OPTIMIZATION OF BIODIESEL PRODUCTION USING HETEROGENOUS CATALYST IN A PACKED BED REACTOR

Submitted in fulfillment of the requirements of the degree of Master
of Engineering: Chemical Engineering in the Faculty of Engineering
and the Built Environment at the Durban
University of Technology

OLAGUNJU OLUSEGUN AYODEJI

August, 2017

Supervisor: Prof. Paul Musonge

DECLARATION

I hereby declare that this dissertation is a record of my original work and research for the obtention of my Master of Engineering qualification in chemical engineering with the Durban University of Technology. The content of this document has not been previously published or written by another person for the award of any other degree at Durban University of Technology (DUT) or any other educational institution. Furthermore, I declare that the content of this dissertation does not violate any copyright as every work of others been indicated has been recognised by means of in text referencing and a comprehensive list of references.

This document must not be reproduced, copied or sold without the consent of the author and the authorities of the Durban University of Technology.

Olagunju Olusegun Ayodeji

Signature: .... Date………………………

Supervisor: Prof. P. Musonge.

Signature: .... Date………………………

DEDICATION

I dedicate this dissertation to my “supporters”:

My father Olagunju SoladoyeSamuel: My hero, my superman. I love you more than anything in this world.

My mother Olagunju Mary Folusho: the strongest woman I have ever known. I will forever relish and folloe your values.

My wife, Olagunju Anuoluwapo: I will forever love and cherish you with all my love, I also dedicate this work to Adeola, Tosin, Muyiwa, Oladele, Solape, Damilola, Mummy Femi, Femi, Sarah, Mummy Samuel and Samuel, as well as my extended family, my dearest friends; and lastly, to my creator, God through my Lord and Saviour Jesus Christ.

ACKNOWLEDGEMENT

Firstly, I would like to thank the Almighty God who made all this possible in my life. My sincere gratitude goes to my Supervisor, Prof. Paul Musonge. I thank you sir for giving me the opportunity to start my Masters with the department of Chemical Engineering and for your guidance and your genuine heart of love and fatherly counsel. I appreciate all your encouragement and all the support you have given me during my studies.

Furthermore, I thank all the laboratory staff and my fellow postgraduates in the Department of Chemical Engineering for their encouragement at all times.

.

ABSTRACT

Industrial development is associated with an increase in pollution levels and rising fuel prices. Research on clean energy contributes to reduction of fossil fuel dependency, decrease in ozone layer depletion and reduction in emission of toxic gases. The development of renewable energies increases the energy independence and reduces the impact of environmental pollution from fossil fuels.

The biodiesel market is among the fastest growing renewable energy markets and its demand in the energy sector has tremendously increased over the last decade due to its environmental friendly qualities. Biodiesel is considered as a promising diesel fuel substitute based on the similarities of its properties with that of petroleum based diesel fuel. However, the high cost of the feedstock, environmental pollution as a result of wastewater generated from a homogeneous process has limited its full implementation. In addition, other technical challenges encountered during the production such as the immiscibility of the reagents and the reversibility of the transesterification reaction calls for innovative technologies to be developed. One promising solution to these issues is the use of membrane technology to serve as a reaction and separating medium for the production of biodiesel.

This study is aimed at optimizing biodiesel production from vegetable oils using heterogeneous catalysts in a ceramic membrane. The objectives were to evaluate the performance of calcium oxide (CaO) as a catalyst supported on activated carbon in a membrane reactor for biodiesel production. Further still, to evaluate the membrane performance regarding permeate quality and to optimize the process using design of experiment. The final objective was to investigate the influence of operating parameters such as temperature, methanol/oil ratio, catalyst amount and reaction time on biodiesel yield.

The transesterification of soya bean oil with methanol in the presence of a supported catalyst was carried out on a laboratory scale. The membrane reactor was designed and assembled for this purpose. The membrane reactor integrated many procedures such as combining reaction and separation in a single unit, continuous mixing of raw materials and maintaining high mass transfer between the immiscible phases during the reaction. The effect of the process parameters on the biodiesel production and FAME (fatty acid methyl ester) yields were investigated.

One factor at a time (OFAT) experiments were conducted to identify the optimum range of the yield. The membrane reactor produced a permeate stream which separated at room temperature into a FAME rich non-polar phase and a methanol polar phase. The optimum range was between 90% - 94% within a reaction time of 60 – 180 minutes, methanol to oil ratio 3:1 - 9:1 and temperature range of 60 ^{0}C - 70 ^{0}C. Methyl ester produced met the ASTM D6751 and SANS 1935 specifications.

The response surface methodology (RSM) based on the central composite design (CCD) was used to optimize the process. The optimization experiments were conducted around the optimum range established by the OFAT method. The optimum condition for transesterification of soya bean oil to fatty acid methyl ester was obtained at 3 g/L catalyst concentration, 65 ^{0}C temperature, 4.5:1 methanol to oil molar ratio and 90 minutes reaction time. At these optimum conditions, the FAME yield was 96.9 %, which is well within the yield of 97.7 % as predicted by the model.

In conclusion, this work presents a study of high quality biodiesel production using a ceramic membrane reactor with the advantage of selectively permeating FAME and methanol. This study therefore showed that the use of a membrane for biodiesel production conserved water for other purposes; eliminates the purification step and wastewater generation thereby reducing the cost of biodiesel production.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

CO_2	-	Carbon dioxide
NaOH	-	Sodium hydroxide
KOH	-	Potassium hydroxide
CaO	-	Calcium Oxide
DUT	-	Durban University of Technology
OFAT	-	One factor at a time
RSM	-	Response Surface Methodology
CCD	-	Central Composite Design
DOE	-	Design of Experiment
IEA	-	International Energy Agency
BRICS	-	Britain Russia Ireland China South Africa
FAME	-	Fatty Acid Methyl Ester
EN	-	European Standard
ASTM	-	American Society for Testing Materials
SANS	-	The South African Bureau of Standards
PPM	-	Parts per Million
DG	-	Diglycerides
TG	-	Triglycerides
FFA	-	Free Fatty Acid
IUPAC	-	International Union of Pure and Applied Chemists
OH	-	Hydroxide
H_2SO_4	-	Sulfuric Acid
TiO_2/Al_2O_3	-	Titanium dioxide/Aluminium Oxide
ANOVA	-	Analysis of Variance
LOF	-	Lack of Fit

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

The continuous growth in population and industrialization has led to an increase in activities that are dependent on fossil fuels such as industrial combustion, transportation and general household demands. This has put a huge constrain on the crude oil reservoir such that it is depleting at a very fast rate. The huge dependency of man on these fossil fuels have led to an increase in environmental pollution through the release of huge amount of CO_2 and other toxic chemicals thereby leading to the depletion of the ozone layer and reduction in the air quality.

The research carried out by British Petroleum (BP, 2009) showed that the world's energy production is largely based on oil (35%), coal (29%) and natural gas (24%) to provide the global energy demand, see Figure 1.1. According to (IEA, 2014), South Africa is considered as one of the top countries in rank contributing to the depletion of the ozone layer. It accounts for almost half of the CO_2 emissions in Africa, and contributes about 1.6% of the world's emissions because its economy majorly depends on energy derived from fossil fuels. In order to resolve this problem, the need to complement the existing crude oil with renewable energy is very important.

.

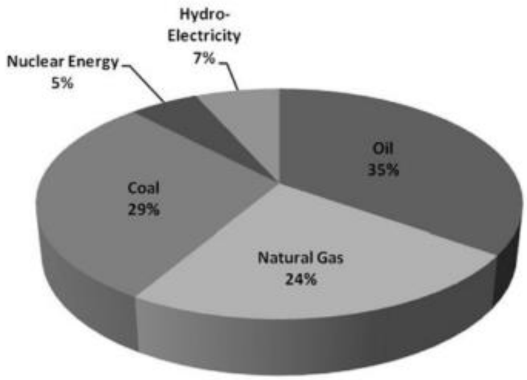


Figure 1.1: World energy production (BP, 2009)

Biodiesel production remains a profitable aspect of renewable energy after the adventure of Rudolf Diesel's test of vegetable oil as fuel for the engine (Nitske and Wilson, 1965). Countries like United States, Germany, Brazil, Argentina, Indonesia, and China are among the top producers of biodiesel in the world. These countries have made ambitious policies in order to assist biofuel industry to grow through renewable fuel standards and economic incentives. The demand and supply for biodiesel are expected to grow over the next two (2) decades if the policies put in place are followed. Global biodiesel production in 2013 was estimated at 24.7 million tons (Pashely, 2013) with European Union (EU) countries, USA and Brazil as the leading producers of biodiesel as shown in Figure 1.2. South Africa is categorized among other countries, which contribute less than 5% to the global biodiesel production. As a result, the South African government plans to pass a regulation that will ensure mandatory blends of biodiesel into petrodiesel fuel, and major biodiesel plant constructions are currently underway in the Eastern Cape (Amigun *et al*., 2011). According to Amigun *et al.* (2011), this province contains large fertile land sites for plantations of feedstock, which may be grown specifically for biodiesel production, thus eliminating the food – fuel debates.

