A STUDY INTO THE PRODUCTION OF BIODIESEL USING HOMOGENOUSLY CATALYZED TRANSESTERIFICATION REACTIONS

By

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Preface

The work presented in this dissertation was carried out in the analytical laboratory at the School of Engineering at the University of KwaZulu-Natal (Howard College Campus), Durban, from January 2019 to November 2019 under the supervision of Professor Amir H. Mohammadi.

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

_____

Muhammad Shezaad Adam

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

_____

Prof. Amir H. Mohammadi

Declaration: Plagiarism

I, Muhammad Shezaad Adam, declare that:

(i) the research reported in this dissertation, except where otherwise indicated or acknowledged, is my original work;

(ii) this dissertation has not been submitted in full or in part for any degree or examination to any other university;

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_____ 13-03- 2020

Muhammad Shezaad Adam Date

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

Abstract

Petro-diesels have a harsh impact on the environment and hence alternate fuels is an important field of study. Biodiesel is a promising alternate to petro-diesel as it can be synthesized from renewable sources such as vegetable oils. Biodiesel is biodegradable and has limited toxicity and its production can be decentralized so that it can help rural economies. Biodiesel is synthesized mainly via transesterification reactions, through which triglycerides (vegetable oils) are converted to their alkyl esters (biodiesel) and glycerol as a by-product. This work aimed to investigate homogenously catalysed transesterification reactions for biodiesel production. A Box-Behnken experimental design was utilised in order to determine the combination of experimental conditions which resulted in the optimum yield of biodiesel from sunflower oil and castor oil. The process variables under investigation were the molar ratio of alcohol to oil, catalyst loading, reaction temperature and reaction time, and the response variable was the yield of biodiesel obtained. Hence, the optimum conditions for biodiesel production through a homogenously catalysed transesterification reaction using was proposed. Due to the high acid number of castor oil, a 2-step method was utilised; the first step involved an esterification reaction with an acid catalyst (sulphuric acid) to reduce the acid number and the second step involved transesterification to biodiesel via a base catalyst (potassium hydroxide). The FFA content of castor oil was reduced by 95% via the esterification process. An optimum sunflower oil biodiesel yield of 98.51% was achieved, while an optimum castor oil biodiesel yield of 95.36% was achieved. The biodiesel produced at the optimum conditions was subject to basic property testing and blending with kerosene to produce bio-jet fuel. Sunflower oil biodiesel met the ASTM standard requirements for fuel, while castor oil biodiesel did not, indicating that only sunflower oil biodiesel may be used in a diesel engine without further modification. Sunflower oil is therefore recommended as a suitable feedstock for biodiesel production, however, castor oil is not. The jet fuel samples met all the ASTM standard requirements, besides the acid value, hence these are not recommended for use in an engine without further modification.

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Chapter 1

Introduction

1.1 Background

With the worldwide evolution of modern civilization and industrialization, there is a growing demand for energy. Currently, most of the world's energy needs are being met with fossil fuels which are a non-renewable source of energy. This means that the amount of fossil fuel available is constantly diminishing, resulting in an increase in fuel prices as the demand for fuels increase while the ability to supply fuels decreases. This problem gives importance to research in the field of fuels produced from renewable sources, such as vegetable oils, which are an attractive alternative to fossil fuels.

The term biodiesel was first used in the year 1992 at the National Soy Diesel Development Board (now the National Biodiesel Board) in the United States of America (Singh & Singh, 2010). Biodiesel is a term that refers to a fuel that is equivalent to diesel fuel but has been obtained from biological sources (Gunstone, 2009), and hence is a renewable energy source. On a molecular level, biodiesel is essentially a mixture of alkyl esters with long-chain fatty acids and is normally synthesized from non-toxic biological resources such as animal fats, vegetable oils, or waste vegetable oils (Leung, et al., 2010).

Biodiesel also has similar properties to petro-diesel, but it also offers several advantages over petro-diesel such as the fact that it has a higher biodegradability than fossil-based fuels, it is renewable and sustainable, it is non-toxic, has exceptional lubricity and is virtually free of sulphur and aromatics (Keera, et al., 2018). Another main advantage of biodiesel is that it can be used in a diesel engine without modification of the current technology (Arshad, et al., 2018).

Using fossil fuels has several negative effects on the environment, with the most significant being that use of fossil fuels increase the amount of carbon dioxide in the atmosphere, and this

directly contributes to global warming. Vegetable oils are an alternative form of renewable fuel to diesel engines, however, direct application of vegetable oil as fuel to diesel engines is not possible due to its higher viscosity (Van Gerpen, 2005). It is therefore necessary to reduce the viscosity of vegetable oils before application in diesel engines. This may be done by using different methods such as blending, pyrolysis, micro-emulsification and transesterification. Transesterification is most commonly used in industry due to the quality of the biodiesel obtained through this method (Fukuda et al., 2001).

1.2. Motivation & significance of the study

Biodiesel production is a very promising field of research due to its increased relevance as a result of the increasing petroleum price as well as the environmental advantages that using biodiesel has over using petro-diesel. In an effort to reduce the effects of global warming by using green diesel (biodiesel), the optimum conditions for production of biodiesel from different vegetable oils and alcohols need to be investigated. Factors that affect biodiesel production are oil to alcohol ratio, presence of water and free fatty acid content, reaction temperature, catalyst concentration and agitation speed (Ma & Hanna, 1999). Most of the biodiesel currently used is produced from edible feedstocks such as rapeseed oil and palm oil (Knothe, 2005). Due to its potential to significantly reduce the emission of greenhouse gases, biodiesel shows a lot of promise to become the replacement for diesel fuel. The main challenge to the large-scale implementation of biodiesel is its cost (Arumugam & Ponnusami, 2014). To reduce the cost, it is necessary to optimise the yield of biodiesel obtained. Competition for land in order for biodiesel feedstocks to be produced is problematic; hence maximising the yield of oil from a given feedstock is critical (Diamantopoulos, et al., 2015).

1.3. Aim & objectives of the study

1.3.1. Aim of the study

The research carried out in this work was aimed at determining the optimum process conditions to maximise the yield of biodiesel obtained from sunflower oil and castor oil via homogenously catalysed transesterification reactions.

1.3.2. Objectives of the study

The following objectives were necessary to meet the aim:

- Conduct a comprehensive literature review to obtain all the information necessary to propose an efficient experimental method for the production of biodiesel using homogenous catalysts.
- Perform property tests on the feedstock to assess its quality.

- Conduct experiments in order to assess the optimal conditions for biodiesel production, and critically analyse the results obtained.
- Perform property testing on the biodiesel obtained to assess its quality.
- Understanding the effect of the various process variables on the transesterification process.
- Assessing the quality of biodiesel obtained by conducting basic property testing.
- Producing bio-jet fuel by blending biodiesel with kerosene.
- Blending of biodiesel with kerosene to produce bio-jet fuel and perform basic property tests on the blends.

1.4. Outline of dissertation structure

Chapter 1 introduces the reader to the topic. The background of the topic is presented so that the reader may understand why there is a need for such a study. The research aims and objectives are also presented here to outline what the intention of the study was, and how this was achieved.

Chapter 2 is a comprehensive review of relevant literature in order to offer the reader the theoretical background necessary to understand the topic. The sections covered include methods of biodiesel production, catalysts used in biodiesel production, factors that affect the production of biodiesel as well as typical feedstocks for the production of biodiesel. The main sources consulted were journal articles.

Chapter 3 provides an outline of the raw materials and experimental equipment used in this study. The chemicals used are reported along with their purity and supplier, and the experimental apparatus used is described along with its purpose.

Chapter 4 focuses on the design of the experiments, as well as the experimental method followed in this study. The experimental design was necessary to optimise the yield of biodiesel.

Chapter 5 presents the results and discussion of the homogenously catalysed transesterification of sunflower oil. The effects of the process variables is investigated and the optimum process conditions that result in a maximum biodiesel yield are proposed.

Chapter 6 provides the results and in-depth discussion of the acid catalysed esterification of castor oil. The effects of the process variables on the free fatty acid content in the oil is investigated and the optimum process conditions for the reduction of the free fatty acid content in castor oil is proposed.

Chapter 7 presents the results and discussion of the transesterification of the esterified castor oil. Similar to chapter 5, the effect of the process variables on the yield of biodiesel obtained

from castor oil is investigated and the conditions that result in the maximum yield are proposed.

Chapter 8 focuses on the property testing of the biodiesel and the blending of biodiesel with kerosene. The properties measured include density, viscosity and acid number. The biodiesel was also analysed by GC-MS.

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

Chapter 2

Theoretical Background

The diesel engine was concocted by Rudolf Diesel in the 1890's (Jääskeläinen, 2019). The engine was intended to be run on vegetable oils, and Dr. Diesel used peanut oil as fuel for his engine (Griffin Shay, 1993). Vegetable oils were the main fuel source used in diesel engines until the 1920's when diesel engine manufacturers changed their design specifications to make the engine more suitable for the viscosity of petroleum based diesel instead of vegetable oil (Demirbas, 2008). This was because of the availability of cheap petroleum and improved methods for refining crude oil to obtain petroleum diesel (Datta & Mandal, 2012). There are several advantages to using vegetable oils as diesel, such as renewability, higher heat content, portability, readily available, lower aromatic and sulphur content, and biodegradability (Demirbas, 2008). The main challenge in using vegetable oils in diesel engines is their high viscosity, this problem can be addressed in four ways: dilution, micro-emulsification, thermal cracking (pyrolysis) and transesterification.

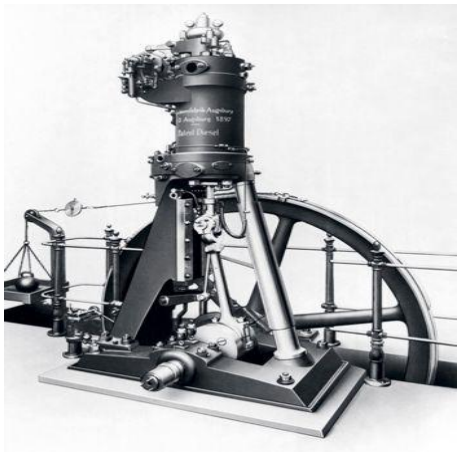

Figure 2-1: Dr. Rudolf Diesel's engine (Jääskeläinen, 2019)

2.1. Direct use of vegetable oils in diesel engines

The diesel engine was originally designed to run on vegetable oil as fuel (Griffin Shay, 1993). However, several disadvantages have been found in directly using vegetable oils in diesel engines. The main challenge of the direct use of vegetable oils is its high viscosity when compared to petroleum diesel (Gunstone, 2009). The high viscosity of vegetable oils can cause several problems in a diesel engine such as poor fuel atomization, carbon deposition on the injector, incomplete combustion and fuel build-up in the lubricant oils (Demirbas, 2008).

2.2. Methods to improve the properties of vegetable oils

There are various processes and methods which can be used to improve the quality of vegetable oils. These methods include blending, thermal cracking (pyrolysis), micro-emulsification and transesterification.

(a) Blending

Even though vegetable oils have similar properties to biodiesel, direct use of vegetable oil in a diesel engine is unfavorable and the vegetable oil would require some chemical modification before it is able to be used in a diesel engine (Gashaw & Teshita, 2014). The main obstacle to the direct use of vegetable oils in diesel engines is the high viscosity of vegetable oils. This problem can be overcome by blending vegetable oils with regular petro-diesel to run the engine (Arshad, et al., 2018).

(b) Micro-emulsification

A micro-emulsion 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" (Gashaw & Teshita, 2014). A biodiesel micro-emulsion may consist of vegetable oils, diesel fuels, alcohols and surfactant and cetane improvers (Gashaw & Teshita, 2014). Alcohols are used as additives to lower viscosity and alkyl nitrates can be used as cetane improvers (Gashaw & Teshita, 2014). Micro-emulsions result in an increase in cetane number, decrease in viscosity and improved spray characteristics (Canakci & Sanli, 2008). Micro-emulsions may improve spray characteristics by explosive vaporisation of the low-boiling constituents (Hardwood, 1984). However, according to Gashaw & Teshita (2014), long term use of micro-emulsified diesel can cause problems such as carbon deposit formation, incomplete combustion, and injector needle sticking.

Table 2-1: Problems, probable causes and potential solutions to problems associated with direct use of vegetable oils in diesel engines (Hardwood, 1984)

Problem	Probable cause	Potential solution
Short term		
1. Cold weather starting	High viscosity, low flash point and low cetane number	Preheat fuel prior to injection Chemically alter fuel to an ester
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) Other ash	Partially refine oil to remove gums Filter to 4 microns
3. Engine knocking	Low cetane number Improper injection timing	Adjust injection timing Use higher compression engines Preheat fuel prior to injection Chemically alter fuel to an ester
Long term		
4. Coking of injectors on piston and head of engine	High viscosity of oil Incomplete combustion of fuel Poor combustion at part load with vegetable oils	Heat fuel prior to injection Switch engine to diesel fuel when operating at part load Chemically alter vegetable oil to an ester
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oils Incomplete combustion of fuels Poor combustion at part load with vegetable oils Free fatty acids in vegetable oils Dilution of engine lubricating oil due to blow-by of vegetable oil	Chemically alter vegetable oil to ester
6. Excessive engine gear	High viscosity of vegetable oil Incomplete combustion of fuel Poor combustion at part load with vegetable oils Possibly free fatty acids in vegetable oils Dilution of engine lubricating oil due to blow-by of vegetable oil	Increase motor oil changes Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerisation	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization starts	Increase motor oil changes Motor oil additives to inhibit oxidation

(c) Pyrolysis (thermal cracking)

Pyrolysis is defined as the conversion of one substance into another via the addition of heat in the absence of oxygen, or via the addition of heat in the presence of a catalyst which results in the splitting of chemical bonds and the formation of various smaller molecules (Gashaw & Teshita, 2014). The thermal cracking of vegetable oil to produce biodiesel produces alkanes, alkenes, alkadienes, carboxylic acids as well as aromatics (Gashaw & Teshita, 2014). The vegetable oil thermally decomposes during this process and the heaviest constituents of the vegetable oil are converted to lighter molecules, thereby reducing the viscosity (Hardwood, 1984). The major disadvantage to this method is its excessive cost. Pyrolysis requires separate distillation columns for separating the different fractions further contributing to the high cost of the process (Schenk, et al., 2008). The biofuels obtained via pyrolysis is similar to gasoline in that it contains sulphur which makes it less environmentally friendly (Arshad, et al., 2018). Gashaw & Teshita (2014) reported that the chemistry of thermal cracking processes is difficult to characterise due to the variety of reaction paths and products that may be obtained from this process. Pyrolysis is also used to reduce the viscosity of fuel oils and is known as visbreaking (Singh & Singh, 2010).

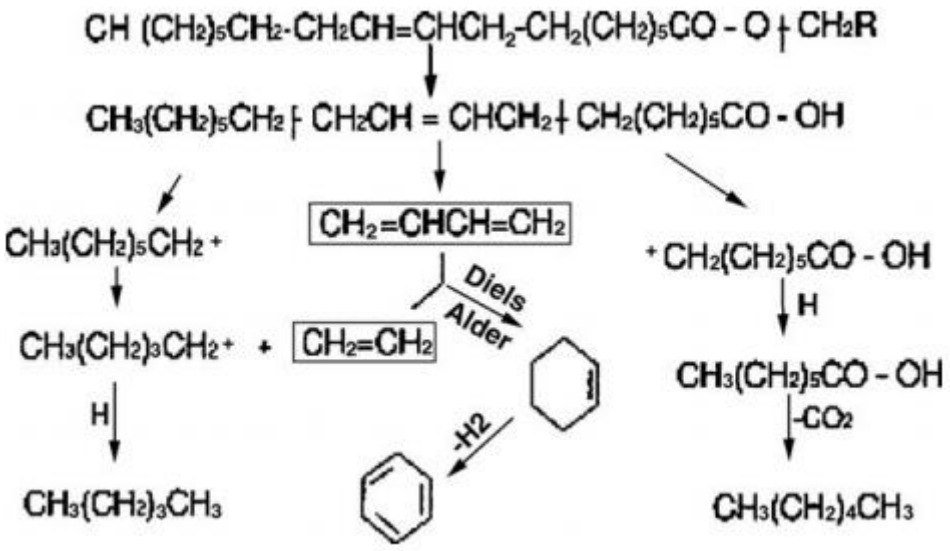

Figure 2-2: Mechanism for pyrolysis of triglycerides (Singh & Singh, 2010)

(d) Transesterification

Transesterification is an ester conversion process which splits up the triglycerides by replacing the glycerol of the triglyceride with the alkyl radical of the alcohol used (Canakci & Sanli, 2008). The transesterification process comprises a sequence of three consecutive reversible reactions: the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and the conversion of monoglycerides to glycerol and each

step yields one ester molecule (Narasimharao, et al., 2007). Usually a catalyst is used to speed up the reaction and improve the yield. The transesterification reaction is reversible, and hence an excess amount of alcohol is required to shift the equilibrium to the product side and promote the forward reaction. Transesterification reduces the viscosity of the vegetable oil by removing the high viscosity component, i.e. glycerol (Gashaw & Teshita, 2014).

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

Methods	Main Process	Advantages	Disadvantages
Blending (dilution)	Preheated vegetable/animal oils were blended with petro-diesel within 10-40% (w/w) ratio. Then the resulted oil-diesel mixture was applied into the diesel engine.	Does not require any chemical process (non-polluting), absence of technical modifications, and easy implementation.	High viscosity, unstable, low volatility, and increase in vegetable/animal oil portion resulted in improper spraying pattern, poor atomization, incomplete fuel combustion, and difficulty in handling by conventional engines.
Microemulsification	The vegetable/animal oils were solubilized in a solvent (alcohol) and surfactant until the required viscosity was obtained.	Simple process and pollution free.	High viscosity, low stability (the addition of ethanol can enhance the quantity of surfactant required to maintain the state of microemulsion), and could lead to sticking, incomplete combustion, and carbon deposition.
Pyrolysis (thermal cracking)	The vegetable/animal oils were preheated and decomposed at elevated temperatures (more than 350 ℃) whether or not the catalyst is present. Different products (gas and liquid) were analysed based on their boiling temperature range to determine the exact product.	The process is effective, simple (no washing, drying or filtering required), wasteless, and pollution free.	Requires high temperature and expensive equipment and produces low purity of biodiesel (contains heterogeneous molecules including ash and carbon residues).
Transesterification	The vegetable/animal oils and fats were reacted with alcohol (ethanol or methanol) and catalyst (alkali or acid). Then the mixture of methyl/ethyl esters (biodiesel) and glycerol (byproduct) will undergo separation and purification steps before further usage.	High conversion with relatively low cost, mild reaction conditions, product properties are closer to the petro-diesel, and applicable for industrial-scale application.	Requires low free fatty acids (FFAs) and water content in the raw material, extensive separation and purification steps, possibility of side reactions occurring, and generation of a large amount of wastewater.

2.3. Transesterification

Of all the methods mentioned in section 2.2, transesterification is the preferred method when the aim is to reduce viscosity, furthermore, glycerol has commercial value and is obtained as a by-product during transesterification (Sharma, et al., 2008).

In Figures 2-3 and 2-4 on page 10, R_1, R_2, and R_3 represent long-chain hydrocarbons, referred to as fatty acids. The alcohol breaks the fatty acid chains in the presence of a catalyst resulting in glycerol and a mixture of fatty acid alkyl esters (biodiesel) (Leung, et al., 2010).

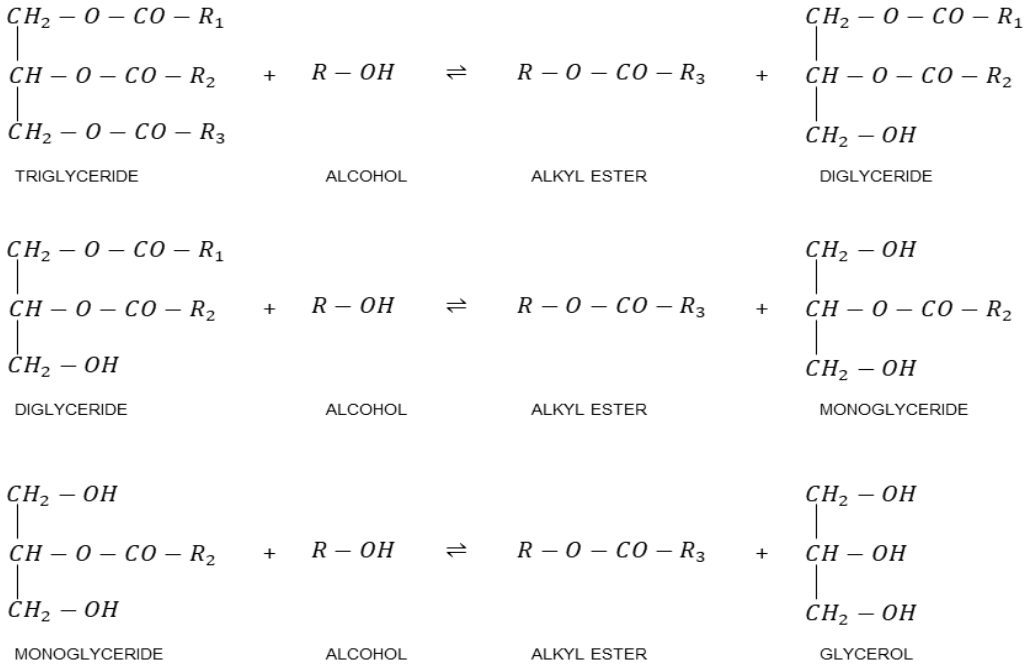

Figure 2-3: Transesterification reaction scheme (Leung, et al., 2010)

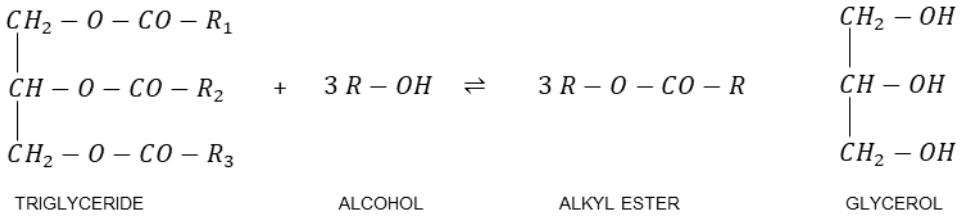

Figure 2-4: Overall transesterification reaction (Leung, et al., 2010)

It can be seen from Figure 2-4 that stoichiometrically, 3 moles of alcohol are required for every mole of triglyceride reacting, however, since the reaction is reversible, an excess amount of alcohol is required to shift the equilibrium towards the product side. It is also seen that the 2 main products of the transesterification reaction are alkyl esters or biodiesel (desired product), and glycerol (by-product).

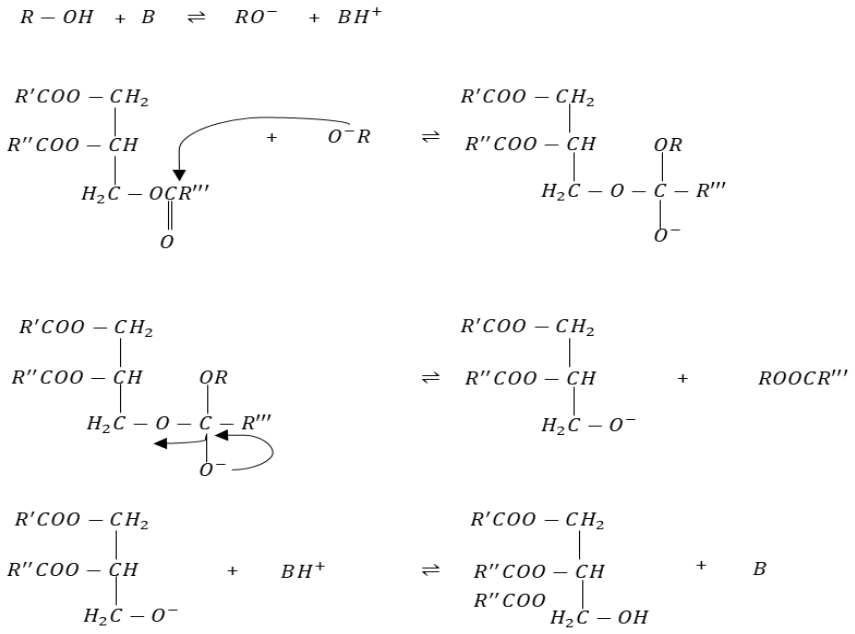

Figure 2-5: Transesterification reaction mechanism (Singh & Singh, 2010)

2.3.1. Factors that affect biodiesel production via tranesesterification

Biodiesel is defined as mono alkyl esters of long chain fatty acids from renewable feedstock such as vegetable oils or animal fats, for use in compression ignition engines (Hossain, et al., 2012). Various factors affect the production of biodiesel via transesterification. These factors include the chosen feedstocks, reaction temperature, alcohol to oil molar ratio, stirrer speed, reaction time and catalyst concentration.

(a) Feedstocks

Different types of feedstocks such as edible and non-edible vegetable oils, animal fats, microalgae and fungi oil can be used to synthesize biodiesel (Marwaha, et al., 2018). As seen in Figure 2-4, the two main reagents required for biodiesel production via transesterification are an alcohol and an oil. First generation biodiesel is produced from edible vegetable oils such as palm, soya, sunflower, etc., while second generation biodiesel is derived from non-edible oils such as Jatropha, neem, castor, etc. (Kansedo, et al., 2009). The feedstock to be used in biodiesel production is based on various factors such as climate and availability in each region (Pinto, et al., 2005). Due to the higher price of edible vegetable oils as compared to non-edible oils, the latter is preferred for use as feedstock in the synthesis of biodiesel (Pinto, et al., 2005). The use of non-edible oils or waste cooking oils avoids the food vs. fuel issue. Gui, et al. (2008) claim that by converting edible vegetable oils into biodiesel, sources of food are being turned into automotive fuels and the large-scale production of fuel from edible vegetable oils could bring about an imbalance to the food supply and demand market. The properties of the biodiesel produced is dependent on the properties of the feedstock used, for

example, biodiesel produced from feedstocks with long chain fatty acids or saturated fatty acids have a high cetane number, high cloud point and can cause nozzle clogging while biodiesel prepared from unsaturated fatty acids have a low cetane number and undergo oxidation easily (Pinto, et al., 2005).

The most commonly used alcohols for transesterification are methanol and ethanol, however, methanol is preferred mainly due to its lower cost (Carter & Halle, 2005). Ethanol has a lower reactivity than methanol during transesterification (Leung, et al., 2010). Longer chain alcohols are rarely used mainly due to their higher cost; however, it is possible to use these alcohols in the transesterification process (Datta & Mandal, 2012).

Choosing the oil to be used is a more involved process than choosing the alcohol as various factors have to be considered, besides the price. Cheaper oils are typically of low quality; cheaper oils have a high free fatty acid (FFA) content resulting in the formation of soap during transesterification, which is undesirable as it reduces both the yield and quality of the biodiesel product obtained (Kemp, 2006).

