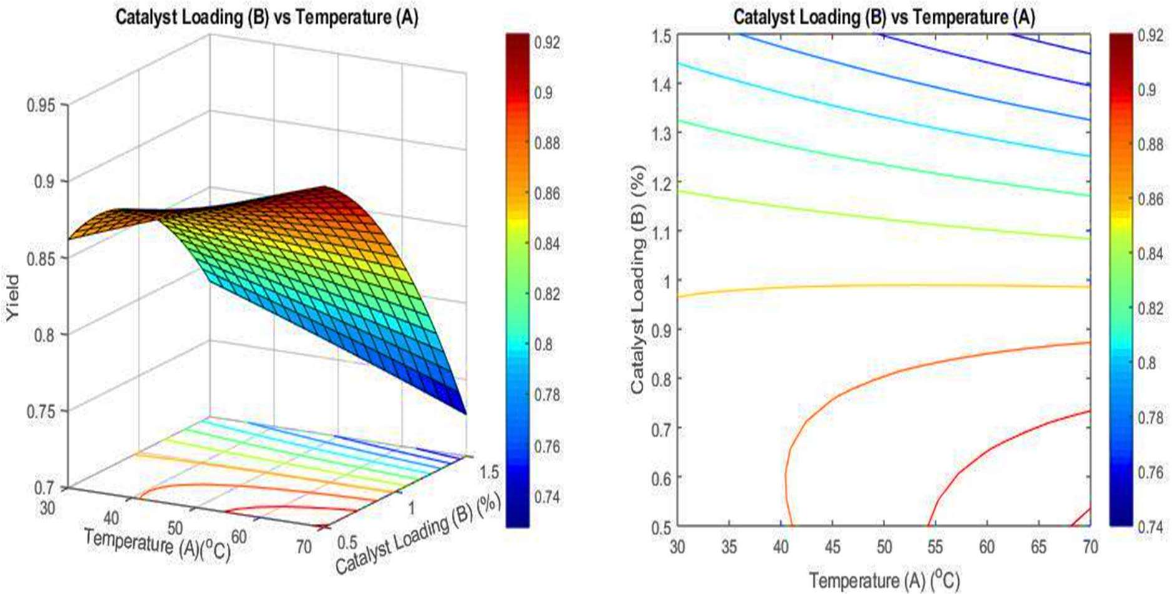
Minitab statistical software was used to generate the optimal conditions to maximize the response (biodiesel yield) in the calcium oxide catalyzed transesterification process. The optimized process conditions are shown below in table 4-5:

Table 4-5: Optimized process conditions for calcium oxide transesterification

Parameters	Optimal result
A - Reaction temperature (℃)	65.73
B - Catalyst loading (wt. %)	0.68
C - Alcohol/oil molar ratio	15.23
D - Reaction time (mins)	55.52
Experimental yield	0.9380
Predicted yield	0.9354

The optimum yield predicted by Minitab statistical software was 0.9354, while the experiment conducted under the proposed optimized conditions produced a biodiesel yield of 0.9380. This supports the fact that the model fits the data well since the percentage difference between the actual and predicted optimal yields is 0.26%.

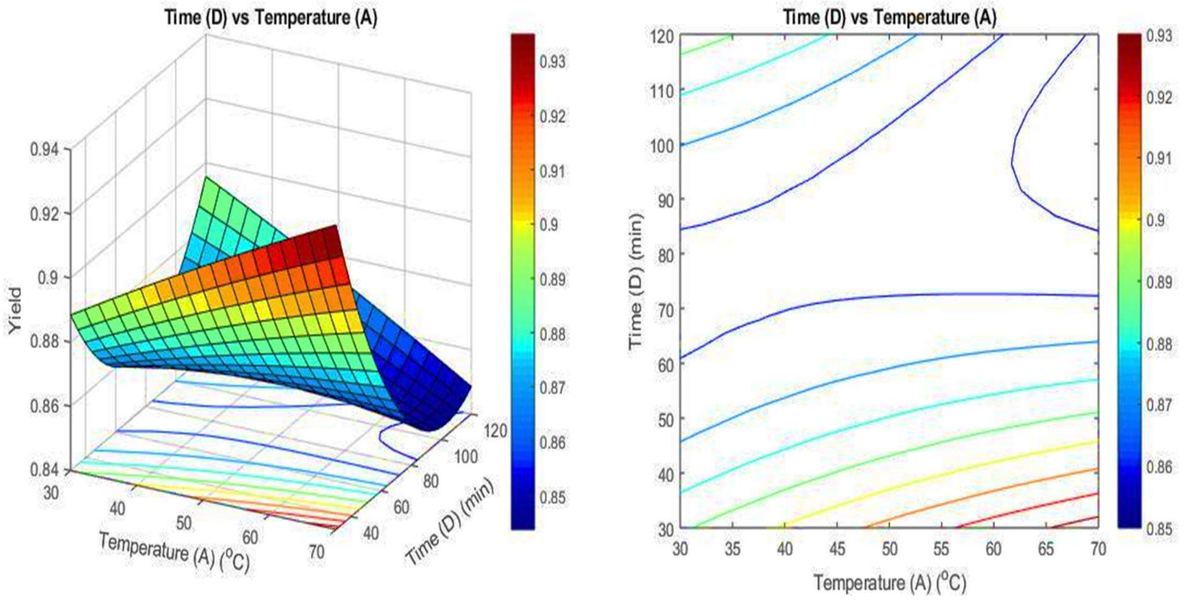
The 2-way interactions between process variables on the biodiesel yield synthesized from canola oil in the presence of calcium oxide catalyst are demonstrated from figures 4-2 to 4-7. Each plot depicts the effect of two process variables across their range within the study, while the two other variables were kept constant at their median values (the median values were 50°C for temperature, 1 wt.% for catalyst loading, 75 minutes for reaction time, and 1:14 for the oil to alcohol molar ratio). The response surface portrays the tendency of each process variable to influence the biodiesel yield. The shape of each contour plot is an indication of the extent and nature of the interactions between the process variables. A contour plot with a circular contour is indicative of an interaction that is insignificant, while a significant interaction is indicated by an elliptical contour (Qiu, et al., 2014).



(a) (b)

Figure 4-2: (a) Response surface showing the effect of catalyst loading (wt.%) and temperature (℃) on biodiesel yield produced using CaO, (b) contour plot showing the effect of catalyst loading (wt.%) and temperature (℃) on biodiesel yield produced using CaO

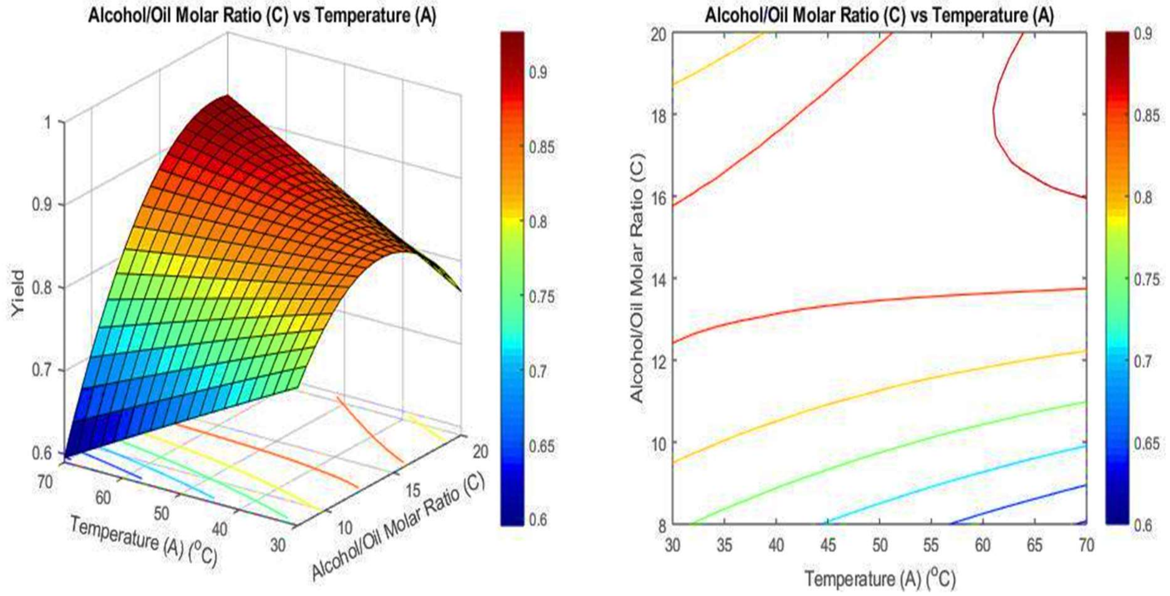
A three-dimensional interaction between catalyst loading and reaction temperature is illustrated in figure 4-2(a). It can be seen that as the reaction temperature increases the yield of biodiesel simultaneously increases, and as the catalyst loading increases the biodiesel yield decreases. Gashaw & Teshita (2014) reported high quantities of alkali catalysts promoting soap formation, this indicates why the biodiesel yield decreases with an increase in catalyst loading. The transesterification reaction is reversible and endothermic in nature; therefore, the reaction favors high temperatures (Lie, et al., 2019). According to Le Chatelier's principle; an endothermic reversible reaction favors the forward reaction; this explains the increase in yield with an increase in temperature. It can be noted that when lower catalyst loadings are used in combination with high reaction temperatures; higher biodiesel yields were attained. Figure 4-2(b) indicates the interaction between reaction temperature and catalyst loading significantly influences the conversion of triglycerides to fatty acid ethyl esters.



(a) (b)

Figure 4-3: (a) Response surface showing the effect of time (min) and temperature (℃) on biodiesel yield produced using CaO, (b) Contour plot showing the effect of time (min) and temperature (℃) on biodiesel yield produced using CaO

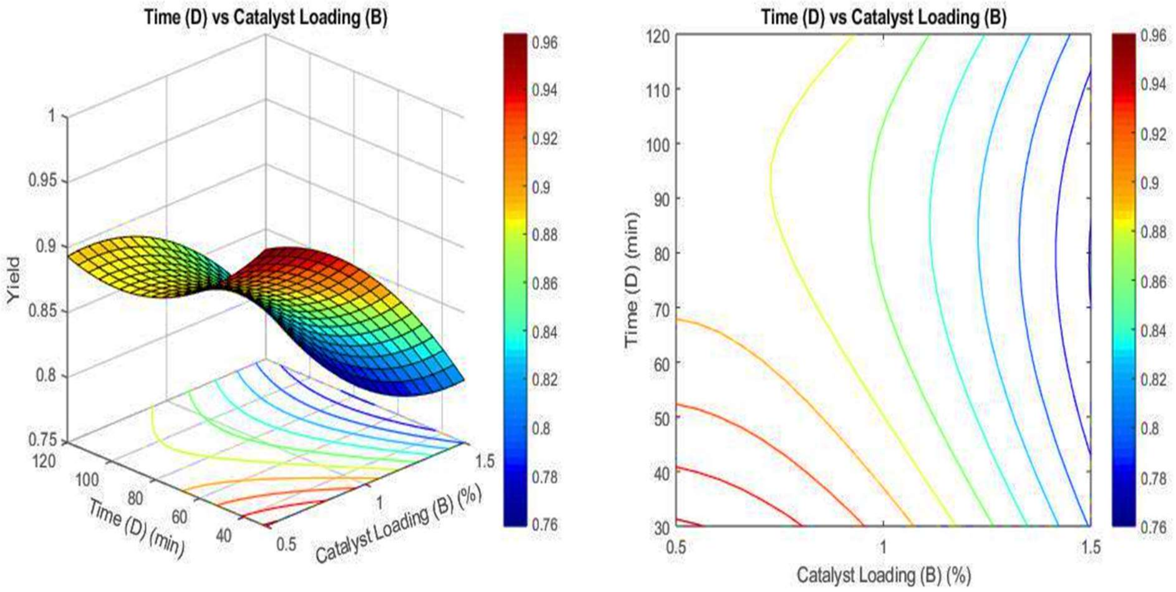
Figure 4-3(a) demonstrates the interaction between reaction temperature and reaction time on the yield of biodiesel. It can be seen that the highest yields were obtained at high reaction temperatures with short reaction times (30 minutes), this can be attributed to the high temperature increasing the rate of reaction, thereby shortening the reaction time due to the reduction in the viscosity of oil (Omar & Amin, 2011). Since the transesterification reaction is reversible, longer reaction times result in a reduced biodiesel yield due to loss of esters (ester hydrolysis), which favors the reverse reaction and causes fatty acids to form soap (Eevera, et al., 2009), this clarifies why the yield decreases over longer reaction times. Figure 4-3(b) indicates that the interaction between the reaction temperature and the reaction time has a significant impact on the yield of biodiesel.