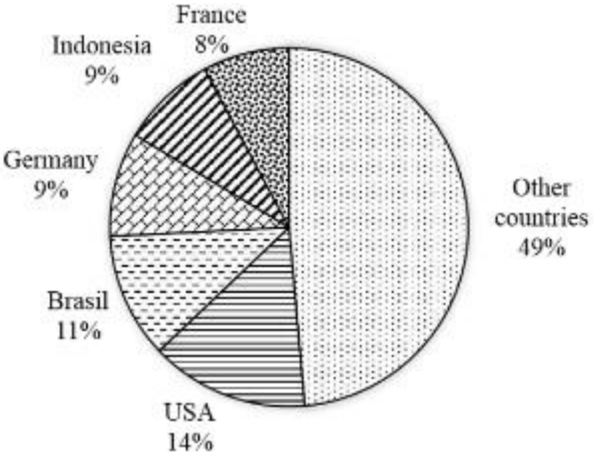


Figure 1.2: Distribution of global biodiesel production in 2013 (Biodiesel, 2014)

Biodiesel can be produced from various sources like vegetable oils, greases, and animal fats. It is chemically known as fatty acid alkyl ester. Biodiesel is a naturally oxygenated fuel because oxygen constitutes about 10% of its formation. Biodiesel can be produced by reacting vegetable oil with alcohol in the presence of an (acid, base or enzyme) catalyst (Zhang *et al*., 2013; Hama *et al*., 2016). Fuel produced from vegetable oil does not add to the CO_2 already in the atmosphere because the green plants absorb the released carbon.

1.2 PROBLEM STATEMENT

The conventional method of producing biodiesel is by transesterification of vegetable oil and animal fat using homogeneous basic catalysts (primarily sodium hydroxide or potassium hydroxide) dissolved in methanol. Using a basic catalyst such as NaOH or KOH has many disadvantages such as soap formation and difficulty in catalyst recovery, which leads to downstream wastewater treatment and hence, increases the production cost of biodiesel. The total cost of producing biodiesel using homogenous catalyst is not sufficiently competitive to fuel produced from crude oil. Therefore, there is need to consider an alternative process, which is safer, cheaper, more environment-friendly and ease the process of separating the catalyst from the product.

Biodiesel produced in South Africa is still in its infancy stage (Hasna, 2013). It is mostly produced in a conventional way using homogeneous base catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). The use of homogeneous base catalyst escalates the production cost because further separation process is required to recover the catalyst, which leads to wastewater generation and disposal issues. Although, acid homogeneous catalysts have also been used but the rate of reaction is slow compared to the base catalyzed reaction.

Heterogeneous catalysis with the use of membrane reactor is an alternative process that can be used to overcome the challenges encountered by the homogenous process. In the heterogeneous process, the catalyst is easily separated from the product and reused for further process. The use of membrane in the process can combine the reaction and separation in a single unit, thereby eliminate purification cost and wastewater generation.

1.3 HYPOTHESIS

The production of biodiesel can be carry out in a single-phase transesterification of vegetable oil using membrane reaction technology thereby eliminating further downstream processes.

1.4 GENERAL OBJECTIVE

This study aims at optimizing biodiesel production from vegetable oils using heterogeneous catalysts in a ceramic membrane.

1.5 SPECIFIC OBJECTIVES

i. To prepare and characterized the catalyst calcium oxide and adhere it to the surface of activated carbon as support.
ii. To design and construct a biodiesel production rig for the main purpose of the experiment.
iii. To evaluate the performance of supported CaO used as catalyst in a membrane reactor for the production of biodiesel.
iv. To evaluate the efficiency of the membrane in terms of selectivity.
v. To evaluate the influence of temperature, methanol/oil ratio, catalyst amount and reaction time on biodiesel yield.
vi. To use an appropriate design tool in order to establish the optimum conditions for biodiesel yield.

1.6 APPROACH

In this study, the biodiesel was produced using a membrane reactor and it also served as a medium for separation to eliminate the use of water in the process. The experimentation for the preliminary study was carried out in the laboratory.

This study was carried out in two stages. The first stage was implemented using the one factor-at-a-time (OFAT) method. The second stage involved the statistical and optimization study using response surface methodology (RSM) based on Central Composite Design (CCD) design. The generated data was analysed and a model equation required to optimize the process was developed.

1.7 DISSERTATION ORGANISATION

This dissertation contains six chapters and it is organized in the following manner:

CHAPTER 1: Introduction

This section will introduce the research title; provide the background of the study, highlights the problem statement, objectives and the scope of the study.

CHAPTER 2: Literature review

This section is a survey of existing studies and findings on this topic. It provides knowledge on the problem-solving strategies and shortcomings encountered by other researchers.

CHAPTER 3: Methodology

The methodology section provides a detail of the means and approaches taken in order to achieve the research aims and objectives. The techniques and strategies used for the design of experiments (DOE), data collection and analysis of results were explained.

CHAPTER 4: Results and discussion

This section provides a detail of the experimental findings and the interpretation of the results. The results generated from the experiments were compared to the findings in literature and were checked against the developed model for validation and reliability.

CHAPTER 5: Statistical and optimization studies

This section presented the statistical and optimization study results. Experiments were carried out using the response surface methodology based on central composite design.

CHAPTER 6: Conclusions and recommendations

This section summarizes the research findings according to the objectives set and demonstrate whether the researcher has met the targets set at the commencement of the study. It also provides recommendations for further research in the light of the results obtained and shortcomings encountered.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

The world’s economy largely depends on fossil fuel energy sources to provide the feedstock needed to maintain and sustain human civilization. According to the studies conducted by IEA (2014), industrial and transportation sector accounted for a larger percentage of the global energy consumption. In Figure 2.1, the industrial sector (manufacturing, agriculture, mining and construction) accounted for 52 % of the global energy consumed in 2014; while the transportation sector accounted for 27 %, the household activities comprised 14 %; and the commercial sector (businesses, institutions and organizations that provide services) comprised 7 % (IEA, 2014). According to British Petroleum (2013), the BRICS countries in which South Africa is a member consumed 36.2 % of world's primary energy (24 % of world's total oil, 20.8 % of total natural gas, and 64.3 % of total coal). The increase in consumption of the fossil fuel has led to increase in its demand and consequently impacted negatively on the environment. In addition, the continuous release of carbon dioxide, Sulphur dioxide, hydrocarbons and volatile organic compounds (VOCs) from the combustion of fossil fuels results in environmental pollution and ozone layer depletion (IEA, 2014). Figure 2.2 shows the million tons of toxic chemical discharged into the atmosphere from 1971 to 2014. Prediction shows that the emission of greenhouse gases from fossil fuels would increase by 39 % in 2030 (Mofijur *et al*., 2012).

Therefore, the development of alternative renewable energy sources has become necessary for sustainable eco-friendly and economic growth. Among many other alternative energy sources that had been discovered, considerable attention has been focused on biodiesel as an alternative energy source to complement conventional petroleum-derived fuels because of its numerous advantages such as its clean and renewable nature. Additionally, it is widely available from various feedstocks which can effectively reduce its production cost.

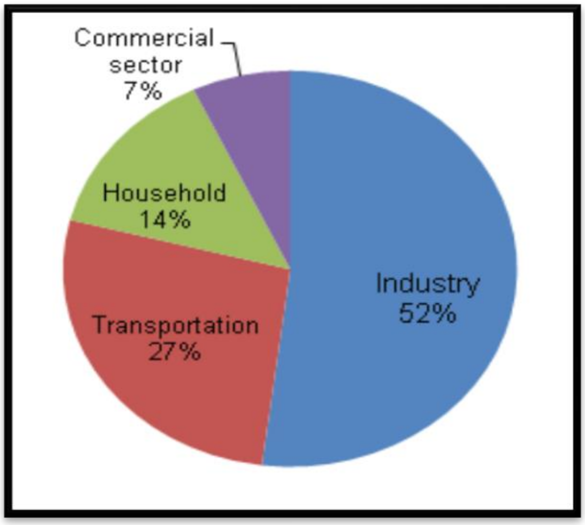


Figure 2.1: Global energy consumption in 2010 (IEA, 2014)

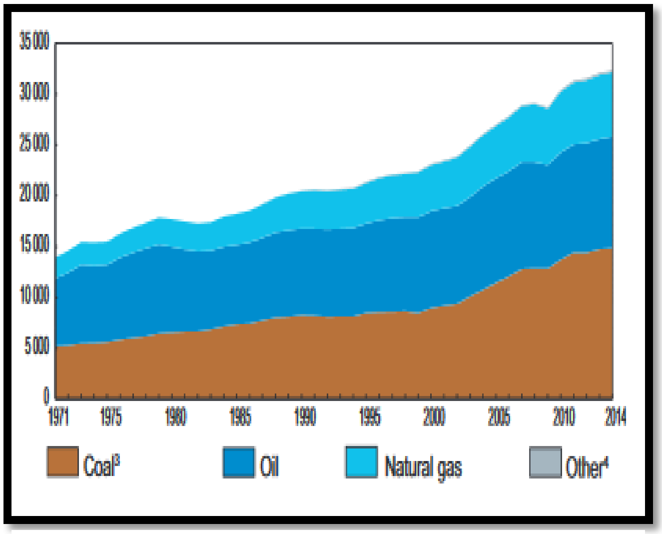


Figure 2.2: World emissions from fuel combustion from 1971 to 2014 by fuel (Mt of CO2) (IEA, 2014)

2.2 BRIEF HISTORY ON BIODIESEL

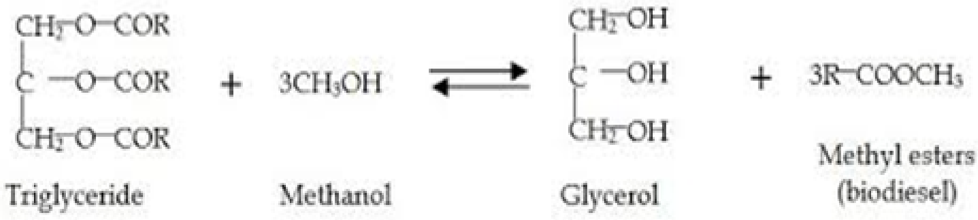
Dr. Rudolf Diesel developed the invention of a diesel engine running on fuels like heavy mineral oil and vegetable oils. The first engine experimentations were not successful but by the year 1900, he was able to overcome this challenge after several other trials and the engine he made to run on 100% peanut oil was showcased at the World Exhibition in Paris. In 1911 he made a profound statement that ‘‘the diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries, which use it’’. In 1912, Diesel said,” the use of vegetable oils for engine fuels may seem insignificant today but such oils may become in the course of time as important as petroleum and the coal-tar products of the present time”. Since Dr. Diesel’s untimely death in 1913, his engine has been modified to run on the polluting petroleum fuel, now known as ‘‘diesel’’. Nevertheless, his ideas on agriculture and his invention provided the foundation for a society fueled with clean, renewable, locally grown fuel (Knothe, 2011).