Another reason that choosing the oil is so important is that the quality of biodiesel obtained is largely dependent on the quality of the base oil used to produce it (Knothe, 2005). Table 2-3 shows the kinematic viscosity of different vegetable oils and the biodiesel produced from these oils. It can be seen that transesterification of vegetable oils reduces the viscosity significantly. It can be seen in table 2-4 that Crambe oil has the highest heating value amongst all the vegetable oils mentioned. Crambe oil is a possible replacement oil for rapeseed oil, in that it is typically derived from older varieties of rapeseed (Singh & Singh, 2010). Crambe oil is mostly available in the United States (Singh & Singh, 2010).

Table 2-3: Kinematic viscosity of different vegetable oils and biodiesel produced from these oils (Leung, et al., 2010)

Oil	Kinematic viscosity of oil (cSt at 40℃)	Kinematic viscosity of biodiesel (cSt at 40℃)
Rapeseed	35.5	4.3-5.83
Soybean	32.9	4.08
Sunflower	32.6	4.9
Palm	39.6	4.42
Peanut	22.72	4.42
Corn	34.9	3.39
Canola	38.2	3.53
Cotton	18.2	4.07
Pumpkin	35.6	4.41

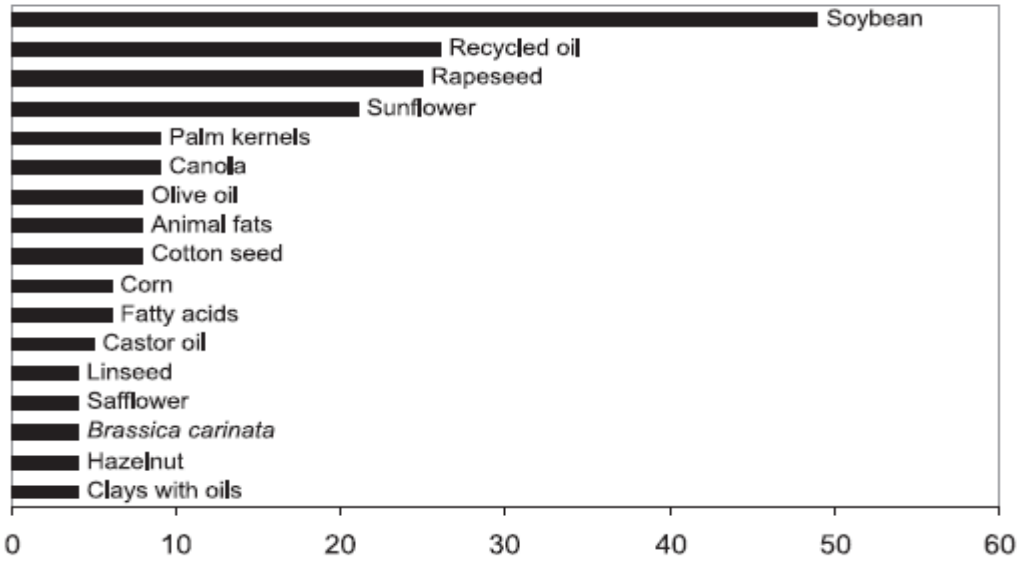

Figure 2-6: Leading sources of biodiesel cited in scientific articles (Pinto, et al., 2005)

Table 2-4: Properties of vegetable oils (Singh & Singh, 2010)

Vegetable Oil	Kinematic viscosity $\left(\frac{mm^2}{s}\right)$ at 38°C	Cetane number (°C)	Heating value $\left(\frac{MJ}{kg}\right)$	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density $\left(\frac{kg}{L}\right)$	Carbon residue (wt %)
Corn	34.9	37.6	39.5	-1.1	-40	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	-15	234	0.9148	0.24
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048	0.23
Linseed	27.2	34.6	39.2	1.7	-15.0	241	0.9236	0.22
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026	0.24
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144	0.25
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133	0.24
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161	0.27
Palm	39.6	42.0	-	31.0	-	267	0.9180	0.23
Babassu	30.3	38.0	-	20.0	-	150	0.9460	-
Diesel	3.06	50	43.8	-	-16	76	0.855	-

Table 2-5: Fatty acid composition of vegetable oils (Singh & Singh, 2010)

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

Given the dependence of biodiesel properties on its parent oil, it is reasonable to postulate that in future genetic engineering could be used to enhance the properties of the parent oil in order to produce biodiesel with desirable properties. The source of biodiesel used is dependent on the availability in each region (Pinto, et al., 2005). The environmental conditions would also dictate the choice of oils, for example, palm oil may be used in regions with a warm climate while in regions with a colder climate it may prove problematic due to its high cloud point value. As seen in table 2-6 below, the yield of oil obtained varies for different oilseeds and this is also a point of consideration when deciding on which oil to use for biodiesel production. The methods of oil extraction include chemical methods such as solvent extraction, as well as mechanical methods such as crushing or pressing (Gunstone, 2009). Chemical methods such as solvent extraction with hexane as solvent was used for soybean and cottonseed oils, while mechanical methods were used for the other oils in table 2-6, this implies that mechanical extraction methods result in higher oil yields.

Table 2-6: Yields of oil and meal obtained by extraction of different oilseeds (Gunstone, 2009)

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

Given that edible vegetable oils have a higher cost than diesel fuel (Pinto, et al., 2005), low cost feedstocks such as waste oils and non-edible crude oils are preferred for biodiesel production.

(i) Sunflower oil

The edible oil obtained from sunflower seeds is of excellent quality in terms of taste and nutritional value (Antolin, et al., 2002). After the extraction of the oil, the remaining cake can be used as livestock feed (Demirbas, 2008). Sunflower oil has low linoleic acid content and may be stored for long periods of time (Canakci & Sanli, 2008). Linoleic acid is unsaturated and hence is more susceptible to oxidation, hence the low amount of linoleic acid in sunflower oil means that it is less susceptible to oxidation and can therefore be stored for longer periods of time (Canakci & Sanli, 2008). The sunflower crops do not require any specialised

agricultural equipment and can grow even under adverse environmental conditions. The oil yield from sunflower seeds is typically 40.9% (Gunstone, 2009).

Table 2-7: Classification of biodiesel feedstocks (Singh & Singh, 2010)

Edible oils	Non-edible oils	Animal fats	Other sources
Almond	Abutilon muticum	Lard	Algae
Soybean	Andiroba	Tallow	Bacteria
Rapeseed	Babassu	Poultry fat	Fungi
Canola	Brassica carinata	Fish oil	Microalgae (Chroellavulgaris)
Safflower	B. napus		Tarpenes
Barley	Camelina		Laxetes
Coconut	Cumaru		Yellow grease
Sunflower	Cynara cadunculus		
Copra	Jatropha curcas		
Cotton seed	Jatropha nana		
Groundnut	Jojoba		
Oat	Pongamia		
Rice	Laurel		
Sorghum	Mahua		
Wheat	Lesquerellafendleri		
Palm	Piqui		
Sesame	Tobacco seed		
	Rubber plant		
	Rice bran		
	Karang		

(ii) Castor oil

Ricinum communis, commonly known as castor bean, is an oilseed crop which belongs to the spurge family called *Euphorbiaceae*, which comprises approximately 6300 species including rubber tree (*Hevea brasiliensis*), cassava (*Manihot esculenta*) and physic nut (*Jatropha curcas*), and its primary economic interest is as a source of castor oil which has various applications such as for the production of high quality lubricants due to its high proportion of the fatty acid ricinoleic acid (Chan, et al., 2010). The castor bean plant is a tropical perennial shrub which finds its origins in Africa but is now cultivated in various tropical and sub-tropical regions of the world (Chan, et al., 2010). One of the largest consumers of castor oil is Brazil,

where attempts are made to extract the ethyl esters using ethanol from sugarcane fermentation which makes it a completely natural and renewable product (Bianchi, et al., 2011). Of all non-edible oils, castor oil is the most widely used for a variety of industrial applications and also has cosmetic, medical and chemical applications (Bianchi, et al., 2011). In addition to being naturally occurring, castor oil is also inexpensive, environmentally friendly and has a good shelf life relative to other vegetable oils (Udoh, et al., 2016). The shelf life of castor oil is due to its major constituent which is ricinoleic acid, a unique hydroxy fatty acid which comprises between 70-90% of castor oil, and does not go rancid unless subjected to high amounts of heat (Huang, et al., 2015). Castor oil is pale-yellow in colour, has a slight distinct nutty odour, is viscous and non-volatile. The high oil content of castor bean seeds and its ease of cultivation in unfavourable environments are the major factors that contribute to its appeal as a crop in tropical developing countries and as a potential raw material for sustainable biodiesel (Chan, et al., 2010). Bianchi, et al. (2011) state that the main limitation for the widespread cultivation of castor beans is that the current practise for harvesting in the largest producer countries (Brazil, India and China) is hand harvesting. Another obstacle noted by Chan, et al. (2010), is that castor beans have a high content of ricin, which is extremely toxic protein and is considered as one of the deadliest natural proteins.

(b) Temperature

Reaction temperature is one of the main factors that affects the yield of biodiesel obtained via a transesterification reaction. High temperatures increase the rate of reaction and result in a shorter reaction time due to the reduction of the viscosity of the vegetable oil (Gashaw & Teshita, 2014). Increasing the temperature above the optimal temperature results in a decrease in biodiesel yield because a high temperature accelerates the saponification of the triglycerides in the vegetable oil (Mathiyazhagan & Ganapathi, 2011). Increasing the reaction temperature beyond the optimal level can also cause the alcohol to vaporise which would result in a decrease in yield of biodiesel (Anitha & Dawn, 2010). Gashaw & Teshita (2014) reported a conversion of up to 78% after 60 minutes at room temperature, indicating that the transesterification reaction can proceed at room temperature but may require longer reaction times. High temperatures increase the energy of the reacting molecules while also improving miscibility of the polar alcohol with a non-polar oil, resulting in quicker reactions (Ogbu & Ajiwe, 2013).

(c) Catalyst loading

Catalyst loading is the amount of catalyst present during a reaction and is typically reported as a percentage of one of the reactants (Fukuda, et al., 2001). The presence of a catalyst is essential for transesterification under atmospheric conditions (Gunstone, 2009). Several

catalysts have been studied in the literature and these include both homogenous and heterogenous catalysts.

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

Heterogenous catalysts include enzymes, titanium silicates, anion exchange resins and alkali earth metals (Arshad, et al., 2018).

Research has also been conducted on the supercritical methanol method which does not require a catalyst, but high temperatures and pressures are required (Sharma, et al., 2008).

Ultrasonic reactors and microwaves have also been investigated. Microwaves are used in combination with a catalyst, but the use of microwaves result in shorter reaction times when compared with conventional heating methods (Mazzocchia, et al., 2004).

The most commonly used catalysts are typically homogenous alkali catalysts such as potassium hydroxide (Saifuddin & Chua, 2004). This could be because this type of catalyst results in faster reaction times without using extreme conditions. The quality of biodiesel obtained when using homogenous base catalysts is also desirable (Kemp, 2006). The main disadvantage of base catalysts is the formation of soap, which is caused by the neutralisation of the free fatty acids in the oil and triglyceride saponification (Mathiyazhagan & Ganapathi, 2011). The saponification reaction is an undesirable side reaction as it partially consumes the catalyst, decreases the yield of biodiesel and complicates the separation and purification steps (Vicente, et al., 2004).

Acid catalysts have not been used as widely as base catalysts. The main advantage of acid catalysts is that they are not sensitive to the free fatty acid content in the oil and can therefore be used to catalyse transesterification of vegetable oils with a high free fatty acid content (Goyal, et al., 2012). Acids can catalyse esterification and transesterification reactions at the same time, which means that instead of soap formation, esters will be formed (Banani, et al., 2015). The main disadvantages of acid catalysts are a slower reaction time, requirement of a larger alcohol to oil molar ratio, high temperature requirements, difficulty in catalyst separation and environmental issues (Lam, et al., 2010). These disadvantages have reduced the potential for large-scale application of acid catalysts for biodiesel production.

Heterogenous catalysts offer the advantage of easy separation and minimal purification steps (Vicente, et al., 2004). However, heterogeneously catalysed transesterification reactions require more extreme reaction conditions (Vicente, et al., 2004).

Biodiesel production via transesterification is affected by the catalyst concentration. Mathiyazhagan & Ganapathi (2011) state that sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the most commonly used catalysts for biodiesel synthesis. Freedman et al. (1984) suggested that sodium methoxide (CH_3NaO) would be a more effective catalyst as mixing sodium hydroxide with methanol may produce a small amount of water which could inhibit the formation of biodiesel and promote saponification. Insufficient catalyst concentration can result in an incomplete conversion of triglycerides to fatty acid esters (Mathiyazhagan & Ganapathi, 2011). The yield of biodiesel generally increases as the catalyst concentration increases due to the availability of a larger number of active sites when using a greater concentration of catalyst (Gashaw & Teshita, 2014). When using alkali catalysts, the yield of biodiesel increases with an increase in catalyst concentration up to an optimal point, after which an increase in catalyst concentration has a negative effect on the yield of biodiesel because an excess of alkali catalyst can result in the formation of soap (Mathiyazhagan & Ganapathi, 2011).

Table 2-8: Advantages and disadvantages of different types of catalysts used in transesterification (Lam, et al., 2010)

Type of catalyst	Advantages	Disadvantages
Homogenous base catalyst	Very fast reaction rate – up to 4000 times faster than acid catalysed transesterification. Reactions can occur under mild conditions and less energy intensive conditions. Catalysts such as KOH and NaOH are relatively cheap and widely available.	Sensitive to FFA content in the oil. Soap will be formed if the FFA content in the oil is greater than 2 wt.%. Too much soap formation will decrease the biodiesel yield and cause problems during purification, especially generating huge amounts of waste water.
Heterogenous base catalyst	Relatively faster reaction rate than acid-catalysed transesterification. Reactions can occur under mild conditions and less energy intensive conditions. Easy separation of catalyst from product.	Poisoning of catalyst when exposed to ambient air. Sensitive to FFA content in the oil due to its basicity. Soap will be formed if the FFA content in the oil is greater than 2 wt.%.

	High possibility to reuse and regenerate the catalyst.	Too much soap formation will decrease the biodiesel yield and cause problems during product purification. Leaching of catalyst active sites may result in product contamination.
Homogenous acid catalyst	Insensitive to FFA and water content in the oil. Preferred method if low-grade oil is used. Esterification and transesterification occur simultaneously. Reactions can occur at mild and less energy intensive conditions.	Very slow reaction rate. Corrosive catalysts such as H_2SO_4 can lead to corrosion on reactor and pipelines. Separation of catalyst from product is problematic.
Heterogenous acid catalyst	Insensitive to FFA and water content in the oil. Preferred method if low-grade oil is used. Esterification and transesterification occur simultaneously. Easy separation of catalyst from product. High possibility to reuse and regenerate the catalyst.	Complicated catalyst synthesis procedures lead to higher cost. Normally, high reaction temperature, high alcohol to oil molar ratio and long reaction time required. Energy intensive. Leaching of catalyst active sites may result in product contamination.
Enzyme	Insensitive to FFA and water content in the oil. Preferred method if low grade oil is used. Transesterification can be carried out at low reaction temperatures, even lower than homogenous base catalysts. Simple purification steps required.	Very slow reaction rate, even slower than acid catalysed transesterification. High cost. Sensitive to alcohol, typically methanol that can deactivate the enzyme.

(d) Alcohol to oil molar ratio

One of the main parameters affecting the yield of biodiesel is the alcohol to oil molar ratio. According to stoichiometry, 3 moles of alcohol are required to react with 1 mole of triglyceride. According to Le Chatelier's principle, an excess amount of methanol would favour the forward reaction and shift the equilibrium to the right. Various alcohols such as methanol, ethanol, propanol and butanol may be used in transesterification reactions, however, methanol is preferred due to its low cost and it is the shortest chain alcohol and is polar (Gashaw & Teshita, 2014). Ethanol is also a preferred alcohol to utilise in transesterification reactions as unlike methanol, ethanol can be derived from agricultural products, is renewable and more environmentally friendly (Gashaw & Teshita, 2014). An increase in the alcohol to oil ratio results in an increase in the yield of biodiesel up to a certain optimal ratio after which a further increase in the oil to alcohol ratio does not increase the yield of biodiesel, but rather increases the difficulty and cost of separation of the biodiesel layer from the glycerol and unreacted alcohol layer (Mathiyazhagan & Ganapathi, 2011). For oils with a high free fatty acid (FFA) content, alkali catalysts are ineffective and acid catalysts should be used; such reactions require a higher amount of alcohol compared to alkali catalysed transesterification reactions (Mathiyazhagan & Ganapathi, 2011). According to the various literature sources studied, the optimum alcohol to oil molar ratio often lied between 6:1 and 12:1, however, this was dependent on various factors such as type of catalyst used, alcohol used, etc.

(e) Reaction time

Freedman et al. (1986) observed an increase in fatty acid conversion when there is an increase in reaction time. In the beginning, the reaction proceeds slowly due to the dispersion and mixing of oil and alcohol, after which the reaction proceeds quickly (Gashaw & Teshita, 2014). In the study conducted by Freedman et al. (1986) the maximum ester conversion was achieved in less than 90 minutes. Increases in reaction time beyond the optimal level results in the reduction of biodiesel due to the reverse reaction resulting in a loss of alkyl esters, as well as soap formation (Jagadale & Jugulkar, 2012).

(f) Free fatty acid and moisture content

Free fatty acids comprise long carbon chains that are disconnected from the glycerol backbone (Lam, et al., 2010). The free fatty acid (FFA) and moisture content of the vegetable oil is an important factor to consider for transesterification reactions. The presence of moisture content is unfavourable as it can cause soap formation and frothing, which could result in an increase in viscosity (Mathiyazhagan & Ganapathi, 2011). Soap formation also consumes the catalyst, resulting in a reduction in its effect (Mathiyazhagan & Ganapathi, 2011). Water content

present in the feedstock can also result in the formation of gels and foams which can cause the separation of glycerol from biodiesel to become increasingly challenging (Demirbas , 2005). Water content could get into the oil during extraction processes and may be present in the oil feedstock as an impurity (Saifuddin & Chua, 2004). Figure 2-7 below shows a typical saponification reaction between oleic acid (FFA) and potassium hydroxide.

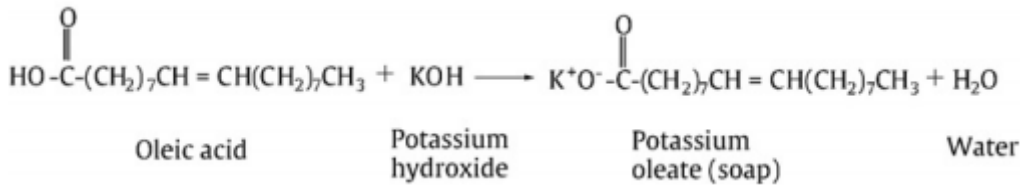

Figure 2-7: Typical saponification reaction (Lam, et al., 2010)

This reaction is highly undesirable as it deactivates the catalyst and thus prevents it from serving its purpose of accelerating the transesterification reaction (Lam, et al., 2010). Excessive soap formation also reduces the yield of fatty acid methyl esters (FAME/biodiesel) and adds a degree of difficulty to the product purification, including water washing and glycerol removal (Kulkarni & Dalai, 2006).

High water or moisture content in the vegetable oil also affects the yield of biodiesel obtained. The presence of water has the ability to hydrolyse triglycerides to diglycerides and form free fatty acids, especially at higher temperatures (Lam, et al., 2010). Figure 2-8 shows a typical hydrolysis reaction. As seen, this reaction results in the formation of free fatty acids which will then go on to react with the base catalyst to form soap as seen in Figure 2-7. It can therefore be concluded that the presence of water in the vegetable oil will result in the excessive formation of soap.

As seen in Figure 2-8, if water is present, then it reacts with the triglyceride to form a diglyceride and fatty acid. This fatty acid (eg. oeic acid) then reacts with the alkali catalyst (eg. KOH) to form a soap (eg. potassium oleate) and water (as seen in Figure 2-7). If water was not present in the feedstock then the triglyceride would not have reacted with it to form the fatty acid and therefore no soap would have formed. It can therefore be deduced that the presence of water in a feedstock does indeed lead to soap formation.

The soaps of saturated fatty acids typically solidify under ambient conditions and therefore a reaction mixture with a lot of soap may gel-up and form a semi-solid mass which is difficult to recover (Felizardo, et al., 2005).

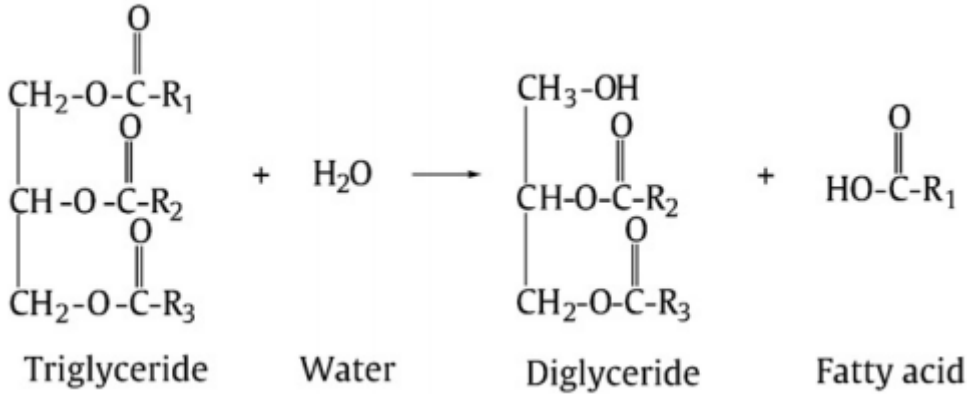

Figure 2-8: Typical hydrolysis reaction of triglyceride to form free fatty acid (Lam, et al., 2010)

Table 2-9: Recommended FFA content for homogenous base catalysed transesterification

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

2.4. Transesterification reaction mechanisms

2.4.1. Homogenous base catalysed transesterification

Biodiesel is currently produced using homogenous base catalysts such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) (Kulkarni & Dalai, 2006). The main reasons these catalysts are so widely used include the fact that they are able to catalyse the transesterification reaction at atmospheric pressure and at low temperatures, they are widely available and inexpensive, and high conversion and yields can be achieved in short periods of time (Lotero, et al., 2005). It was reported by Kulkarni & Dalai (2006) and Fukuda, et al. (2001) that base catalysed transesterification reaction rates would be 4000 times faster than acid catalysed reactions. However, these catalysts cannot be used for all vegetable oils as they are very sensitive to the FFA content of the oil. Wang, et al. (2006) reported that homogenous base catalysts should only be used with oils that have an FFA content of lower than 0.5 wt.%, while Felizardo, et al. (2005) reported that homogenous base catalysts can be used in conjuction with

oils that have an acid value below 1 $\frac{mg\ KOH}{g}$. However, as seen in table 2-9, other researchers have recommended FFA values of up to 2 wt.%.

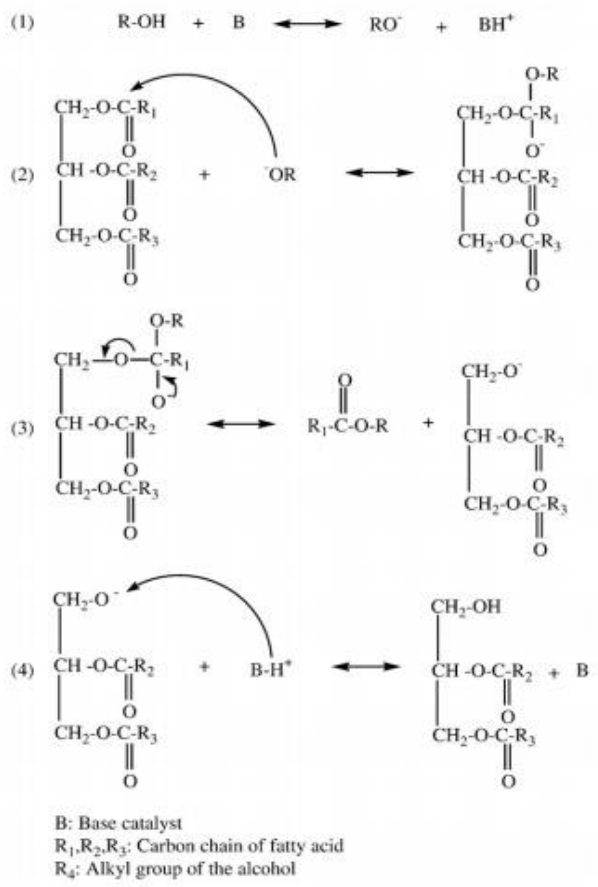

Figure 2-9: Reaction mechanism for homogenous base catalysed transesterification: (1) production of the active species , RO^-, (2) nucleophilic attack of RO^- to carbonyl group on triglycerides forming a tetrahedral intermediate, (3) intermediate breakdown, (4) regeneration of the RO^- active species (Lotero, et al., 2005)

2.4.2. Homogenous acid catalysed transesterification

The use of acid catalysts has been reported in the literature mainly for use with oils that have a high free fatty acid content. The most investigated homogenous acid catalysts are hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) (Lam, et al., 2010). Transesterification via acid catalysis offers two main advantages over base catalysis; acid catalysts are insensitive to free fatty acids in the oil (Kulkarni & Dalai, 2006), and acid catalysts are able to catalyse esterification and transesterification simultaneously (Jacobson , et al., 2008).

Esterification is a chemical reaction wherein an alcohol and acid react to form an ester (Lam, et al., 2010). It was widely reported in the literature that acid catalysts are more efficient when the amount of free fatty acids in the vegetable oil is greater than 1 wt.% (Zhang, et al., 2003; Canakci & Van Gerpen, 1999; Freedman, et al., 1984; Gashaw & Teshita, 2014;

Mathiyazhagan & Ganapathi, 2011). Zhang, et al. (2003) reported that since acid catalysed reactions are a one-step process, they are more economical compared to base catalysts which require two steps for vegetable oils with high free fatty acid content.

When it comes to commercial application however, acid catalysts are not a viable option because they have slower reaction rates, require high reaction temperatures, require high alcohol to oil molar ratios, catalyst separation is difficult and they result in environmental issues (Wang, et al., 2006).

Lotero, et al. (2005) investigated the difference between homogenous acid and base catalysed transesterification reaction mechanisms in an attempt to explain why acid catalysts have a longer reaction time. A comparison of Figures 2-9 and 2-10 show that for acid catalysed reactions, the main step is the protonation of the carbonyl group. This increases the electrophilicity of the adjoining carbon atom, causing the intermediate molecules to be susceptible to nucleophilic attack (Lam, et al., 2010). Base catalysts on the other hand take on a more direct route; the alkoxide ion which is created initially acts as a strong nucleophile (Lam, et al., 2010). This different reaction path; formation of electrophilic species via acid catalyst and formation of stronger nucleophile via base catalyst, is essentially responsible for the difference in catalytic activity between acid and base catalysed transesterification (Lam, et al., 2010).