(a) (b)

Figure 4-4: (a) Response surface showing the effect of alcohol/oil molar ratio and temperature (℃) on biodiesel yield produced using CaO, (b) contour plot showing the effect of alcohol/oil molar ratio and temperature (℃) on biodiesel yield produced using CaO

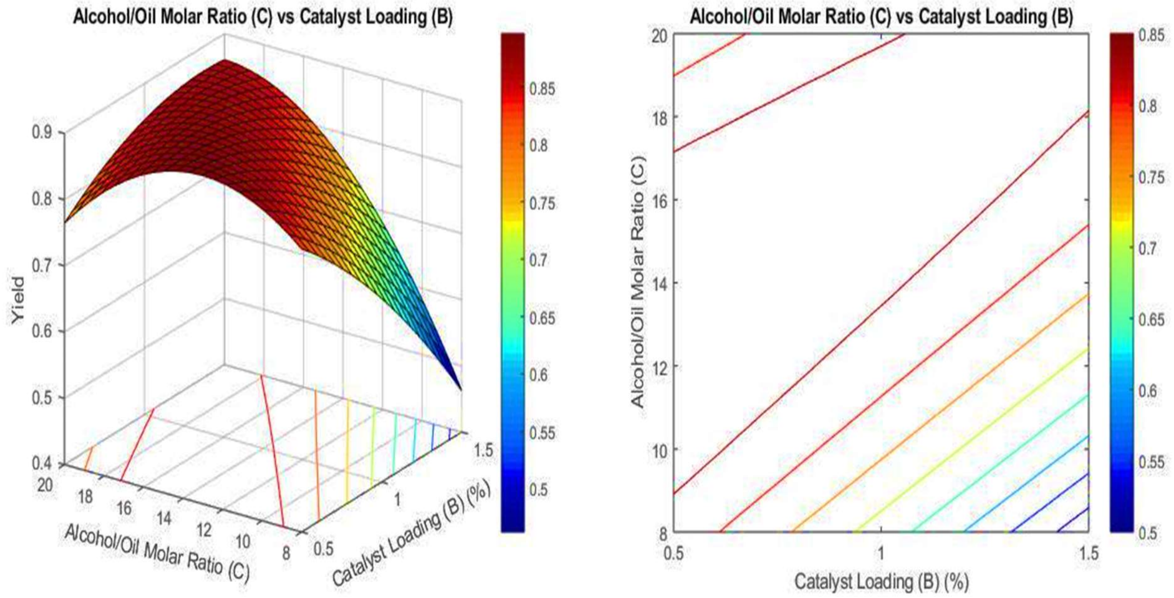
The effect of the interaction between the alcohol to oil molar ratio and reaction temperature on the biodiesel yield is exhibited in figure 4-4(a). From the response surface plot, it can be seen that the highest yields were achieved at ethanol to oil molar ratios between 12:1 and 16:1 in combination with high reaction temperatures. The endothermic nature of the transesterification reaction decreases the dielectric constant of ethanol due to the weakening of the hydrogen bonding in the alcohol, which therefore makes the oil miscible with ethanol and the reaction mixture, thus resulting in an increase in the recovery of fatty acid ethyl esters (Gunawan, et al., 2014). When lower ethanol/oil ratios were used in combination with high reaction temperatures, low yields were synthesized due to insufficient alcohol present, thus the reaction does not proceed to completion. Furthermore, high reaction temperatures may have also evaporated ethanol which reduces the contact between alcohol and oil (Eevera, et al., 2009), which explains why low yields were attained at lower ratios. Figure 4-4(b) the contour plot indicates that the interaction between alcohol/oil molar ratio and reaction temperature has a significant effect on the production of biodiesel from canola oil in the presence of CaO catalyst.



(a) (b)

Figure 4-5: (a) Response surface showing the effect of time (min) and catalyst loading (wt.%) on biodiesel yield produced using CaO, (b) contour plot showing the effect of time (min) and catalyst loading on biodiesel yield produced using CaO

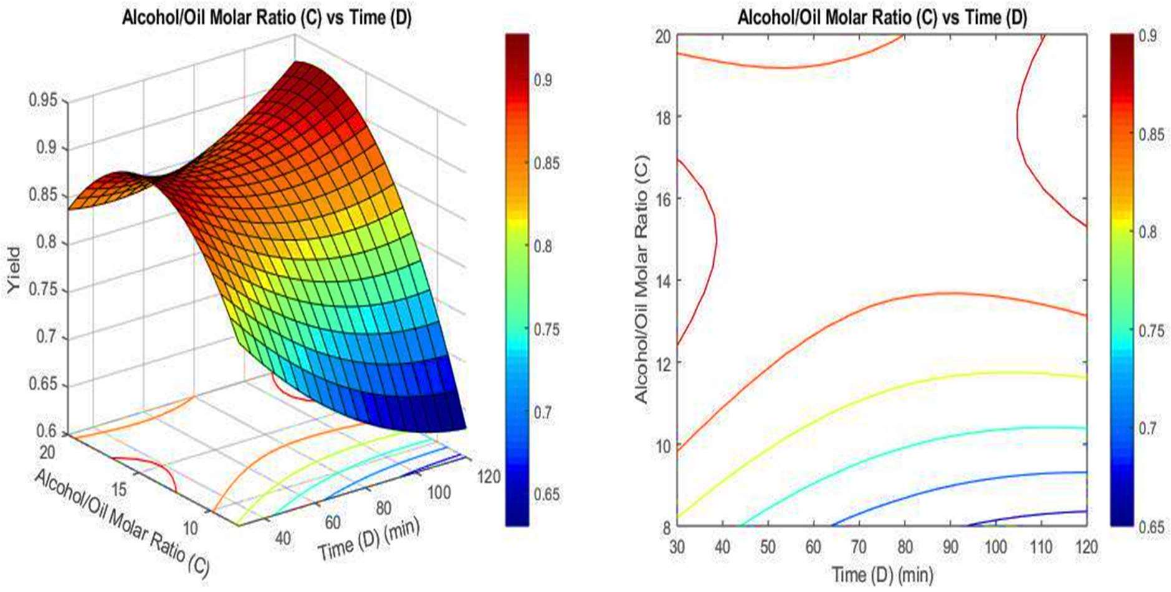
The three-dimensional response surface plot in figure 4-5(a) exhibits the interaction between reaction time and catalyst loading on the yield of biodiesel. It can be observed that the lowest biodiesel yields were obtained at high catalyst loadings and lengthy reaction times. This can be attributed to excess calcium oxide causing more triglycerides to participate in the saponification reaction which resulted in a reduction of ester yield (Leung & Guo, 2006), while more glycerol forms over time which tends to dissolve in ethanol reducing the rate of the forward reaction. Overall, long reaction times coupled with high catalyst loadings should be avoided due to the excess of these variables promoting the reverse reaction and soap formation (Eevera, et al., 2009). Figure 4-5(b) displays a circular nature in the contour plot indicating the interaction does not significantly influence the conversion of triglycerides to fatty acid ethyl esters.



(a) (b)

Figure 4-6: (a) Response surface showing the effect of alcohol to oil molar ratio and catalyst loading (wt.%) on biodiesel yield produced using CaO, (b) contour plot showing the effect of alcohol to oil molar ratio and catalyst loading on biodiesel yield produced using CaO

The response surface plot in figure 4-6(a) illustrates how the interaction between alcohol/oil molar ratio and catalyst loading affects the yield of biodiesel. As the alcohol to oil molar ratio increases, the biodiesel ester yield increases but only up to a point, thereafter as the ratio increases the yield decreases. It can be noted that high yields were obtained at lower catalyst loadings. An increase in catalyst loading resulted in a decrease in the yield of biodiesel. A sufficient amount of catalyst and ethanol is necessary to drive the transesterification reaction forward, however, increasing both these process variables beyond optimal conditions favors the reverse reaction and results in soap formation, and thus, a reduced yield is obtained. Figure 4-6(b) reveals no interaction between alcohol to oil molar ratio and catalyst loading.



(a) (b)

Figure 4-7: (a) Response surface showing the effect of alcohol to oil molar ratio and time (min) on biodiesel yield produced using CaO, (b) contour plot showing the effect of alcohol to oil molar ratio and time (min) on biodiesel yield produced using CaO

A visual illustration of the effect of the interaction between alcohol to oil molar ratio and reaction time on the ester yield synthesized in the presence of CaO catalyst can be seen in figure 4-7(a). From observation, a combination of lengthy reaction times and low alcohol to oil molar ratios result in the lowest yields. This combination should be avoided as it significantly hinders the forward reaction. The long reaction times (reaction times beyond an optimal point) result in reduced yields due to the loss of esters (ester hydrolysis), which favors the reverse reaction and causes fatty acids to form soap (Eevera, et al., 2009), while there is also insufficient alcohol available to shift the equilibrium to the right and drive the reaction forward and thus, reduced biodiesel yields are obtained. Figure 4-7(b) depicts the interaction between alcohol to oil molar ratio and reaction time significantly impacts the biodiesel yield.

The majority of the response surface plots had a parabolic effect where the yield would increase to an optimal point, and thereafter decrease with further increases in the process variables. The response surface trends produced in this study are aligned with the findings of Gashaw & Teshita (2014), Lie, et al. (2019), Gunawan, et al. (2014), Omar & Amin (2011), Evera, et al. (2009), and Kafuku & Mbarawa (2010).

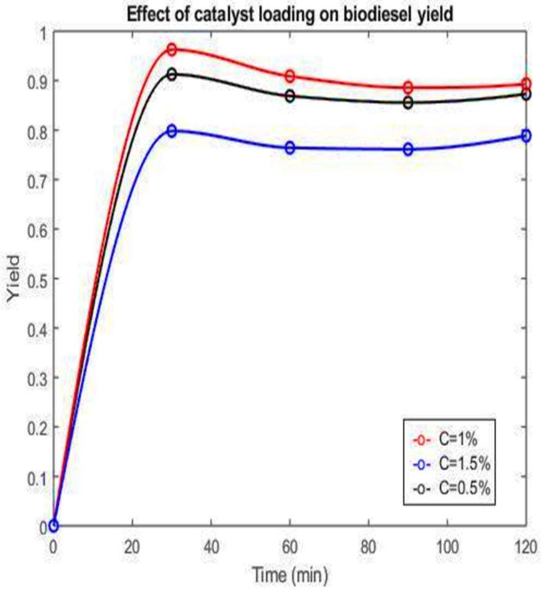


Figure 4-8: *Effect of catalyst loading (wt.%) on biodiesel yield produced from canola oil in the presence of CaO*

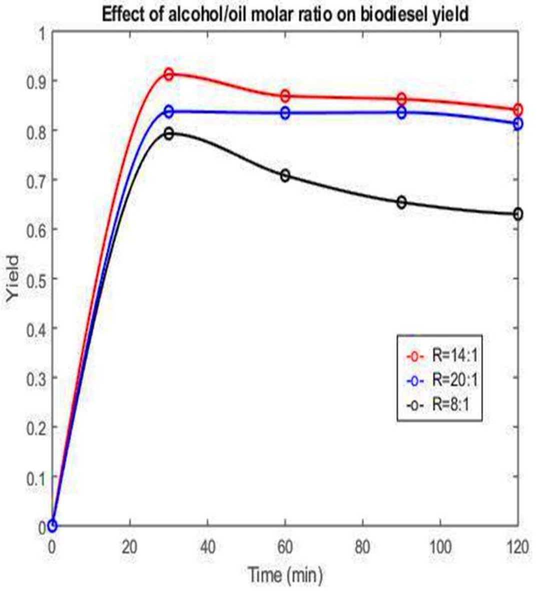


Figure 4-9: Effect of alcohol to oil molar ratio on biodiesel yield produced from canola oil in the presence of CaO

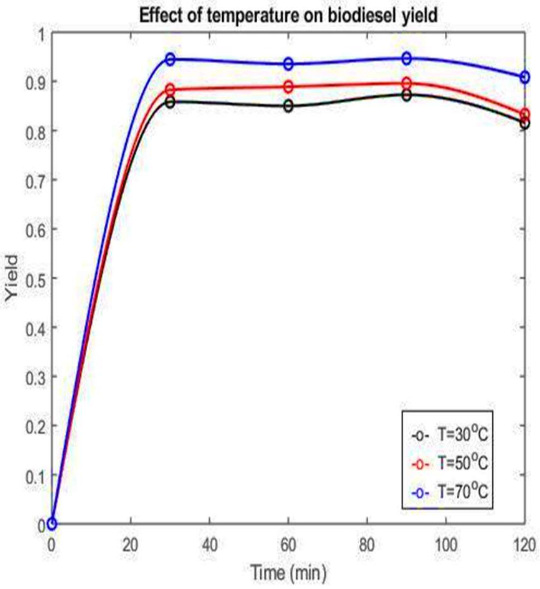


Figure 4-10: Effect of temperature (℃) on biodiesel yield produced from canola oil in the presence of CaO

Figures 4-8 to 4-10 illustrate interaction plots which were attained by varying only one variable in order to display the effect it has on the yield of biodiesel against time, while the remaining variables were kept constant at their median values. The median values are as follows:

Reaction temperature: 50 °C
Catalyst loading: 1 wt.%
Alcohol to oil molar ratio: 14:1
Reaction time: 75 min
This was done to understand the interaction between the variables at different levels.

Figure 4-8 shows that increasing the catalyst loading from 0.5 wt.% to 1 wt.% resulted in an increase in biodiesel yield attained, whereas a further increase in catalyst loading to 1.5 wt.% resulted in a reduction in biodiesel yield. This is due to catalyst loading exceeding the optimal quantity for biodiesel production which promotes soap formation. Gashaw & Teshita (2014) reported high quantities of alkali catalysts promoting soap formation. This indicates why the biodiesel yield decreases with an increase in catalyst loading. Soap formation inhibits glycerol separation from the reaction mixture and the purification of fatty acid ethyl esters with water (Thanh, et al., 2012), thus resulting in a lower yield.