Vegetable oils were used as an alternative to diesel during emergency in the 1930s and 1940s (Knothe, 2011). In addition, due to the fluctuation in crude oil prices and environmental problems, more attention has been drawn to vegetable oils and animal fats to make biodiesel among other alternatives to fossil fuel. Continuous reliance on crude oil as a major source of energy had deepened local air pollution and magnified the global warming problems caused by carbon emission; a specific instance is that of the release of the toxic compound in the closed environment of underground mines. However, biodiesel has the prospect of reducing the high level of air contaminants and carcinogens into the atmosphere (Vellguth, 1983; Pryde, 1984; Meher *et al*., 2006).

The common international standards for biodiesel are EN 14214 and ASTM D 6751(Demirbas and Demirbas, 2010) but in South Africa, biodiesel is restricted by the SANS 1935 automotive standard to being a fatty acid methyl ester (FAME) derived only from vegetable oils (The South African Bureau of Standards, 2006). This means that either oil seeds or their subsequent crude vegetable oil can be used for the production of biodiesel or FAME (fatty acid methyl ester) in South Africa.

2.3 CHEMISTRY OF BIODIESEL

Biodiesel is described as a fuel for diesel engines produced from chemically converted animal fats or vegetable oils. It comprises of esters derived from the transesterification of vegetable oil. Hence, they are produced when a vegetable oil or similar feedstock reacts with an alcohol (methanol, ethanol, and butanol) in the presence of a catalyst. Glycerol and ester constitute the end product (Friedrich, 2003). Equation 2.1 shows the reaction mechanism for transesterification of triglycerides with alcohol.



(Equation 2.1)

The vegetable oils are composed of triglycerides, of which three free fatty acids are attached to a glycerol molecule. Fatty acids are long chain hydrocarbons, and are categorized into saturated and unsaturated fats. Saturated fats are triglycerides that contain only single carbon bonds along its chain whereas unsaturated fats contain at least one double bond (monounsaturated fats) or multiple double bonds (polyunsaturated fats) along its carbon chain (Tariq *et al*., 2015). The system names and structural formula for fatty acids are shown in Table 2.1.

Table 2.1: Structural formula for fatty acid (Tariq et al., 2015)

Structures Of common Fatty Acids Found In Vegetable Oils			
System name	**Common name**	**Symbol**	**Formula**
	Saturated		
Decanoic	Capric	$C_{10:0}$	$C_{10}H_{20}O_2$
Dodecanoic	Lauric	$C_{12:0}$	$C_{12}H_{24}O_2$
Tetradecanoic	Myristic	$C_{14:0}$	$C_{14}H_{28}O_2$
Hexadecanoic	Palmitic	$C_{16:0}$	$C_{16}H_{32}O_2$
Octadecanoic	Stearic	$C_{18:0}$	$C_{18}H_{36}O_2$
Eicosanoic	Arachidic	$C_{20:0}$	$C_{20}H_{40}O_2$
Docosanoic	Behenic	$C_{22:0}$	$C_{22}H_{44}O_2$
Tetracosanoic	Lignoceric	$C_{24:0}$	$C_{24}H_{48}O_2$
	Monounsaturated		
Hexadecenoic	Palmitoleic	$C_{16:1}$	$C_{16}H_{30}O_2$
Octadecenoic	Petroselinic	$C_{18:1}$	$C_{18}H_{34}O_2$
Octadecenoic	Oleic	$C_{18:1}$	$C_{18}H_{34}O_2$
Octadecenoic	Elaidic	$C_{18:1}$	$C_{18}H_{34}O_2$
Octadecenoic	Vaccenic	$C_{18:1}$	$C_{18}H_{34}O_2$
Eicosenoic		$C_{20:1}$	$C_{20}H_{38}O_2$
Eicosenoic	Gadoleic	$C_{20:1}$	$C_{20}H_{38}O_2$
Eicosenoic	Gondoic	$C_{20:1}$	$C_{20}H_{38}O_2$
Docosenoic	Erucic	$C_{22:1}$	$C_{22}H_{42}O_2$
	Polyunsaturated		
Hexadecanoic		$C_{16:2}$	$C_{16}H_{28}O_2$
Octadecadienoic	Linoleic	$C_{18:2}$	$C_{18}H_{32}O_2$
Octadecatrienoic	Linolenic-α	$C_{18:3}$	$C_{18}H_{30}O_2$
Octadecatrienoic	Linolenic-γ	$C_{18:3}$	$C_{18}H_{30}O_2$
Octadecatrienoic	Eleostearic	$C_{18:3}$	$C_{18}H_{30}O_2$
Octadecatrienoic	Calendic	$C_{18:3}$	$C_{18}H_{30}O_2$

The major material for producing biodiesel is the oil source, which is categorized into four groups, namely; pure vegetable oils, used cooking oils, animal fats, and non-edible oils. The feedstock extracted from rapeseed, soybean, and sunflower seeds are known as a pure vegetable oil (Demirbas, 2008), while waste cooking oils are known as the oils that have been used for frying and are no longer suitable for human consumption. (Azocar *et al*., 2010; Conservation ADOE, 2011; Lam *et al.*, 2010). Oil from animal fats include tallow, lard and yellow grease (Atadashi *et al*., 2010), while the non-edible oils are from seeds like Jatropha (Shuit *et al*., 2010; Yee *et al.*, 2009), rubber seed, sea mango, Palanga (Demirbas, 2008) and microalgae (Ahmad *et al.*, 2011).

2.4 THE USE OF BIODIESEL

Biodiesel can be used in its pure state which is known as B100 or as a blend with petrol-diesel. When it is used in its pure form, it gives maximum reduction with regards to exhaust elements and carbon dioxide. Using biodiesel as fuel in its pure form does not have a harmful effect on the engine but the properties of the solvents used might cause deposit in the engine and thereby degrade or damage the fuel line.

Another alternative to be considered is blending biodiesel with another petrol-diesel. This helps to prevent the problems encounter using B100. This mixing is commonly reported in percentages like B10, which implies that biodiesel content of the fuel mix is 10%. This percentage can still be extended to B20, B30, etc., depending on the preferred blend. The advantage of blending is that; cost and emission are reduced. According to Friedrich (2003), such reductions are proportional to the blending percentage of the biodiesel that is used. The Energy Policy (2007) reported the most common blend mix as 20% biodiesel with 80% petroleum diesel or B20 under recent scientific investigations. In South Africa, the current regulation stipulates a maximum of 5 % biodiesel in the blend.

Biodiesel serves as good additives and improves lubrication efficiently. The use of 1% biodiesel is adequately enough to turn a low lubricity product into a fuel that is well acceptable (Friedrich, 2003). According to Knothe and Steidley (2005), biodiesel as an alternative fuel has liquid nature portability, ready availability, renewability, higher combustion efficiency, lower sulfur, and aromatic content.

2.5 ADVANTAGES AND DISADVANTAGES OF BIODIESEL

2.5.1 Advantages of Biodiesel

The use of biodiesel offers varieties of benefits to users, engines and the environment. Below are some of the advantages:

- It is environmentally friendly. It combusts better than petrol-diesel and thus, carbon (II) oxide emission into the atmosphere is reduced.
- There are less sulfur (IV) oxide discharges in exhaust fumes compared to diesel.
- Modification of engine is not required
- It is renewable in nature.
- It is less toxic when compared to other hydrocarbon fuel sources. It also decays naturally.
- It has better lubricating efficiency than petroleum diesel.

Other general advantages of biodiesel are as follows:

- Biodiesel is plant-based and considered carbon neutral, as it adds almost no CO_2 to the environment.
- Its flash point doubles that of petroleum diesel, which makes it unlikely to ignite in a car accident.

2.5.2 Disadvantages of Biodiesel

Although numerous advantages presented makes biodiesel very attractive, there are also some problems associated with using this alternative fuel and they are listed below:

- The storage conditions of biodiesel must be observed carefully as biodiesel has a low stability in terms of oxidation.
- The volumetric energy density is usually low.
- It has a higher cold filter plugging point (CFPP) temperature than petroleum diesel. This implies that it will turn into a gel at low temperatures.
- Fuel filter might likely need to be replaced at the initial use of biodiesel.