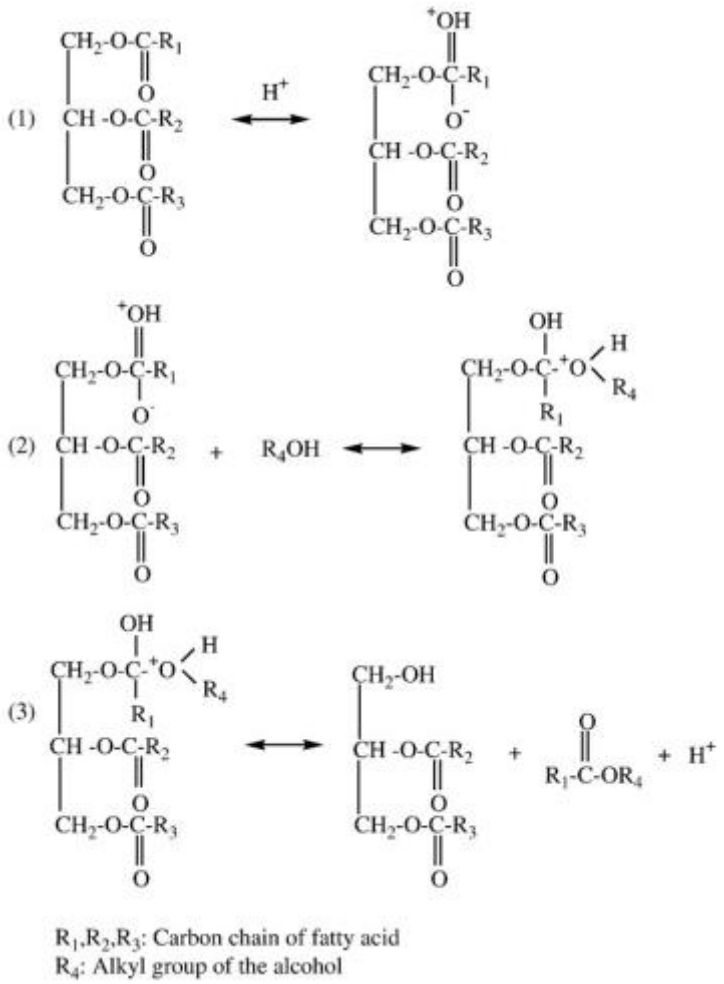

Figure 2-10: Reaction mechanism for homogenous acid catalysed transesterification: (1) protonation of carbonyl group by acid catalyst, (2) nucleophilic attraction of the alcohol forming a tetrahedral intermediate, (3) proton migration and breakdown of the intermediate (Lotero, et al., 2005)

2.4.3. Heterogenous base catalysed transesterification

Several solid (heterogenous) base catalysts such as basic zeolites, hydrotalcites and alkaline earth metals have been studied for biodiesel production via transesterification (Lam, et al., 2010). Calcium oxide (CaO) has a high basic strength, low solubility in methanol and can be synthesized via cheap sources such as limestone and hence has attracted a lot of attention as a potential catalyst for biodiesel production (Zabeti, et al., 2009).

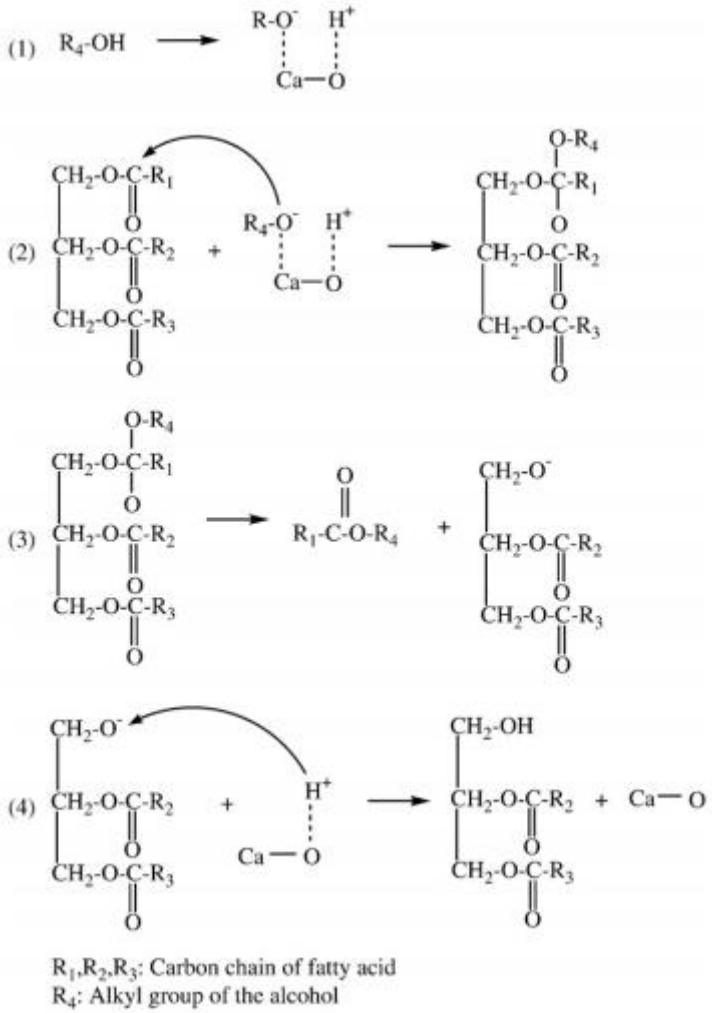

Figure 2-11: Reaction mechanism for heterogenous base catalysed transesterification: (1) abstraction of proton from methanol by basic sites to form methoxide anion, (2) methoxide anion attacks carbonyl carbon in a molecule of the triglyceride leading to formation of alkoxycarbonyl intermediate, (3) alkoxycarbonyl intermediate transformed into more stable form (FAME and anion of diglyceride), (4) methoxide cation attracts the anion of diglyceride leading to formation of diglyceride (Lotero, et al., 2005)

2.5. Properties of biodiesel

The properties of biodiesel are dependent on the properties of the oil and alcohol used in its production. The structural features such as degree of unsaturation, chain length and branching of the vegetable oil and alcohol also affects such properties of biodiesel as viscosity, cetane number, heat of combustion and oxidative stability (Marwaha, et al., 2018). Although most properties of biodiesel are comparable to petroleum-based diesel fuel, the low temperature properties of biodiesel make it unsuitable for direct use in an engine, however, these properties may be improved by blending the biodiesel with kerosene and ethanol (Marwaha, et al., 2018).

2.5.1. Viscosity

Viscosity is defined as “a measure of resistance to flow of a liquid due to internal friction of one part of a fluid moving over another” (Saxena, et al., 2013). According to Canakci & Sanli (2008), the viscosity of a fuel is one of its most critical properties as it plays a dominant role in the fuel spray, mixture formation and combustion process. The kinematic viscosity determines the degree of atomization that biodiesel has inside the combustion chamber (Anguebes-Franseschi, et al., 2019). The main issue with the direct use of vegetable oils as fuels is their high viscosity. The high viscosity affects the injection process and leads to insufficient fuel atomization (Canakci & Sanli, 2008). The mean diameter of the fuel droplets from the injector and their penetration increases with increasing viscosity (Choi & Reitz, 1999). This contributes to nozzle clogging, injector choking and incomplete combustion within the engine (Kumar, et al., 2017). The afforementioned issues can also result in a reduced engine life. Viscosity increases as the chain length (number of carbon atoms) of an organic molecule increases. Viscosity also increases with an increasing degree of saturation (Knothe, 2005). Methanol is preferred for the production of biodiesel via transesterification as the viscosity of methyl esters is lower than that of ethyl esters (Knothe, 2005). Bianchi, et al. (2011) claim that the necessary fuel characeristics are dependent on the intended application of the fuel, for instance, engines used for the production of energetic power allow the use of fuels with a higher viscosity. The viscosity of biodiesel is higher than that of petro-diesel typically by a factor of approximately two (Saxena, et al., 2013).

2.5.2. Density

According to Bianchi, et al. (2011), the density dictates the energy content of a fuel, where higher desities indicate a higher amount of thermal energy for the same amount of fuel, resulting in a better fuel economy. Density is an important fuel property because injection systems and pumps must deliver a precisely adjusted amount of fuel to provide proper combustion (Dzida & Prusakiewicz, 2008). Density values of biodiesel should be maintained within certain limits in order to allow optimal air to fuel ratios for complete combustion (Ismail & Ali, 2015). High density biodiesel or blends thereof can lead to particulate matter emmissions as well as incomplete combustion (Ismail & Ali, 2015). Typically, the density of biodiesel is slightly higher than that of petro-diesel, and increasing the level of biodiesel blends increases the blend’s density (Saxena, et al., 2013). The density of biodiesel is dependent on the raw materials used in its production as well as the alkyl ester profile of the biodiesel (Blangino, et al., 2008), with the degree of unsaturation being a major influence on the density of biodiesel; a higher degree of unsaturation results in a higher density (Saxena, et al., 2013). Chain length also affects biodiesel density with an increase in chain length leading to a

decrease in density (Saxena, et al., 2013). The density of biodiesel at 40 ℃ specified in ASTM D6751 is 0.82-0.9 $\frac{g}{cm^3}$.

2.5.3. Iodine value

The iodine value is an indication of the number of double bonds in biodiesel and hence is used to quantify the degree of unsaturation of biodiesel (Bianchi, et al., 2011). The iodine value is constant for a specific oil or fat and is a useful parameter when studying oxidative rancidity, as well as chemical stability of different oils and biodiesel (Ismail & Ali, 2015). The presence of a high amount of double bonds indicate a greater potential to polymerise and hence, a low stability (Ismail & Ali, 2015).

2.5.4. Cetane number

Cetane number (CN) is a measure of a fuel's auto-ignition quality characteristics. The cetane number is a similar concept to octane number for gasoline. Biodiesel comprises mainly long-chain hydrocarbon groups with no branching or aromatic structures, hence biodiesel typically has a higher cetane number than petroleum diesel (Saxena, et al., 2013). The cetane number of pure fatty acid methyl esters (FAME) increases with chain length, however, this effect is not prominent when considering blends of FAME fuels (Saxena, et al., 2013). Saxena, et al. (2013) report that the cetane number decreases as the degree of unsatration increases.

2.5.5. Acid value

The acid value (AV) measures the content of acidic substances in biodiesel, and is also used to monitor the degree of degradation that may occur during storage (Anguebes-Franseschi, et al., 2019).

2.5.6. Saponification value

The saponification value (SV) is an indication of the amount of saponifiable units (acyl groups) per unit weight of oil (Ismail & Ali, 2015). A high saponification value indicates a higher proportion of low molecular weight fatty acids, while a low saponification value indicates a lower proportion of low molecular weight fatty acids (Ismail & Ali, 2015). According to Ismail & Ali (2015), the saponification value can be used to calculate the average molecular weight of oil and is expressed in miligrams of potassium hydroxide per gram of oil.

2.5.7. Heating value

The heating value of a fuel is defined as the amount of heat released during the combustion of a specified amount of the fuel (Arshad, et al., 2018). Due to the high oxygen content of biodiesel, it has lower mass energy values than petroleum diesel (Ismail & Ali, 2015). As the

chain length inceases for a constant level of unsaturation, the amount of oxygen decreases resulting in an increase in heating value (Ismail & Ali, 2015).

2.5.8. Flash point

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

2.5.9. Cloud point

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

2.5.10. Pour point

Pour point (PP) is the temperature at which the amount of wax out of solution is sufficient to gel the fuel (Arshad, et al., 2018). Biodiesel has a higher pour point than petroleum diesel (Singh & Singh, 2010).

Table 2-10: Some physical and chemical properties of diesel and biodiesel produced from different feedstocks (Kumar, et al., 2017)

Edible and non-edible oil esters	Kinematic viscosity at 38°C $\left(\frac{mm^2}{s}\right)$	Cetane number	Heating value $\left(\frac{MJ}{kg}\right)$	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density $\left(\frac{kg}{m^3}\right)$
Peanut	4.9	54	33.6	5	-	176	883
Soybean	4.5	45	33.5	1	-7	178	885
Babassu	3.6	63	31.8	4	-	127	875
Palm	5.7	6	33.5	13	-	164	880
Sunflower	4.6	49	33.5	1	-	183	860
Jatropha	2.37	61	39.1	-	2	135	880
Karanja	4.78	42	37.0	19	6	144	860
Castor	10.7	-	3.4	-	-13	160	900
Diesel	3.06	50	43.8	-	-16	128	855

2.6. Esterification

Free fatty acids in oils are saponified by homogenous alkali catalysts during transesterification reactions, resulting in a loss of catalyst as well as increased purification costs (Narasimharao, et al., 2007). Free fatty acids react with the basic catalyst and form soap as an unwanted by-product resulting in a portion of the catalyst being neutralised and therefore unavailable for transesterification (Narasimharao, et al., 2007). It is therefore necessary to first esterify the free fatty acids to alkyl esters in the presence of an acidic catalyst prior to transesterification of oils with a high free fatty acid content.

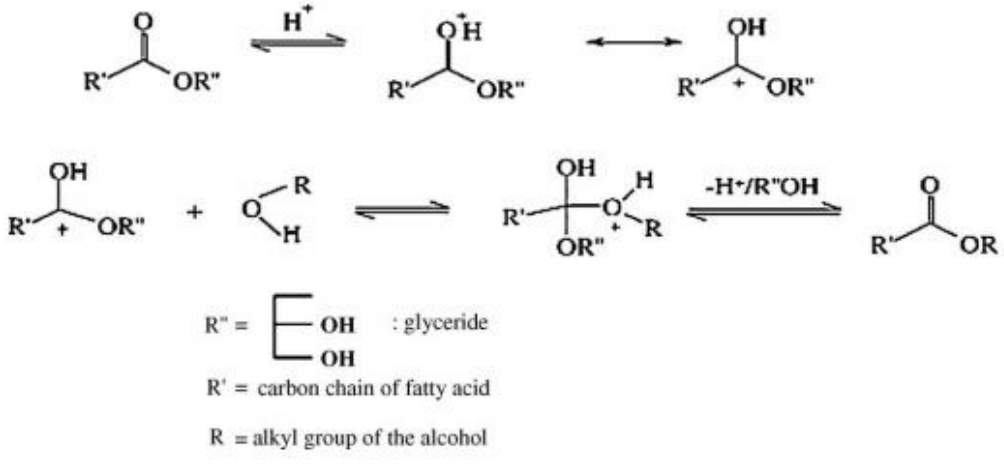

Figure 2-12: Esterification reaction mechanism (Singh & Singh, 2010)

Table 2-11: Major 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 on feedstocks and equipment	Lower sulphur 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		

Chapter 3

Equipment & Feedstock Description

Various experiments were conducted in this study, and this chapter provides an outline of the feedstocks and chemicals used during the study, as well as the experimental equipment used. Castor oil and sunflower oil were the chosen vegetable oil feedstocks used in this study. These oils were subjected to a transesterification reaction with methanol using potassium hydroxide as a catalyst in order to produce biodiesel. The following chemicals were used during this study without any further purification:

Table 3-1: Chemicals used for esterification and transesterification reactions

Chemical	Supplier	Purity
Organic sunflower oil	Lichro Chemical and Laboratory Supplies	
Organic castor oil	Lichro Chemical and Laboratory Supplies	
Methanol	Sigma-Aldrich	≥99.8%
Hydrochloric acid	Sigma-Aldrich	Analytical Reagent (AR)
Potassium hydroxide	Radchem	Analytical Reagent (AR)
Sulphuric acid	Radchem	98% AR
Toluene	Merck	≥99%
Isopropyl alcohol	Radchem (Pty) Ltd	Analytical Reagent (AR)
Kerosene	Lichro Chemical and Laboratory Supplies	
Phenolphthalein	Lichro Chemical and Laboratory Supplies	1% in 96% ethanol

Table 3-2: Description of equipment used in this study

Equipment	Purpose	Key
Heating mantle and magnetic stirrer	Provide heat to the reaction mixture	1
Magnetic stirrer bar	Provide vigorous stirring of the reaction mixture	
Thermometer	Measure temperature of reaction mixture to allow for temperature control	2
3-Necked round bottom flask	Contains the reaction mixture	3
Reflux condenser	Condense any vapours during the reaction	4
Water bath and chiller	Supply cold water to the reflux condenser	5
Separation funnel	Facilitate the separation of biodiesel and glycerol	
Volumetric flask	Facilitate the mixing of alcohol and catalyst	
Scale	To measure the mass of sample	
Volumetric cylinder	Measure required oil quantity	
Rotary evaporator	Purify the biodiesel obtained after water washing	
Burette	Used in titrations for determination of acid number	
Dropper	Used to add indicator to the sample being titrated	
Viscometer	Measure viscosity	
Hydrometer	Measure specific gravity	

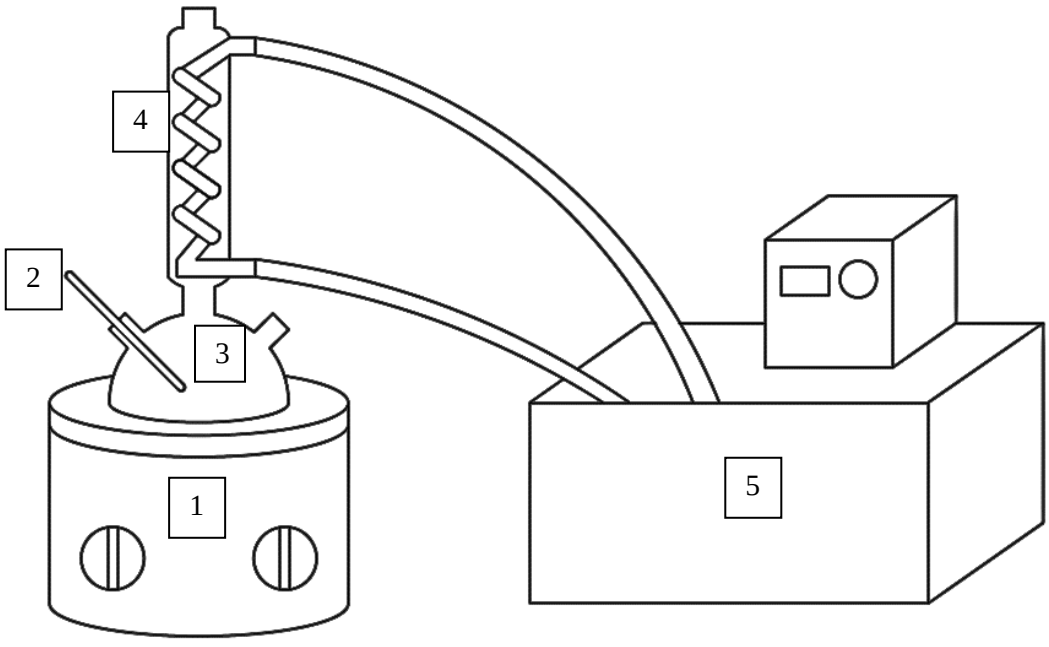

Figure 3-1: Experimental set-up

Figure 3-2: Picture of experimental set-up

Figure 3-3: Sunflower oil biodiesel (top layer) and glycerol (bottom layer)

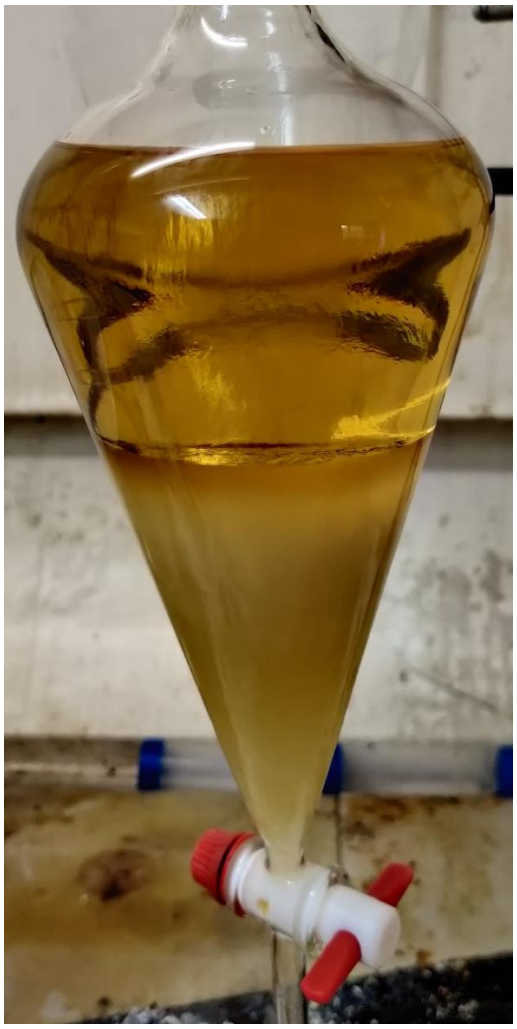

Figure 3-4: Castor oil biodiesel (top layer) and glycerol (bottom layer)

Chapter 4

Experimental Design & Methods

4.1. Experimental Design

The experimental design method employed in this study was the Box-Behnken design, which is a response surface methodology (RSM) design which requires only three levels to run an experiment. Statistical approaches such as the Box-Behnken design can greatly reduce the number of experimental trials required without reducing the accuracy of the optimisation when compared to traditional factorial design methods (Qiu, et al., 2013).

Most research in the literature have focused on a one variable at a time (OVAT) approach to determine the effect of different variables on the yield of biodiesel and to optimise the yield of biodiesel, however, an OVAT approach does not consider the interactions between the variables investigated and hence, a statistical approach which considers the interactions between different variables was deemed appropriate for this study. The Box-Behnken approach was chosen as it avoids using a combination of the extreme values of all variables simultaneously and hence avoids experiments performed under extreme conditions which are costly and may exhibit unsatisfactory results (Ferreira, et al., 2007). This means that the response variable would not be determined when all 4 variables are simultaneously at their extreme values, however this was not an issue for this study as the optimum conditions are expected to lie within the range of the chosen variables.

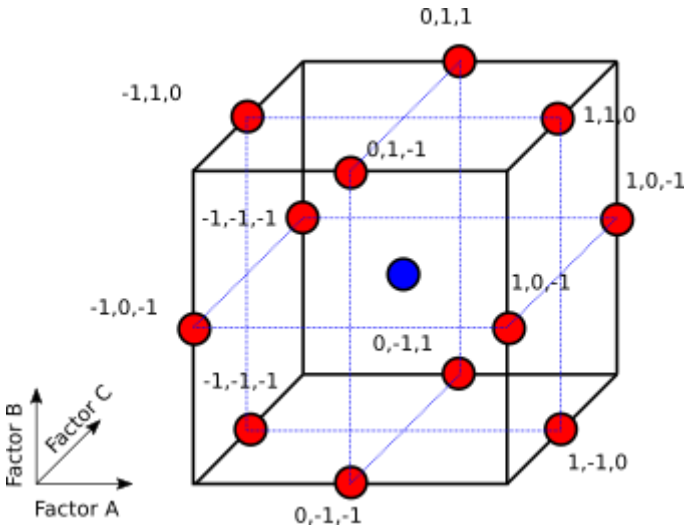

Figure 4-1: Box-Behnken design (Develve, 2018)

The number of experiments (N) required for a Box-Behnken design can be calculated as follows (Ferreira, et al., 2007):

$$N = 2k(k-1) + C_0$$

Where N is the number of experiments, k is the number of factors and C_0 is the number of central points. So, for 4 factors with 3 central points, the number of experiments required would be:

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

The experimental design and optimisation were done on Minitab software (version 17). Four factors were varied; reaction time, reaction temperature, catalyst loading and alcohol to oil molar ratio. This resulted in a total of 27 experimental runs, including 3 replicates which help improve accuracy. Tables 4-1, 4-2 and 4-3 on pages 39, 40 and 41, respectively show the experimental conditions for all 27 experimental runs for castor oil esterification, castor oil transesterification and sunflower oil transesterification, respectively.

Table 4-1: Castor oil esterification experimental design

Run Order	Temperature (℃)	Catalyst Loading (wt. % oil)	Time (min)	Alcohol/Oil Molar Ratio
1	30	3.25	75	9.5
2	64	0.25	75	9.5
3	47	1.75	75	9.5
4	47	0.25	120	9.5
5	64	1.75	120	9.5
6	47	0.25	30	9.5
7	47	1.75	75	9.5
8	47	1.75	75	9.5
9	64	3.25	75	9.5
10	64	1.75	75	4
11	30	0.25	75	9.5
12	47	0.25	75	4
13	47	1.75	30	4
14	30	1.75	30	9.5
15	47	3.25	75	15
16	30	1.75	75	15
17	47	3.25	120	9.5
18	47	1.75	120	4
19	47	3.25	75	4
20	30	1.75	75	4
21	47	3.25	30	9.5
22	64	1.75	30	9.5
23	47	0.25	75	15
24	47	1.75	120	15
25	47	1.75	30	15
26	30	1.75	120	9.5
27	64	1.75	75	15

Table 4-2: Castor oil transesterification experimental design

Run Order	Temperature (°C)	Catalyst Loading (wt. % oil)	Time (min)	Alcohol/Oil Molar Ratio
1	47	0.5	30	9.5
2	64	1.5	75	15
3	47	0.5	75	4
4	47	1.5	75	9.5
5	47	1.5	30	15
6	47	1.5	75	9.5
7	47	1.5	75	9.5
8	47	2.5	30	9.5
9	47	1.5	120	4
10	47	2.5	75	4
11	47	1.5	120	15
12	64	2.5	75	9.5
13	30	2.5	75	9.5
14	30	1.5	120	9.5
15	47	0.5	75	15
16	30	1.5	30	9.5
17	64	1.5	120	9.5
18	64	1.5	30	9.5
19	47	2.5	120	9.5
20	30	0.5	75	9.5
21	64	0.5	75	9.5
22	30	1.5	75	4
23	47	2.5	75	15
24	64	1.5	75	4
25	30	1.5	75	15
26	47	0.5	120	9.5
27	47	1.5	30	4

Table 4-3: Sunflower oil transesterification experimental design

Run Order	Temperature (°C)	Catalyst Loading (wt. % oil)	Time (min)	Alcohol/Oil Molar Ratio
1	47	2.5	75	4
2	30	1.5	30	9.5
3	47	1.5	30	15
4	64	1.5	120	9.5
5	47	0.5	75	15
6	47	1.5	120	15
7	47	1.5	75	9.5
8	64	0.5	75	9.5
9	30	1.5	75	15
10	47	0.5	30	9.5
11	47	2.5	30	9.5
12	47	2.5	120	9.5
13	30	0.5	75	9.5
14	64	1.5	75	4
15	47	1.5	75	9.5
16	30	1.5	75	4
17	30	1.5	120	9.5
18	64	2.5	75	9.5
19	47	0.5	75	4
20	47	1.5	75	9.5
21	30	2.5	75	9.5
22	47	0.5	120	9.5
23	47	1.5	30	4
24	64	1.5	75	15
25	47	2.5	75	15
26	64	1.5	30	9.5
27	47	1.5	120	4

4.2. Experimental Method

It should be noted that due to the high acid value of castor oil, a 2-step method was employed. The first step was esterification with an acid catalyst (sulphuric acid) in order to reduce its acid value, and the second step was transesterification of the pre-treated oil with a base catalyst (potassium hydroxide). Sunflower oil had a low acid value and hence did not require acid catalysed pre-treatment. The only difference between the transesterification procedures for both oils was that raw sunflower oil was used, while pre-treated castor oil was used. The method for transesterification and esterification were very similar with minor differences as outlined below. The following steps were conducted for esterification of castor oil, transesterification of pre-treated castor oil, and transesterification of sunflower oil:

- First, 300 ml of oil was weighed, and this mass was converted into moles. The oil was then heated while being stirred.
- Using the appropriate molar ratio of alcohol to oil, the mass of methanol required was obtained.
- The amount of catalyst required (as a weight percentage of oil used) was weighed and dissolved into the methanol.
- Once the oil was at the desired temperature, the alcohol and catalyst mixture was added to the oil.
- After the appropriate reaction time had elapsed, the mixture was poured into a separation funnel and allowed to settle.
- Two distinct layers were observed in the funnel, the top layer being biodiesel and the bottom layer being glycerol.
- Upon removing the bottom glycerol layer from the funnel, hot water was added to remove any additional impurities from the biodiesel as biodiesel is insoluble in water.
- The biodiesel was then further purified in a rotary evaporator at 150 mbar and 90 ℃.