Figure 4-9 illustrates the effect of the alcohol to oil molar ratio on the biodiesel yield against time. The lowest ratio of 8:1 synthesized low ester yields due to insufficient alcohol present to drive the reaction forward. When the ratio was increased to 14:1, the excess amount of ethanol was sufficient enough to drive the reaction forward and thus, resulted in an increase in the biodiesel yield. A further increase in the alcohol to oil molar ratio of 20:1 caused a decrease in the yield, this is due to glycerol dissolving in the excess ethanol which inhibits the forward reaction (Kafuku & Mbarawa, 2010).

Figure 4-10 exhibits the effect of temperature on the yield of biodiesel against time. It can be seen that the highest yield is obtained at 70 °C and the lowest yield is obtained at 30 °C. The transesterification reaction is endothermic in nature (Daramola, et al., 2016), high temperatures would favor the endothermic reaction due to endothermic reactions consuming energy. Sufficient thermal energy is required to overcome the diffusion resistance between the two phases in the reaction mixture (i.e. oil phase and alcohol phase) (Ismail, et al., 2016).

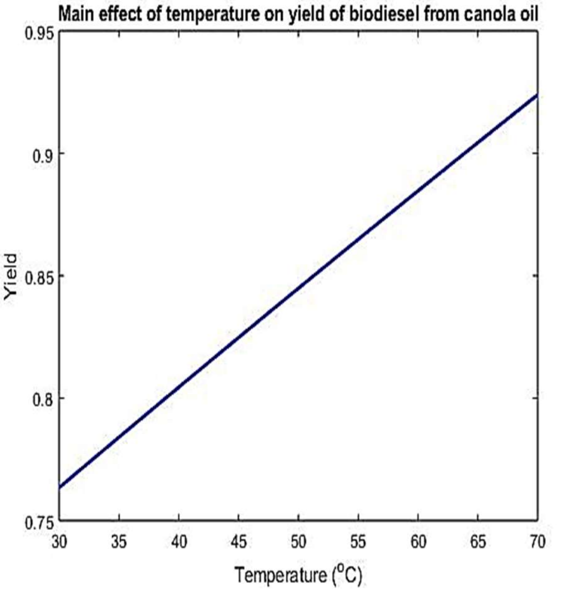


Figure 4-11: Main effect of temperature on the yield of biodiesel from CaO catalyzed transesterification

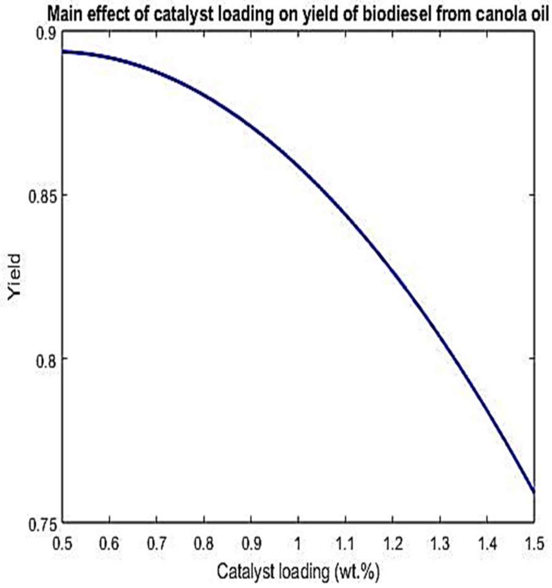


Figure 4-12: Main effect of catalyst loading on the yield of biodiesel from CaO catalyzed transesterification

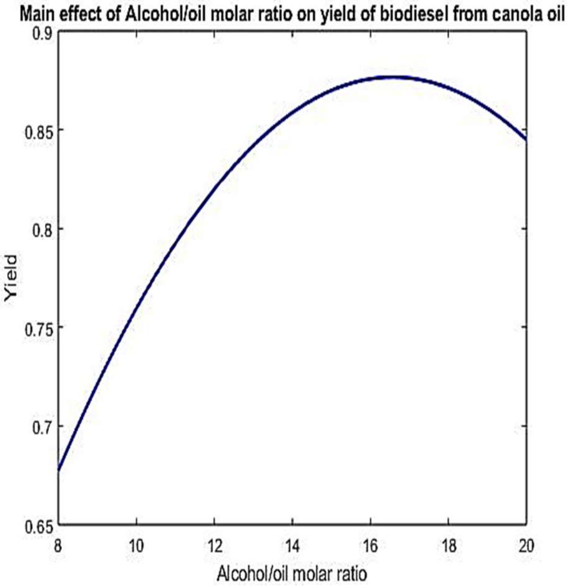


Figure 4-13: Main effect of alcohol/oil molar ratio on the yield of biodiesel from CaO catalyzed transesterification

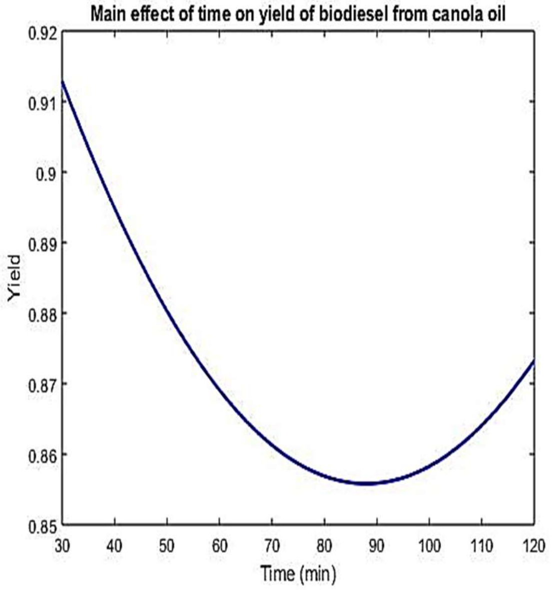


Figure 4-14: Main effect of time on the yield of biodiesel from CaO catalyzed transesterification

The main effects of each individual process variable illustrated on page 78 (figures 4-11 to 4-14) were determined by varying one variable, while holding all the other variables at their median values.
These plots were used to study the effect of each individual variable on the biodiesel yield. These plots don’t take into account the interactions between variables.

Figure 4-11 demonstrates the main effect of temperature on the yield of biodiesel. It can be seen that the reaction temperature and biodiesel yield share a directly proportional relationship, as the temperature increases the biodiesel yield also increases as expected. In addition, according to Le Chatelier’s principle, an increase in reaction temperature results in an increase in the product. This effect is in agreement with the reported results of Daramola, et al. (2016). Figure 4-12 illustrates the individual effect of catalyst loading on the biodiesel yield. It can be seen as the catalyst loading increases from 0.5% to approximately 1.5%, the yield of biodiesel decreases, this can be attributed to high catalyst loadings promoting soap formation which reduces the biodiesel yield. Figure 4-13 exhibits a parabolic effect of the alcohol to oil molar ratio on the yield obtained. When the ratio increases from 8:1 to 14:1, the biodiesel yield increases, however, further increase in the ratio beyond the optimal point results in a decrease in the yield produced. This result is due to excess alcohol increasing the solubility of glycerol in biodiesel thus, increasing the difficulty of separation of biodiesel from glycerol which leads to a reduced yield (Kafuku & Mbarawa, 2010). Figure 4-14 shows reaction time has a parabolic effect on the biodiesel yield. The yield decreases from 30 minutes to approximately 90 minutes, thereafter the yield starts to increase. This can be attributed to excess catalyst loading present in the reaction system which requires longer reaction times to increase mass transfer resistance due to insufficient coverage of the catalyst surface by ethanol (Todorovic, et al., 2019). However, the difference between the maximum and minimum yields is less than 0.06, which indicates that the individual effect of time on biodiesel yield can be deemed insignificant.

Chapter 5 Magnesium Oxide Catalyzed Transesterification Results and Discussion

This chapter focuses on the synthesis of biodiesel via heterogeneously-catalyzed transesterification whereby magnesium oxide was used to catalyze the reaction. Canola oil was chosen for this study as well. Canola oil biodiesel is an excellent fuel alternative because it has attractive fuel properties which are environmentally friendly, it has great advantages in comparison to other biodiesel fuels. Canola oil is primarily composed of triglycerides with a triglyceride concentration varying between 94.4 wt.% to 99.1 wt.%, and it has a FFA content of less than 1.4 wt.% as reported by Gaurav, et al. (2019). As mentioned in the previous chapter, as a result of preliminary property testing conducted, canola oil attained a FFA percentage of 0.042% which falls below the stipulated limits, thus making it acceptable for base-catalyzed transesterification. Magnesium oxide was the selected heterogeneous catalyst because it has a low environmental impact, high basic strength, and produces high biodiesel yields (Ashok, et al., 2018).

In this study, canola oil was reacted with ethanol while magnesium oxide catalyzed the transesterification reaction. The Box-Behnken design method was employed to determine the optimum reaction conditions that would produce a maximized biodiesel yield. The experimental conditions used in this chapter are the same as those discussed in chapter 4, except for the catalyst loading; which was ranged between 1% to 2%.

The response surface Box-Behnken design generated 27 experimental runs in total, 3 of which were replicated. Upon completing all the required experiments, Minitab was utilized to fit a regression equation to the data. The results obtained from the 27 experimental runs are shown in table 5-1 using coded variables. The coded variables are as follows:

A: Reaction temperature (°C)
B: Catalyst loading (%)
C: Alcohol to oil molar ratio
D: Reaction time (min)

Table 5-1: Canola oil with magnesium oxide transesterification results

Run Order	**A**	**B**	**C**	**D**	**Experimental Yield**	**Predicted Yield**
1	50	1.5	8	120	0.8801	0.8672
2	50	2	20	75	0.8059	0.8016
3	30	1.5	20	75	0.8859	0.8985
4	50	1	20	75	0.9449	0.9388
5	70	2	14	75	0.7089	0.7257
6	70	1.5	8	75	0.8189	0.8035
7	50	1	14	30	0.8752	0.8605
8	50	1.5	20	120	0.8751	0.8621
9	50	2	14	30	0.8641	0.8594
10	50	1.5	14	75	0.9371	0.9341
11	70	1.5	14	120	0.8750	0.8729
12	30	2	14	75	0.9647	0.9432
13	50	2	8	75	0.8055	0.8073
14	70	1	14	75	0.9512	0.9798
15	70	1.5	14	30	0.887	0.8684
16	50	1.5	20	30	0.8939	0.9140
17	70	1.5	20	75	0.9343	0.9250
18	30	1	14	75	0.8819	0.8723
19	50	1	8	75	0.8532	0.8532
20	30	1.5	14	30	0.9369	0.9347
21	50	1	14	120	0.9423	0.9442
22	50	1.5	14	75	0.9168	0.9341
23	50	1.5	8	30	0.8089	0.8290
24	30	1.5	14	120	0.9023	0.9166
25	30	1.5	8	75	0.9336	0.9401
26	50	2	14	120	0.7502	0.7621
27	50	1.5	14	75	0.9485	0.9341

With reference to table 5-1, the highest biodiesel yield was obtained in experimental run 12 which synthesized a yield of 0.9647 at a reaction temperature of 30 ℃, a catalyst loading of 2 wt.% of oil, an alcohol to oil molar ratio of 14, and a reaction time of 75 minutes. The lowest biodiesel yield of 0.7089 was attained in experimental run 5 at a temperature of 70 ℃, a catalyst loading of 2 wt. % of oil, an alcohol to oil molar ratio of 14, and a reaction time of 75 minutes. It can be noted that the only difference in the process variables in run 5 and run 12 is the reaction temperature. The yield obtained in run 5 can be attributed to the high temperature which could have resulted in vaporization of ethanol, thus decreasing the contact between the alcohol and oil and therefore resulted in a low biodiesel yield. The high reaction temperature increased the rate of reaction and the excess catalyst loading present promoted the saponification reaction faster. Run 12 also had a high catalyst loading of 2 wt. % however, it was reacting in a system with a low reaction temperature of 30 ℃ which therefore produced a negligible amount of soap.

Table 5-2: Canola oil with magnesium oxide transesterification model summary

Model	**R^2**	**R^2 adjusted**	**R^2 predicted**	**S**
Linear	0.3678	0.2529	0.0454	0.0553
Linear + squares	0.5272	0.3170	0.0000	0.0529
Linear + interactions	0.7952	0.6673	0.5069	0.0369
Full quadratic	0.9546	0.9016	0.7554	0.0200

It can be seen from table 5-2 that the full quadratic model is the most significant with a high coefficient of determination (R^2) of 0.9546 and a high adjusted R^2 value of 0.9016, both of which are higher than the recommended value of 0.8; indicating that the full quadratic model generated fits the experimental data exceptionally well. The linear, linear with squares, and linear with interactions models had R^2 values lower than 0.8, suggesting that they are insufficient to describe the experimental data obtained. The magnesium oxide catalyzed transesterification reaction is explained extremely well by the full quadratic response model obtained at a 95% confidence level. Halder, et al. (2015) stated that if the difference between the R^2 value and the adjusted R^2 value is less than 0.1; this would signify the reliability of the model. The difference between the R^2 and adjusted R^2 values for the full quadratic model was 0.053, therefore implying that the full quadratic model provides a good fit to the data attained and may be used to adequately predict biodiesel yield within the range of this study. The predicted R^2 value of 0.7554 specifies that outside the range of this study the full quadratic response model may only be approximately 75% accurate in predicting the biodiesel yield. The model fit is demonstrated in figure 5-1 (page 83), which displays the experimental biodiesel yields (actual yields) achieved against the predicted model. The majority of the actual yield values lie close to the 45-degree line, thus demonstrating a high degree of correlation between the experimental and predicted values. The coefficient of determination (R^2) of 0.9546 suggests that only approximately

4.54% of the total variation is unaccounted for by the model. The predicted R^2 value being lower than the R^2 and adjusted R^2 values is indicative of the model being tailored specifically to the data attained in this study, thus the model can be used to accurately predict the yield of biodiesel strictly within the range of this study. The standard deviation is represented by the S-value as depicted in table 5-2. The S-value indicates the distance between the experimental data values and the predicted values. The low S-value of 0.02 indicates that the data points deviation is low from the predicted response, further emphasizing that the regression equation fits the attained data well. Table 5-3 on page 84 exhibits a probability (p-value) of 0 and a high F-value of 18.01 at a 95% confidence level, indicating the quadratic model is significant. According to Ye, et al. (2017) for a 95% confidence level, a p-value less than 0.05 indicates the developed models are significant. The lower p-values imply that the variable plays a more important role in affecting the responses, and a p-value greater than 0.1 is indicative of an insignificant model.