2.6 BIODIESEL FEEDSTOCK

Vegetable oils, animal fats, used vegetable oils, non-edible oils and short chain alcohols are feedstocks for biodiesel production. Vegetable oil (edible and non-edible oil) emerges as a viable and promising feedstock for the production of biodiesel and different types of oils have been considered in the literature. The oils most used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (South Africa, Argentina and the United States of America), palm (Asian and Central American countries) and sunflower. Although other oils including peanut, linseed, safflower, used vegetable oils, and animal fats are also used. The use of animal fats is uncommon due to the feedstock becoming a solidified wax phase at normal room temperature (Atabani *et al.*, 2012). The current study places focus on virgin edible vegetable oils in the determination of its objectives. The production of biodiesel also requires a short chain alcohol and methanol is the most frequently used alcohol because it is relatively cheap.

2.7 COMPOSITION OF VEGETABLE OILS

Vegetable oils are composed of triglycerides, which contain in its molecule, three fatty acid chains (acyl group) that are bonded to a glycerol backbone (glycerol group). Fatty acids are long chain hydrocarbons, which may be categorized into saturated and unsaturated fats. Saturated fats are triglycerides that contain single bond along its carbon chain whereas unsaturated fats contain at least one double bond (monounsaturated fats) or multiple double bonds (polyunsaturated fats) along its carbon chain. The length of the carbon chains usually falls in the range of 10 – 24 carbons. The fatty acids are commonly denoted by a notation such as $C_{16}{:}_0$ which suggests that the acid is composed of a 16 carbon chain of which 0 double bonds are present. This example indicates a saturated fat. Typical fatty acids and their structures found in triglycerides are shown in Table 2.1.

The type of fatty acid that makes up the molecule is the defining factor between the different type of vegetable oils. Each type of vegetable oil contains different compositions. Table 2.2 shows the composition of various vegetable oils. It has been reported that biodiesel fuel properties are affected greatly by the fatty acid composition of the vegetable oil (Ramirez *et al.*, 2012). The composition of the acids is also important in determining the molecular weight of the oil as well as the degree of saturation or unsaturation of the oil.

2.8 BIODIESEL PRODUCTION PROCESS

Worldwide, in other to be as close to the properties of diesel fuels, there have been considerable efforts to develop and improve vegetable oil properties. It is observed that high viscosity, low volatility and polyunsaturated characters are the mostly associated problems with crude vegetable oils. These challenges can be overcome by three methods, namely; pyrolysis, micro-emulsion and transesterification (Srivastava and Prasad, 2000; Demirbas, 2008; Canakci and Sanli, 2010; Balat and Balat, 2010; Lin *et al.*, 2011).

2.8.1 Pyrolysis

This process involves the thermal decomposition of organic matters in the absence of oxygen and in the presence of a catalyst. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. Researchers have studied the pyrolysis of triglycerides to obtain suitable fuels for a diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, aromatics and carboxylic acids (Balat and Balat, 2010; Srivastava and Prasad, 2000; Parawira, 2010; Yusuf *et al.*, 2011). It has been observed that pyrolysis process is effective, simple and pollution free (Singh and Singh, 2010). According to Sharma *et al.* (2008), pyrolysis of the vegetable oil can produce a product that has high cetane number, low viscosity, acceptable amounts of sulfur, water and sediments contents and acceptable copper corrosion values. However, ash contents, carbon residues, and pour points were unacceptable.

Table 2.2: Structural formula of fatty acids adapted from (Pantoja, 2013)

Fatty acid compositions of vegetable oils.												
Vegetable oils		Fatty acid composition (wt%)										
Common name	**Species**	**12:00**	**14:00**	**16:00**	**16:01**	**18:00**	**18:01**	**18:02**	**18:03**	**20:00**	**22:00**	**22:01**
Canola	Brassica campestris	–	–	3.1	0.2	1.3	56.6	22.4	14	0.4	0.2	0.1
Canola	Brassica napus	–	–	4.3	0.3	1.7	61	20.8	9.3	0.6	0.3	–
Black mustard	Brassica nigra	–	1.5	5.3	0.2	1.3	11.7	16.9	2.5	9.2	0.4	41
Oriental mustard	Brassica juncea	–	–	2.3	0.2	1	8.9	16	11.8	0.8	5.7	43.3
Brown mustard	Brassica juncea	–	–	2.2	0.2	1.2	17.4	20.5	14.1	0.7	0.5	28.1
Wild mustard	Brassica juncea	–	0.1	2.6	0.2	0.9	7.8	14.2	13	0.8	1.5	45.7
White mustard	Sinapis alba	–	–	3.1	0.2	0.7	9.1	11.7	12.5	0.7	–	46.5
White mustard	Sinapis alba	–	0.1	2.8	0.2	1.1	25	11.6	8.6	0.7	0.6	32.8
Abyssinian mustard	Brassica carinata	–	–	3.1	–	1	9.7	16.8	16.6	0.7	–	42.5
Soybean	Glycine max	–	–	10.1	–	4.3	22.3	53.7	8.1	–	–	–
Soybean	GMO a<comma> b	–	–	3.5	0.1	2.8	22.7	60.3	9.8	0.2	0.2	–
Soybean	GMO a<comma> c	–	0.1	10.9	0.1	5.7	27.5	51.5	3	0.5	0.4	–
Soybean	GMO a<comma> d	–	0.1	23.8	0.7	3.8	15.4	44.1	11	0.4	0.6	–
Soybean	GMO a<comma> e	–	–	8	0.1	24.7	17.2	39.2	8.3	1.5	0.7	–
Palm	Elaeis guineensis	0.3	1.2	44.3	–	4.3	39.3	10	–	–	–	–
Palm	Elaeis oleifera	–	0.2	18.7	1.6	0.9	56.1	21.1	–	–	–	–
Palm kernel	Elaeis guineensis	50.1	15.4	7.3	–	1.8	14.5	2.4	–	–	–	–
Palm kernel	Elaeis oleifera	29.3	25.7	10.1	–	1.8	26.4	4.5	–	–	–	–
Palm kernel	Aiphanes acanthophylla	41.5	20.5	10.2	–	3.4	15.8	7.4	–	–	–	–
Palm kernel	Buttia capitata	39.2	6.4	4.2	–	3	11.9	3.5	–	–	–	–
Palm oleinf		0.3	1.2	40.6	0.2	4.3	41.9	11.9	0.4	0.4	–	–
Palm stearinf		0.3	1.5	61.1	0.1	4.8	25.8	6.5	0.4	0.5	–	–
Sunflower	Helianthus annuus	–	–	5.2	0.1	3.7	33.7	56.5	–	–	–	–
Sunflower	GMO a<comma> g	–	–	3.1	0.1	1.5	91.5	2.1	–	0.2	0.7	0.1
Sunflower	GMO a<comma> g	–	–	4.4	–	4.2	78.3	10.9	–	0.3	1	–
Sunflower	GMO a<comma> c	–	0.1	7.5	0.1	1.9	13.3	76	0.1	0.1	0.4	–
Sufflower		–	0.1	6.4	–	2.3	11.6	79.3	–	0.3	–	–
Groundnut	Arachis hypogea	–	–	11.2	–	3.6	41.1	35.5	0.1	–	–	–
Corn	Zea mays	–	–	11.6	–	2.5	38.7	44.7	1.4	–	–	–
Olive	Olea europea	–	–	13.8	1.4	2.8	71.6	9	1	–	–	–
Olive (wild)	Ximenia americana	–	–	–	–	1.2	60.8	6.7	–	–	–	–
Cottonseed	Gossypium hirsutum	–	–	23	–	2.3	15.6	55.6	0.3	–	–	–
Linseed	Linum usitatissimum	–	–	5.6	–	3.2	17.7	15.7	57.8	–	–	–
Coconut	Cocos nucifera	50.9	21.1	9.5	–	4.9	8.4	0.6	–	–	–	–
Sesame	Sesamum	–	–	9.6	0.2	6.7	41.1	41.2	0.7	–	–	–
Rice bran	Oryza sativa	–	–	22.1	–	2	38.9	29.4	0.9	–	–	–
Jatropha	Jatropha curcas	–	–	18.5	–	2.3	49	29.7	–	–	–	–
Karanjaf	Pongamia glabra	–	–	5.8	–	5.7	57.9	10.1	–	3.5	–	–
Karanja	Pongamia Pinnata	–	–	11.7	–	7.5	51.6	16.5	2.7	–	–	–
Neemf	Azadirachta indica	–	–	17.8	–	16.5	51.2	11.7	–	2.4	–	–
Salf	Shorea robusta	–	–	6.2	–	43	41.3	2.1	–	5.5	–	–

2.8.2 Micro Emulsion

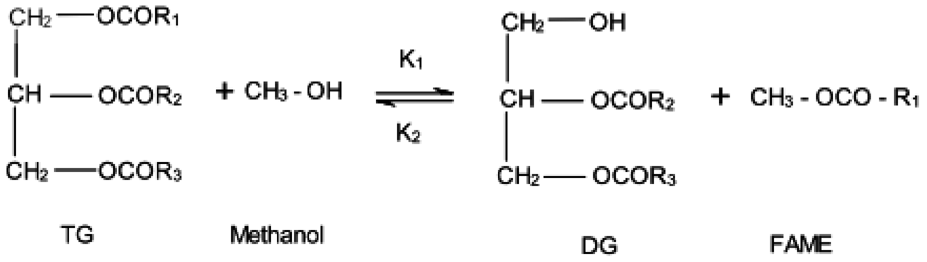
A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions between 1–150 nm range formed spontaneously from two normally immiscible liquids. Micro-emulsions using solvents such as methanol, ethanol, hexanol, butanol and 1-butanol have been investigated by many researchers. It has been demonstrated that short-term performances of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil are close to diesel fuel (Balat and Balat, 2010; Singh and Singh, 2010; Parawira, 2010; Jain and Sharma, 2010).