The following steps were conducted only for the esterification of castor oil:

- The purpose of esterification of castor oil was to reduce its acid number, hence after being purified in the rotary evaporator, acid tests were conducted on the sample according to the method described in ASTM D974.
- The optimum conditions to reduce the acid value of castor oil was determined using Minitab software and several reactions were conducted under these conditions to ensure that there was sufficient pre-treated castor oil for transesterification.

The following steps were conducted for the transesterification of castor oil and sunflower oil:

- After being purified in the rotary evaporator, the sample was allowed to cool before being weighed.
- The mass of biodiesel obtained was then recorded and used to determine the yield of biodiesel obtained according to the following equation (Fereidooni, et al., 2017):

$$Yield = \frac{mass\ of\ biodiesel\ produced}{mass\ of\ oil\ used} \quad (1)$$

Chapter 5

Sunflower Oil Transesterification: Results & Discussion

Preliminary property testing of sunflower oil indicated that its properties were desirable for the production of biodiesel. The main issue with the direct use of vegetable oils in diesel engines is their high viscosity (Antolin, et al., 2002). Sunflower oils low dynamic viscosity of 29.3 cP made it an attractive feedstock for biodiesel production. Sunflower oil is also cheaper than other vegetable oils, is easily obtained and its low acid value of 0.32 $\frac{mg\ KOH}{g}$ meant that it could be transesterified using a base catalyst to produce biodiesel in a single step resulting in low production costs.

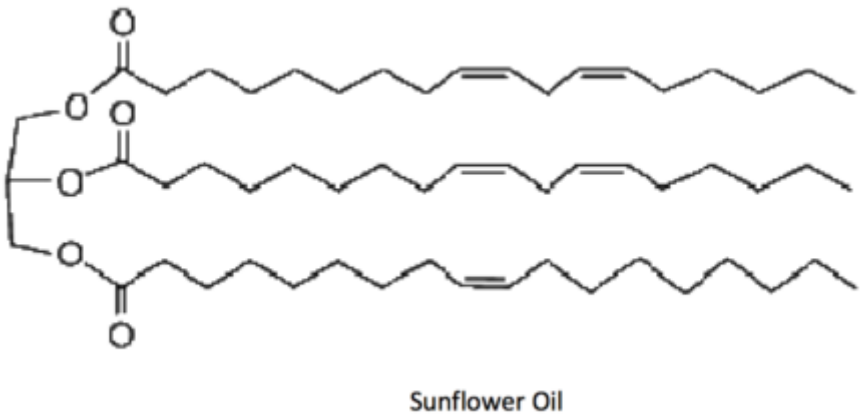

Figure 5-1: Chemical structure of sunflower oil (Guinda, et al., 2003)

Table 5-1: Summary of properties of sunflower oil

Density $\left(\frac{kg}{m^3}\right)$	916
Dynamic viscosity (cP)	29.3
Acid number $\left(\frac{mg\ KOH}{g}\right)$	0.32
FFA%	0.16
Refractive index	1.47252

Table 5-2: Composition of sunflower oil

Component	Chemical formula	%
Palmitic acid	$C_{16}H_{32}O_2$	5.8
Palmitoleic acid	$C_{16}H_{30}O_2$	0.1
Stearic acid	$C_{18}H_{36}O_2$	3.9
Oleic acid	$C_{18}H_{34}O_2$	32.6
Linoleic acid	$C_{18}H_{32}O_2$	56.2
Linolenic acid	$C_{18}H_{30}O_2$	0.1
Arachidic acid	$C_{20}H_{40}O_2$	0.3
Behenic acid	$C_{22}H_{44}O_2$	0.7

Table 5-1 shows the measured properties of sunflower oil. Table 2-9 on page 23 shows the FFA % recommendations of different researchers for base catalysed transesterification. Since sunflower oil had a very low acid number, a single step base catalysed transesterification process was sufficient to convert sunflower oil into biodiesel.

In this study, potassium hydroxide (KOH) was used to catalyse the transesterification of sunflower oil with methanol. The Box-Behnken design was done on Minitab (version 17) and was implemented in order to determine the conditions which resulted in the greatest yield of biodiesel from sunflower oil. Reaction temperature was varied from 30℃ to 64℃ as the boiling point of methanol is 64.7℃ and it is recommended that the reaction temperature should not exceed the boiling point of methanol as this would result in the vaporisation of methanol and therefore decreased contact between the oil and alcohol (Mathiyazhagan & Ganapathi, 2011). The catalyst loading was varied from 0.5 wt % of oil to 2.5 wt % of oil. The alcohol to oil molar ratio was varied from 4:1 to 15:1. Stoichiometrically, a ratio of 3:1 is required for the reaction, however, an excess amount of alcohol is desirable in order to shift the equilibrium to the right and promote the forward reaction. An excess amount of alcohol also helps the dissolution of water produced from the reaction (Fereidooni, et al., 2017). The reaction time

was varied from 30 minutes to 120 minutes. Freedman, et al. (1986) reported that the conversion of triglycerides increases with an increase in time, but the maximum conversion was achieved in less than 90 minutes. This trend is further supported by the findings of Chai, et al. (2014), Gashaw & Teshita (2014), Goyal, et al. (2012) and Mathiyazhagan & Ganapathi (2011), however, the vegetable oil used in these studies were different and hence a maximum reaction time of 120 minutes was chosen for this study to cover a wider range.

The Box-Behnken design resulted in a total of 27 experimental runs, including 3 replicates. Upon completion of all 27 experiments, Minitab was used to fit a regression equation to the data. The results of these experiments are shown in table 5-3 (page 47) using coded variables. The coded variables are as follows:

A = Reaction temperature (℃) B = Catalyst loading (%)

C = Reaction time (min) D = Alcohol/oil molar ratio

As seen in table 5-3 on page 47, the maximum experimental yield of 0.9658 was obtained for experimental run 21 with a temperature of 30 ℃, a catalyst loading of 2.5%, a reaction time of 75 minutes and an alcohol to oil molar ratio of 9.5, while the lowest experimental yield of 0.7300 was obtained in experiment 18 with a temperature of 64 ℃, a catalyst loading of 2.5%, a reaction time of 75 minutes and an alcohol to oil molar ratio of 9.5. The low yield can be attributed to the high temperature which could've resulted in the evaporation of methanol leading to decreased contact between the oil and alcohol and therefore a reduced yield. Experiment 18 also had a high catalyst loading of 2.5% which resulted in soap formation which was observed during the water washing process, the soap formation resulted in a reduced biodiesel yield. Even though experiment 21, which saw the highest experimental yield, also had a catalyst loading of 2.5%, it had a low temperature of 30 ℃ and therefore a high amount of catalyst did not have a negative effect on the yield in this case.

Table 5-3: Sunflower oil transesterification results

Run Order	A	B	C	D	Yield (Experimental)	Yield (Predicted)
1	47	2.5	75	4	0.8166	0.8149
2	30	1.5	30	9.5	0.9480	0.9437
3	47	1.5	30	15	0.9050	0.9245
4	64	1.5	120	9.5	0.8861	0.8768
5	47	0.5	75	15	0.9560	0.9464
6	47	1.5	120	15	0.8862	0.8650
7	47	1.5	75	9.5	0.9582	0.9451
8	64	0.5	75	9.5	0.9623	0.9838
9	30	1.5	75	15	0.8970	0.9048
10	47	0.5	30	9.5	0.8863	0.8711
11	47	2.5	30	9.5	0.8752	0.8700
12	47	2.5	120	9.5	0.7613	0.7650
13	30	0.5	75	9.5	0.8930	0.8837
14	64	1.5	75	4	0.83	0.8125
15	47	1.5	75	9.5	0.9279	0.9451
16	30	1.5	75	4	0.9447	0.9465
17	30	1.5	120	9.5	0.9134	0.9185
18	64	2.5	75	9.5	0.7300	0.7396
19	47	0.5	75	4	0.8643	0.8609
20	47	1.5	75	9.5	0.9596	0.9451
21	30	2.5	75	9.5	0.9658	0.9445
22	47	0.5	120	9.5	0.9534	0.9472
23	47	1.5	30	4	0.8200	0.8396
24	64	1.5	75	15	0.9454	0.9339
25	47	2.5	75	15	0.8170	0.8091
26	64	1.5	30	9.5	0.8981	0.8805
27	47	1.5	120	4	0.8912	0.8702

Table 5-4: Model summary for sunflower oil transesterification

Terms	S	R^2	R^2 (adjusted)	R^2 (predicted)
Linear	0.0542	0.3708	0.2564	0.0568
Linear + squares	0.0509	0.5465	0.3449	0.0000
Linear + interactions	0.0373	0.7828	0.6471	0.4965
Full quadratic	0.0188	0.9585	0.9102	0.7830

The coefficient of determination (R^2) value is defined as the ratio of the explained variation to the total variation and is a measure of the degree to which the regression equation fits the data (Qiu, et al., 2013). Joglekar & May (1987) suggested that an R^2 value of at least 0.8 is indicative of a good model fit. It can be seen from table 5-4 above that only a full quadratic model had an R^2 value higher than 0.8, implying that only a full quadratic model provides a good fit to the data obtained and may be used to adequately predict the biodiesel yield within the range of this study. This means that the full quadratic response model obtained in this study explains the transesterification of sunflower oil very well, with an R^2 value of 0.9585 and an adjusted R^2 value of 0.9102 at a 95% confidence level. The fit of the model to the data can be seen visually in Figure 5-2 (page 49). The predicted R^2 value of 0.7830 indicates that the model may only be approximately 78% accurate in predicting the yield of biodiesel outside the range of the study. This value being lower than the other two R^2 values could be an indication that the model is tailored specifically to the data obtained in this study, hence the model can be used to accurately predict the yield of biodiesel inside the range of this study only. The S-value in table 5-4 represents the standard deviation of the distance between the data values and the fitted values. The extremely low S-value of 0.0188428 indicates a low deviation of data points from the predicted responses, indicating that the regression equation fits the data obtained well. The model is also very significant, as indicated by its high F-value of 19.82 and very low probability (p) value of 0 (seen in table 5-5 on page 49). For a 95% confidence level, a p-value less than 0.05 indicates statistical significance, while a value higher than 0.1 indicates statistical insignificance (Zhang & Zheng, 2009).

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

$$\begin{aligned} Yield = {} & 0.356 + 0.00306A + 0.4281B + 0.004284C + 0.01997D - 0.000027\,A^2 \\ & -0.04939B^2 - \ 0.000016\,C^2 - 0.001252\,D^2 - 0.004487\,AB \\ & +0.000007AC + 0.000436AD - 0.001006BC - 0.00415BD \\ & -0.000091CD \end{aligned}$$

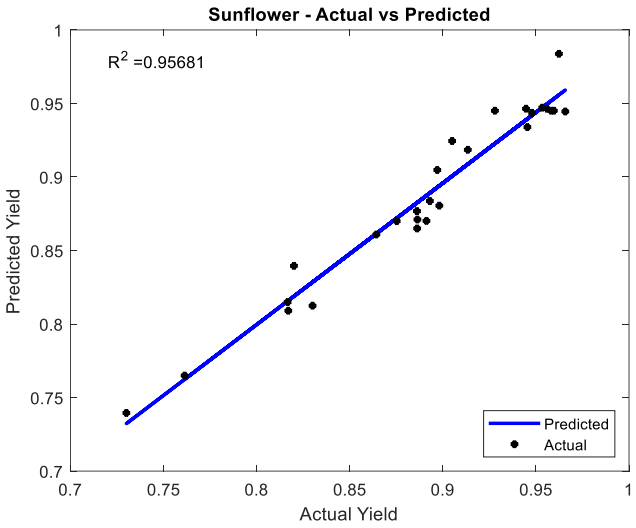

Figure 5-2: Model predicted yield of sunflower oil biodiesel vs actual yield

Table 5-5: Analysis of variance (ANOVA) for sunflower oil transesterification (full quadratic model)

Analysis of Variance						
Source	Degrees of freedom	Sum of squares	Mean squares	F-value	p-value	Characteristics
Model	14	0.098504	0.007036	19.82	0	Significant
Linear	4	0.038101	0.009525	26.83	0	Significant
A	1	0.008004	0.008004	22.54	0	Significant
B	1	0.025163	0.025163	70.87	0	Significant
C	1	0.000140	0.000140	0.39	0.542	Not Significant
D	1	0.004794	0.004794	13.50	0.003	Significant
Square	4	0.018057	0.004514	12.71	0	Significant
A^2	1	0.000326	0.000326	0.92	0.357	Not Significant
B^2	1	0.013012	0.013012	36.65	0	Significant
C^2	1	0.005299	0.005299	14.92	0.002	Significant
D^2	1	0.007650	0.007650	21.55	0.001	Significant
2-Way interaction	6	0.042345	0.007058	19.88	0	Significant
AB	1	0.023273	0.023273	65.55	0	Significant
AC	1	0.000127	0.000127	0.36	0.561	Not significant
AD	1	0.006649	0.006649	18.73	0.001	Significant
BC	1	0.008190	0.008190	23.07	0	Significant
BD	1	0.002082	0.002082	5.86	0.032	Significant
CD	1	0.002024	0.002024	5.70	0.034	Significant
Error	12	0.004261	0.000355			
Lack of fit	10	0.003622	0.000362	1.13	0.556	Not significant
Pure error	2	0.000639	0.000319			
Total	26	0.102765				

Table 5-5 shows the results of the analysis of variance (ANOVA) for the obtained full quadratic model. The ANOVA analysis is a statistical technique which can be used to identify

the importance of the model and model parameters (Qiu, et al., 2013). It can be seen that the coefficients for the linear term for time is not significant, indicating that time does not have a very large impact on the yield of biodiesel predicted by the model, while the coefficients for the linear terms of the other variables are all very significant indicating that these variables largely impact the yield of biodiesel obtained from sunflower oil when using a homogenous base catalyst, as predicted by the proposed model equation. It can also be noted from table 5-5 that the coefficient for the quadratic term of temperature is not significant, while all the other quadratic coefficients are very significant indicating that the quadratic coefficient of temperature does not impact the yield predicted by the model as significantly as the quadratic coefficients of the other variables. It can be further noted that the interaction between temperature (A) and reaction time (C) has a p-value of 0.561 indicating that the interactions between these variables are not significant while the interactions between all the other variables are highly significant when using the full quadratic model. The model's lack of fit has a p-value of 0.556 indicating that the lack of fit is not significant, further supporting the observation that the model fits the data well. The inclusion of the insignificant terms in the model resulted in the lower predicted R^2 value of 0.7830. This value could be improved by modifying the model by removing the insignificant terms, however, the current predicted R^2 value is only slightly lower than the recommended value of 0.8 (Joglekar & May, 1987), and for the purpose of this study it was deemed more important to understand the effects of the process variables within the range of the study and for this purpose the unmodified model was still a good fit to the data. Furthermore, modifying the model does not necessarily mean that it could be used to predict the yield of biodiesel obtained outside the range of the study, further experiments would be needed to verify this.

Minitab was used to determine the optimum conditions to maximise the yield of sunflower oil biodiesel obtained via the esterification process, the optimisation results are shown in table 5-6 below:

Table 5-6: Optimum conditions for sunflower oil transesterification

Temperature (℃)	Catalyst loading (%)	Time (min)	Alcohol/oil molar ratio	Predicted Yield	Experimental Yield
55.3607	0.8625	86.48	12.6056	0.98293	0.9851

The optimum yield suggested by Minitab was 0.98293, while experiments under the proposed optimum conditions resulted in a yield of 0.9851, which results in an error of 0.22% further indicating that the model fits the data well.

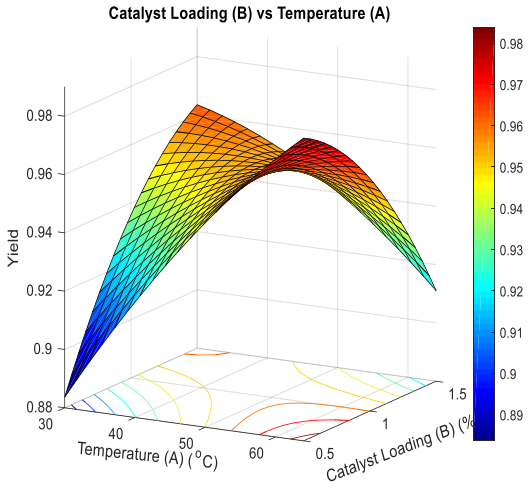

Figure 5-3(a): Effect of catalyst loading and temperature on yield of biodiesel from sunflower oil response surface

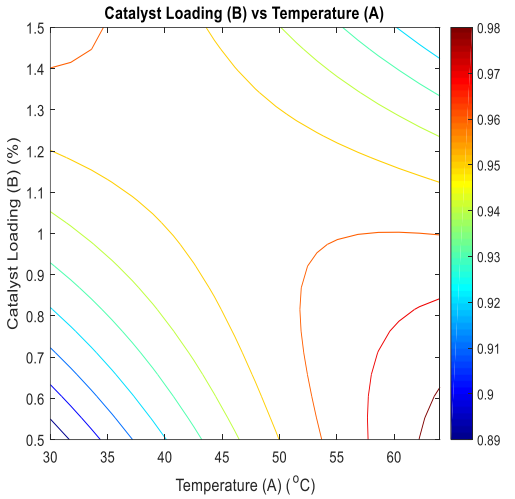

Figure 5-3(b): Effect of catalyst loading and temperature on yield of biodiesel from sunflower oil contour plot

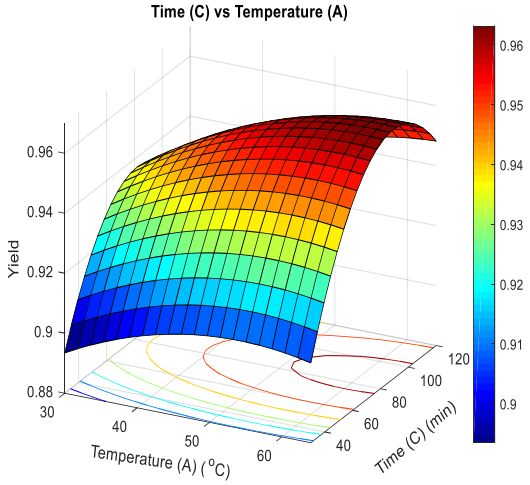

Figure 5-4(a): Effect of time and temperature on yield of biodiesel from sunflower oil response surface

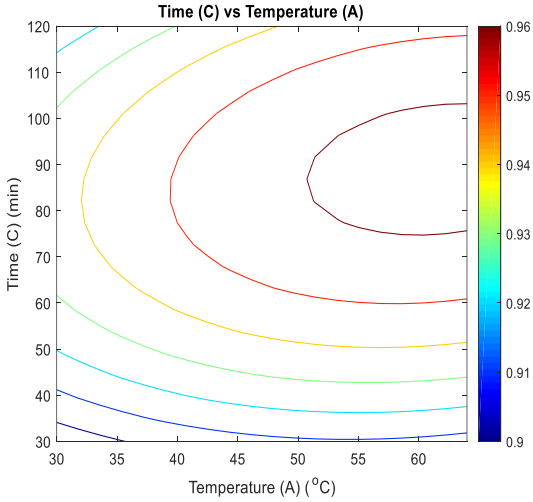

Figure 5-4(b): Effect of time and temperature on yield of biodiesel from sunflower oil contour plot

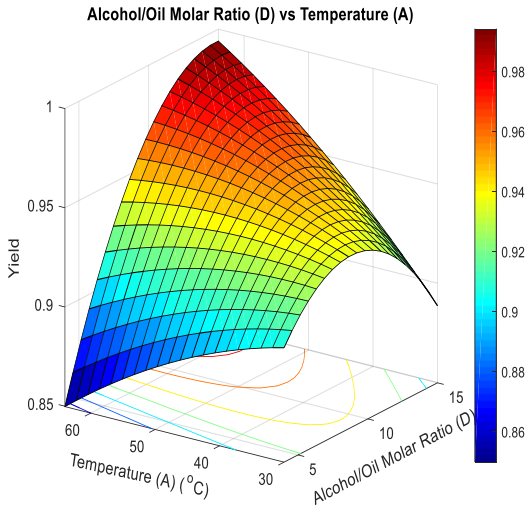

Figure 5-5(a): Effect of alcohol/oil molar ratio and temperature on yield of biodiesel from sunflower oil response surface

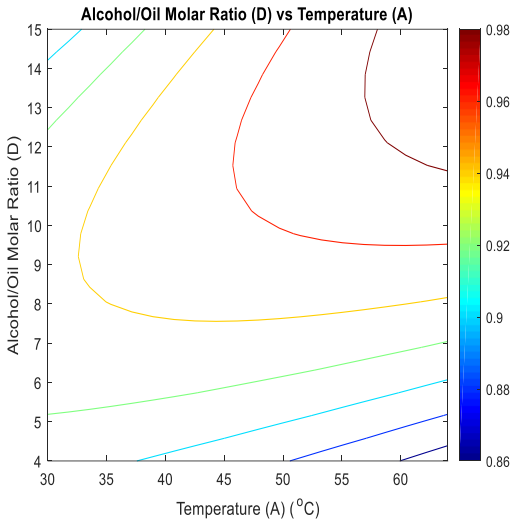

Figure 5-5(b): Effect of alcohol/oil molar ratio and temperature on yield of biodiesel from sunflower oil contour plot

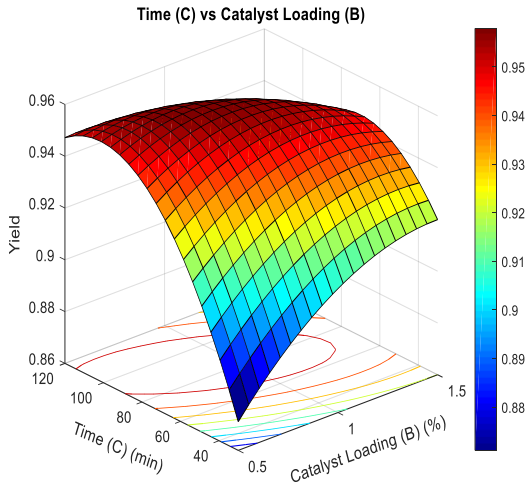

Figure 5-6(a): Effect of time and catalyst loading on yield of biodiesel from sunflower oil response surface

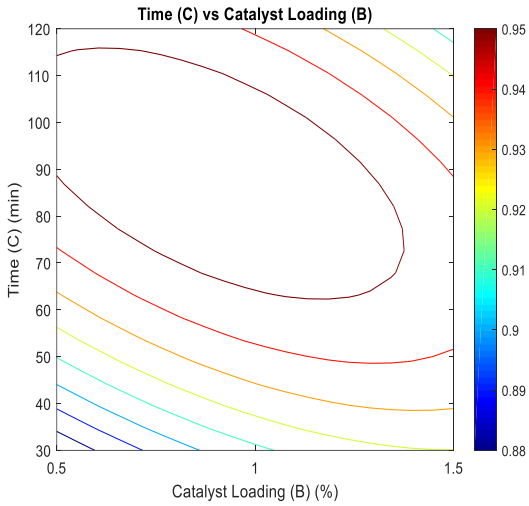

Figure 5-6(b): Effect of time and catalyst loading on yield of biodiesel from sunflower oil contour plot

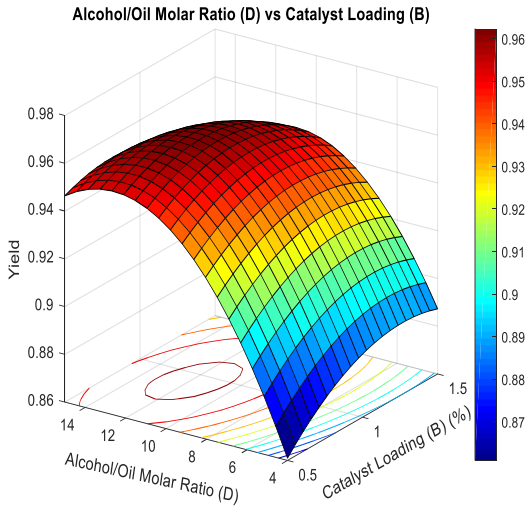

Figure 5-7(a): Effect of alcohol/oil molar ratio and catalyst loading on yield of biodiesel from sunflower oil response surface

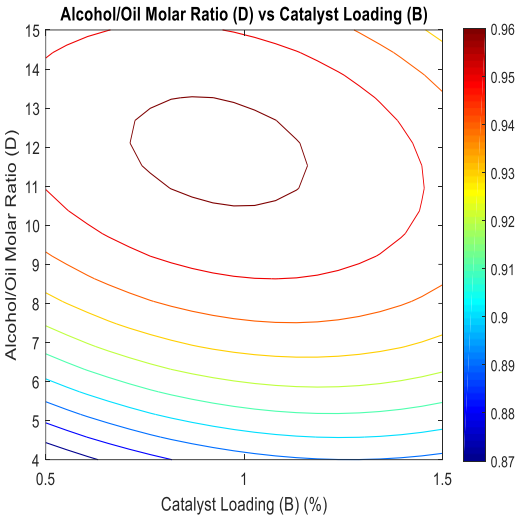

Figure 5-7(b): Effect of alcohol/oil molar ratio and catalyst loading on yield of biodiesel from sunflower oil contour plot

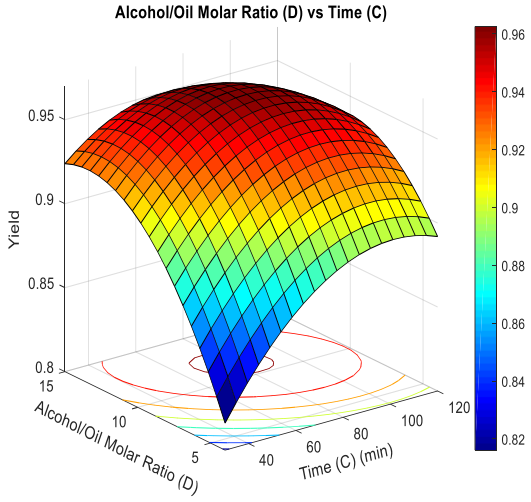

Figure 5-8(a): Effect of alcohol/oil molar ratio and time on yield of biodiesel from sunflower oil response surface

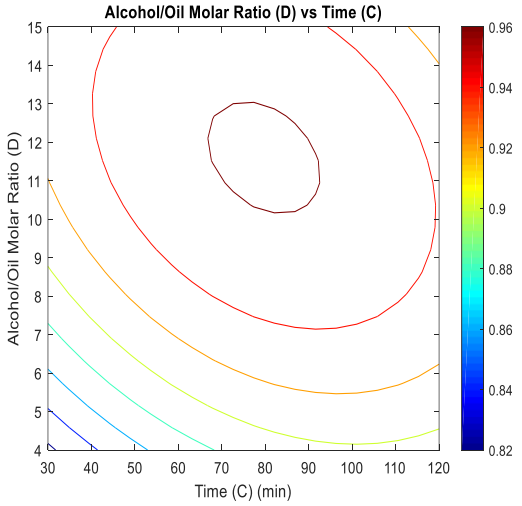

Figure 5-8(b): Effect of alcohol/oil molar ratio and time on yield of biodiesel from sunflower oil contour plot

The effects of the 4 variables studied on the yield of biodiesel obtained from sunflower oil are shown in Figures 5-3 to 5-8 above. Each plot shows the effect of 2 variables across their range within the study, with the other 2 variables fixed at their median value. The response surface visually represents the tendency of each factor to influence the yield. The shape of the contour plots are an indication of the extent and nature of the interactions between the factors. A prominent interaction is indicated by an elliptical contour plot, while a more circular contour plot is indicative of a negligible interaction (Qiu, et al., 2013).