The full quadratic regression equation is shown below using coded variables:

$$\begin{aligned}\text{Yield} = {} & -0.47 + 0.00713A + 1.145B + 0.03216C + 0.006D - 0.000015A^2 - 0.1909B^2 \\ & - 0.001006C^2 - 0.000015D^2 - 0.00813AB + 0.00034AC + 0.000006AD \\ & - 0.00761BC - 0.002011BD - 0.000083CD\end{aligned} \quad [5.1]$$

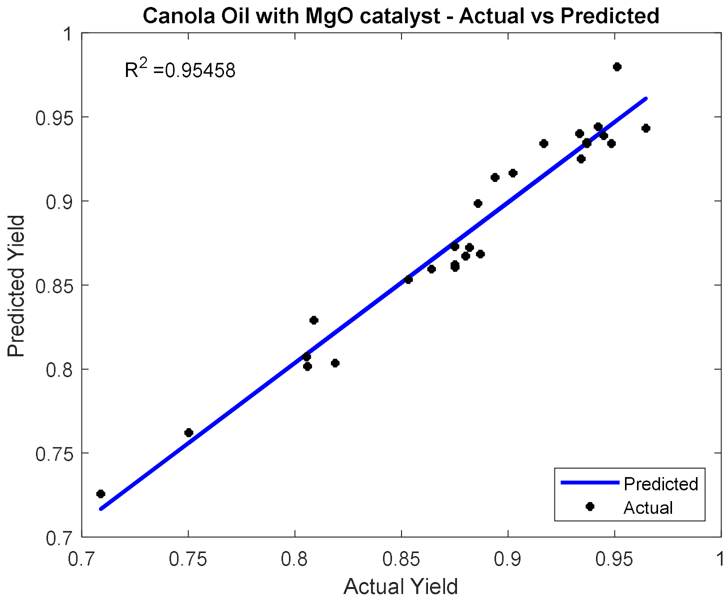


Figure 5-1: Model predicted yield vs actual yield for canola oil biodiesel production in the presence of MgO catalyst

Table 5-3: Full quadratic model analysis of variance (ANOVA) for canola oil transesterification in the presence of MgO catalyst

Analysis of Variance						
Source	Degrees of freedom	Sum of squares	Mean squares	F-value	P-value	Significance
Model	14	0.101623	0.007259	18.01	0.000	Significant
Linear	4	0.022384	0.005596	13.89	0.000	Significant
A	1	0.008675	0.008675	21.53	0.001	Significant
B	1	0.002961	0.002961	7.35	0.019	Significant
C	1	0.005498	0.005498	13.64	0.003	Significant
D	1	0.005250	0.005250	13.03	0.004	Significant
Square	4	0.016962	0.004241	10.52	0.001	Significant
A^2	1	0.000202	0.000202	0.50	0.492	Not significant
B^2	1	0.012150	0.012150	30.15	0.000	Significant
C^2	1	0.006991	0.006991	17.35	0.001	Significant
D^2	1	0.004753	0.004753	11.80	0.005	Significant
2-way interaction	6	0.045500	0.007583	18.82	0.000	Significant
AB	1	0.026423	0.026423	65.57	0.000	Significant
AC	1	0.006650	0.006650	16.50	0.002	Significant
AD	1	0.000128	0.000128	0.32	0.584	Not significant
BC	1	0.002084	0.002084	5.17	0.042	Slightly Significant
BD	1	0.008190	0.008190	20.33	0.001	Significant
CD	1	0.002025	0.002025	5.03	0.045	Slightly Significant
Error	12	0.004836	0.000403			
Lack-of-fit	10	0.004320	0.000432	1.68	0.431	Not significant
Pure error	2	0.000516	0.000258			
Total	26	0.106458				

Table 5-3 exhibits the results of the analysis of variance (ANOVA) for the full quadratic obtained model. It can be seen that all the coefficients for the linear terms are significant, this indicates that all the coefficients for the linear terms have a significant impact on the biodiesel yield in the magnesium oxide catalyzed transesterification reaction as predicted by the proposed model. It can be noted that the coefficients for the quadratic terms are all significant except for the reaction temperature (A) which has a low F-value of 0.50 and a p-value of 0.492, this suggests the quadratic coefficient of temperature (A) does not influence the yield predicted by the regression equation as significantly as the quadratic coefficients of the other variables. It can further be noted that the interaction between the reaction temperature (A) and reaction time (D) is insignificant as it has a probability greater than 0.1, which means that the interaction between the reaction temperature and reaction time is not as significant in comparison to the other variable interactions used in the quadratic model. The interactions between catalyst loading (B) and alcohol to oil molar ratio (C) as well as the interaction between alcohol to oil molar ratio (C) and reaction time (D) are both slightly significant therefore leaving the interaction between catalyst loading (B) and reaction time (D) as the most significant in the model. Further validation of the model is noted by the model's lack-of-fit which has an insignificant p-value of 0.431, which confirms the model fits the data well. The inclusion of the terms that were not significant in the model attributed to a lower predicted R^2 value of 0.7554. However, for the purpose of this study, it was deemed more important to understand the effects of the process variables within the chosen range, as the optimum conditions were expected to lie within this range, and hence the model was left unmodified.

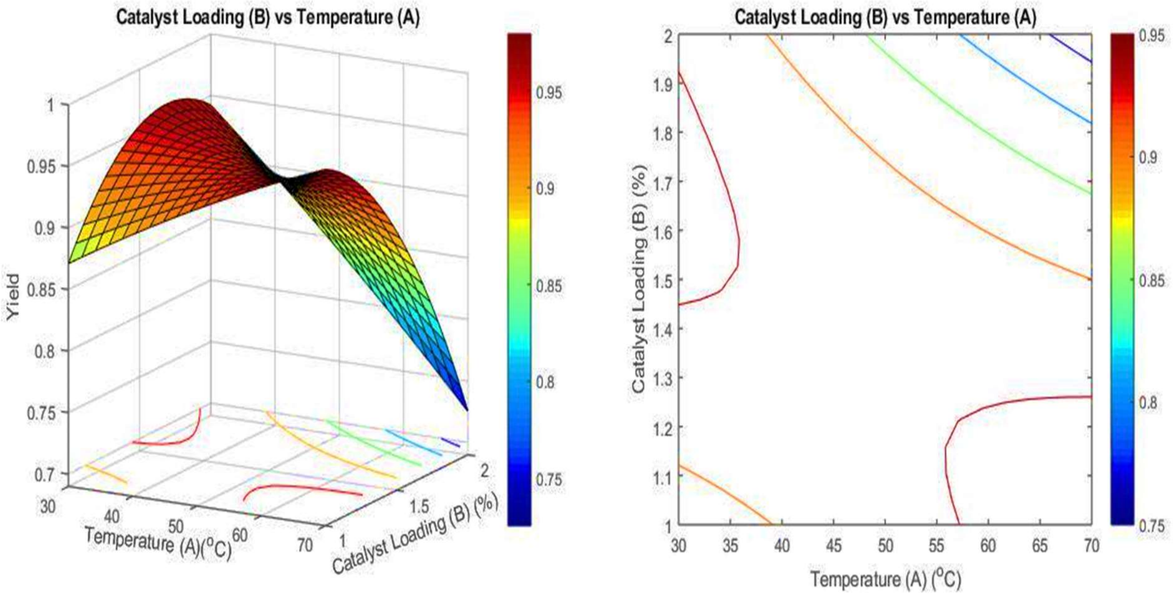
Minitab statistical software was used to generate the optimal conditions in order to maximize the response (biodiesel yield) in the magnesium oxide catalyzed transesterification process. The optimized process conditions are shown below in table 5-4:

Table 5-4: Optimized process conditions for magnesium oxide transesterification

Parameters	**Optimal result**
A - Reaction temperature (℃)	61.64
B - Catalyst loading (wt. %)	1.04
C - Alcohol/oil molar ratio	14.22
D - Reaction time (mins)	80.62
Experimental yield	0.9690
Predicted yield	0.9729

The optimum yield suggested by Minitab statistical software was 0.9729, while the experiment conducted under the proposed optimized conditions produced a biodiesel yield of 0.9690. This supports the fact that the model fits the data well since the difference between the predicted and actual optimal yields is 0.39%.

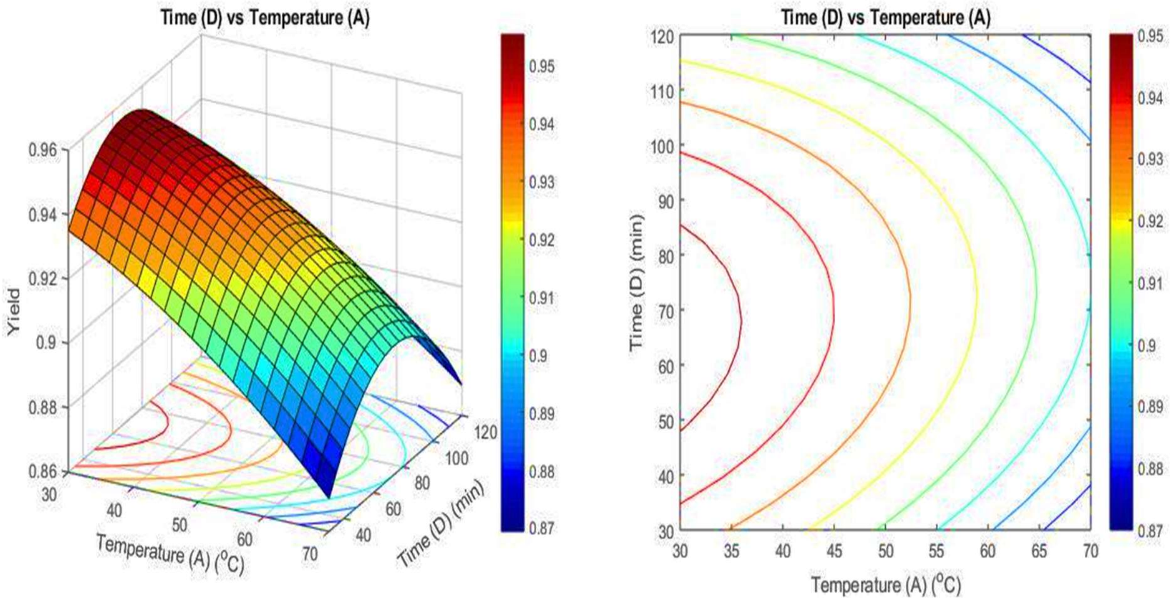
The effects of the four process variables on the biodiesel yield synthesized from canola oil in the presence of magnesium oxide catalyst are demonstrated below in figures 5-2 to 5-7. Each plot depicts the effect of two process variables across their range within the study, while the two other variables were fixed at their median values. The response surface portrays the tendency of each process variable to influence the biodiesel yield. The shape of each contour plot is an indication of the extent and nature of the interactions between the process variables. A contour plot with a circular contour is indicative of an interaction that is insignificant, while a significant interaction is indicated by an elliptical contour (Qiu, et al., 2014).