Soybean oil pyrolysed distillate had a cetane number of 43, exceeding that of soybean oil (37.9) and the ASTM minimum value of 40. However, the viscosity of the distillate is 10.2 mm^2/s at 311 K, which is higher than the ASTM specification for diesel fuel (1.9 – 4.1 mm^2/s) but considerably below that of soybean oil (32.6 mm^2/s) (Balat and Balat, 2010).

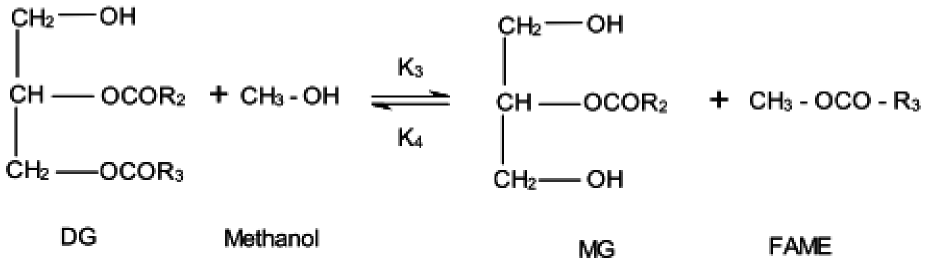
2.8.3 Transesterification

Transesterification is referred to the process used in synthesizing biodiesel (Cao *et al.*, 2008a; Qiu *et al.*, 2010). It is the general term used to define a carbon-based reaction, where there is a transformation of one ester to another through the exchange of alkyl group. It is an equilibrium process and the transformation occurs mainly when the reactants are mixed together. In the transesterification of vegetable oils, the reaction occurs between triglyceride and alcohol (methanol, ethanol) in the presence of a strong acid or base catalyst to produce a mixture of fatty acids alkyl esters and glycerol. The stoichiometric reaction requires 1 mole of a triglyceride and 3 moles of the alcohol. However, the alcohol is required in excess in order to increase alkyl ester yield and to allow phase separation from the byproduct formed. Transesterification is a stepwise-based reaction as shown in the equation below (Equation 2.2, 2.3 and 2.4). In the first step reaction, triglycerides (TG) are converted to diglycerides (DG) and later to monoglycerides (MG). Subsequently, the monoglycerides are converted to glycerol. The overall reaction that takes place in transesterification is simplified by equations 2.2, 2.3

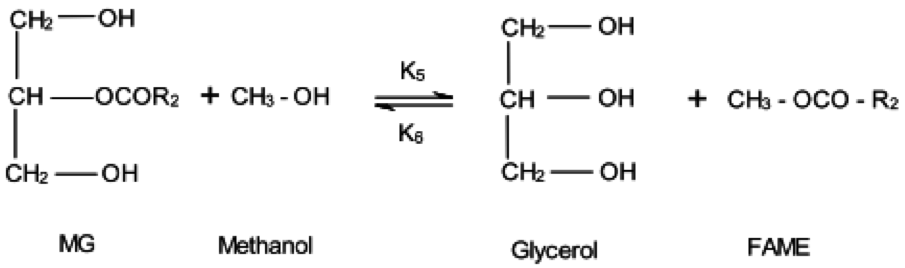
and 2.4. Where R_1, R_2 and R_3 are long chain hydrocarbons (e.g., palmitic acid - $(CH_2)_{14}$-CH_3), which is occasionally called fatty acid chains (Cao *et al.*, 2008).



(Equation 2.2)



(Equation 2.3)



(Equation 2.4)

In general, transesterification process can be carried out by two methods; catalytic (homogeneous and heterogeneous) and non-catalytic method. Figure 2.3 shows the detailed classification of transesterification processes.

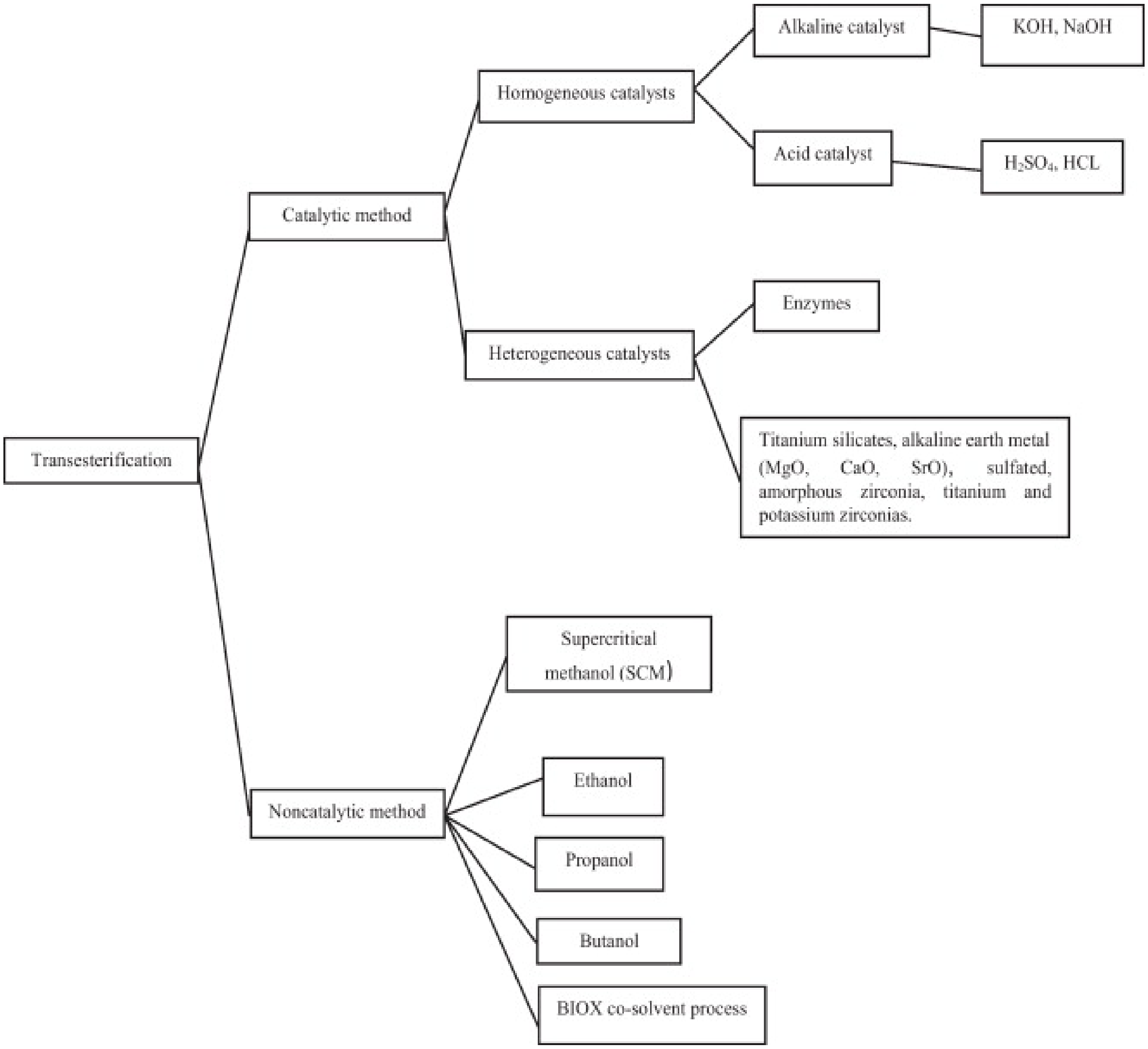


Figure 2.3: Classification of transesterification processes (Chouhan and Sarmav, 2011).

The catalytic transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol in the presence of some catalyst to form esters and glycerol. A triglyceride has a glycerin molecule as its base with three long chain fatty acids attached. The characteristics of the oil/fat are determined by the nature of the fatty acids attached to the glycerin. The nature of the fatty acids can in turn, affect the characteristics of the biodiesel (Karmakar, 2010).

2.8.3.1 Homogeneous catalyzed transesterification

Homogeneous catalyzed transesterification involves the use of a catalyst (base, acid) in the reaction process of biodiesel production and this catalyst is in the same phase as the reactants. Conventionally, the production of biodiesel involves the use of a homogeneous base catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Kulkarni *et al*., 2006). These catalysts are generally being employed in the industries due to the following advantages:

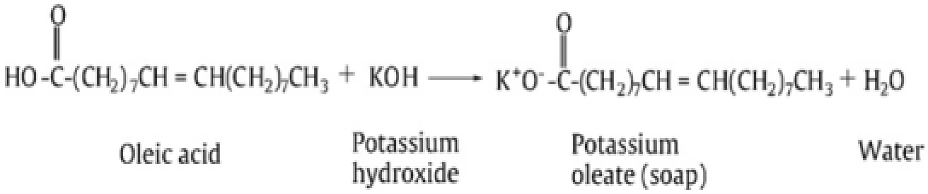
- Ability to catalyze the reaction at low temperature and pressure.
- High conversion rates within a short time.
- Readily available and economical (Lotero et al., 2005).