Figure 5-3(a) shows the 3-dimensional response surface interactions between temperature and catalyst loading. The yield is seen to increase with an increase in temperature and a decrease in catalyst loading. This could be due to the endothermic nature of the transesterification reaction (Antolin, et al., 2002), since endothermic reactions absorb energy, high temperatures favour these reactions. High amounts of alkali catalysts result in the formation of soap and hence a reduction in the yield of biodiesel (Gashaw & Teshita, 2014), and this explains why the yield of biodiesel decreases as the catalyst loading increases. It can be noted that high biodiesel yields can be obtained when using low catalyst loading combined with high reaction temperatures. Figure 5-3(b) indicates that the interaction between temperature and catalyst loading has a significant impact on the yield of biodiesel.

Figure 5-4(a) indicates that the yield increases with temperature, however, it is clear from this figure that the reaction time has a more significant effect on the yield. The yield is seen to increase with time up to a point, after which a further increase in temperature results in a decrease in yield possibly due to the reverse reaction resulting in a loss of esters and formation of soap. Figure 5-4(b) displays an elliptical shape, indicating that the interaction between temperature and time is significant.

Figure 5-5(a) shows that the alcohol/oil molar ratio has a parabolic effect on the yield of biodiesel. Initially, an increase in the ratio results in an increase in yield, however after a point any further increase in the ratio results in a decrease in the yield. While an excess amount of methanol is required to shift the equilibrium to the right and favour the forward reaction according to Le Chatelier's principle, an increase in the methanol amount beyond an optimal point interferes with the separation of the glycerol layer from the biodiesel layer resulting from an increase in solubility (Kafuku & Mbarawa, 2010); the glycerol in the solution shifts the equilibrium back to the left promoting the reverse reaction and decreasing the yield of biodiesel. It can be seen that the lowest yields can be obtained when using a high temperature combined with a low alcohol/oil molar ratio, this is due to the low alcohol to oil ratios being insufficient to drive the forward reaction. Figure 5-5(b) indicates that the interaction between the alcohol/oil molar ratio and temperature has a significant effect on the yield of biodiesel.

Figure 5-6(a) indicates that the yield of biodiesel obtained from sunflower oil increases with both time and catalyst loading up to a point, after which it starts to decrease. This can be attributed to the fact that while a sufficient amount of time is required for the reaction to proceed, as time passes and more products are formed, the equilibrium tends to shift to the left favouring the reverse reaction and reducing the yield. Similarly, a sufficient amount of catalyst is required in order to drive the reaction, but the use of high amounts of base catalysts result in the formation of soap which reduces the biodiesel yield. Figure 5-6(b) shows that the

interaction between the catalyst loading and time has a significant impact on the yield of biodiesel obtained from sunflower oil.

Figure 5-7(a) shows the effect of the interactions between the alcohol/oil molar ratio on catalyst loading on the yield of biodiesel. It can be seen that the biodiesel yield increases with both the alcohol to oil ratio and catalyst loading up to an optimum point after which the yield starts to decrease with a further increase in the ratio and catalyst loading. While a sufficient excess of methanol and a sufficient catalyst loading is required to drive the forward reaction, increasing both these factors beyond an optimal point causes the formation of soap and favours the reverse reaction thus reducing the yield of biodiesel that is obtained. Addition of high amounts of base catalyst also result in a product with a high viscosity which further complicates the separation of the biodiesel from glycerol (Fereidooni, et al., 2017), and high viscosity biodiesel is undesirable for use in diesel engines and hence should be avoided.

The effect of the interaction between the alcohol/oil molar ratio and time on the yield of sunflower oil biodiesel is shown visually in Figure 5-8(a). It was observed that the yield of biodiesel obtained increased as the alcohol to oil ratio and time increased up to a point, while further increases in the reaction time and alcohol to oil ratio hinder the production of biodiesel. The lowest yields are obtained at low ratios of alcohol to oil and short reaction times due to an insufficient amount of methanol to drive the forward reaction and a too short reaction time for the reaction to occur. At higher reaction times, more soap formation was observed during the water washing process caused by the hydrolysis of esters which cause the fatty acids to form soap.

The parabolic shape of most of the surface plots indicate that there is an optimum point at which the yield of biodiesel obtained is a maximum and any further increases result in a decrease in the biodiesel yield. These trends are consistent with the findings of Kafuku & Mbarawa (2010), Fereidooni, et al. (2017) and Demirbas (2007).

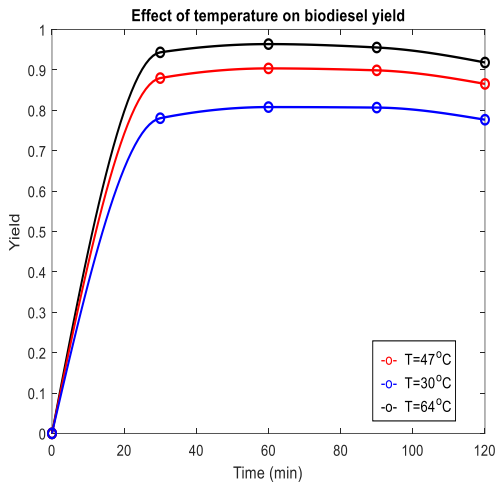

Figure 5-9: Effect of temperature on yield of biodiesel from sunflower oil

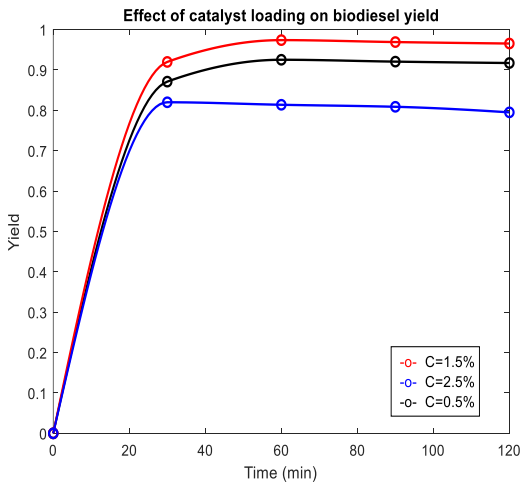

Figure 5-10: Effect of catalyst loading on yield of biodiesel from sunflower oil

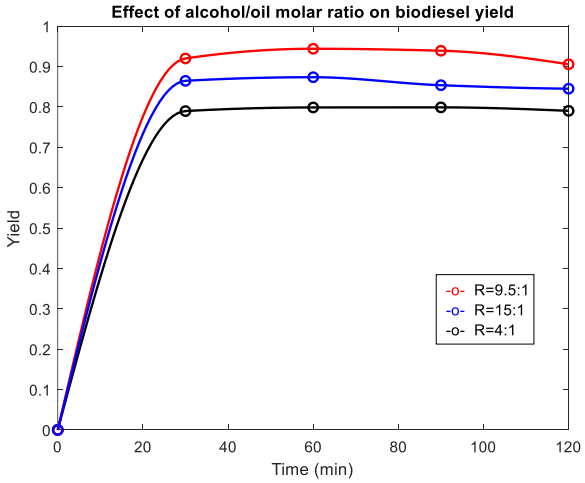

Figure 5-11: Effect of alcohol/oil molar ratio on yield of biodiesel from sunflower oil

The interaction plots in Figures 5-9 to 5-11 above were obtained by varying only one variable and showing its effect on the biodiesel yield against time, while holding all other variables constant at their median value. The median values are as follows:

Temperature = 47 ℃ Catalyst loading = 0.5 %

Reaction time = 75 minutes Alcohol to oil molar ratio = 9.5

This is done in order to understand the interaction between the variables at their different levels.

Figure 5-9 shows that increasing the temperature results in an increase in the yield obtained. This is largely due to the endothermic nature of the transesterification reaction; since endothermic reactions consume energy, high temperatures would favour the endothermic reaction. The reaction mixture consists of 2 phases, i.e. the alcohol phase and the oil phase, therefore sufficient thermal energy is needed to overcome the diffusion resistance between the different phases (Ismail, et al., 2016).

According to Figure 5-10, increasing the catalyst loading from 0.5% to 1.5% resulted in an increase in the yield obtained, while a further increase of the catalyst loading to 2.5% caused a sharp decrease in the yield. This is because high amounts of alkali catalyst tend to promote the saponification of the fatty acids in the oil thereby causing a reduction in the yield of biodiesel obtained. Excess amounts of catalyst also tend to increase the viscosity, thereby lowering the yield, as reported by Ismail, et al. (2016).

Figure 5-11 shows the effect of the alcohol to oil molar ratio on the yield of biodiesel against time. It is evident that the low ratio of 4 resulted in the lowest yield, this is because an excess amount of methanol is required to shift the reaction towards the product side; therefore, an increase in the ratio to 9.5 caused the yield to increase. A further increase in the alcohol to oil molar ratio to 15 resulted in a decrease in the yield, this is because glycerol tends to dissolve in methanol which inhibits the forward reaction and reduces the yield.

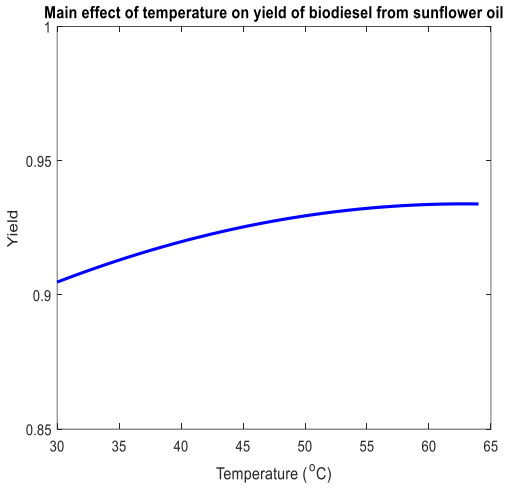

Figure 5-12: Main effect of temperature on the yield of biodiesel from sunflower oil

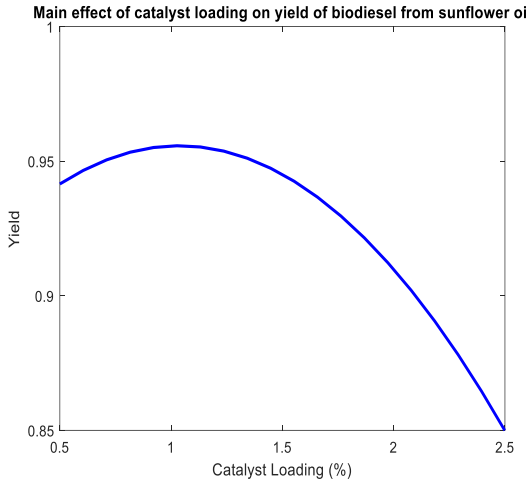

Figure 5-13: Main effect of catalyst loading on the yield of biodiesel from sunflower oil

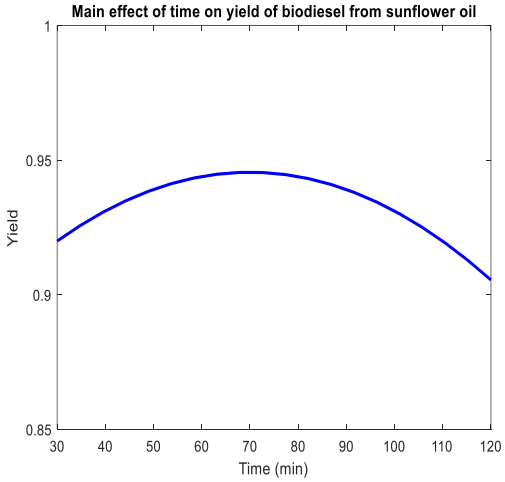

Figure 5-14: Main effect of time on the yield of biodiesel from sunflower oil

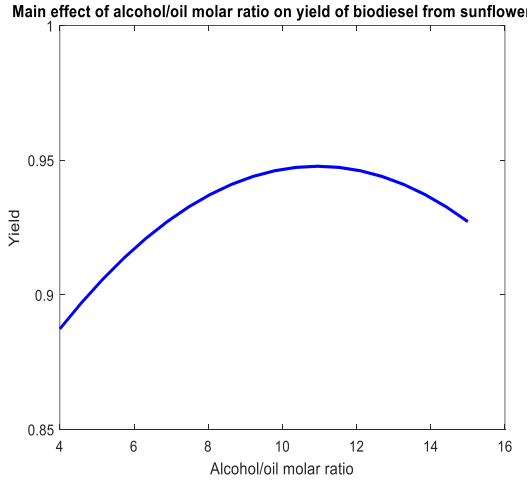

Figure 5-15: Main effect of alcohol/oil molar ratio on the yield of biodiesel from sunflower oil

The main effect plots shown above were obtained by varying one variable, while holding all the other variables at their median values as listed on page 57. Figure 5-12 indicates that increasing the temperature caused the yield to increase, while all other variables were at their median values. This is attributed mainly to the fact that the transesterification reaction is endothermic (Antolin, et al., 2002) and an increase in temperature favours endothermic reactions. Figure 5-13 shows that the yield increases as catalyst loading increases up to approximately 1%, a further increase in catalyst loading causes a steady decrease in the yield. This is due to high amounts of base catalyst promoting the formation of soap, thereby reducing the yield of biodiesel obtained. Figure 5-14 shows that time has a parabolic effect on the yield. After 70 minutes, the yield of biodiesel starts to decrease as time increased. This is because with the passage of time, more glycerol is formed causing the equilibrium to shift to the left and favouring the reverse reaction resulting in a decreased yield. According to Figure 5-15, the yield of biodiesel initially increases sharply as the alcohol to oil molar ratio increases up

to a value of approximately 11, thereafter, a further increase in the ratio results in a decrease in yield. This is because very high alcohol to oil ratios cause increased solubility of glycerol in biodiesel thereby increasing the separation difficulty causing a reduction in the yield of biodiesel obtained.

These trends are supported by the findings of Antolin, et al. (2002) and Demirbas (2007).

It should be noted that the interaction plots and main effect plots are mainly to understand the effect of one variable while the others remain constant and these plots were not used to determine the optimum conditions as truly optimised conditions can only be determined by varying all the variables and considering all their interactions. This is why the Box-Behnken design, and the response optimiser was used on Minitab. The yield was constrained on Minitab to lie between 0 and 1, as yields higher than 1 are not possible, and all process variables were constrained to lie between their minimum and maximum values used in this study because the model may not be able to accurately represent the trends that may be observed outside the range considered in this study.

Chapter 6

Castor Oil Esterification: Results & Discussion

Due to the poisonous nature of the castor bean, it is not suitable for human consumption and hence the use of castor oil as a feedstock for biodiesel production avoids the food vs fuel issue. Castor oil was chosen for this study due to the fact that it is non-edible, inexpensive, environmentally friendly and has a good shelf life in comparison with other vegetable oils (Udoh, et al., 2016). Castor bean seeds have a high oil content and can be easily cultivated even in harsh environments (Chan, et al., 2010).

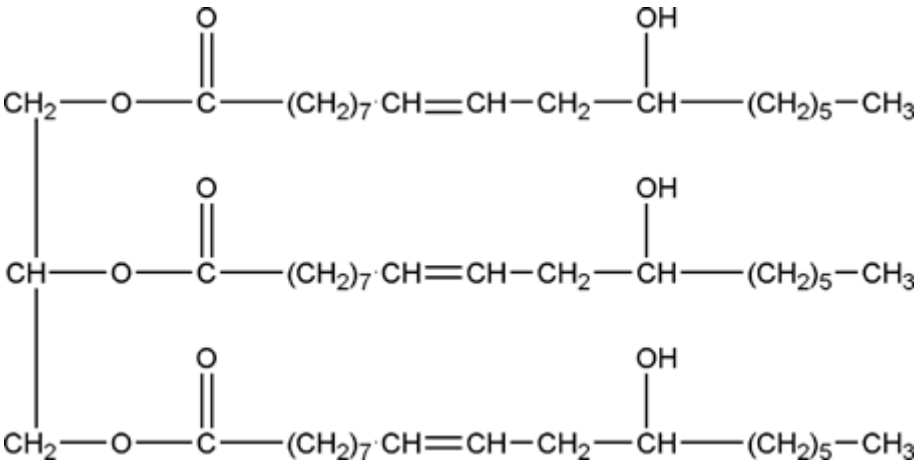

Figure 6-1: Chemical structure of castor oil (Hablot, et al., 2008)

Table 6-1: Summary of properties of castor oil

Density $\left(\frac{kg}{m^3}\right)$	955
Dynamic viscosity (cP)	244.77
Acid number $\left(\frac{mg\ KOH}{g}\right)$	28.61
FFA%	14.31
Refractive index	1.48

Table 6-1 shows the measured properties of castor oil. It was noted that castor oil had a very high acid number and this necessitated a 2-step process; first esterification (pre-treatment) of castor oil with an acid catalyst to reduce its acid number and hence FFA content, and then transesterification of the pre-treated oil via a base catalyst to produce biodiesel. Gashaw & Teshita (2014) and Sattanathan (2015) recommend that an acid number of less than 3 is required for base catalysed transesterification. The free fatty acid content in the oil is neutralized by the base catalyst which can result in the formation of soap and water and this also decreases the catalyst activity and negatively impacts the yield of the required product (Mathiyazhagan & Ganapathi, 2011). During esterification, the excess acid content in the oil is reacted and the acid value of the oil is thus reduced (Sattanathan, 2015).

In this study, sulphuric acid (H_2SO_4) was used to catalyse the esterification of castor oil with methanol. The Box-Behnken design was done on Minitab (version 17) and was implemented in order to determine the conditions which resulted in the greatest reduction of the FFA content in the oil. Reaction temperature was varied from 30℃ to 64℃ as the boiling point of methanol is 64.7℃ and it is recommended that the reaction temperature should not exceed the boiling point of methanol as this would result in the vaporisation of methanol and therefore decreased contact between the oil and alcohol (Mathiyazhagan & Ganapathi, 2011). The catalyst loading was varied from 0.25 wt % of oil to 3.25 wt % of oil. The alcohol to oil molar ratio was varied from 4:1 to 15:1. Stoichiometrically, a ratio of 3:1 is required for the reaction, however, an excess amount of alcohol is desirable in order to shift the equilibrium to the right and promote the forward reaction. The reaction time was varied from 30 minutes to 120 minutes.

The Box-Behnken design resulted in a total of 27 experimental runs, including 3 replicates. Upon completion of all 27 experiments, Minitab was used to fit a regression equation to the data.

The results of these experiments are shown in table 6-2 using coded variables. The coded variables are as follows:

A = Reaction temperature (℃) B = Catalyst loading (%)

C = Reaction time (min) D = Alcohol/oil molar ratio

Table 6-2: Castor oil esterification results

Run Order	A	B	C	D	FFA % (Experimental)	FFA % (Predicted)
1	30	3.25	75	9.5	9.588	9.459
2	64	0.25	75	9.5	1.538	1.596
3	47	1.75	75	9.5	6.923	6.525
4	47	0.25	120	9.5	1.269	1.324
5	64	1.75	120	9.5	3.076	2.720
6	47	0.25	30	9.5	1.495	1.665
7	47	1.75	75	9.5	6.177	6.525
8	47	1.75	75	9.5	6.499	6.525
9	64	3.25	75	9.5	6.091	6.915
10	64	1.75	75	4	11.434	11.671
11	30	0.25	75	9.5	2.417	1.519
12	47	0.25	75	4	8.223	8.795
13	47	1.75	30	4	10.846	10.684
14	30	1.75	30	9.5	5.961	6.085
15	47	3.25	75	15	12.651	11.845
16	30	1.75	75	15	9.306	9.326
17	47	3.25	120	9.5	6.076	6.164
18	47	1.75	120	4	10.086	9.473
19	47	3.25	75	4	11.937	11.689
20	30	1.75	75	4	8.460	8.611
21	47	3.25	30	9.5	9.881	10.084
22	64	1.75	30	9.5	6.401	5.463
23	47	0.25	75	15	1.466	1.480
24	47	1.75	120	15	4.880	4.974
25	47	1.75	30	15	7.486	8.025
26	30	1.75	120	9.5	3.860	4.566
27	64	1.75	75	15	3.692	3.800

The lowest experimental FFA % of 1.269 % was observed in run 4 at a temperature of 47 ℃, catalyst loading of 0.25%, reaction time of 120 minutes and an alcohol to oil molar ratio of 9.5.

Table 6-3: Model summary for castor oil esterification

Terms	S	R^2	R^2 (adjusted)	R^2 (predicted)
Linear	2.3379	0.6110	0.5403	0.3870
Linear + squares	1.5590	0.8585	0.7956	0.6816
Linear + interactions	2.2598	0.7357	0.5705	0.1164
Full quadratic	0.6592	0.9831	0.9635	0.9060

It can be seen in table 6-3 that both a full quadratic model and a linear + squares model have an R^2 value higher than 0.8 indicating that these models fit the data well. However, the linear + squares model displays a higher standard deviation value, and lower adjusted and predicted R^2 values than the full quadratic model, indicating that the full quadratic model fits the data better. This means that the full quadratic response model obtained in this study explains the esterification of castor oil very well, with an R^2 value of 0.9831 and an adjusted R^2 value of 0.9635 at a 95% confidence level. The fit of the model to the data is seen visually in Figure 6-2 on page 64. The S-value in table 6-3 above represents the standard deviation of the distance between the data values and the fitted values. The low S-value of 0.659158 indicates a low deviation of data points from the predicted responses, indicating that the regression equation fits the data obtained well. The predicted R^2 value of 0.9060 is also greater than 0.8 indicating that the model has a high predictive ability even outside the range of this study. The model is also very significant, as evidenced by its high F-value of 49.96 and very low probability (p) value of 0 (seen in table 6-4 on page 64). For a 95% confidence level, a p-value less than 0.05 indicates statistical significance, while a value higher than 0.1 indicates statistical insignificance (Zhang & Zheng, 2009).

The regression equation is shown below using coded variables:

$$FFA\ (\%) = -6.15 + 0.542\,A + 3.469\,B + 0.1056C\ - 1.201\,D - 0.003034\,A^2 \\ -0.345B^2 -\ 0.000464\,C^2 + 0.0893\,D^2 - 0.0257\,AB - 0.0004\,AC \\ -0.02296\,AD - 0.01326\,BC + 0.2264\,BD - 0.00186\,CD$$

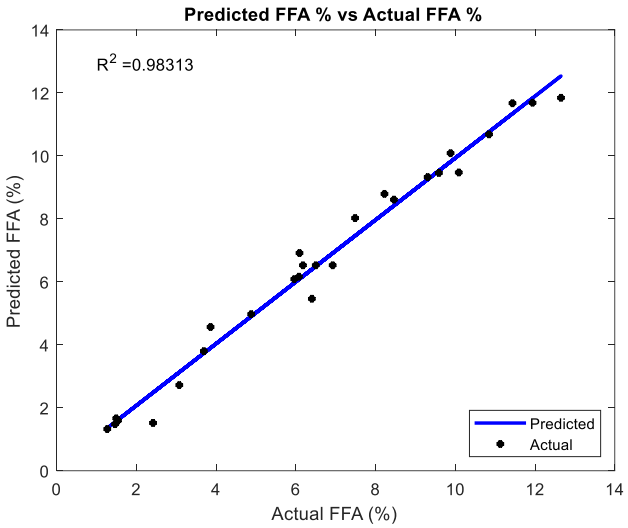

Figure 6-2: Model predicted FFA % vs actual FFA % for castor oil esterification

Table 6-4: Analysis of variance (ANOVA) for castor oil esterification (full quadratic model)

Analysis of Variance						
Source	Degrees of freedom	Sum of squares	Mean squares	F-value	p-value	Characteristics
Model	14	303.894	21.707	49.96	0	Significant
Linear	4	188.865	47.216	108.67	0	Significant
A	1	4.514	4.514	10.39	0.007	Significant
B	1	132.109	132.109	304.06	0	Significant
C	1	13.702	13.702	31.54	0	Significant
D	1	38.539	38.539	88.70	0	Significant
Square	4	76.495	13.124	44.01	0	Significant
A^2	1	4.100	4.100	9.44	0.01	Significant
B^2	1	3.210	3.210	7.39	0.019	Significant
C^2	1	4.715	4.715	10.85	0.006	Significant
D^2	1	38.982	38.982	89.72	0	Significant
2-Way interaction	6	38.535	6.422	14.78	0	Significant
AB	1	1.713	1.713	3.94	0.07	Slightly significant
AC	1	0.375	0.375	0.86	0.371	Not significant
AD	1	18.438	18.438	42.44	0	Significant
BC	1	3.202	3.202	7.37	0.019	Significant
BD	1	13.954	13.954	32.12	0	Significant
CD	1	0.852	0.852	1.96	0.187	Not significant
Error	12	5.214	0.434			
Lack of fit	10	4.934	0.493	3.52	0.241	Not significant
Pure error	2	0.280	0.140			
Total	26	309.108				

Table 6-4 shows the results of the analysis of variance (ANOVA) for the obtained model. The ANOVA analysis is a statistical technique which can be used to identify the importance of the model and model parameters (Qiu, et al., 2013). It can be seen that the coefficients for the quadratic and linear terms are very significant, indicating that all 4 variables investigated in this study have very large effects on the FFA content in the oil. It can also be noted from table 6-4 that the interaction between temperature (A) and reaction time (C), and the interaction between reaction time (C) and alcohol/oil molar ratio (D) is insignificant, while the interaction between temperature (A) and catalyst loading (B) is slightly significant.