(a) (b)

Figure 5-2: (a) Response surface showing the effect of catalyst loading (wt.%) and temperature (℃) on biodiesel yield produced using MgO, (b) contour plot showing the effect of catalyst loading (wt.%) and temperature (℃) on biodiesel yield produced using MgO

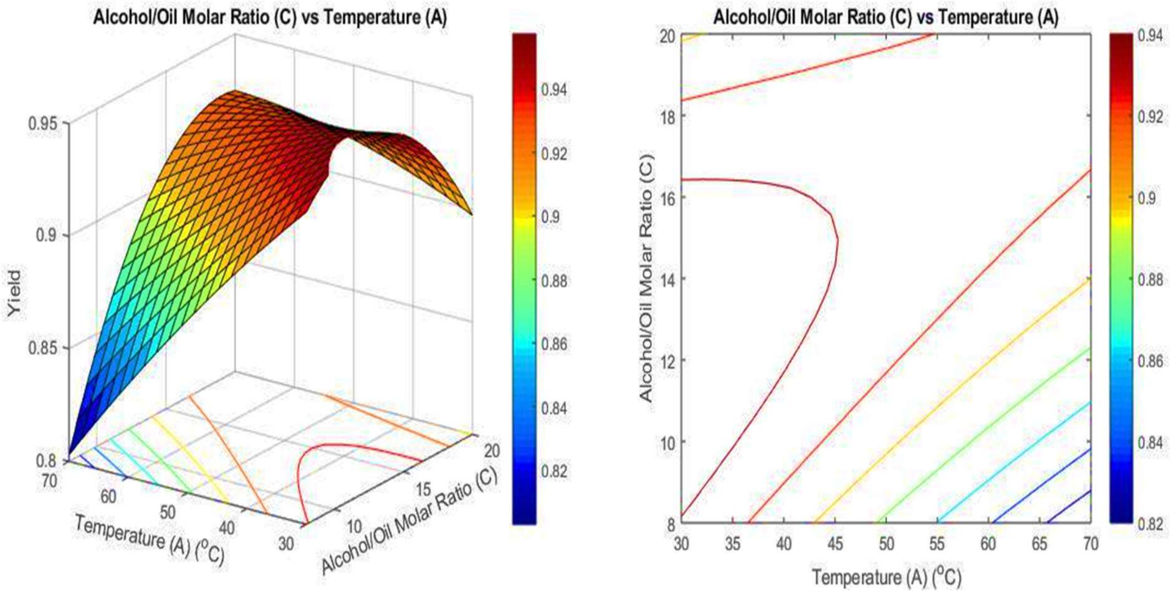
The response surface plot in figure 5-2(a) illustrates a three-dimensional interaction between catalyst loading and reaction temperature. It can be noted that the biodiesel yield increases with an increase in temperature and decreases with an increase in catalyst loading. This could be a result of the transesterification reaction being endothermic in nature (Antolin, et al., 2002), since endothermic reactions absorb energy, high temperatures favor these reactions. Gashaw & Teshita (2014) reported high quantities of alkali catalysts results in soap formation. This indicates why the biodiesel yield decreases with an increase in catalyst loading. Soap formation inhibits glycerol separation from the reaction mixture and the purification of fatty acid ethyl esters with water (Thanh, et al., 2012), thus resulting in a lower yield. It can be noted that when lower catalyst loadings were used in combination with high reaction temperatures; higher biodiesel yields were attained. Figure 5-2(b) depicts the interaction between catalyst loading and reaction temperature significantly impacts the biodiesel yield.



(a) (b)

Figure 5-3: (a) Response surface showing the effect of time (min) and temperature (℃) on biodiesel yield produced using MgO, (b) contour plot showing the effect of time (min) and temperature (℃) on biodiesel yield produced using MgO

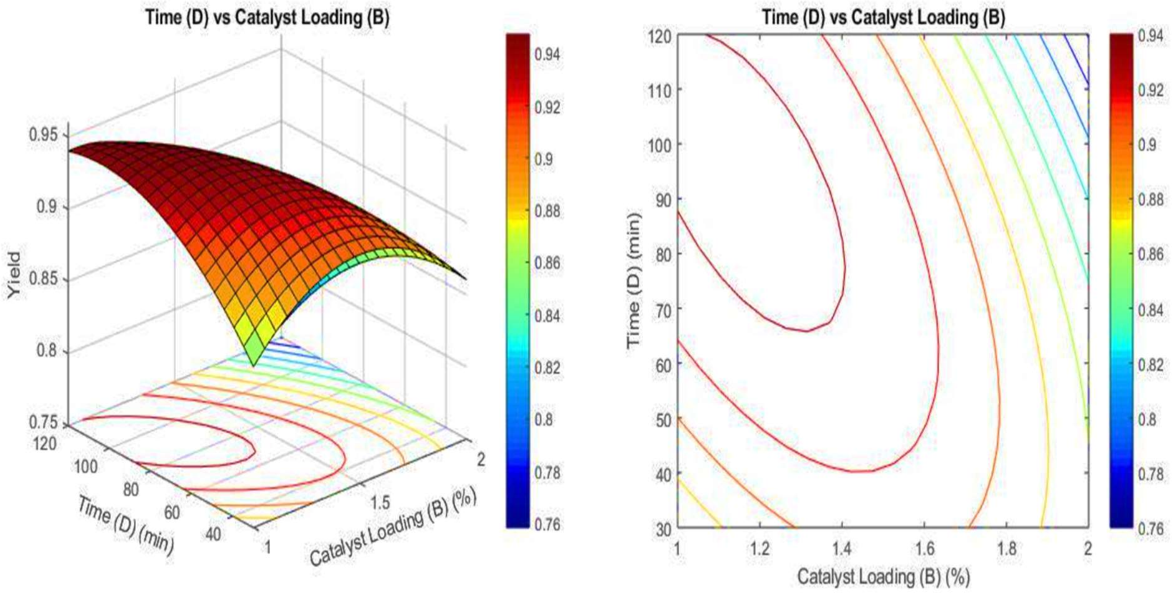
Figure 5-3(a) indicates as the reaction temperature and reaction time increases the yield of biodiesel decreases. It was recommended that the reaction temperature should not exceed the boiling point of ethanol (78.37 ℃), however at the highest reaction temperature of 70 ℃ ethanol may have vaporized during some experimental runs, this slows down the transesterification reaction rate as there is more ethanol in the vapor phase than in the liquid phase which decreases the contact between the alcohol and oil which resulted in a low biodiesel yield. Furthermore, high reaction temperature beyond an optimum temperature leads to a decrease in biodiesel production due to higher temperatures accelerating saponification of triglycerides (Chozhavendhan, et al., 2020). An excess in reaction time beyond the optimal value may lead to a reduction in the biodiesel yield due to the backward transesterification reaction being favored. Figure 5-3(b) shows a more circular contour indicating the interaction between time and temperature is insignificant.



(a) (b)

Figure 5-4: (a) Response surface showing the effect of alcohol/oil molar ratio and temperature (℃) on biodiesel yield produced using MgO, (b) contour plot showing the effect of alcohol/oil molar ratio and temperature (℃) on biodiesel yield produced using MgO

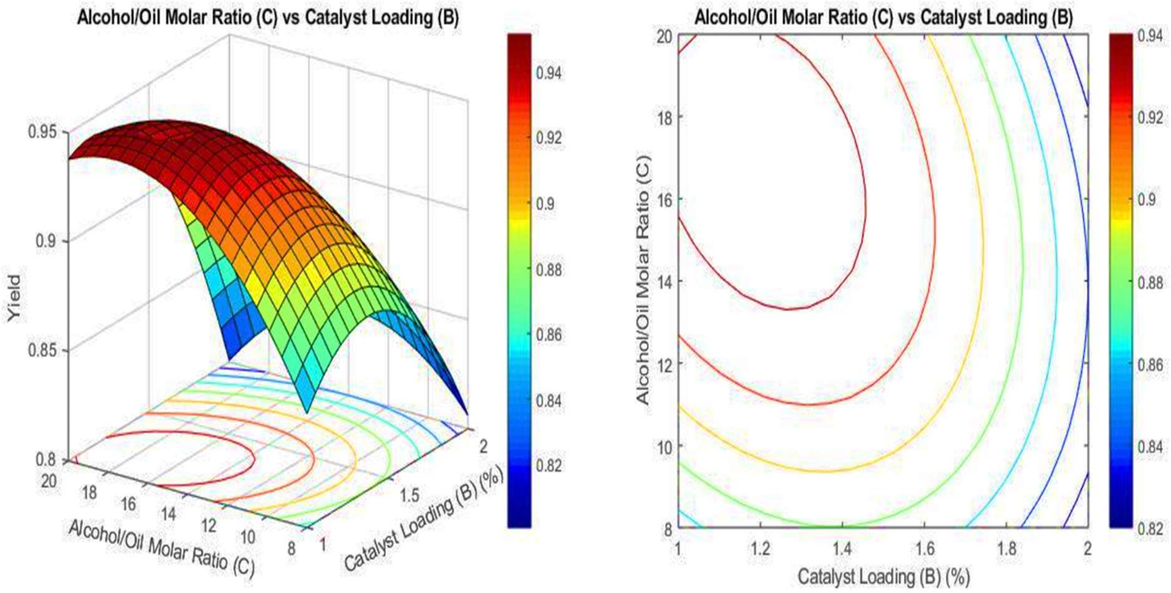
The response surface plot in figure 5-4(a) illustrates the interaction between alcohol/oil molar ratio and reaction temperature. It can be seen that the alcohol/oil molar ratio demonstrates a parabolic effect on the biodiesel yield. Initially, an increase in the alcohol/oil molar ratio led to an increase in biodiesel yield, however, after a certain point an increase in the ratio resulted in a decreased yield. According to Le Chatelier’s principle, an excess amount of ethanol is needed to shift the reactions equilibrium to the right and favor the forward reaction. Nevertheless, according to Kafuku & Mbarawa (2010), a high alcohol/oil ratio beyond an optimal point will negatively affect the separation of glycerol from biodiesel resulting from an increase in solubility, equilibrium is shifted to the left by the glycerol present in the solution which promotes the reverse reaction, resulting in a decreased biodiesel yield. It can be noted that when the lowest alcohol/oil molar ratio was used in combination with high reaction temperature, the lowest biodiesel yields were produced due to insufficient alcohol. Furthermore, high reaction temperatures also accelerate the side saponification reaction of triglycerides (Eevera, et al., 2009), which explains why low yields were obtained. Figure 5-4(b) indicates a significant interaction between the alcohol to oil molar ratio and the reaction temperature on biodiesel yield.



(a) (b)

Figure 5-5: (a) Response surface showing the effect of time (min) and catalyst loading (wt.%) on biodiesel yield produced using MgO, (b) contour plot showing the effect of time (min) and catalyst loading (wt.%) on biodiesel yield produced using MgO

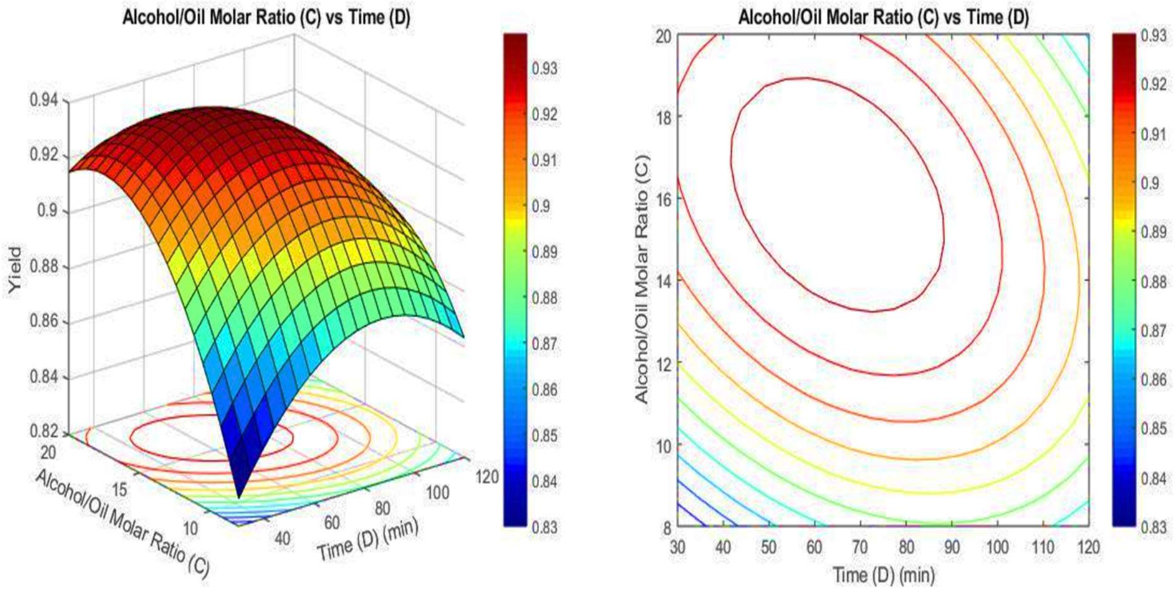
Figure 5-5(a) shows the interaction between reaction time and catalyst loading. It can be seen that as both the catalyst loading and reaction time are increased so does the biodiesel yield, but only up to a point, after which the yield decreases. This can be attributed to the reaction requiring a sufficient amount of catalyst to drive the reaction; however, the biodiesel yield is decreased when high amounts of catalysts are used due to soap formation. Similarly, an adequate amount of reaction time is necessary for the transesterification reaction to proceed, as time passes more products are formed, the equilibrium tends to shift to the left favoring the reverse reaction and thus, resulting in a reduced biodiesel yield. Figure 5-5(b) displays an elliptical contour which indicates that the interaction between reaction time and catalyst loading has a significant impact on the production of biodiesel from canola oil in the presence of MgO catalyst.



(a) (b)

Figure 5-6: (a) Response surface showing the effect of alcohol/oil molar ratio and catalyst loading (wt.%) on biodiesel yield produced using MgO, (b) contour plot showing the effect of alcohol/oil molar ratio and catalyst loading (wt.%) on biodiesel yield produced using MgO

The response surface plot in figure 5-6(a) illustrates how the interaction between alcohol/oil molar ratio and catalyst loading affects the yield of biodiesel. As the alcohol to oil molar ratio increases so does the yield of biodiesel. Similarly, as the catalyst loading increases the biodiesel yield simultaneously increases, however, this happens only happens up to an optimal point, thereafter as the catalyst loading increases the yield decreases. Even though a sufficient quantity of catalyst and excess ethanol is necessary to drive the transesterification reaction forward, increasing both these process variables above optimum conditions favors the reverse reaction as this results in soap formation which reduces the biodiesel yield. High amounts of catalyst also increase the viscosity of the product which complicates the separation process, production of biodiesel with high viscosity should be avoided as it is undesirable for use in diesel engines (Fereidooni, et al., 2017). Figure 5-6(b) indicates that the interaction between alcohol to oil molar ratio and catalyst loading has a slightly significant impact on the yield of biodiesel.