In addition, Fukuda *et al*., (2009) and Kulkami *et al*., (2010) reported base catalyzed reaction was faster than acid catalyzed reaction. However, the homogeneous base catalyst is not adequate for refined vegetable oil which has more than 2 wt.% FFA (Wang *et al.*, 2012) or acid value more than 1 mg KOH/g (Kulkami *et al.*, 2010). Some scholars have also stated that base catalyst cannot tolerate higher content of FFA as shown in Table 2.3.

Table 2.3: Level of FFA recommended for homogeneous base catalyst (Lam et al., 2010)

Author	**Recommended FFA (wt.%)**
Ma and Hanna (1999)	< 1
Zhang *et al., (2003a)*	< 0.5
Ramadas *et al., (2005)*	≤ 2
Kumar Tiwari *et al., (2007)*	< 1
Sahoo *et al., (2007)*	≤ 2

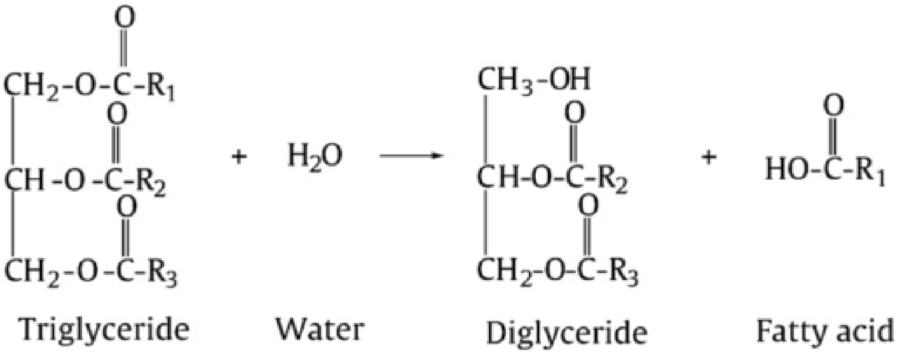
The recommendation from Table 2.3 shows that FFA content in oil feedstock should be minimal (ranging between 0.5 wt. % to 2 wt. %) for base-catalyzed transesterification reaction. Thus, if oil feedstock contains a high FFA content (> 2 wt. %), base catalyst is definitely not the appropriate catalyst to be used (Lotero *et al.*, 2005). FFA contains long chains of carbon, which are separated from glycerol backbone. They are occasionally called carboxylic acids. When oil or fat having a high content of FFA is used as feedstock, the base catalyst will react with the FFA to form soap, which is highly undesirable. (Kulkarni *et al*., 2010). Equation 2.5 displays a typical reaction between FFA (oleic acid) and base catalyst (KOH). This reaction is highly undesirable because the catalyst is hindered from accelerating the transesterification reaction. In addition, excess soap formed in the product stream can extremely decrease the fatty acid methyl ester (FAME) yield and hinder the purification process of biodiesel, including glycerol separation and water washing (Kulkarni *et al.*, 2010).



$$HO\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH=CH(CH_2)_7CH_3 + KOH \longrightarrow K^+O^-\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_7CH=CH(CH_2)_7CH_3 + H_2O$$

(Equation 2.5)

Furthermore, the presence of water in the oil feedstock also affects the methyl ester yield. The presence of water particularly at high temperatures will hydrolyze triglycerides to diglycerides and free fatty acid formation. Equation 2.6 shows the hydrolysis reaction.



(Equation 2.6)

2.8.3.2 Homogeneous acid-catalyzed transesterification

Liquid base-catalyzed transesterification process is known to be associated with many challenges particularly for oil feedstock with high FFA concentration, therefore, homogeneous acid catalysts are recommended as the best substitute for oil or fat with a high concentration of FFA. The most common studied catalysts for the acid-catalyzed process are sulfuric acid (H_2SO_4) and hydrochloric acid. Acid catalyzed transesterification have significant advantages over the base-catalyzed process, because the acid catalyst is insensitive to the presence of FFAs in the feedstock (Kulkarni *et al*., 2010) and can undergo esterification and transesterification process simultaneously. Esterification process is an organic reaction involving two reactants, usually an alcohol (methanol) and an acid (FFA) reacting to form an ester. Previous studies show that acid catalysis is more efficient when the amount of FFA in the oil is over 1 wt. % (Zhang *et al*., 2003). Furthermore, economic analysis has established that acid catalyzed method, being a one-step process, is cost-effective than the base-catalyzed method which needs an extra step to convert FFA to methyl esters (Zhang *et al*., 2003).

However, the acid-catalyzed process is a rare choice for commercial applications due to its slower rate of reaction, higher reaction temperature, higher molar ratio of alcohol to oil required, difficulties in catalyst recovery, severe environmental and corrosion associated problem (Wang *et al*., 2006). In a study conducted on acid-catalyzed transesterification of oil feedstock with high FFA using H_2SO_4, Wang *et al.* (2008) reported that the yield of FAME increased with longer reaction time, higher methanol to oil ratio and higher catalyst loading. The feedstock conversion was more than 90 % during a reaction time of 10 hours. In another study, 99 % oil conversion by using 1 mol % of H_2SO_4 and methanol to oil ratio 30:1 for 69 hours reaction time was reported (Freedman *et al*., 1984). These data indicate that acid-catalyzed transesterification process requires more severe reaction conditions (such as longer reaction time) than base-catalyzed reaction.

2.9 LIMITATIONS IN CONVENTIONAL BIODIESEL CONVERSION TECHNOLOGY

The conversion of vegetable oil by transesterification process is highly dependent on the proportion of the reactants and the conditions of the transesterification process. According to Le Chatelier's principle, large quantity of alcohol is required to shift the equilibrium of the reaction to the product side and increase the yield of biodiesel (Baroutain *et al.,* 2011). Unfortunately, excess usage of alcohol will lead to higher production cost. Although, the consumption of alcohol could be reduced by using acid or alkaline catalysts, which could improve the reaction rate and biodiesel yield. However, homogeneous acid solutions that catalyze transesterification processes, such as sulphuric (Sahoo *et al.*, 2007) and hydrochloric (Wang *et al*., 2008), have been largely disregarded because they require longer process time, higher reaction temperature and are corrosive in nature.

Heterogeneous catalyst has been viewed as an alternative solution to replace the homogeneous catalyst because it is non-corrosive and environmentally friendly. However, the heterogeneous catalytic reaction usually faces a mass transfer resistance problem because the constitution of the three-phase system (triglycerides, alcohol, and solid catalyst) in the reaction mixture limits the pore diffusion process and reduces the active site availability for the catalytic reaction, thereby decreasing the reaction rate (Mbaraka and Shanks, 2006). Catalyst support can minimize the mass transfer limitation, but the active species in the supported catalyst can easily be corroded by alcohol, shortening the catalyst lifecycle (Liu *et al.*, 2008). The biodiesel obtained from the biocatalytic transesterification process that uses an enzyme as a catalyst seems attractive and encouraging because the product is easily separable without side reactions (Jegannathan *et al.*, 2008), but biodiesel from this process is not yet commercially viable because of the requirement of longer reaction time and the unfavourable reaction yield in comparison to the alkaline catalyst. It has been reported that the enzymatic transesterification process requires 24 h to achieve a biodiesel yield of 90% (Oda *et al*., 2005). Most importantly, the major obstacle to this process is the high cost of the enzyme. The enzyme also requires very specific reaction conditions because deactivation of feed impurity could decrease its efficiency (Dizge *et al.*, 2009).

Supercritical alcohol transesterification provides a new path for the production of biodiesel without the aid of a catalyst. The supercritical condition could overcome the mass transfer limitation by enabling the mixture of triglyceride and alcohol to become a homogeneous phase (Pinnarat and Savage, 2008). However, the major drawbacks of this non-catalytic process are its large energy requirement and its infeasibility for large-scale industrial application because of the increased production cost imposed by the high reaction temperature and pressure (Yin *et al.*, 2008). Moreover, the supercritical process is potentially hazardous and requires attention to personal risk and safety. Both the catalytic and non-catalytic transesterification downstream processes will receive a mixture of product, biodiesel, and glycerol, as well as unreacted reactant and catalyst. Ineffective biodiesel separation and purification may cause severe diesel engine problems, such as plugging of filters, choking on injectors, carbon deposits, excessive engine wear, oil ring sticking, engine knocking, and thickening and gelling of lubricant oil (Demirbas, 2007). In order to obtain high purity biodiesel, the downstream of the transesterification process will undergo various complementary separation stages, such as glycerol separation, catalyst neutralization, and biodiesel purification. The multiple downstream processes are time-consuming and require additional cost. Research revealed that the current downstream processing alone constituted over 60 – 80 % of the total cost of a transesterification process plant and in addition, the multiple separation and purification stages could cause loss of the biodiesel, resulting in a decrease in the pure biodiesel yield (Tai-Shung, 2010).

2.10 PROCESS INTENSIFICATION TECHNOLOGIES IN BIODIESEL PRODUCTION

There are numerous challenges associated with the use of conventional methods for producing biodiesel and some of them include; purification of the product which leads to wastewater generation (Xie and Li, 2011), limited mass transfer (Mbaraka and Shanks, 2006), thermodynamic equilibrium (Cao *et al.*, 2008), high energy requirement (Yin *et al*., 2008) and multiple downstream processing steps (Tai-Shung, 2010). These limitations can be overcome by using process intensification technologies. These technologies involve the use of novel reactors or coupled reaction/separation processes to enhance the reaction rate and to reduce the residence time (Qiu *et al*., 2010). Recently, novel reactors, such as the microchannel reactor, microwave reactor, oscillatory flow reactor, and cavitation reactor, have been developed and applied to improve the mixing and mass/heat transfer between the oil and methanol in biodiesel production (Qiu *et al*., 2010).