Minitab was used to determine the optimum conditions to reduce the FFA content of castor oil via the esterification process, the optimisation results are shown in table 6-5 below:

Table 6-5: Optimum conditions for castor oil esterification

Temperature (℃)	Catalyst loading (%)	Time (min)	Alcohol/oil molar ratio	Predicted FFA %	Experimental FFA %
61.94	0.6063	35.6162	13.4071	0.64375	0.7153

The optimum FFA % suggested by Minitab was 0.64375 %, while experiments under the proposed optimum conditions yielded an FFA % of 0.7153 %. This further supports the fact that the model fits the data well. The FFA content in castor oil was reduced by 95% via the esterification procedure. The reduced FFA content meant that a base catalyst could be used for the transesterification of the pre-treated castor oil.

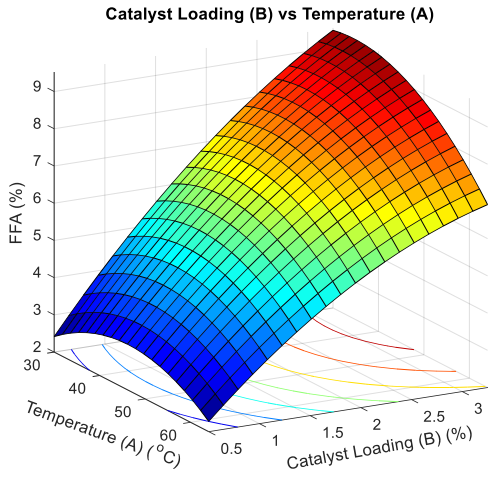

Figure 6-3(a): Effect of catalyst loading and temperature on FFA (%) response surface

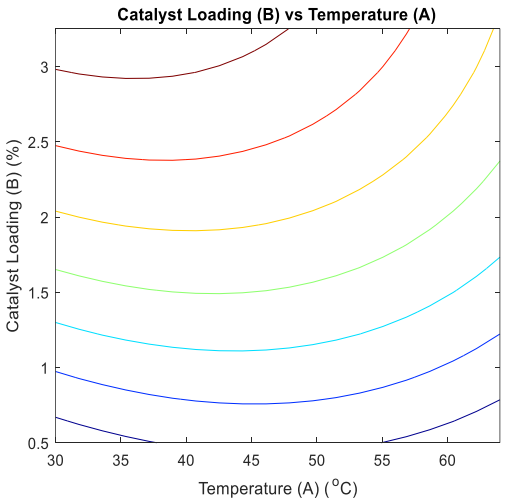

Figure 6-3(b): Effect of catalyst loading and temperature on FFA (%) contour plot

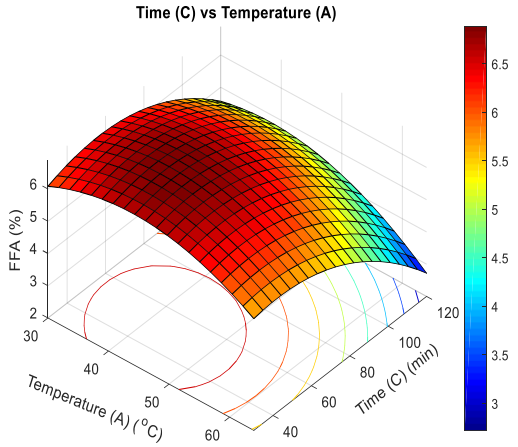

Figure 6-4(a): Effect of time and temperature on FFA (%) response surface

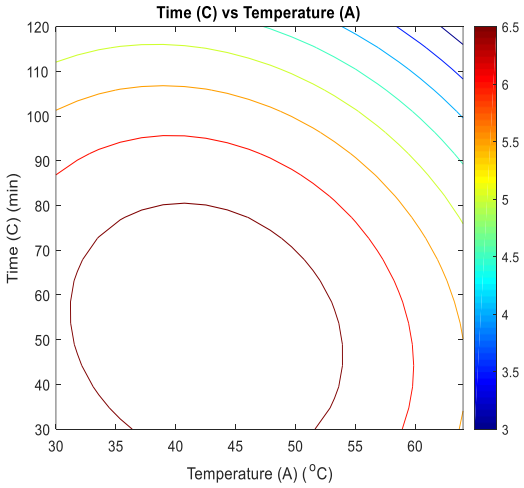

Figure 6-4(b): Effect of time and temperature on FFA (%) contour plot

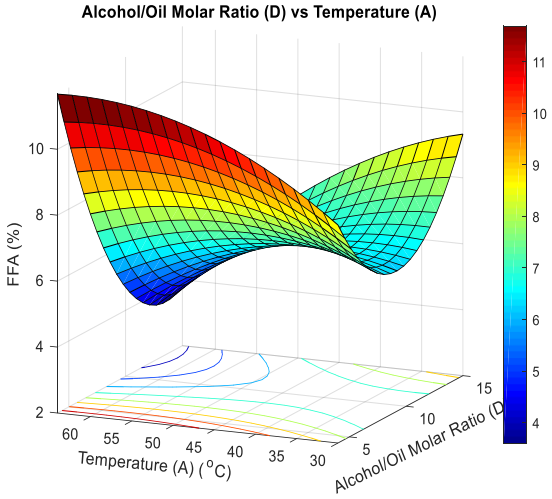

Figure 6-5(a): Effect of alcohol/oil molar ratio and temperature on FFA (%) response surface

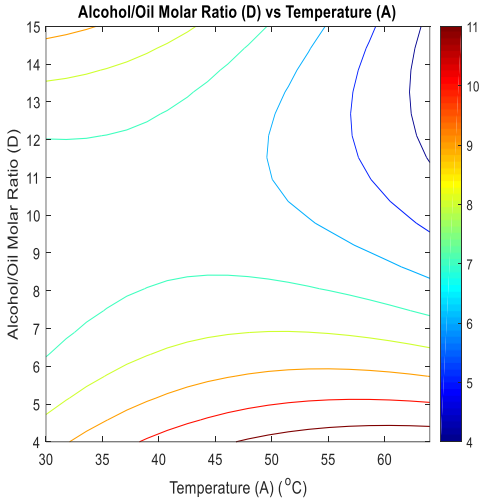

Figure 6-5(b): Effect of alcohol/oil molar ratio and temperature on FFA (%) contour plot

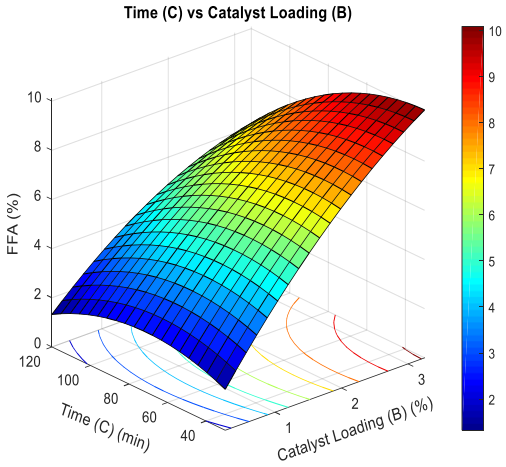

Figure 6-6(a): Effect of time and catalyst loading on FFA (%) response surface

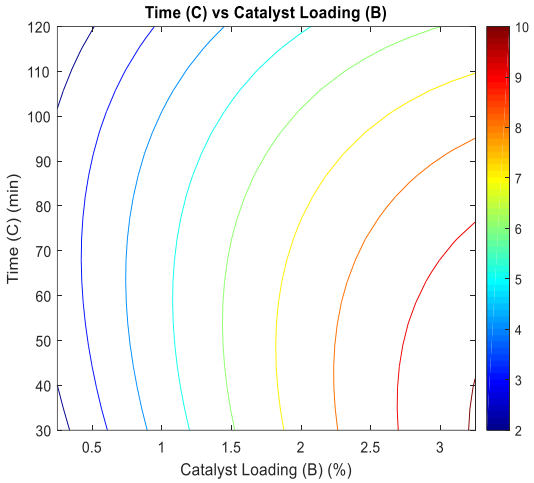

Figure 6-6(b): Effect of time and catalyst loading on FFA (%) contour plot

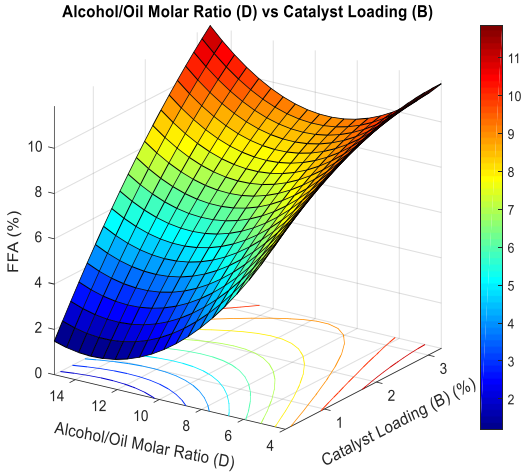

Figure 6-7(a): Effect of alcohol/oil molar ratio and catalyst loading on FFA (%) response surface

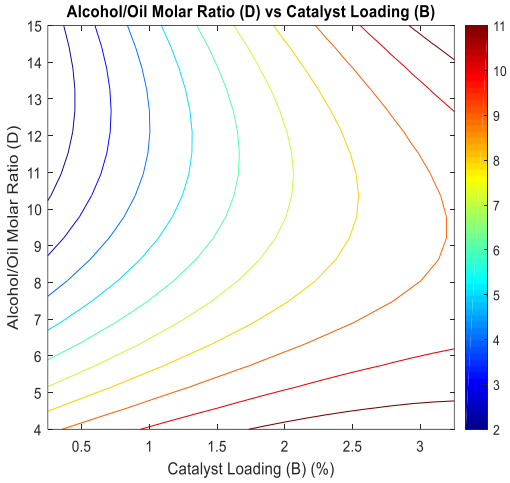

Figure 6-7(b): Effect of alcohol/oil molar ratio and catalyst loading on FFA (%) contour plot

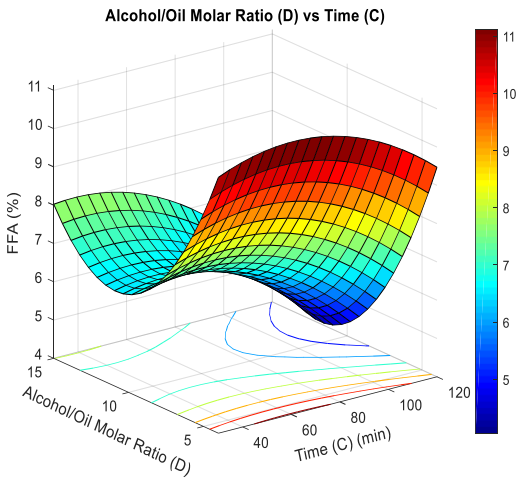

Figure 6-8(a): Effect of alcohol/oil molar ratio and time on FFA (%) response surface

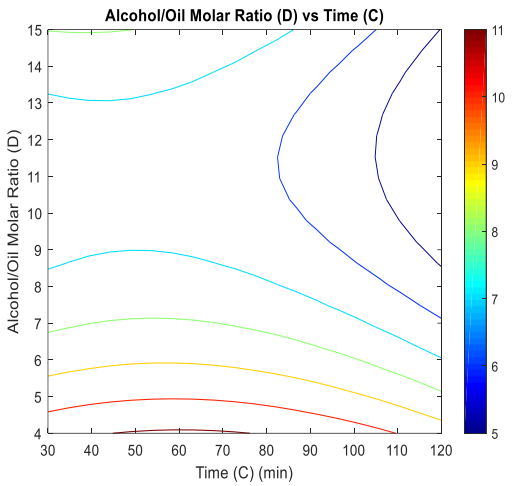

Figure 6-8(b): Effect of alcohol/oil molar ratio and time on FFA (%) contour plot

The effects of the 4 variables studied on the FFA content of castor oil are shown in Figures 6-3 to 6-8. Each plot shows the effect of 2 variables across their range within the study, with the other 2 variables fixed at their median value. The response surface visually represents the tendency of each factor to influence the castor oil FFA content. The shape of the contour plots are an indication of the extent and nature of the interactions between the factors. A prominent interaction is indicated by an elliptical contour plot, while a more circular contour plot is indicative of a negligible interaction.

Figure 6-3(a) shows the 3-dimensional response surface interactions between temperature and catalyst loading. The FFA content is seen to increase with temperature up to approximately 42℃ after which the FFA content is seen to decrease. An increase in the catalyst loading is observed to result in an increase in FFA content. This is possibly due to the presence of moisture content in the oil (Halder, et al., 2015). The circular nature of Figure 6-3(b) indicates that the interactions between temperature and catalyst loading is not significant.

Figures 6-4 show the effect of time and temperature on the FFA % of the oil. The circular shape of the contour plot indicates that the interactions between time and temperature is not significant. With the passage of time, the FFA % is seen to decrease due to longer contact time between the oil and alcohol. Halder, et al. (2015) reported that for reaction times longer than 120 minutes, the FFA% increases with time possibly caused by the formation of water during esterification, hence, the maximum reaction time considered in this study was 120 minutes.

Figure 6-5(a) displays the effect of the alcohol/oil molar ratio and temperature on the FFA %. It is seen that the FFA% decreases as the alcohol/oil molar ratio increases up to a point, after which the FFA% is seen to increase. Increasing the alcohol/oil molar ratio also increases the difficulty in separating the aqueous layer from the organic layer upon completion of the

reaction. The elliptical nature of the contour plot seen in Figure 6-5(b) indicates that the interaction between the oil/alcohol molar ratio and temperature has a significant impact on the FFA%.

Figure 6-6(a) further shows that high catalyst loadings result in high FFA %. This is possibly because the high acid content in castor oil paired with high amounts of acid catalyst result in reduced catalyst activity resulting in the FFA in the oil not reacting (Banani, et al., 2015). Low catalyst loadings are also preferable due to its low cost. As time proceeded, the FFA% is seen to decrease, as noted above, due to the longer contact time between the reacting species. Figure 6-6(b) provides an indication that the interaction between the catalyst loading and time is significant.

Figures 6-7 show the effect of the alcohol/oil molar ratio and catalyst loading on the FFA%. The trends observed are similar to the ones noted above; an increase in the oil/alcohol molar ratio decreases the FFA% up to an optimal point, after which the FFA% is seen to increase again, and increasing the catalyst loading results in an increase in FFA%. The highly elliptical nature of Figure 6-7(b) indicates that the interaction between the alcohol/oil molar ratio and catalyst loading has a significant impact on the FFA%.

Figure 6-8(a) shows the 3-dimensional response surface interactions between time and the alcohol/oil molar ratio. It can be seen that as time increases, the FFA content decreases due to increased contact time for the reaction to occur, while the alcohol/oil molar ratio has a parabolic effect on the FFA% with the FFA content decreasing as the ratio increases initially, thereafter the FFA% is seen to increase as the alcohol/oil ratio is increased further.

The trends observed are in agreement with the trends noted by Banani, et al. (2015) , Goyal, et al. (2012), Sathya & Manivannan (2013) and Chai, et al. (2014).

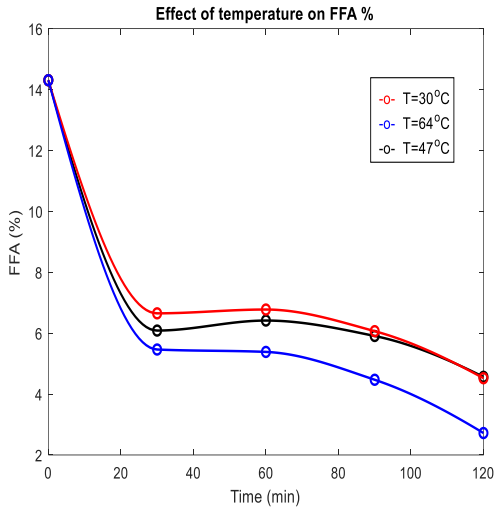

Figure 6-9: Effect of temperature on FFA (%)

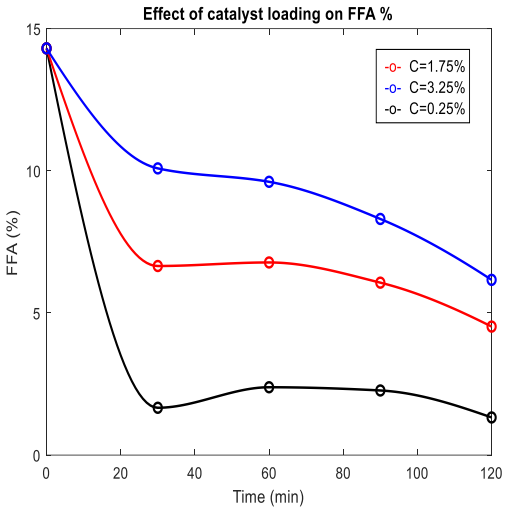

Figure 6-10: Effect of catalyst loading on FFA (%)

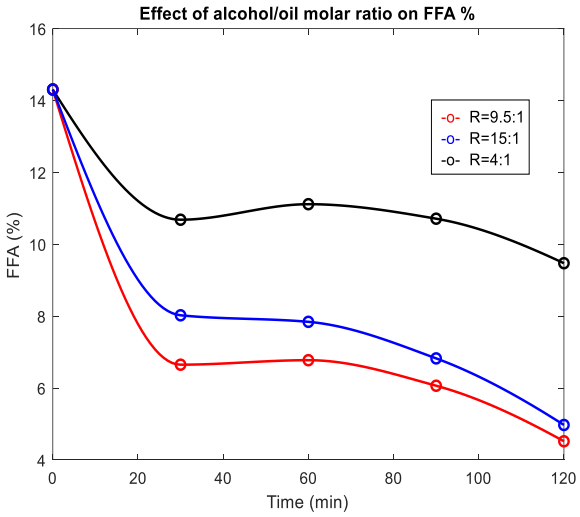

Figure 6-11: Effect of alcohol/oil molar ratio on FFA (%)

The interaction plots seen in Figures 6-9 to 6-11 were obtained by varying only one variable and showing its effect on the FFA % against time, while holding all other variables constant at their median value. The median values are as follows:

Temperature = 47 ℃ Catalyst loading = 1.75 %

Reaction time = 75 minutes Alcohol to oil molar ratio = 9.5

Figure 6-9 shows that increasing the temperature results in a decrease in FFA %. Increasing the temperature from 30 ℃ to 47 ℃ has results in only a slight reduction in FFA content, however after 90 minutes there is virtually no difference. Increasing the temperature to 64 ℃ had a more significant on the reduction of the FFA %.

Figure 6-10 shows that increasing the catalyst loading results in a higher FFA %. The reduction in FFA % is significantly increased when decreasing the catalyst loading from 1.75% to 0.25%. As seen in Figure 6-11 increasing the alcohol/oil molar ratio from 4:1 to 9.5:1 results in a significantly lower FFA %, however a further increase in the ratio from 9.5:1 to 15:1 results in a slightly higher FFA % indicating that the optimum alcohol/oil molar ratio is less than 15:1.

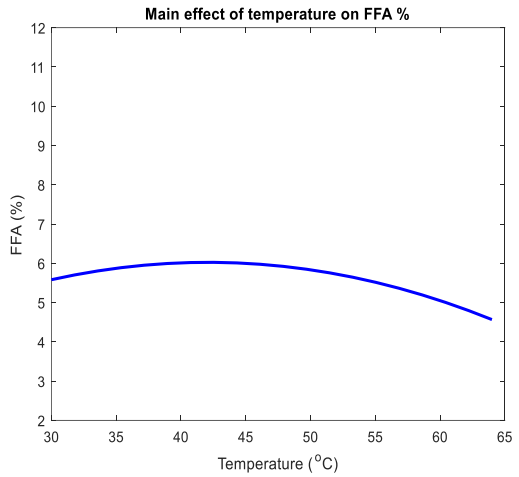

Figure 6-12: Main effect of temperature on FFA (%)

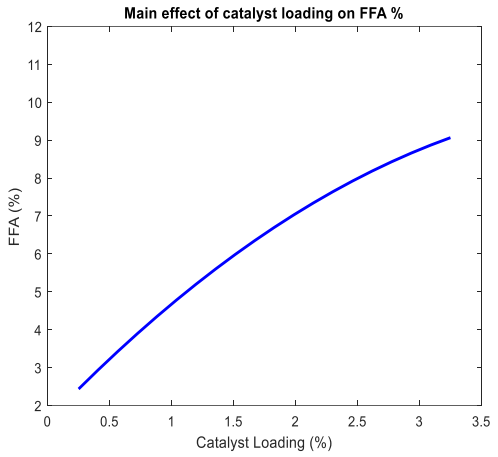

Figure 6-13: Main effect of catalyst loading on FFA (%)

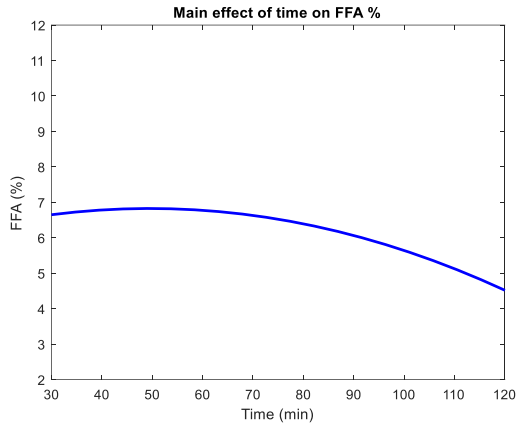

Figure 6-14: Main effect of time on FFA (%)

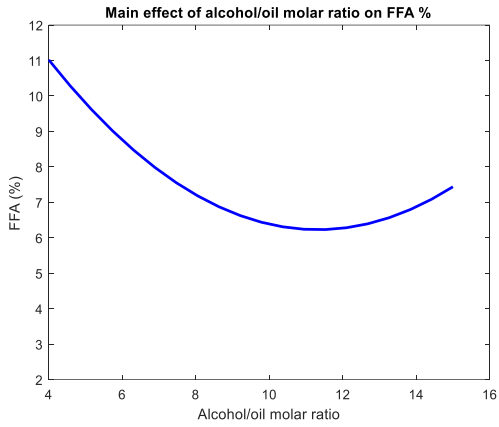

Figure 6-15: Main effect of alcohol/oil molar ratio on FFA (%)

The main effect plots shown above were obtained by varying one variable, while holding all the other variables at their median values as listed on page 70. Figure 6-12 indicates that temperature did not have a very significant effect on the FFA %. Increasing the temperature from 30 ℃ to 64 ℃ resulted in a decrease in FFA % of less than 1%. Figure 6-13 further supports the finding that high catalyst loading values result in high FFA percentages. It can be seen from Figure 6-14 that increasing the time from 30 minutes to 120 minutes reduced the FFA percentage by approximately 2%. Figure 6-15 shows the parabolic effect that the

alcohol/oil molar ratio has on the FFA %. The FFA content decreases as the ratio increases up to a value of approximately 11:1, after which a further increase in the ratio results in an increase in the FFA %. All these trends are consistent with the findings of Sathya & Manivannan (2013) and Banani, et al. (2015).

As in chapter 6, the interaction plots and main effect plots were used to understand the effects of the process variables on the FFA %, and not to optimise the FFA % as for true optimisation the interactions between the process variables need to be considered. The optimisation was therefore done on Minitab.

Chapter 7

Castor Oil Transesterification: Results & Discussion

The esterification of castor oil under the optimum conditions discussed in chapter 6 resulted in a decrease in the acid number of castor oil from 28.61 to 1.4306. This means that the FFA % was reduced from 14.3055% to 0.7153%. The acid number of the pre-treated castor oil was less than 2, meaning that a base catalyst could now be used for transesterification to produce biodiesel.

In this study, potassium hydroxide (KOH) was used to catalyse the transesterification of the pre-treated castor oil with methanol. The Box-Behnken design was done on Minitab (version 17) and was implemented in order to determine the conditions which resulted in the greatest yield of biodiesel from the esterified castor oil. The reasons for choosing the experimental conditions are the same as those discussed in the chapter 5.

The Box-Behnken design resulted in a total of 27 experimental runs, including 3 replicates. Upon completion of all 27 experiments, Minitab was used to fit a regression equation to the data. The results of these experiments are shown in table 7-1 using coded variables. The coded variables are as follows:

A = Reaction temperature (℃)

B = Catalyst loading (%)

C = Reaction time (min)

D = Alcohol/oil molar ratio

Table 7-1: Castor oil transesterification results

Run Order	A	B	C	D	Yield % (Experimental)	FFA % (Predicted)
1	47	0.5	30	9.5	0.9123	0.9503
2	64	1.5	75	15	0.8939	0.9118
3	47	0.5	75	4	0.8474	0.8157
4	47	1.5	75	9.5	0.8510	0.8475
5	47	1.5	30	15	0.8513	0.8249
6	47	1.5	75	9.5	0.8200	0.8475
7	47	1.5	75	9.5	0.8764	0.8475
8	47	2.5	30	9.5	0.8043	0.7869
9	47	1.5	120	4	0.5981	0.6221
10	47	2.5	75	4	0.4192	0.4568
11	47	1.5	120	15	0.8908	0.9121
12	64	2.5	75	9.5	0.7247	0.7158
13	30	2.5	75	9.5	0.7867	0.7791
14	30	1.5	120	9.5	0.9029	0.8861
15	47	0.5	75	15	0.8059	0.7564
16	30	1.5	30	9.5	0.8593	0.8767
17	64	1.5	120	9.5	0.8676	0.8378
18	64	1.5	30	9.5	0.9161	0.9202
19	47	2.5	120	9.5	0.8149	0.7804
20	30	0.5	75	9.5	0.8449	0.8516
21	64	0.5	75	9.5	0.9045	0.9101
22	30	1.5	75	4	0.7622	0.7480
23	47	2.5	75	15	0.8286	0.8485
24	64	1.5	75	4	0.5880	0.5842
25	30	1.5	75	15	0.7454	0.7528
26	47	0.5	120	9.5	0.8630	0.8838
27	47	1.5	30	4	0.8059	0.7824

The lowest yield of 0.4192 was obtained in experiment 10 with a temperature of 47 ℃, a catalyst loading of 2.5%, a reaction time of 75 minutes and an alcohol to oil molar ratio of 4. The low alcohol to oil ratio not being sufficient to drive the forward reaction, combined with the high catalyst loading of 2.5% resulting in the formation of soap could explain the low yield

of biodiesel obtained in this run. The formation of soap was observed during the experiment, and this became more apparent during the water washing process. This added a degree of difficulty to the separation of the biodiesel after decanting. The highest experimental yield of 0.9161 was obtained in experimental run 18 with a temperature of 64℃, a catalyst loading of 1.5%, a reaction time of 30 minutes and an alcohol to oil molar ratio of 9.5. The high temperature favoured the forward reaction, which is endothermic, thus shifting the equilibrium to the left and increasing the yield obtained. The catalyst loading of 1.5% and the alcohol to oil ratio of 9.5 were both sufficient to drive the forward reaction without causing the formation of soap and hindering the production of biodiesel.