(a) (b)

Figure 5-7:(a) Response surface showing the effect of alcohol/oil molar ratio and time (min) on biodiesel yield produced using MgO, (b) contour plot showing the effect of alcohol/oil molar ratio and time (min) on biodiesel yield produced using MgO

A visual illustration of the effect of the interaction between alcohol to oil molar ratio and reaction time on the yield of biodiesel synthesized in the presence of MgO catalyst can be seen in figure 5-7(a). From observation, it can be noted that as the reaction time and ratio increase so does the yield of biodiesel, however, this occurs only up to a point after which further increase in the reaction time and ratio results in a decrease in the yield, as excess alcohol and reaction time hinders biodiesel production. At short reaction times and low alcohol/oil molar ratios, the lowest biodiesel yields were obtained. This is due to the insufficient quantity of alcohol required to drive the reaction forward and a too short reaction time for the reaction to produce sufficient product. At longer reaction times, more soap formation was observed during water washing caused by the hydrolysis of esters which cause the fatty acids to form soap. Figure 5-7(b) depicts the interaction between alcohol to oil molar ratio and reaction time has a slight impact on the biodiesel yield.

The majority of the response surface plots had a parabolic effect where the yield would increase to an optimal point and therefore decrease with further increases in the process variables. The response surface trends produced in this study are in line with the findings of Demirbas (2008), Kafuku & Mbarawa (2010) and Fereidooni, et al. (2017).

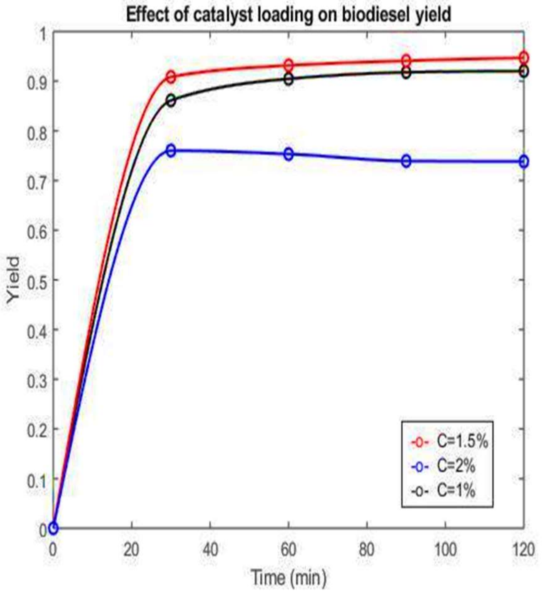


Figure 5-8: Effect of catalyst loading (wt.%) on biodiesel yield produced from canola oil in the presence of MgO

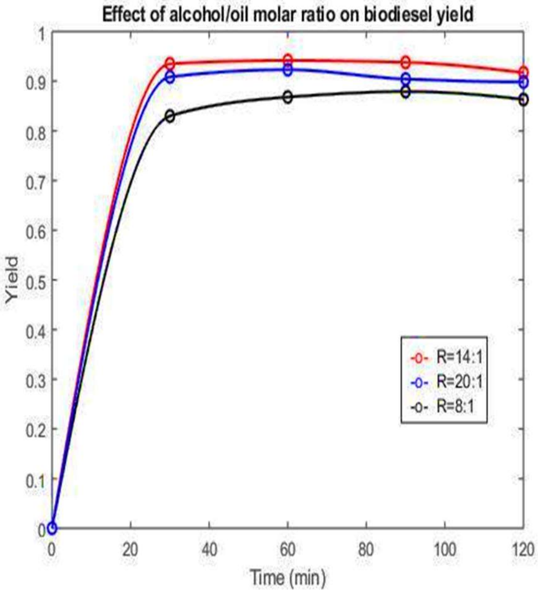


Figure 5-9: Effect of alcohol/oil molar ratio on biodiesel yield produced from canola oil in the presence of MgO

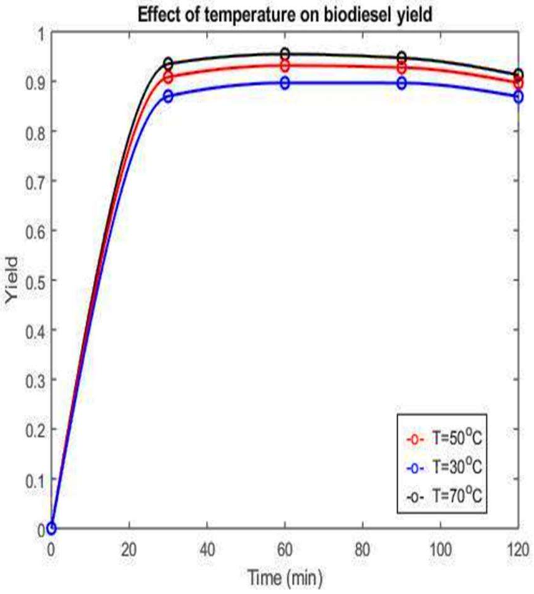


Figure 5-10: Effect of temperature (℃) on biodiesel yield produced from canola oil in the presence of MgO

Figures 5-8 to 5-10 illustrate interaction plots which were attained by varying only one variable in order to display the effect it has on the yield of biodiesel against time, while the remaining variables were kept constant at their median value. The median values are as follows:

Reaction temperature: 50 ℃
Catalyst loading: 1.5 wt.%
Alcohol to oil molar ratio: 14:1
Reaction time: 75 min

This was done to understand the interaction between the variables at their different levels.

Figure 5-8 shows that increasing the catalyst loading from 1 wt.% to 1.5 wt.% resulted in an increase in biodiesel yield attained, whereas a further increase in catalyst loading to 2 wt.% resulted in a sharp decrease in biodiesel yield. The reduction in biodiesel yield is due to soap formation in the presence of high amounts of catalyst. When 1wt.% and 1.5wt.% of catalyst were used, the formation of soap was negligible due to small amounts of catalyst present in the reaction (Thanh, et al., 2012). Furthermore, excess amounts of catalyst increases the viscosity of the reactants which results in lowering the biodiesel yield.

Figure 5-9 illustrates the effect of the alcohol to oil molar ratio on the biodiesel yield against time. The lowest ratio of 8:1 produced the lowest biodiesel yield. When the ratio was increased to 14:1, the excess amount of ethanol resulted in an increase in the biodiesel yield. A further increase in the alcohol to oil molar ratio of 20:1 caused a decrease in the yield; this is due to glycerol dissolving in the excess ethanol which inhibits the forward reaction and reduces the yield.

Figure 5-10 shows that the highest yield is obtained at 70 ℃ and the lowest yield is obtained at 30 ℃. The transesterification reaction is endothermic in nature (Daramola, et al., 2016), high temperatures would favor the endothermic reaction due to endothermic reactions consuming energy. Sufficient thermal energy is required to overcome the diffusion resistance between the two phases in the reaction mixture (i.e., oil phase and alcohol phase) (Ismail, et al., 2016).

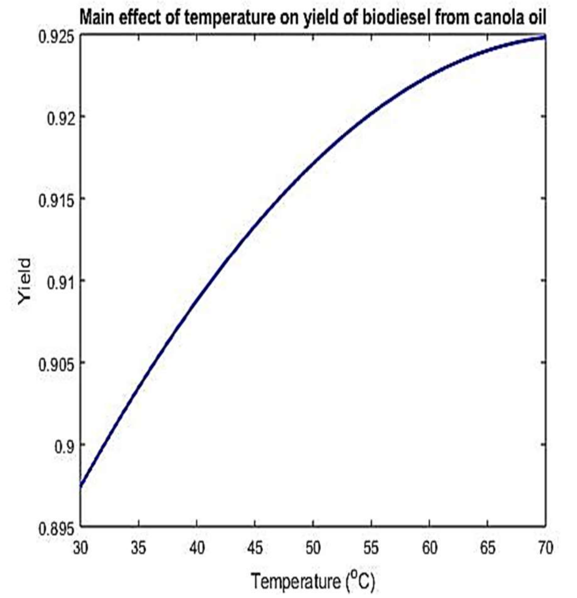


Figure 5-11: Main effect of temperature on the yield of biodiesel from MgO catalyzed transesterification

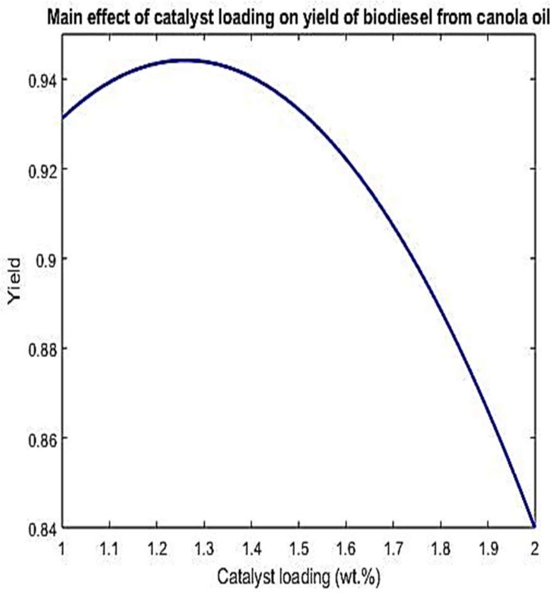


Figure 5-12: Main effect of catalyst loading on the yield of biodiesel from MgO catalyzed transesterification

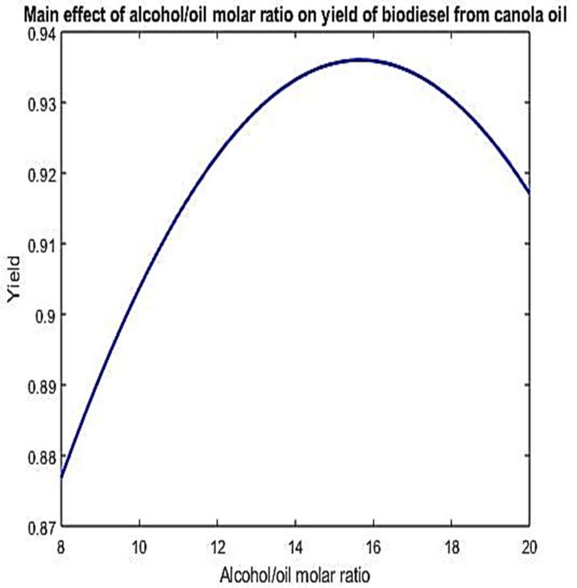


Figure 5-13: Main effect of alcohol/oil molar ratio on the yield of biodiesel from MgO catalyzed transesterification

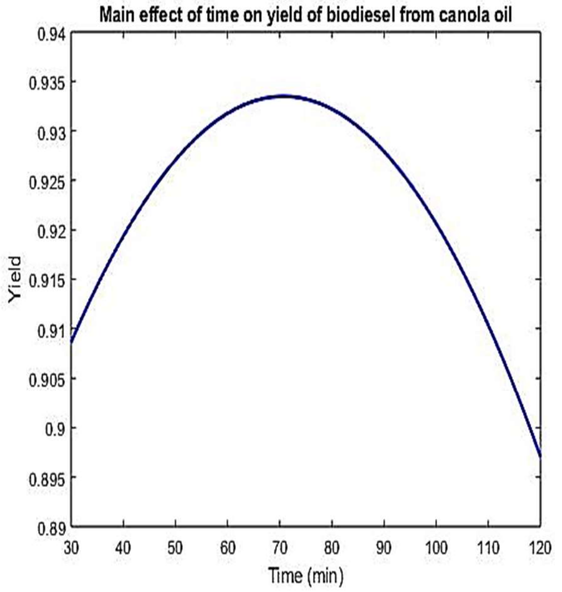


Figure 5-14: Main effect of time on the yield of biodiesel from MgO catalyzed transesterification

The main effects of each individual process variable illustrated on page 95 (figures 5-11 to 5-14) were determined by varying one variable while holding all the other variables at their median values.
These plots were used to study the effect each individual variable has on the biodiesel yield. These plots don't take into account the interactions between variables.

Figure 5-11 shows the main effect of temperature on the yield of biodiesel. It can be seen as temperature increases the biodiesel yield also increases as expected. The transesterification of triglycerides is endothermic in nature, high temperatures favor the endothermic reactions due to endothermic reactions consuming energy. Moreover, according to Le Chatelier's principle, an increase in reaction temperature results in an increase in product. This effect is in agreement with the reported results of Daramola, et al. (2016). Figure 5-12 illustrates the individual effect of catalyst loading on the biodiesel yield. It can be seen as the catalyst loading increases from 1% to approximately 1.3%, the yield of biodiesel also increases, however, with further increase in catalyst loading the biodiesel yield starts to decrease. This can be attributed to high catalyst loadings promoting soap formation which reduces the biodiesel yield. Figure 5-13 displays a parabolic effect of alcohol to oil molar ratio on the yield obtained. When the ratio increases from 8 to approximately 16, the biodiesel yield increases, however, further increase in the ratio beyond 16 results in a decrease in the yield produced. This result is due to excess alcohol increasing the solubility of glycerol in biodiesel thus, increasing the difficulty of separation of biodiesel from glycerol which leads to a reduced yield (Kafuku & Mbarawa, 2010). Figure 5-14 shows reaction time has a parabolic effect on the biodiesel yield. The yield increases from 30 minutes to 70 minutes, thereafter the yield starts to decrease. This can be attributed to longer reaction times resulting in the equilibrium shifting to the left due to excess glycerol formation which favors the reverse reaction, thus reducing the biodiesel yield obtained.