The microchannel reactors are of different types and quite a few have been used in the production of biodiesel; T- or Y- flow structures, zigzag micro-channel reactors (Wen *et al.,* 2009) and slit channel reactor (Kalu *et al.*, 2011). According to Wen *et al.*, (2009) and Qui *et al.,* (2010) these reactors consume less energy as compared to the normally stirred tank reactor, they can achieve rapid reaction rate because of a high volume/surface ratio, exhibit short diffusion distance, efficient heat dissipation and mass transfer. However, the microchannel reactor suffers from the drawback of low production throughput, which is attributed to the limitations of the micro-fabrication technology that is used to produce the micro-channel. Furthermore, the high investment cost of the microchannel reactor prohibits the addition of more reactors in parallel to amplify the production of biodiesel (Kalu *et al*., 2011).

The microwave reactor is another intensification technology for biodiesel production. The main function of a microwave reactor is not to improve the mixing of oil and methanol but to use its irradiation to transfer energy directly into the reactants and thus accelerate the transesterification. Microwave reactor plays an important role in the more efficient heating of reactants to the desired temperature because of the energy interactions at the molecular level (Barnard *et al*., 2011). Compared to a conventional thermal heating reactor, a microwave reactor is able to achieve similar biodiesel conversion with a shorter reaction time and in a more energy-efficient manner (Qiu *et al*., 2010).

The oscillatory flow reactor is a type of continuous plug flow reactor (PFR) (Phan *et al*., 2011) in which the orifice plate baffles are equally spaced, and a piston is used to produce oscillatory flow (Qiu *et al.,* 2010). The combination of baffles and oscillatory motion intensifies the radial mixing by the formation of periodic vortices in the bulk fluid, causing an increase in mass and heat transfer while maintaining plug flow (Qiu *et al.*, 2010; Phan *et al*., 2011). In addition, the oscillatory flow reactor can also improve the residence time distribution (RTD) and multi-phase suspension (Zheng et al., 2007).

The cavitation reactor is another type of novel reactor that has been used successfully in biodiesel production (Kelkar *et al*., 2008; Gogate and Kabadi, 2009; Pal *et al.,* 2010; Qiu *et al.,* 2010). Cavitation is defined as the generation of cavities followed by their growth and violent collapse, causing high local energy densities, temperatures and pressures (Gogate and Kabadi, 2009; Qiu *et al*., 2010). Cavitation enhances the mass transfer rate of the reaction by creating conditions of local intense turbulence and liquid microcirculation currents in the reactor (Gogate and Kabadi, 2009; Qiu *et al*., 2010).

The entire above-mentioned novel reactors intensify the transesterification by either enhancing the mixing of oil and methanol or improving the heat transfer between the two liquid phases. However, none of these novel reactors, except the membrane reactor, is able to overcome the limitation caused by chemical equilibrium in transesterification. Therefore, the membrane reactor technology would be used to conduct transesterification process in this current study.

2.11 CONCEPT OF MEMBRANE REACTOR

A membrane reactor is also known as a membrane-based reactive separator (Sanchez Marcano and Tsotsis, 2012). According to IUPAC, a membrane reactor is defined as a device that combines reaction and separation in a single unit (Caro, 2008). Generally, membrane technology can be classified based on four concepts (Ertl *et al.,* 2008): the reactor design (extractor, distributor or contactor), how the membrane is used in the reaction (organic, inorganic, porous or dense membrane), whether it is an inert or catalytic membrane reactor and the type of reaction that occurs in the reactor such as dehydrogenation (Caro, 2008), esterification (Caro, 2008; Buonomenna *et al*., 2010), wastewater treatment (Drioli *et al*., 2008). In addition to providing the separation, a membrane reactor also enhances the selectivity, control the addition of reactants to the reaction mixture, intensify the contact between reactants and catalyst (Baroutian *et al*., 2011). As illustrated in Figure 2.4, there are two basic configurations of membrane reactor namely; conventional and integrated membrane reactor system (Lipnizki *et al*., 2009a). Figure 2.4a shows the layout of a membrane reactor system in which the membrane reactor appears as an external process unit. On the other hand, the membrane reactor shown in Figure. 2.4b combines the reactor and membrane separator into a single unit. In comparison to the conventional biodiesel production process, the main advantage offered by the membrane reactor, especially the integrated membrane system is the reduction of the capital and operating costs because of the elimination of the intermediate processing steps (Sanchez Marcano and Tsotsis, 2012). Recently, the membrane reactor has been applied as a promising technology in biodiesel production (Dubé *et al*., 2007; Cao *et al*., 2008b; Baroutian *et al*., 2011).

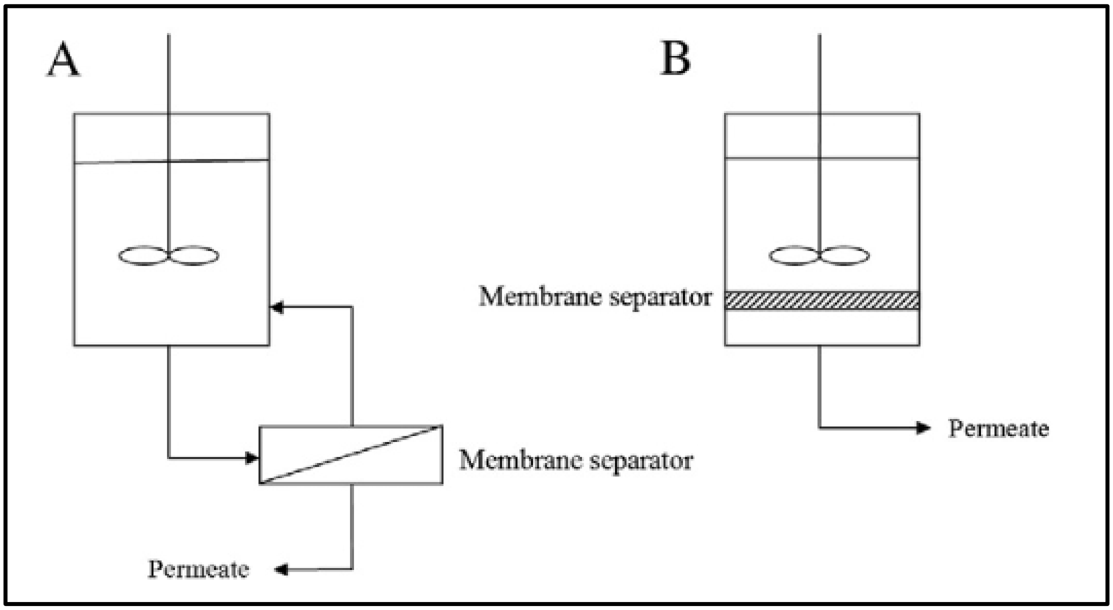


Figure 2.4: Basic layout of membrane reactor (a) a conventional membrane reactor system (b) an integrated membrane reactor system (Lipnizki et al., 2009a).

2.12 MEMBRANE TECHNOLOGY IN BIODIESEL PRODUCTION

2.12.1 Concepts and principles

Membrane separation involves the use of a selective barrier (membrane) to regulate the transport of substances, such as gases, vapors, and liquids, at different mass transfer rates (Böddeker, 2008). The mass transfer rates of different substances are controlled by the permeability of the feed components toward the barrier (Böddeker, 2008). In the production of biodiesel, the membrane plays an important role by removing glycerol from the product (biodiesel) stream (Guerreiro *et al*., 2009; Saleh *et al*., 2010) or retaining the unreacted triglycerides within the membrane (Dubé *et al*., 2007; Cao *et al*., 2008b; Baroutian *et al*., 2011) as shown in Figures. 2.5 and 2.6 respectively. There are two basic principles of operation in biodiesel production via membrane technology; separation based on oil droplet size (Cao *et al*., 2008a, 2008b) and membrane catalysis (Shao and Huang, 2007; Guerreiro *et al*., 2009, 2010).

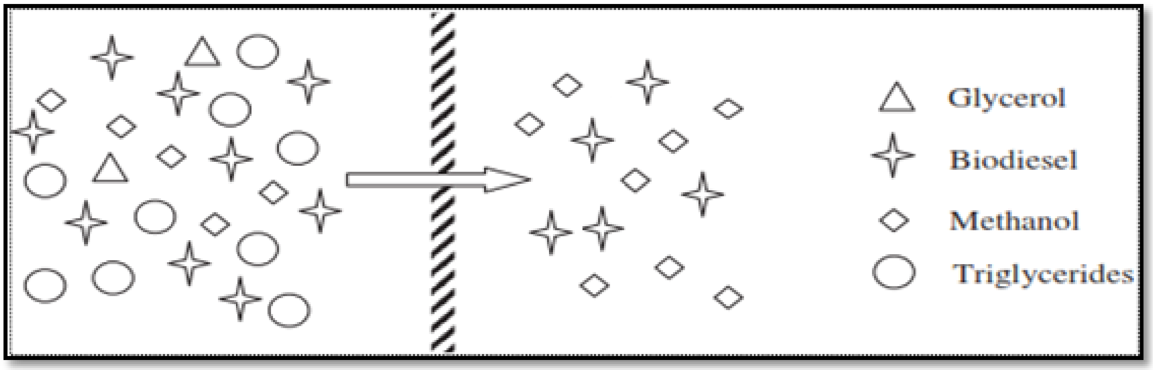


Figure 2.5: Schematic diagram of the membrane to remove glycerol from the product stream.