Table 7-2: Model summary for castor oil transesterification

Terms	S	R^2	R^2 (adjusted)	R^2 (predicted)
Linear	0.0938	0.4186	0.3129	0.0936
Linear + squares	0.0794	0.6592	0.5077	0.2331
Linear + interactions	0.0770	0.7153	0.5373	0.0934
Full quadratic	0.0350	0.9558	0.9042	0.7623

Table 7-2 shows that the high coefficient of determination (R^2) value of 0.9558 and adjusted R^2 value of 0.9042 for a full quadratic model are both significantly higher than 0.8 indicating an excellent fit of the model equation to the experimental data. All the other models displayed lower coefficients of determination, meaning that they were insufficient to describe the data. The full quadratic response model obtained in this study explains the transesterification of the pre-treated castor oil very well at a 95% confidence level. The model fit can be seen in Figure 7-1 (page 76). The S-value in table 7-2 above represents the standard deviation of the distance between the data values and the fitted values. The extremely low S-value of 0.0350395 indicates a low deviation of data points from the predicted responses, indicating that the regression equation fits the data obtained well. The predicted R^2 value of 0.7623 is slightly less than 0.8 indicating that while the model fits the experimental data well, it may not be as accurate in predicting the yield of biodiesel outside the range of this study. The model is also very significant, as evidenced by its high F-value of 18.53 and very low probability (p) value of 0. For a 95% confidence level, a p-value less than 0.05 indicates statistical significance, while a value higher than 0.1 indicates statistical insignificance (Zhang & Zheng, 2009).

The regression equation is shown below using coded variables:

$$\begin{aligned} Yield = {} & 1.222 - 0.00277\,A - 0.1075\,B - 0.00442\,C - 0.0143\,D - 0.000006\,A^2 \\ & -0.0316\,B^2 + 0.000017\,C^2 - 0.003192\,D^2 - 0.00179\,AB \\ & -0.00003\,AC + 0.000863\,AD + 0.000333 + 0.0205\,BD + 0.00025\,CD \end{aligned}$$

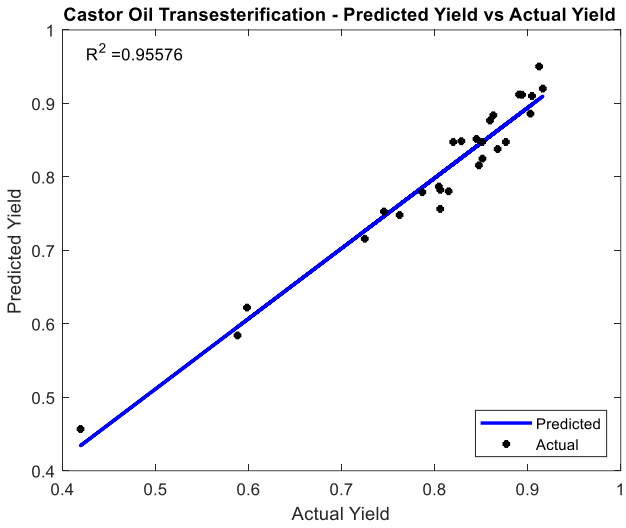

Figure 7-1: Model predicted yield of castor oil biodiesel vs actual yield

Table 7-3: Analysis of variance (ANOVA) for castor oil transesterification (full quadratic model)

Analysis of Variance						
Source	Degrees of freedom	Sum of squares	Mean squares	F-value	p-value	Characteristics
Model	14	0.31855	0.022574	18.53	0	Significant
Linear	4	0.060275	0.015069	12.27	0	Significant
A	1	0.003574	0.003574	2.91	0.114	Not Significant
B	1	0.005526	0.005526	4.50	0.055	Slightly Significant
C	1	0.000695	0.000695	0.57	0.466	Not Significant
D	1	0.050577	0.050577	41.19	0	Significant
Square	4	0.080161	0.020040	16.32	0	Significant
A^2	1	0.000014	0.000014	0.01	0.917	Not Significant
B^2	1	0.005316	0.005316	4.33	0.060	Slightly Significant
C^2	1	0.00642	0.006420	5.23	0.041	Significant
D^2	1	0.04972	0.049720	40.50	0	Significant
2-Way interaction	6	0.098862	0.016477	13.42	0	Significant
AB	1	0.003698	0.003698	3.01	0.108	Not Significant
AC	1	0.00212	0.00212	1.73	0.213	Not significant
AD	1	0.026037	0.026037	21.21	0.001	Significant
BC	1	0.000897	0.000897	0.73	0.410	Not Significant
BD	1	0.050826	0.050826	41.40	0	Significant
CD	1	0.015284	0.015284	12.45	0.004	Significant
Error	12	0.014733	0.001228			
Lack of fit	10	0.013129	0.001313	1.64	0.438	Not significant
Pure error	2	0.001604	0.000802			
Total	26	0.333283				

Table 7-3 shows the results of the analysis of variance (ANOVA) for the obtained model. It can be seen that the coefficients for the quadratic and linear terms of temperature, and the linear term of time are not significant, however the coefficients for the linear and quadratic terms of all the other variables are significant, thereby indicating that all the variables besides temperature and time have a significant effect on the yield predicted by the model. It can be further noted that the interactions between temperature (A) and catalyst loading (B), temperature (A) and reaction time (C), and catalyst loading (B) and reaction time (C) are not significant. The inclusion of all the insignificant terms resulted in the lower predicted R^2 value. However, for the purposes 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 equation was left unmodified.

Minitab was used to determine the optimum conditions to maximise the yield of castor oil biodiesel obtained via the transesterification process, the optimisation results are shown in table 7-4 below:

Table 7-4: Optimum conditions for castor oil transesterification

Temperature (℃)	Catalyst loading (%)	Time (min)	Alcohol/oil molar ratio	Predicted Yield %	Experimental Yield %
62.79	0.7203	45.49	10.1011	0.96022	0.9536

The optimum yield suggested by Minitab was 0.96022, while experiments under the proposed optimum conditions gave a yield of 0.9536. This further supports the fact that the model fits the data well as the difference between the actual and predicted optimum yield is 0.69%.

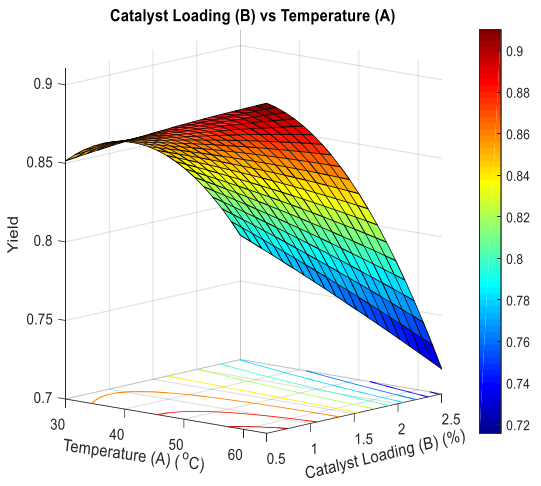

Figure 7-2(a): Effect of catalyst loading and temperature on yield of castor oil biodiesel response surface

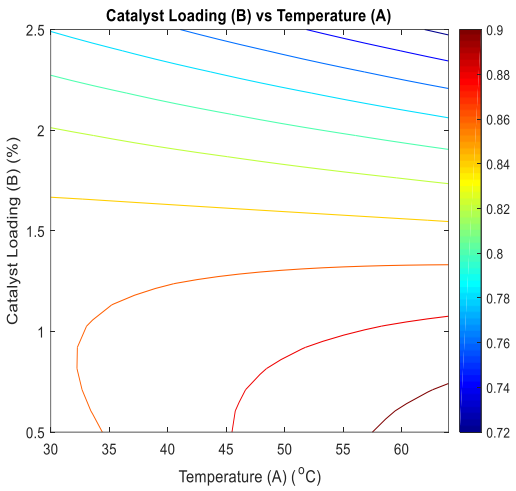

Figure 7-2(b): Effect of catalyst loading and temperature on yield of castor oil biodiesel contour plot

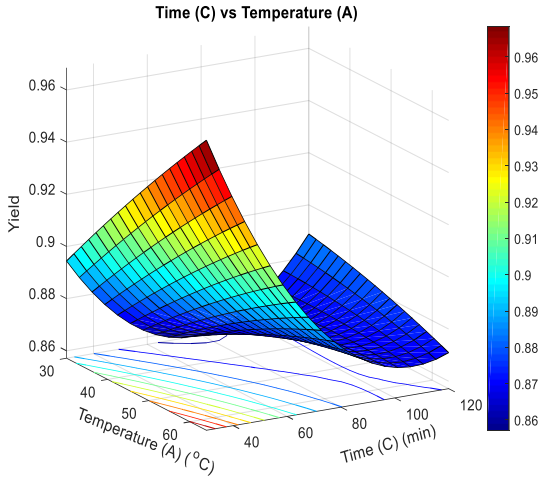

Figure 7-3(a): Effect of time and temperature on yield of castor oil biodiesel response surface

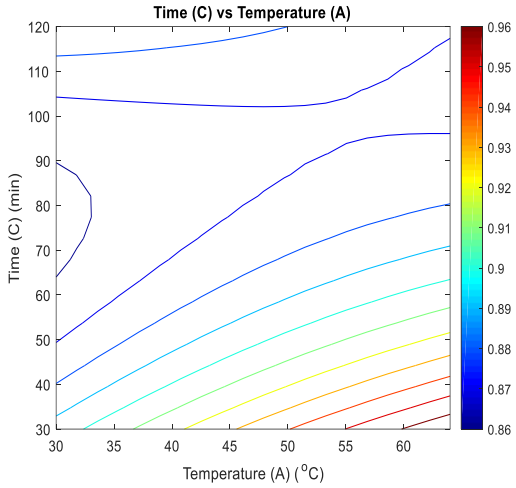

Figure 7-3(b): Effect of time and temperature on yield of castor oil biodiesel contour plot

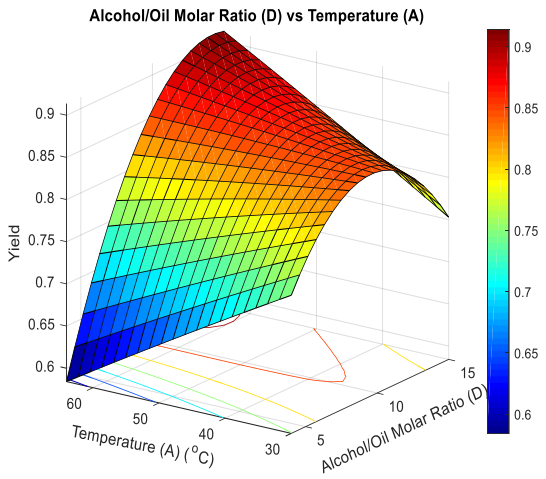

Figure 7-4(a): Effect of alcohol/oil molar ratio and temperature on yield of castor oil biodiesel response surface

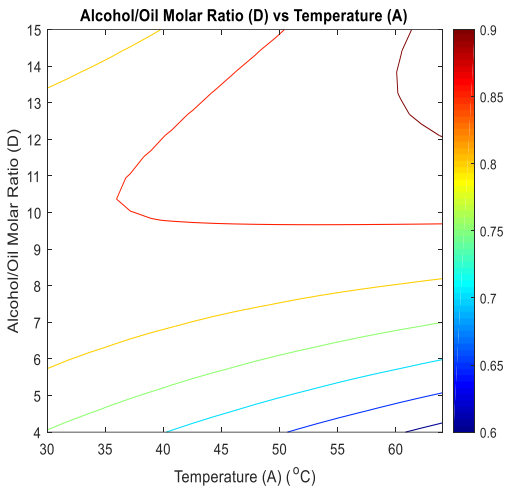

Figure 7-4(b): Effect of alcohol/oil molar ratio and temperature on yield of castor oil biodiesel contour plot

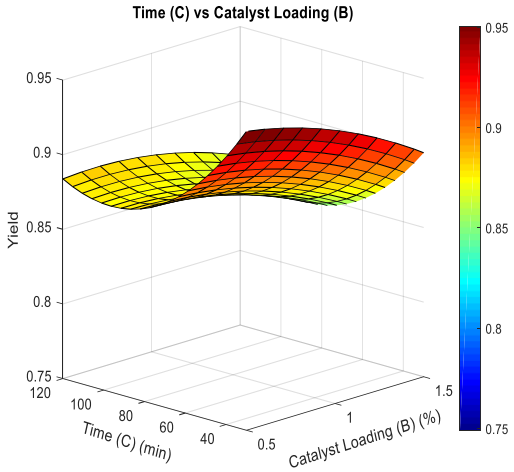

Figure 7-5(a): Effect of time and catalyst loading on yield of castor oil biodiesel response surface

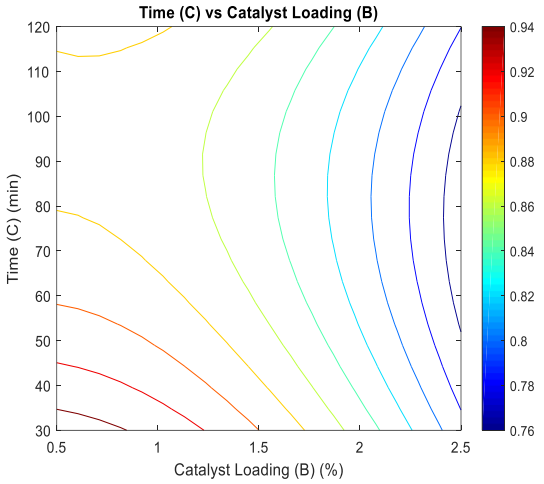

Figure 7-5(b): Effect of time and catalyst loading on yield of castor oil biodiesel contour plot

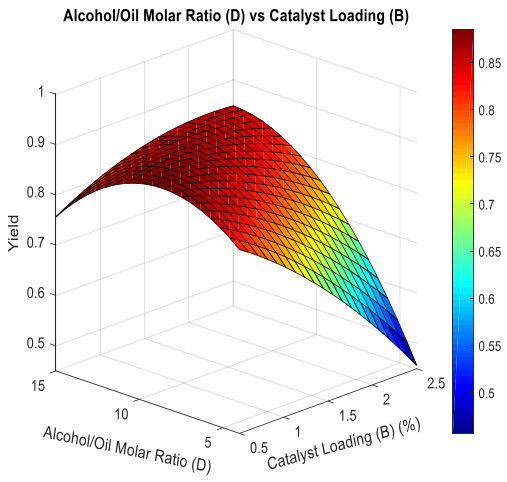

Figure 7-6(a): Effect of alcohol/oil molar ratio and catalyst loading on yield of castor oil biodiesel response surface

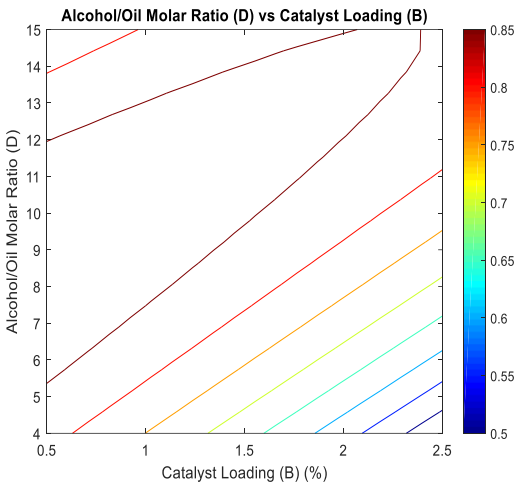

Figure 7-6(b): Effect of alcohol/oil molar ratio and catalyst loading on yield of castor oil biodiesel contour plot

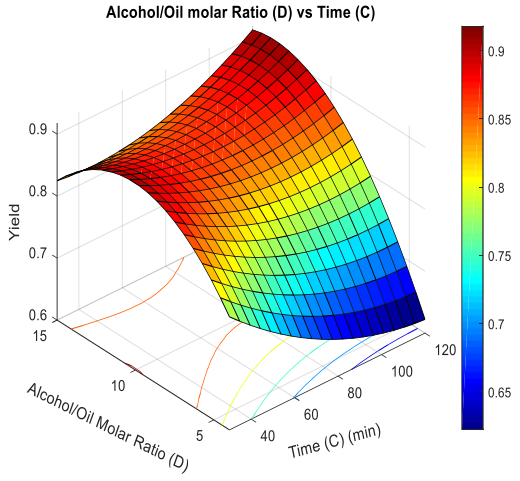

Figure 7-7(a): Effect of alcohol/oil molar ratio and time on yield of castor oil biodiesel response surface

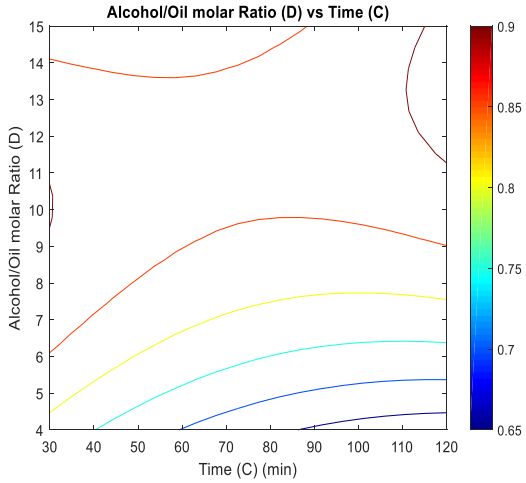

Figure 7-7(b): Effect of alcohol/oil molar ratio and time on yield of castor oil biodiesel contour plot

The effects of the 4 variables studied on the yield of castor oil biodiesel are shown in Figures 7-2 to 7-7. Each plot shows the effect of 2 variables across their range within the study, with the other 2 variables fixed at their median value. The response surface visually represents the tendency of each factor to influence the biodiesel yield.

Figures 7-2 show the effect of the variation of temperature and catalyst loading on the yield of castor oil biodiesel. It can be seen that the yield of biodiesel decreases as the catalyst loading increases, which is expected because high amounts of catalyst promote the formation of soap, reducing the yield. Figure 7-2(b) indicates that the interactions between temperature and catalyst loading has a significant effect on the yield of biodiesel.

Figure 7-3(a) shows the effect of the interactions between time and temperature on the yield of biodiesel. It can be seen that the yield increased as temperature increased owing to the endothermic nature of the reaction. It can be noted that with long durations, the yield observed is low, this can be attributed to the reverse reaction; as time passes and the reaction reaches equilibrium, the reverse reaction becomes more prominent resulting in a decreased yield. The contour plot shown in Figure 7-3(b) indicates that the interactions between time and temperature have a significant effect on the yield of biodiesel.

Figure 7-4(a) displays the 3-dimensional response surface interactions between the alcohol to oil molar ratio and temperature. It can be seen that at high temperatures, a high yield can be obtained with a high alcohol to oil ratio. This may be because the alcohol is more likely to evaporate at high temperatures, meaning that more alcohol would be required to drive the reaction. Although the maximum reaction temperature was 64 ℃, the temperature control system was manual and hence the reaction temperature may have reached the boiling point of methanol (64.7℃) at some stage during the reaction, however, this was accounted for by the presence of the reflux system. Nevertheless, if methanol did evaporate, there would be a small amount of time with reduced contact between the alcohol and oil. The highly elliptical nature of Figure 7-4(b) means that the interactions between the alcohol to oil molar ratio and temperature have a significant impact on the yield of biodiesel.

The relatively flat shape of Figure 7-5(a) implies that the interactions between reaction time and catalyst loading do not significantly impact the yield of biodiesel. This is further supported by the circular nature of Figure 7-5(b). It can still be noted that high yields can be obtained in low amounts of time, with low values of catalyst loading.

The effect of the interactions between catalyst loading and alcohol to oil molar ratio on the yield of castor oil biodiesel is displayed in Figures 7-6 (a) and (b). It can be seen that the lowest yield occurs at high catalyst loading values and low alcohol to oil ratios. This is because this combination of factors significantly hinders the forward reaction; the low amount of alcohol isn't sufficient to drive the forward reaction and the high amount of base catalyst promotes the formation of soap. This combination should be avoided. Figure 7-6 (b) shows that the interactions between the ratio of alcohol to oil and catalyst loading significantly impacts the biodiesel yield.

Figure 7-7(a) shows the effect of the interactions between the alcohol to oil molar ratio and time on the yield of castor oil biodiesel in the form of a 3-dimensional response surface. It can be seen that a combination of a low alcohol to oil molar ratio and large amount of time corresponds to the lowest yield and hence, this combination of factors should be avoided. This can be because with the passage of time and the formation of glycerol, the glycerol tends to

dissolve in the methanol reducing the rate of the forward reaction, while a low alcohol to oil molar ratio is not sufficient to shift the equilibrium to the right. Figure 7-7(b) implies that the interactions between the alcohol to oil molar ratio and time have a significant impact on the yield of castor oil biodiesel obtained.

The trends observed are in agreement with the trends noted by Banani, et al. (2015) , Goyal, et al. (2012), Sathya & Manivannan (2013) and Chai, et al. (2014).

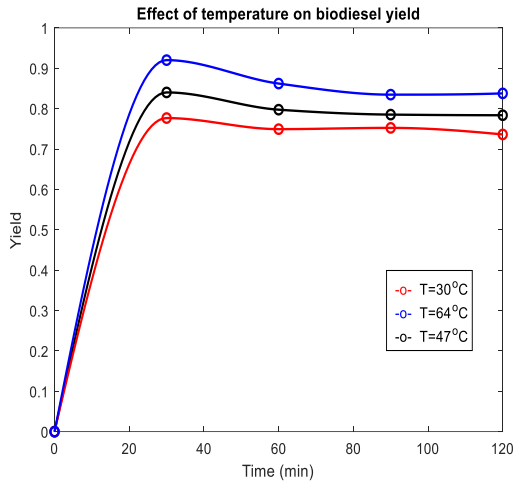

Figure 7-8: Effect of temperature on castor oil biodiesel yield

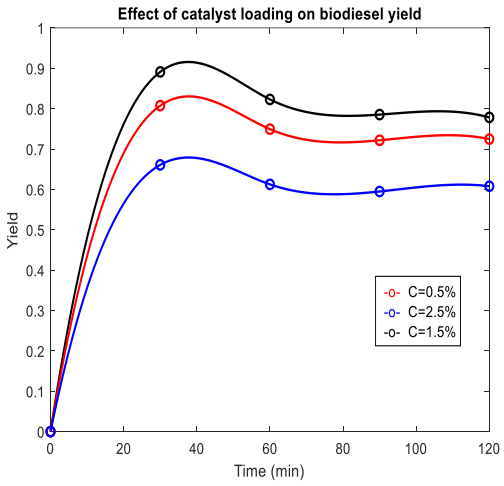

Figure 7-9: Effect of catalyst loading on castor oil biodiesel yield

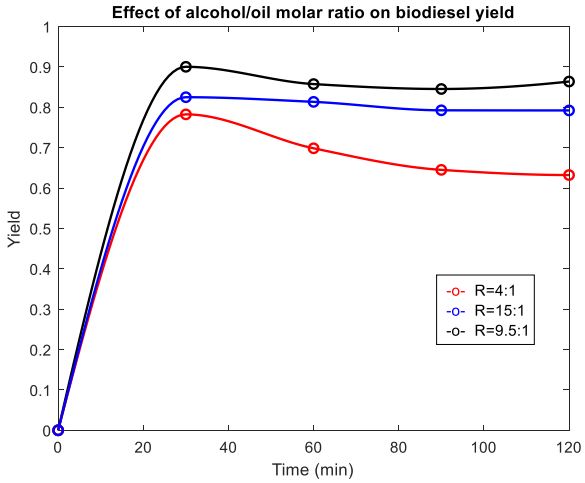

Figure 7-10: Effect of alcohol/oil molar ratio on castor oil biodiesel yield

Figures 7-8 to 7-10 were obtained by varying only one variable and showing its effect on the yield of biodiesel against time, while holding all other variables constant at their median value.

The median values are as follows:

Temperature = 47 ℃ Catalyst loading = 0.5 %

Reaction time = 75 minutes Alcohol to oil molar ratio = 9.5

These plots help understand the effect of the interactions between the variables at their different levels and time, and their effect on the biodiesel yield.

Figure 7-8 demonstrates that the yield of castor oil biodiesel increases as temperature increases, while the alcohol to oil ratio and catalyst loading remain fixed at their median values of 9.5 and 1.5% respectively. Increasing the temperature from 30 ℃ to 47 ℃ resulted in the biodiesel yield increasing from 0.75 to 0.8, while further increasing the temperature to 64 ℃ saw the yield increase to 0.9. This is because the increase in temperature offers more thermal energy to overcome the diffusion resistance between the 2 reacting phases (alcohol and oil). The increase in temperature also favours the forward reaction, which is endothermic.

Figure 7-9 represents the yield of castor oil biodiesel at different catalyst loadings (0.5%-2.5%) and reaction times (30-120 min) while maintaining the alcohol to oil ratio at 9.5 and the temperature at 47℃ (their median values). It can be seen that a catalyst loading of 0.5% resulted in a maximum yield of 0.8, while increasing the catalyst loading to 1.5% resulted in the maximum yield increasing to 0.9. A further increase in the catalyst loading to 2.5% results in a significant reduction in yield to 0.66. This behaviour is typical of base catalysts; the increase in catalyst amount favours the saponification reaction which results in the formation of soap and the reduction in yield of methyl esters (biodiesel).

Figure 7-10 displays the yield of biodiesel against time at different alcohol/oil molar ratios, while maintaining the temperature and catalyst loading at their median values of 47 ℃ and 1.5%, respectively. A ratio of 4 resulted in a yield of 0.75. Increasing the alcohol to oil ratio to 9.5 caused the yield to increase to 0.9, however, a further increase in the ratio to 15 resulted in the yield dropping to 0.8. The high ratio causing a decreased yield is possibly due to the accumulation of methanol and the viscous nature of the fluid, while the low ratio's low yield can be attributed to the reversible nature of the transesterification reaction; an excess of alcohol is required to drive the forward reaction.

These findings are similar to those of a recent study done by Keera, et al. (2018).