These trends are in agreement with the trends reported by Daramola, et al. (2016), Kafuku & Mbarawa (2010) and Thanh, et al. (2012). It should be noted that the main effect plots and interaction plots were used solely to see the effect of an individual variable while the other variables were kept constant. The main effect and interaction plots were not used to attain the optimized result as it does not take all the interactions between all variables into consideration. This is why the Minitab Box-Behnken design along with its response optimizer was utilized to generate the transesterification reactions optimal conditions. The response and process variables were all constrained between their minimum and maximum values used in this study because the regression model generated by Minitab may not be able to accurately represent trends observed outside the range of this study.

Chapter 6 Property Testing and Blending

This chapter is focused on physical property testing which was performed on the biodiesel produced. This was done in order to evaluate whether the biodiesel synthesized is suitable for direct use in diesel engines without further modification. The property testing was done in accordance with the international fuel standards. The properties examined included density, kinematic viscosity, acid value, flash point, pour point, and heat of combustion. The samples analyzed were inclusive of biodiesel produced from canola oil using calcium oxide catalyst as well as biodiesel produced from canola oil using magnesium oxide as a catalyst. The samples were also blended with kerosene in an effort to produce bio-jet fuel. Two different blends were created. The blending was done in ratios of 10% biodiesel with 90% kerosene and 20% biodiesel with 80% kerosene. For convenience, the 10% biodiesel with 90% kerosene blend will be referred to as BK10 and the 20% biodiesel with 80% kerosene will be referred to as BK20 in this chapter.

6.1 Density

As per the ASTM D941, the limit for density is 900 $\frac{kg}{m^3}$. From table 6-1, it can be seen; biodiesel produced from canola oil in the presence of calcium oxide had a density of 891 $\frac{kg}{m^3}$ and the biodiesel produced from canola oil in the presence of magnesium oxide had a density of 888 $\frac{kg}{m^3}$. Both biodiesel sample densities fall below the limit. The bio-jet fuel acceptable density range is 775-840 as outlined in ASTM D1655. From table 6-1, it can be seen all biodiesel blends are within the standard range. The digital density meter used to measure the density had an uncertainty of $\pm$ 0.02 $\frac{kg}{m^3}$.

Table 6-1: Density measurements

Sample	**Density $\left(\frac{kg}{m^3}\right)$**			**Average density$\left(\frac{kg}{m^3}\right)$**
	Test 1	**Test 2**	**Test 3**	
Canola oil at $\mathbf{15}$℃	916	915	916	916
Biodiesel (CaO) at $\mathbf{15}$℃	890	892	891	891
Biodiesel (MgO) at $\mathbf{15}$℃	887	890	888	888
Blends				
Biodiesel blend BK10 (CaO) at $\mathbf{15}$℃	812	813	812	812
Biodiesel blend BK20 (CaO) at $\mathbf{15}$℃	815	813	816	815
Biodiesel blend BK10 (MgO) at $\mathbf{15}$℃	811	810	812	811
Biodiesel blend BK20 (MgO) at $\mathbf{15}$℃	813	816	814	814

6.2 Kinematic viscosity

As stated in ASTM D445; the limit for kinematic viscosity for fuel is 6 $\frac{mm^2}{s}$. It can be seen in table 6-2, both biodiesel samples are above the limit (15.59 $\frac{mm^2}{s}$ and 13.72 $\frac{mm^2}{s}$). The jet fuel maximum kinematic viscosity limit as indicated by ASTM D1665 is 8$\frac{mm^2}{s}$ at 20 ℃. It can be seen in table 6-2, all biodiesel blends with kerosene are above the maximum limit. The viscometer used to measure the dynamic viscosity had an uncertainty value of $\pm$ 0.02 $\frac{mm^2}{s}$.

Table 6-2: Kinematic viscosity measurements

Sample	**Kinematic viscosity** $\left(\frac{mm^2}{s}\right)$			**Average kinematic viscosity** $\left(\frac{mm^2}{s}\right)$
	Test 1	**Test 2**	**Test 3**	
Canola oil at $\mathbf{25}$ ℃	59.52	59.53	58.91	59.32
Biodiesel (CaO) at $\mathbf{40}$ ℃	15.67	15.36	15.75	15.59
Biodiesel (MgO) at $\mathbf{40}$ ℃	13.77	13.82	13.56	13.72
Blends				
Biodiesel blend BK10 (CaO) at $\mathbf{20}$ ℃	11.81	11.56	11.21	11.52
Biodiesel blend BK20 (CaO) at $\mathbf{20}$ ℃	12.56	12.66	12.56	12.59
Biodiesel blend BK10 (MgO) at $\mathbf{20}$ ℃	9.77	9.82	9.56	9.72
Biodiesel blend BK20 (MgO) at $\mathbf{20}$ ℃	10.69	10.94	10.63	10.75

6.3 Acid value

The acid values in table 6-3 was determined as outlined in Chapter 3.

Table 6-3: Acid value results

Sample	**Acid value** $\left(\frac{mg\ KOH}{g}\right)$			**Average acid value** $\left(\frac{mg\ KOH}{g}\right)$
	Test 1	**Test 2**	**Test 3**	
Canola oil	0.083	0.085	0.084	0.084
Biodiesel (CaO)	0.22	0.22	0.21	0.217
Biodiesel (MgO)	0.19	0.21	0.22	0.207
Blends				
Biodiesel blend BK10 (CaO)	0.22	0.22	0.22	0.220
Biodiesel blend BK20 (CaO)	0.22	0.21	0.22	0.217
Biodiesel blend BK10 (MgO)	0.21	0.20	0.23	0.213
Biodiesel blend BK20 (MgO)	0.23	0.21	0.19	0.210

As stipulated in ASTM D974, the acid value should not be higher than 0.5 $\frac{mg\ KOH}{g}$. It can be seen from table 6-3 above, biodiesel produced in the presence of CaO had an acid value of 0.217 $\frac{mg\ KOH}{g}$ and biodiesel produced in the presence of MgO had an acid value of 0.207 $\frac{mg\ KOH}{g}$, both biodiesel acid values fall below the limit. With regards to jet fuel, the maximum allowable acid value is 0.015 $\frac{mg\ KOH}{g}$, which means that all the biodiesel blends with kerosene lie above the allowable limit.

6.4 Flash point (closed cup)

The flash point presented in table 6-4 was determined as outlined in Chapter 3.

Table 6-4: Flash point results

Sample	**Flash point** (°C)			**Average flash point** (°C)
	Test 1	**Test 2**	**Test 3**	
Biodiesel (CaO)	99	101	100	100
Biodiesel (MgO)	101	100	101	101
Blends				
Biodiesel blend BK10 (CaO)	56	58	55	56
Biodiesel blend BK20 (CaO)	66	64	65	65
Biodiesel blend BK10 (MgO)	54	59	58	57
Biodiesel blend BK20 (MgO)	65	63	66	65

The biodiesel produced in the presence of CaO and MgO had flash points of 100°C and 101°C respectively, these values fall between the required flash point range of 93 °C - 170°C as outlined in ASTM D93. According to ASTM D1655, the jet fuel flash point should be higher than 38 °C. It can be seen in table 6-4, all biodiesel blends are well above 38 °C.

6.5 Pour point

As specified in ASTM D6751, the acceptable pour point values range between -15 °C to 10 °C. From table 6-5, it can be seen both biodiesel samples lie within the acceptable range. ASTM D1655 states a pour point of -47°C is required for jet fuel and due to equipment limitations, this could not be tested.

Table 6-5: Pour point results

Sample	**Pour point** (°C)			**Average pour point** (°C)
	Test 1	**Test 2**	**Test 3**	
Biodiesel (CaO)	5	6	5	5
Biodiesel (MgO)	5	4	4	4

6.6 API gravity

API gravity was determined for the bio-jet fuel samples using the following formula (Speight, 2002):

$$\text{API gravity} = \frac{141.5}{\text{SG}} - 131.5 \qquad [6.1]$$

Where SG represents specific gravity. The API gravity was determined for three specific gravity values which were attained during density testing.

Table 6-6: API gravity results

Sample	**API gravity**			**Average API gravity**
Blends	**Test 1**	**Test 2**	**Test 3**	
Biodiesel blend BK10 (CaO)	42.76	42.55	42.76	42.69
Biodiesel blend BK20 (CaO)	42.12	42.55	41.91	42.19
Biodiesel blend BK10 (MgO)	42.98	43.19	42.76	42.98
Biodiesel blend BK20 (MgO)	42.55	41.91	42.33	42.26

6.7 Heat of combustion

The heat of combustion was determined for the bio-jet fuel samples using the following formula (Speight, 2002):

$$\text{Heat of combustion} = 12400 - 2100(\text{SG})^2 \qquad [6.2]$$

Where SG represents specific gravity. The heat of combustion was determined for three specific gravity values which were attained during density testing.

Table 6-7: Heat of combustion results

Sample	**Heat of combustion $\left(\frac{BTU}{lb}\right)$**			**Average heat of combustion $\left(\frac{BTU}{lb}\right)$**
Blends	**Test 1**	**Test 2**	**Test 3**	
Biodiesel blend BK10 (CaO)	11015.38	11011.97	11015.38	11014.24
Biodiesel blend BK20 (CaO)	11005.13	11011.97	11001.70	11006.27
Biodiesel blend BK10 (MgO)	11018.79	11022.19	11015.38	11018.78
Biodiesel blend BK20 (MgO)	11011.97	11001.70	11008.55	11007.41

6.8 Gas chromatography-mass spectrometry (GC-MS) analysis

6.8.1 Canola oil biodiesel synthesized via CaO catalyzed transesterification GC-MS results

Biodiesel synthesized at optimum conditions which produced the highest yield was subjected to GC-MS analysis. The optimized conditions as outlined in chapter 4 (table 4-5):

Temperature: 65.73 ℃ Reaction time: 55.52 mins

Catalyst loading: 0.68 wt.% Alcohol/oil molar ratio: 15.23:1

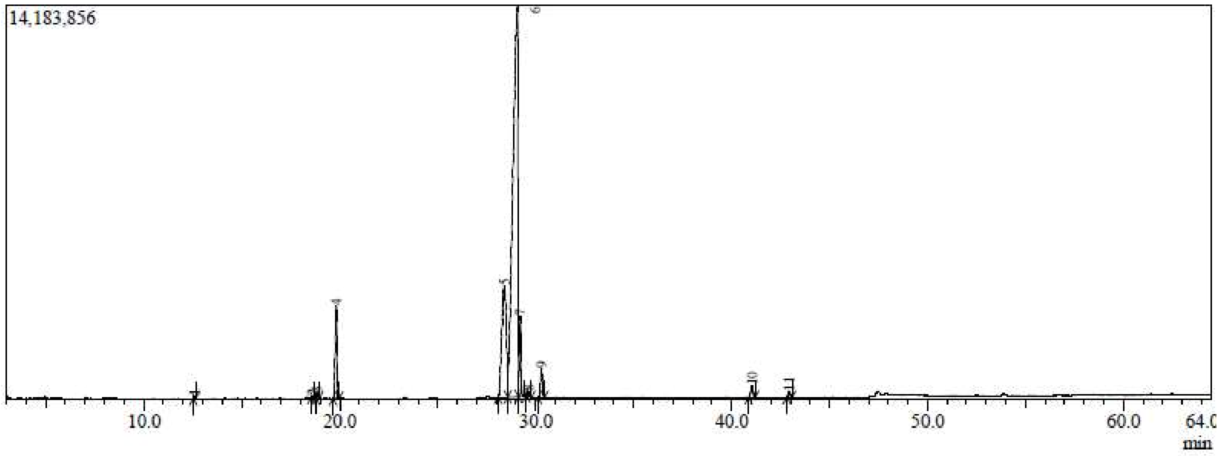


Figure 6-1: Canola oil biodiesel produced in the presence of CaO chromatogram

Table 6-8: Canola oil biodiesel produced in the presence of CaO GC-MS results

Peak Number	Retention Time (mins)	Area %	Name	Chemical Formula
1	12.580	0.06	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$
2	18.603	0.08	9,12,15-Octadecatrienoic acid, ethyl ester	$C_{20}H_{34}O_2$
3	18.848	0.26	9-Hexadecanoic acid, ethyl ester	$C_{18}H_{34}O_2$
4	19.829	5.36	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$
5	28.394	16.65	Linoleic acid, ethyl ester	$C_{20}H_{36}O_2$
6	29.073	69.48	Ethyl Oleate	$C_{20}H_{38}O_2$
7	29.220	4.29	(E)-9-Octadecenoic acid, ethyl ester	$C_{20}H_{38}O_2$
8	29.622	0.29	Ethyl 9,12,15-octadecatrienoate	$C_{20}H_{34}O_2$
9	30.308	2.12	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$
10	41.039	0.96	(E)-9-Octadecenoic acid, ethyl ester	$C_{20}H_{40}O_2$
11	42.941	0.43	Eicosanoic acid, ethyl ester	$C_{22}H_{44}O_2$