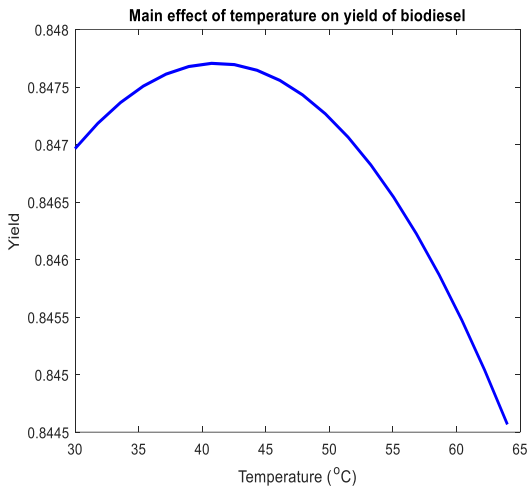

Figure 7-11: Main effect of temperature on castor oil biodiesel yield

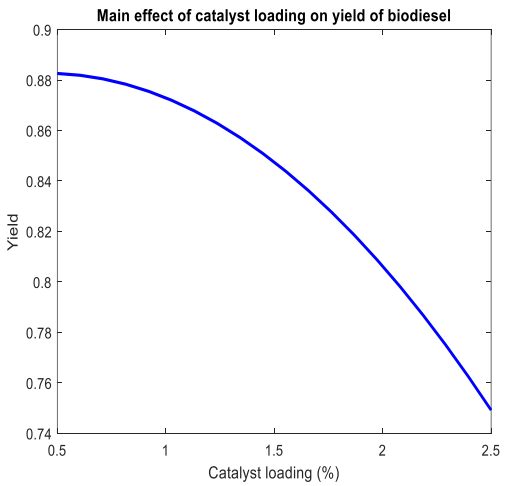

Figure 7-12: Main effect of catalyst loading on castor oil biodiesel yield

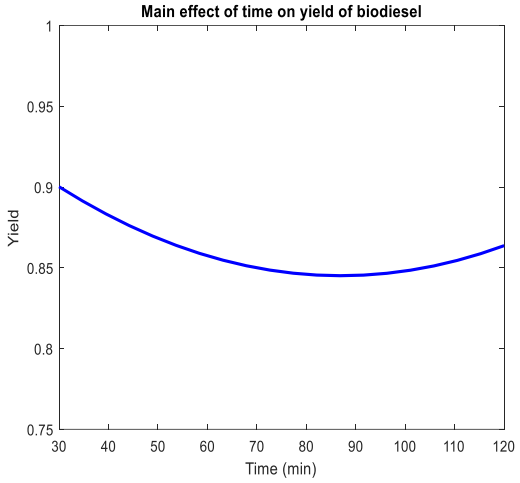

Figure 7-13: Main effect of time on castor oil biodiesel yield

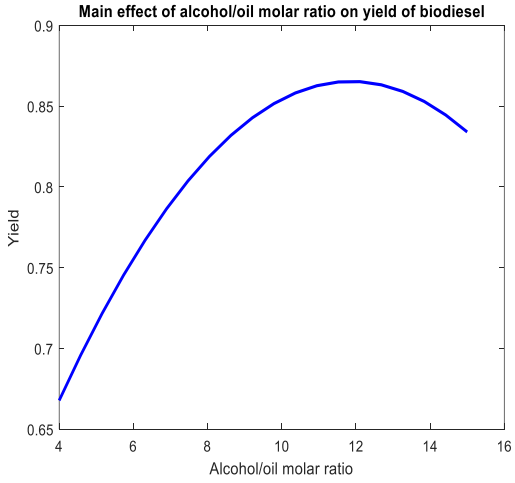

Figure 7-14: Main effect of alcohol/oil molar ratio on castor oil biodiesel yield

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

Figure 7-11 indicates that the yield increased with temperature initially, and then the yield decreased as temperature increased. However, the difference between the highest and lowest yield value is 0.003 indicating that the effect of temperature on the yield of biodiesel obtained from castor oil is not prominent. Figure 7-12 shows that the yield of biodiesel decreases as the catalyst loading increases. This is explained by the fact that high amounts of alkaline catalyst promote the formation of soap and inhibit the production of biodiesel resulting in a decrease in yield. The main effect of time on the yield of castor oil biodiesel is seen in Figure 7-13. The difference between the highest and lowest yield values is less than 0.05, indicating that the

effect of time on the yield of biodiesel obtained from pre-treated castor oil is not significant. Figure 7-14 displays the effect of the alcohol to oil molar ratio on the yield of biodiesel obtained. It can be seen that the alcohol to oil ratio has the most significant effect on the yield of biodiesel. The yield first increases as the ratio increases, however, after an alcohol to oil ratio of 12, the yield begins to decrease as the ratio increases. Once again, this is due to the excessive amount of alcohol contributing to the difficulty in separation of the biodiesel from the glycerol layer, thereby decreasing the yield.

Chapter 8

Property Testing & Blending

Simple property testing was conducted on the biodiesel produced in this study in order to determine if the biodiesel was in line with international standards and classify if it could be used in diesel engines without any further modification. Properties of the feedstocks (sunflower oil, castor oil and esterified castor oil) as well as the biodiesel produced from these feedstocks, and blends of biodiesel with kerosene were assessed. Biodiesel was blended with kerosene in an attempt to produce bio-jet fuel. Two blends were produced; 10% biodiesel and 90% kerosene, as well as 20% biodiesel and 80% kerosene. For convenience, the 10% biodiesel and 90% kerosene blend is referred to in this chapter as BK10, and the 20% biodiesel and 80% kerosene blend is referred to as BK20.

8.1. Density

The density of the samples was measured using a hydrometer. A sufficient volume of the sample was poured into a measuring cylinder and the hydrometer was then spun and dropped into the sample and the specific gravity was recorded. The density of the sample was then calculated by multiplying the specific gravity with the reference density of water of 1000 $\frac{kg}{m^3}$. This process was carried out 3 times and an average value was taken to improve the accuracy of the results. The density of all samples was measured at a standard reference temperature of 15 ℃ as specified in ASTM D941. The limit for density as specified in ASTM D941 is 900 $\frac{kg}{m^3}$. It can be seen in table 31, that castor oil biodiesel had a density of 910 $\frac{kg}{m^3}$ which is slightly above the limit, while sunflower oil biodiesel had a density of 890 $\frac{kg}{m^3}$ which is below the limit. The acceptable density range for jet fuel is 775-840 $\frac{kg}{m^3}$ according to ASTM D1655. It can be

seen that all the biodiesel blends were well within the range. The hydrometer used to measure the density had an uncertainty of ± 0.02 mm.

Table 8-1: Density measurements

Sample	Density $\left(\frac{kg}{m^3}\right)$			Average density $\left(\frac{kg}{m^3}\right)$
Sunflower oil	915	914	916	916
Castor oil	953	956	956	955
Esterified castor oil	942	943	947	944
Sunflower oil biodiesel	889	891	890	890
Castor oil biodiesel	912	911	909	910
Blends				
Sunflower oil biodiesel BK10	811	812	810	811
Sunflower oil biodiesel BK20	816	813	813	814
Castor oil biodiesel BK10	818	816	814	816
Castor oil biodiesel BK20	830	829	825	828

8.2. Kinematic viscosity

The dynamic (absolute) viscosity of the samples were measured using a viscometer. A water bath was used to bring the sample to its desired temperature (40 ℃ for biodiesel, 25 ℃ for oils and 20 ℃ for jet fuels) before recording the measurement. Spindle S21 was used to measure the viscosity. Once the sample was at the desired temperature, the spindle was placed into the sample and the rotation speed was set to 60 rpm. The dynamic viscosity was then recorded in centipoise (cP) and this value was divided by the density of the sample to obtain the kinematic viscosity. This process was done 3 times for each sample and an average value was taken.

As seen in table 8-2, castor oil biodiesel had a kinematic viscosity of 9.1 $\frac{mm^2}{s}$, which is above the limit of 6 $\frac{mm^2}{s}$ as specified in ASTM D445. Sunflower oil biodiesel had a lower density of 2.3 $\frac{mm^2}{s}$ which is well below the limit. ASTM D1665 outlines a maximum kinematic viscosity of 8 $\frac{mm^2}{s}$ for jet fuels at 20 ℃. It can therefore be noted that all biodiesel blends with kerosene met this requirement. The apparatus used to measure the viscosity had an uncertainty value of $\pm$ 0.02 $\frac{mm^2}{s}$.

Table 8-2: Viscosity measurements

Sample	Kinematic viscosity $\left(\frac{mm^2}{s}\right)$			Average kinematic viscosity $\left(\frac{mm^2}{s}\right)$
Sunflower oil	33.6	32.3	29.8	31.9
Castor oil	257	255.8	256.1	256.3
Esterified castor oil	85.7	85.9	84.6	85.4
Sunflower oil biodiesel	2.1	2.6	2.2	2.3
Castor oil biodiesel	9.0	9.4	8.9	9.1
Blends				
Sunflower oil biodiesel BK10	1.2	1.3	1.2	1.2
Sunflower oil biodiesel BK20	1.2	1.2	1.2	1.2
Castor oil biodiesel BK10	1.9	1.8	1.7	1.8
Castor oil biodiesel BK20	1.2	1.2	1.3	1.2

8.3. Acid value

Acid tests were conducted in accordance with the method outlined in ASTM standard D974. Prior to conducting the acid test, a titration solvent was prepared by mixing toluene, water and isopropyl alcohol in the ratio 100:1:99. A 0.1 M potassium hydroxide (KOH) solution was also prepared and added into a burette.

A blank titration of the titration solvent was then conducted to determine the amount of reactive substances in the titration solvent, and this allowed for a correction of error in subsequent titrations using the titration solvent. The blank titration was conducted as follows:

- 100 mL of titration solvent was added to an Erlenmeyer flask followed by 0.5 mL of phenolphthalein indicator and a blank titration of the titration solvent was conducted. The volume of KOH solution required to titrate the titration solvent was recorded.

The following procedure was followed to determine the acid value as outlined by ASTM standard D974:

- 2g of the sample was weighed into an Erlenmeyer flask.
- 100mL of the titration solvent was added to the sample, followed by 0.5mL of phenolphthalein indicator and the sample was swirled until it was entirely dissolved by the titration solvent.

- The sample was then titrated with the potassium hydroxide solution until the endpoint (when the solution turned pale pink) was reached.
- The volume titrated was recorded and the acid number was calculated by the following equation:

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

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 sample used (g).

Table 8-3: Acid value measurements

Sample	Acid value $\left(\frac{mg\ KOH}{g}\right)$			Average acid value $\left(\frac{mg\ KOH}{g}\right)$
Sunflower oil	0.34	0.33	0.29	0.32
Castor oil	28.73	28.32	28.78	28.61
Esterified castor oil	1.40	1.44	1.45	1.43
Sunflower oil biodiesel	0.22	0.22	0.19	0.21
Castor oil biodiesel	0.63	0.61	0.56	0.60
Blends				
Sunflower oil biodiesel BK10	0.22	0.21	0.20	0.21
Sunflower oil biodiesel BK20	0.21	0.21	0.20	0.21
Castor oil biodiesel BK10	0.56	0.54	0.55	0.55
Castor oil biodiesel BK20	0.53	0.57	0.55	0.55

According to ASTM D974, the acid value of biodiesel should not be larger than 0.5 $\frac{mg\ KOH}{g}$. Castor oil biodiesel had an acid value of 0.60 $\frac{mg\ KOH}{g}$ which is above the allowable limit, while sunflower oil biodiesel's acid value of 0.32 $\frac{mg\ KOH}{g}$ was below the limit. For jet fuel, the maximum allowable acid value is 0.015 $\frac{mg\ KOH}{g}$, which means that all the jet fuel samples were above this limit.

8.4. Flash point (closed cup)

A flash point apparatus was used to determine the flash point of the biodiesel and jet fuel samples. A small volume of the sample was placed in a lidded cup in the flash point apparatus. The sample was heated within the cup and the lid of the cup was opened in 1 ℃ intervals and the sample was exposed to an ignition source. The lowest temperature at which the vapour above the fuel flashed was recorded as the flash point. The test was performed 3 times for each sample and an average value was taken. The flash point apparatus used provides results with an uncertainty of $\pm$ 0.01℃.

Table 8-4: Flash point measurements

Sample	Flash point (℃)			Average flash point (℃)
Sunflower oil biodiesel	100	101	99	100
Castor oil biodiesel	154	159	155	156
Blends				
Sunflower oil biodiesel BK10	55	55	58	56
Sunflower oil biodiesel BK20	65	66	61	64
Castor oil biodiesel BK10	58	61	58	59
Castor oil biodiesel BK20	65	64	69	66

According to ASTM D93, the flash point of biodiesel should be between 93 ℃ and 170 ℃. It can be seen from table 34 that both sunflower oil biodiesel and castor oil biodiesel lied within this range. ASTM D1655 states that the flash point of jet fuels should be higher than 38 ℃ and it can be seen that all the jet fuels sample had a flash point higher than 38 ℃.

8.5. Pour point

The pour point of the biodiesel samples were determined by surrounding a beaker containing the biodiesel with dry ice. The lowest temperature at which the mixture was able to be poured was recorded as the pour point. ASTM D1655 states a pour point of -47 ℃ for jet fuel and due to equipment limitations, this could not be tested. Therefore, only the pour point of the biodiesel samples were tested. As seen in table 8-5, both samples had a pour point that lied within the range of -15 ℃ to 10 ℃ as specified in ASTM D6751.

Table 8-5: Pour point measurements

Sample	Pour point (℃)			Average pour point (℃)
Sunflower oil biodiesel	-3	-3	0	-2
Castor oil biodiesel	6	5	4	6

8.6. API Gravity

The API gravity for jet fuel samples was calculated using the following equation (Speight, 2002):

$$\text{API gravity} = \frac{141.5}{SG} - 131.5$$

The API gravity was calculated for the 3 specific gravity values obtained when conducting the density measurements and an average value was taken.

Table 8-6: API gravity results

Sample	API gravity			Average API gravity
Blends				
Sunflower oil biodiesel BK10	42.98	42.76	43.19	42.98
Sunflower oil biodiesel BK20	41.91	42.55	42.55	42.34
Castor oil biodiesel BK10	41.48	41.91	42.33	41.91
Castor oil biodiesel BK20	38.98	39.19	40.02	39.40

8.7. Heat of combustion

The heat of combustion for the jet fuel samples were calculated according to the following equation (Speight, 2002):

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

The heat of combustion was calculated for the 3 specific gravity values obtained when conducting the density measurements, and an average value was taken.

Table 8-7: Heat of combustion results

Sample	Heat of combustion $\left(\frac{BTU}{lb}\right)$			Average heat of combustion $\left(\frac{BTU}{lb}\right)$
Blends				
Sunflower oil biodiesel BK10	11018.79	11015.38	11022.19	11018.79
Sunflower oil biodiesel BK20	11001.70	11011.97	11011.97	11008.55
Castor oil biodiesel BK10	10994.84	11001.70	11008.55	11001.70
Castor oil biodiesel BK20	10953.31	10956.79	10970.69	10960.26

8.8. GC-MS Analysis

The composition of the biodiesel samples obtained at the optimum conditions were analysed using gas chromatography – mass spectrometry. A Shimadzu GC-MS machine equipped with an ultra-alloy column was used for the analysis. Table 8-8 shows the column specifications:

Table 8-8: GC-MS column specifications

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

The following column oven temperature program was used:

Table 8-9: GC column oven temperature program

Rate $\left(\frac{℃}{min}\right)$	Final temperature (℃)	Hold time (min)
-	120	0
2	240	7

Table 8-10: GC conditions

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

8.8.1. Sunflower oil biodiesel GC-MS results

GC-MS analysis was conducted of sunflower oil biodiesel at the optimum conditions as outlined in chapter 5 on page 50 (table 5-6). These were the conditions that resulted in the highest yield of biodiesel and are listed below:

Temperature: 55.36 ℃ Catalyst loading: 0.86%

Time: 86.48 minutes Alcohol/oil molar ratio: 12.61

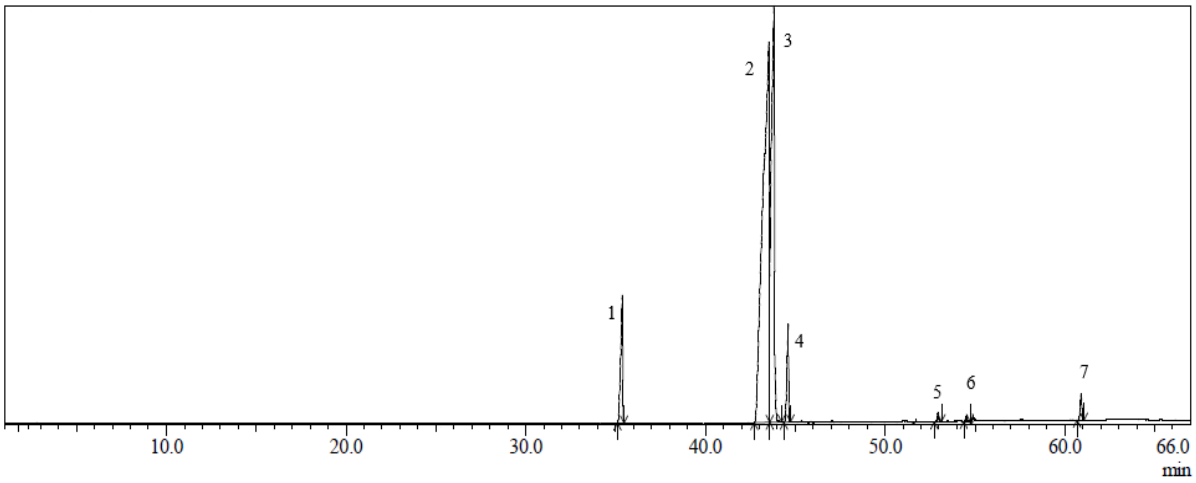

Figure 8-1: Sunflower oil biodiesel chromatogram

Table 8-11: Sunflower oil biodiesel GC-MS results

Peak no.	Retention time (min)	Area (%)	Name	Chemical formula
1	35.376	6.09	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$
2	43.532	56.22	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$
3	43.821	31.61	9-Octadecenoic acid, methyl ester, (E)-	$C_{19}H_{36}O_2$
4	44.611	3.84	Methyl stearate	$C_{19}H_{38}O_2$
5	52.952	0.33	cis-11-Eicosenoic acid, methyl ester	$C_{21}H_{40}O_2$
6	54.935	0.18	Eicosanoic acid, methyl ester	$C_{21}H_{42}O_2$
7	60.914	0.92	Docosanoic acid, methyl ester	$C_{23}H_{46}O_2$

8.8.2. Castor oil biodiesel GC-MS results

GC-MS analysis was conducted of castor oil biodiesel at the optimum conditions as outlined in chapter 7 on page 77 (table 7-4). These were the conditions that resulted in the highest yield of biodiesel and are listed below:

Temperature: 62.79 ℃ Catalyst loading: 0.72%

Time: 45.49 minutes Alcohol/oil molar ratio: 10.10

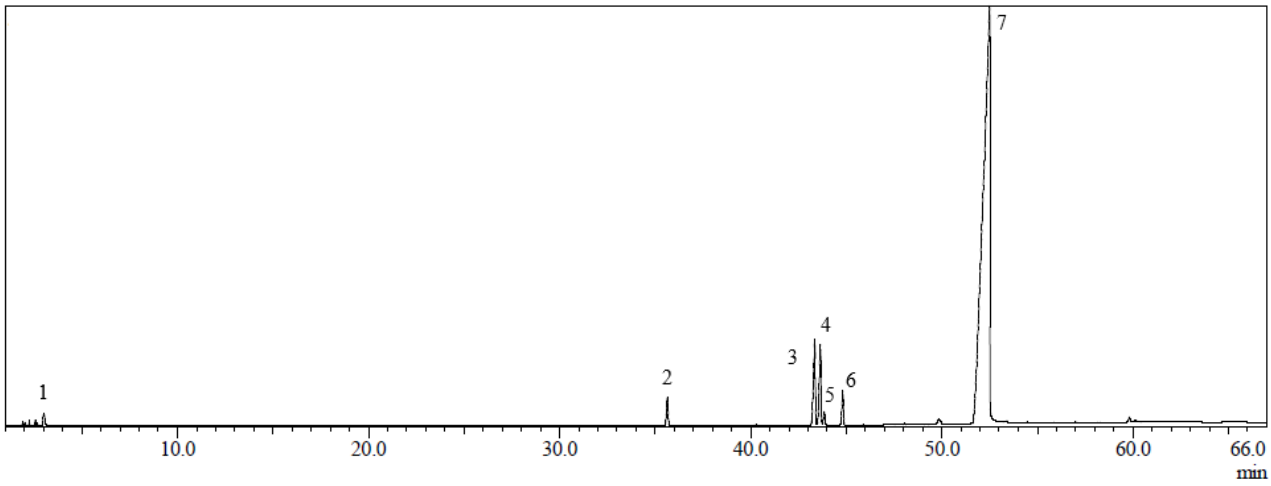

Figure 8-2: Castor oil biodiesel chromatogram

Table 8-12: Castor oil biodiesel GC-MS results

Peak no.	Retention time (min)	Area (%)	Name	Chemical formula
1	3.033	0.58	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$
2	35.641	1.21	9,12-Octadecadienoic acid, (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$
3	43.353	4.95	Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester	$C_{18}H_{34}O_2$
4	43.647	4.26	11-Octadecenoic acid, methyl ester	$C_{19}H_{36}O_2$
5	43.843	0.55	Octadecanoic acid, 9,10-dihydroxy-, methyl ester	$C_{19}H_{38}O_4$
6	44.818	1.54	Methyl stearate	$C_{19}H_{38}O_2$
7	52.496	86.73	Ricinoleic acid, methyl ester	$C_{19}H_{36}O_3$

Chapter 9

Conclusions & Recommendations

9.1. Conclusions

The following conclusions were drawn from this study:

- Sunflower oil had a low acid value of 0.32 $\frac{mg\ KOH}{g}$ and hence could be used to produce biodiesel through a single-step base catalysed transesterification reaction.
- When producing biodiesel from sunflower oil and methanol using potassium hydroxide as catalyst, the maximum experimental yield of 0.9658 was obtained at a temperature of 30 ℃, a catalyst loading of 2.5%, reaction time of 75 minutes and methanol to sunflower oil molar ratio of 9.5.
- A regression equation was fitted to the data and showed a strong coefficient of determination (R^2) value of 0.9585 indicating an excellent fit.
- The predicted optimum yield was 0.98293 at a temperature of 55 ℃, a catalyst loading of 0.86%, reaction time of 86.5 minutes and an alcohol to oil ratio of 12.61. However, the experimental yield at these conditions was 0.9851 which slightly exceeded the predicted optimum.
- It can therefore be concluded that the optimum yield of biodiesel from sunflower oil when using methanol and KOH as catalyst can be obtained at a reaction temperature of 55 ℃, reaction time of 86.5 minutes, catalyst loading of 0.86% and methanol to sunflower oil molar ratio of 12.61.
- Sunflower oil biodiesel properties were within the limits specified in the ASTM standards and can therefore be used in a diesel engine without modification.

- Castor oil had a high free fatty acid content, with an acid value of 28.61 $\frac{mg\ KOH}{g}$ and an FFA % of 14.31% which meant that the oil needed be esterified via an acid catalyst to reduce its FFA content before it was able to be transesterified with a base catalyst.
- Sulphuric acid was used as catalyst for the esterification process. The lowest experimental FFA% of 1.269 % occurred at a temperature of 47℃, a catalyst loading of 0.25%, reaction time of 120 minutes and an alcohol to oil ratio of 9.5.
- The regression equation had a high coefficient of determination (R^2) value of 0.9831 indicating an excellent fit.
- The predicted optimum FFA % was 0.644% at a temperature of 61.9 ℃, catalyst loading of 0.61%, reaction time of 35.6 minutes and an alcohol to oil ratio of 13.41. The experimental FFA % at these conditions was 0.715% meaning that the esterified castor oil could be used in base catalysed transesterification to produce biodiesel.
- The esterified castor oil was transesterified using KOH as catalyst.
- The regression equation for the castor oil transesterification had a high R^2 value of 0.9558.
- The predicted optimum yield for castor oil biodiesel of 0.96 was at a temperature of 62.8 ℃, catalyst loading of 0.72%, reaction time of 45.5 minutes and alcohol to oil ratio of 10.1. The experimental yield obtained under these conditions was 0.95.
- It was therefore concluded that the optimum castor oil biodiesel yield can be obtained at a reaction time of 45.5 minutes, temperature of 62.8 ℃, catalyst loading of 0.72% and alcohol to oil ratio of 10.1.
- The properties of castor oil biodiesel did not lie within the limits outlined in the ASTM standards and hence is not suitable for use in a diesel engine without further modification.

9.2. Recommendations

- Several other feedstocks/combinations of feedstocks could be investigated.
- Other catalysts and alcohols could be investigated.
- A kinetic study should be done in order to understand the transesterification reaction at a molecular level.
- Other reaction conditions, such as pressure, etc. should be varied in order to study the effect they have on the production of biodiesel.
- Properties of biodiesel blends with petro-diesel should also be studied.

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Appendix A - Sample calculations

All sample calculations are shown with respect to sunflower oil. The same calculations were done for castor oil.

Molar mass

The molar mass of sunflower oil and castor oil was determined according to the following equation (Huaping, et al., 2006):

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

Where SV is the saponification value, and AV is the acid value of the oil, both in units of $\frac{mg\ KOH}{g}$.

The saponification value was determined according to the method suggested by Muhammad, et al. (2019). Five drops of phenolphthalein indicator was added to a mixture of 2g of oil and 25mL of a 0.1N ethanolic potassium hydroxide solution. The solution turned pink upon adding the indicator. The solution was then titrated with a 0.5M hydrochloric acid solution until the pink colour faded away, and this volume was recorded as the volume titrated. A blank titration of the ethanol and KOH solution was also done and the saponification value was calculated according to the following equation (Muhammad, et al., 2019):

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

Where V_b is the volume titrated during the blank titration, V_t is the volume titrated and m is the mass of sample. The blank titration volume was 20 mL, while the volume titrated for sunflower oil was 6.28 mL, and the volume titrated for castor oil was 5.02 mL. The calculation for the saponification value of sunflower oil is shown below:

$$SV_{sunflower\ oil} = \frac{56.1 \times 0.5 \times (20 - 6.28)}{2} = 192.42\ \frac{mg\ KOH}{g}$$

The same calculation was done for castor oil resulting in a saponification value of 210.16 $\frac{mg\ KOH}{g}$.

The acid value was determined as outlined in chapter 8 (page 88). The sample calculation for sunflower oil is shown below:

$$Acid\ value = \frac{(1.34 - 0.2) \times 0.1 \times 56.1}{20} = 0.32\ \frac{mg\ KOH}{g}$$

The molar mass of sunflower oil was therefore:

$$Molar\ mass_{sunflower\ oil} = \frac{56.1 \times 1000 \times 3}{192.42 - 0.32} = 876.11\ \frac{g}{mol}$$

The above calculations were repeated for castor oil resulting in a molar mass of 927 $\frac{g}{mol}$.

Amount of alcohol required

300 mL of sunflower oil weighed 274.8g. The number of moles of sunflower oil was calculated as follows:

$$n_{oil} = \frac{m}{Molar\ mass} = \frac{274.8}{876.11} = 0.3137\ mol$$

For an alcohol to oil molar ratio of 4, the amount of alcohol required is:

$$n_{alcohol} = 4 \times 0.3137 = 1.255\ mol$$

Methanol has a molar mass of 32.04 $\frac{g}{mol}$. The mass of methanol required is calculated as follows:

$$m_{alcohol} = 1.255 \times 32.04 = 40.21\ g$$

Amount of catalyst required

For a catalyst loading of 0.5%, the mass of catalyst required is:

$$m_{catalyst} = \frac{0.5}{100} \times 274.8 = 1.374\ g$$

Yield

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

$$Yield = \frac{mass\ of\ biodiesel\ produced}{mass\ of\ oil\ used} = \frac{224.402}{274.8} = 0.8166$$