6.8.2 Canola oil biodiesel synthesized via MgO catalyzed transesterification GC-MS results

Biodiesel synthesized at optimum conditions which produced the highest yield was subjected to GC-MS analysis. The optimized conditions as outlined in chapter 5 (table 5-4):

Temperature: 61.64 °C
Reaction time: 91.54 mins
Catalyst loading: 1.04 wt.%
Alcohol/oil molar ratio: 14.22:1

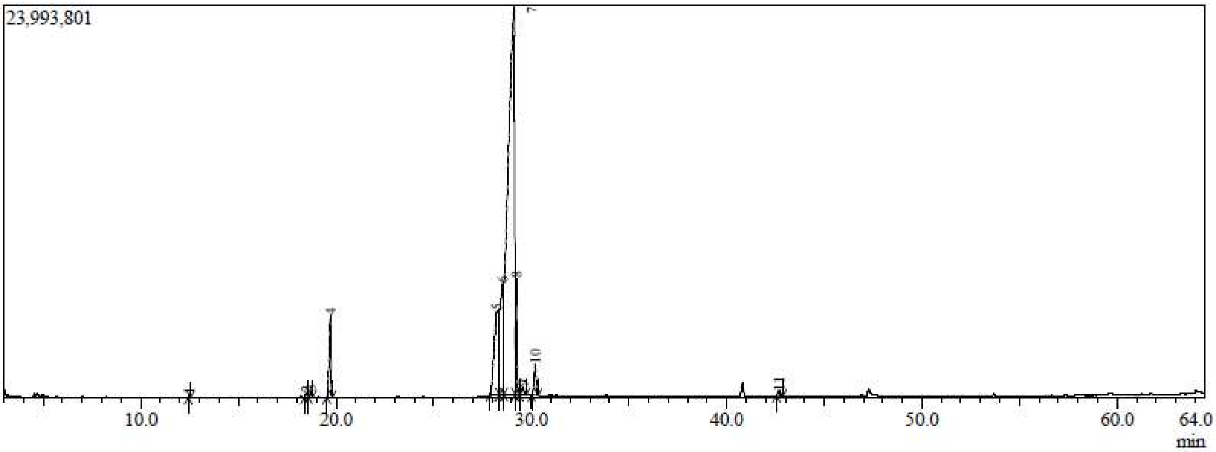


Figure 6-2: Canola oil biodiesel produced in the presence of MgO chromatogram

Table 6-9: Canola oil biodiesel produced in the presence of MgO GC-MS results

Peak Number	Retention Time (mins)	Area %	Name	Chemical Formula
1	12.481	0.06	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O$
2	18.461	0.17	9,12,15-Octadecatrienoic acid, ethyl ester	$C_{20}H_{34}O_2$
3	18.703	0.21	9-Hexadecnoic acid, ethyl ester	$C_{18}H_{34}O_2$
4	19.704	3.80	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$
5	28.233	10.55	Linoleic acid, ethyl ester	$C_{20}H_{36}O_2$
6	28.533	11.11	Linoleic acid, ethyl ester	$C_{20}H_{36}O_2$
7	29.125	67.36	Ethyl Oleate	$C_{20}H_{38}O_2$
8	29.238	4.33	(E)-9-Octadecenoic acid, ethyl ester	$C_{20}H_{38}O_2$
9	29.575	0.43	Ethyl 9,12,15-octadecatrienoate	$C_{20}H_{34}O_2$
10	30.200	1.66	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$
11	42.698	0.32	Eicosanoic acid, ethyl ester	$C_{22}H_{44}O_2$

Chapter 7 Conclusion and Recommendations

7.1 Conclusions

The following conclusions were drawn from this study:

- The use of calcium oxide heterogeneous base-catalyst to achieve a maximized biodiesel yield from canola oil was successful. Calcium oxide was able to convert triglycerides to free fatty ethyl esters without the need for esterification pretreatment, taking into account canola oil had a low acid number of 0.084 $\frac{mg\ KOH}{g}$ which indicated it had a low FFA content, thus reducing production costs due to single-step transesterification.
- The maximum experimental yield achieved for canola oil transesterification in the presence of calcium oxide was 0.9272. This yield was synthesized at a reaction temperature of 70 ℃, a catalyst loading of 1 wt.% of oil, an alcohol to oil molar ratio of 14:1, and a reaction time of 30 minutes.
- A regression equation was generated in line with the experimental data and the coefficient of determination (R^2) for the regression model was 0.9543 which suggested that only 4.57% of the total variation was unaccounted for by the model indicating that the equation was a good fit to the data obtained.
- The optimized conditions for the CaO study predicted a yield of 0.9354 at a reaction temperature of 65.73 ℃, a catalyst loading of 0.68 wt.%, an alcohol to oil molar ratio of 15.23, and a reaction time of 55.52 minutes. However, the experimental yield obtained at these conditions was 0.9380 which exceeded the predicted yield by 0.26%.
- The results obtained from the GC-MS confirmed that biodiesel can be produced at the optimum operating conditions. Therefore, it can be concluded that the generated regression model could adequately predict the effects of all the conditions on the yield of biodiesel from the transesterification reaction with calcium oxide.
- All the biodiesel properties tested fell within the specified ranges in accordance with the ASTM standards, except for the kinematic viscosity which was higher than the stipulated limit. It can therefore be concluded that biodiesel synthesized from canola oil reacting with ethanol in the presence of calcium oxide cannot directly be used in a diesel engine without further modification.

- The use of magnesium oxide heterogeneous base-catalyst to achieve a maximized biodiesel yield from canola oil was also successful. It was found that the magnesium oxide catalyst produced higher biodiesel yields in comparison to the calcium oxide catalyst, this can be attributed to calcium oxide forming more soap.
- The maximum experimental yield achieved for canola oil transesterification in the presence of magnesium oxide was 0.9647. This yield was synthesized at a reaction temperature of 30 ℃, a catalyst loading of 2 wt.% of oil, an alcohol to oil molar ratio of 14:1, and a reaction time of 75 minutes.
- A regression equation was fitted to the experimental data and it showed a strong coefficient of determination (R^2) of 0.9546 indicating a suitable fit as there was only 4.54% of the total variation unaccounted for by the model.
- The optimized conditions for the MgO study obtained predicted a yield of 0.9729 at a reaction temperature of 61.64 ℃, a catalyst loading of 1.04 wt.%, an alcohol to oil molar ratio of 14.22, and a reaction time of 91.54 minutes. The experimental optimized yield obtained was 0.9690 which was only 0.39% lower than the predicted yield.
- The results obtained from the GC-MS confirmed that biodiesel can be produced at the optimum operating conditions. Therefore, it can be concluded that the generated regression model could adequately predict the effects of all the process conditions on the yield of biodiesel from the transesterification of canola oil in the presence of magnesium oxide catalyst.
- All the biodiesel properties tested fell within the specified ranges in accordance with the ASTM standards except for the kinematic viscosity, similar to biodiesel produced in the presence of calcium oxide, which was also higher than the stipulated limit. However, the kinematic viscosity of the biodiesel produced in the presence of MgO was a bit lower than the kinematic viscosity of the biodiesel produced in the presence of CaO.
- It can therefore be concluded that biodiesel synthesized from canola oil reacting with ethanol in the presence of magnesium oxide cannot be used directly in a diesel engine as further engine modification or blending of biodiesel with petroleum diesel would be required.
- It can further be concluded that MgO catalyst is better at producing higher biodiesel yields with lower kinematic viscosities; with the reactants used in this study.

From the observation of the transesterification reactions using both heterogeneous catalysts, the following can be concluded:

- The oil viscosity was reduced when high reaction temperatures were employed, thus increasing the reaction rate and shortening the reaction time. Saponification of triglycerides was noticed when the reaction temperature was higher than an optimal temperature. The reaction temperature and biodiesel yield had a directly proportional relationship.
- Free fatty ethyl ester production was decreased in the presence of excess catalyst as it caused triglycerides to participate in the saponification reaction.
- The transesterification of esters was left incomplete in the absence of sufficient ethanol, however, ethanol in excess beyond the optimal quantity resulted in a reduced yield.
- Longer reaction times (120 minutes) did not promote the production of biodiesel as it favored the reverse reaction which resulted in a reduced yield.

7.2 Recommendations

Future studies should be conducted on:

- Waste vegetable cooking oils and non-edible oils so that it avoids the food vs. fuel crisis.
- The reusability of solid heterogeneous catalysts and catalyst deactivation in biodiesel production.
- Calcination temperature plays a vital role in catalytic activity as it modifies the active sites on the catalyst surface. Hence, the effect of heterogeneous catalyst calcination temperature has on biodiesel production should be studied.
- A variety of other alcohols and catalysts can be investigated.
- The life cycle of biodiesel produced from waste feedstocks.
- The present study was carried out at atmospheric pressure. Thus, the production of biodiesel should be investigated at high pressure.
- To ensure the diesel engine fuel compatibility and reliability with biodiesel, the physical properties of the produced biodiesel should be studied in more detail.
- Biodiesel from various feedstocks blended with petroleum diesel should also be studied.
- To understand the transesterification reaction at a molecular level a kinetic study should be conducted.

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Appendix A – Sample Calculations

The following sample calculations are shown for canola oil and calcium oxide catalyst respectively.

Canola oil molar mass determination

The following equation was used in the determination of canola oil molar mass (Huaping, et al., 2006):

$$Molar\ Mass\ \left(\frac{g}{mol}\right) = \frac{56.1 \times 1000 \times 3}{SV - AV} \qquad [A1]$$

Where SV represents the saponification value $\left(\frac{mg\ KOH}{g}\right)$, and AV is the acid value $\left(\frac{mg\ KOH}{g}\right)$ of the oil.

A method suggested by Muhammed, et al. (2019) was used to calculate the saponification value as follows:

A mixture of 2 g of canola oil and 25mL of 0.1 ethanolic potassium hydroxide solution was prepared, thereafter, 5 drops of phenolphthalein indicator was added to the mixture. Upon adding phenolphthalein, the solution turned pink. Thereafter, with a 0.5M hydrochloric acid solution, the solution was titrated until the pink color faded away, and this volume was recorded as the titrated volume. A blank titration on the ethanolic potassium hydroxide solution was also conducted.

The following equation was used in the determination of canola oil saponification value (Muhammad, et al., 2019):

$$SV\left(\frac{mg\ KOH}{g}\right) = \frac{56.1 \times 0.5 \times (V_b - V_t)}{m} \qquad [A2]$$

Where V_b is the volume titrated during the blank titration, V_t is the volume titrated, and m is the mass of sample. On conduction of the blank titration, a titrated volume of 20 mL was obtained while the titrated volume for canola oil was 6.30 mL for a sample mass of 2 g. Therefore, the saponification value was determined as follows:

$$SV_{Canola\ oil} = \frac{56.1 \times 0.5 \times (20 - 6.30)}{2} = 192.07\ \frac{mg\ KOH}{g}$$

Acid tests were conducted in accordance with the method specified in ASTM D974. The procedure is outlined in chapter 3. The titrated volume was noted and therefore the acid number was determined by the following formula:

$$Acid\ number\ \left(\frac{mg\ KOH}{g}\right) = \frac{(A-B)M \times 56.1}{W} \qquad [A3]$$

Where A is the volume of KOH solution required for titration of the sample (mL), B is the volume of KOH solution required for the blank titration (mL), M is the molarity of the KOH solution, and W is the mass of the sample used (g).

The blank titrated volume was 0.5 mL and the 20 g of oil titrated volume was 0.8 mL. Therefore, the acid value was determined as follows:

$$Acid\ number\ = \frac{(0.8-0.5) \times 0.1 \times 56.1}{20} = 0.084\ \left(\frac{mg\ KOH}{g}\right)$$

The molar mass of canola oil was therefore:

$$Molar\ Mass_{canola\ oil} = \frac{56.1 \times 1000 \times 3}{192.07 - 0.084} = 876.60\left(\frac{g}{mol}\right)$$

Transesterification reaction process variable requirements

Amount of Alcohol required

250 mL of canola oil weighed 224.17g. The number of moles of canola oil was determined as follows:

$$n\ (mol) = \frac{mass}{Molar\ mass} \qquad [A4]$$

$$n_{\ oil} = \frac{m_{oil}}{Molar\ mass} = \frac{224.17}{876.6} = 0.256\ mol$$

For an alcohol to oil molar ratio of 8:1, the mass of alcohol required in grams:

$$n_{alcohol} = n_{\ oil} \times ratio = 0.256 \times 8 = 2.05\ mol$$

The molar mass of ethanol is 46.07 g/mol, therefore the mass of alcohol is determined by rearranging equation A4:

$$\therefore m_{alcoh} \quad = n_{alcohol} \times molar\ mass\ of\ ethanol = 2.05 \times 46.07 = 94.25\ g$$

Amount of catalyst required

For a catalyst loading of 0.5 wt.% oil, the mass of the required is determined as:

$$m_{catalyst} = 0.05 \times 224.17 = 1.12\ g$$

Yield of biodiesel

The mass of biodiesel was recorded and the overall yield of biodiesel produced in accordance to Fereidooni, et al. (2017) equation as follows:

$$Yield = \frac{Mass\ of\ biodiesel\ produced}{Mass\ of\ oil\ used} \quad [A5]$$

$$Yield = \frac{192.45}{224.17} = 0.8585\ \therefore 0.8585 \times 100 = 85.85\%$$