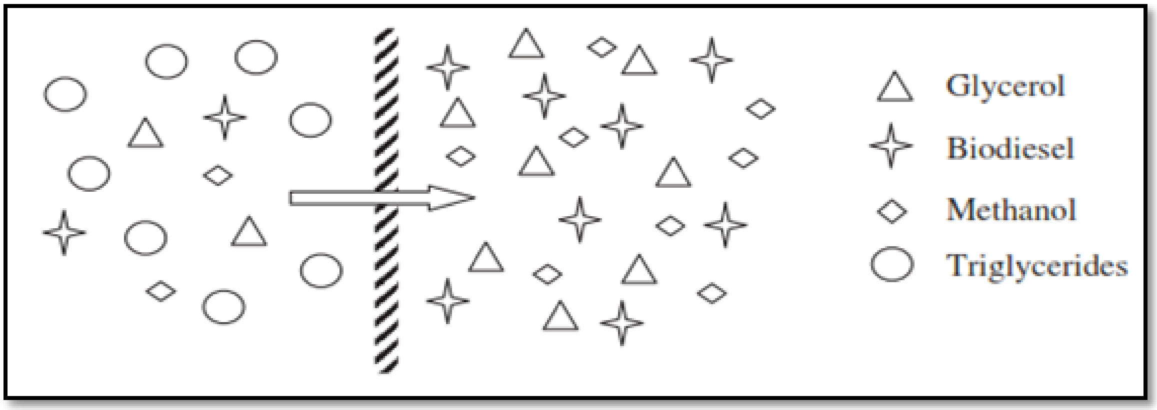


Figure 2.6: Schematic diagram of the membrane to retain unreacted triglycerides within the membrane.

2.12.2 Membrane separation based on oil droplet size

Membrane separation based on oil droplet size requires a microporous membrane, which is typically a ceramic membrane (Cao *et al*., 2008a; Baroutian *et al*., 2011) or a carbon membrane (Dubé *et al*., 2007). The operation principle used in membrane technology for biodiesel production is illustrated in Figure 2.7 (Dubé *et al*., 2007). Methanol is immiscible in oil because of the differences in polarity (Cao *et al*., 2008a; Shuit *et al*., 2010a). Therefore, a mixture of methanol and oil will exist in a two-phase system or as an emulsion of lipid droplets suspended in a methanol-rich phase (Cao *et al.*, 2008a; Dubé *et al*., 2007). The immiscibility of the oil and the methanol is the main cause of the mass transfer limitation in the transesterification reaction, but this emulsified system is favored in the operation of a membrane reactor (Dubé *et al*., 2007).

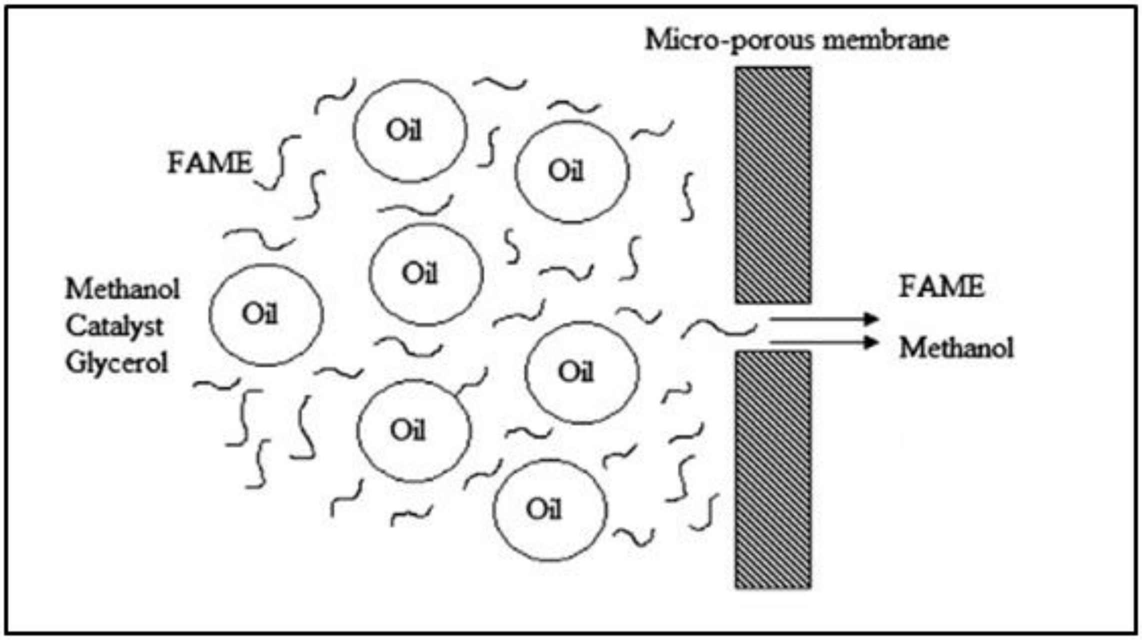


Figure 2.7: Separation of oil and FAME by a micro-porous membrane (Dubé et al., 2007).

In an emulsified system, transesterification is believed to occur at the interface between oil droplets and the continuous methanol phase in which they are dispersed (Ataya *et al.*, 2006). Researchers have reported that biodiesel and glycerol, as well as the catalysts (both acid and alkaline catalysts), are soluble in methanol (Zhou *et al*., 2006; Cao *et al*., 2008a). Thus, the unreacted oils will be suspended and dispersed in a mixture of methanol, biodiesel, glycerol and catalyst on the membrane retentate side (Cao *et al*., 2008a). The smaller molecular size, methanol and other soluble components, such as biodiesel are able to pass through the micro porous membrane into the permeate stream when the transmembrane pressure (TMP) is increased (Baroutian *et al.,* 2011). Meanwhile, the emulsified oil droplets with larger molecular size are trapped within the membrane to be continuously converted into biodiesel (Dubé *et al.,* 2007; Cao *et al.*, 2008a; Baroutian *et al.,* 2011).

2.12.3 Membrane separation based on catalytic membrane

Membrane separation based on the catalytic membrane involves a non-porous dense polymer membrane, such as poly vinyl alcohol (PVA) (Guerreiro *et al*., 2009, 2010; Shi *et al*., 2010). According to Guerreiro *et al*., (2009) the operation of this type of membrane is based on the interaction between the target component and the polymer functional groups of the membrane. They further explained that biodiesel production via this type of catalytic membrane; biodiesel and methanol are able to form hydrogen bonds with the OH groups in the polymer membrane. Therefore, the biodiesel and methanol are continuously removed from the mixture during the reaction (Guerreiro *et al*., 2009; Saleh *et al*., 2010). Meanwhile, Guerreiro *et al.*, (2009) maintained that the unreacted oils and glycerol are retained within the membrane based on their chemical properties with the polymer group of the membrane. In this process, the separation is carried out under atmospheric pressure.

2.13 EFFECT OF PROCESS PARAMETERS IN BIODIESEL PRODUCTION BY MEMBRANE REACTOR

In addition to the typical process parameters (reaction temperature, methanol to oil ratio and catalyst concentration), other process variables, such as the reactant flow rate, trans-membrane pressure, membrane thickness and pore size (for membrane separation based on oil droplet selection), also have a great influence on the biodiesel yield and need to be taken into consideration when biodiesel is produced by membrane technology. In order to produce biodiesel in a more sustainable and cost-effective manner, the important process parameters that should be taken into consideration will be discussed in the following section (Guerreiro *et al*., 2010).

2.13.1 Effect of reaction temperature

Temperature has an effect on the production of biodiesel. Transesterification process can be carried out at a different temperature, depending on the physical and chemical properties of the oil used (Phan and Phan, 2008). Several studies reported that 50–70 ^{0}C would be the best temperature range to obtain the highest biodiesel yield (Meng *et al*., 2008). According to Cvengros and Cvengrosova (2009), the ideal reaction temperature is often near the boiling point of alcohol. However, Chen *et al*. (2010) reported that transesterification process, with a lipase catalyst, should not be carried out above 50 ^{0}C because the stability and the usage life of lipase may be affected.

Transesterification with a minimum temperature of 60 °C and a high yield have been reported with the use of a dense membrane (Guerreiro *et al*., 2009, 2010). A possible reason for this result is due to the thermal mobility of the molecules inside the membrane, which increases at higher reaction temperatures and thus generates extra free volume space (Ong *et al*., 2011), thereby enhancing the permeation of larger molecules such as glycerol. Moreover, glycerol demonstrates a significant decrease in viscosity at higher reaction temperatures. If the viscosity is reduced, the circulation of the mixture becomes easier (Gomes *et al*., 2010).

Irrespective of the type of process used to synthesize biodiesel, the conversion of oil to FAME has been found to be positively affected by increasing the reaction temperature (Dubé *et al.*, 2007). This increase can be easily justified because transesterification is an endothermic process (Samart *et al.*, 2009). Therefore, from Le Chatelier's principle, by increasing the temperature, the equilibrium of the reaction is shifted to the forward direction, which favors the conversion of oil into FAME (Ong *et al*., 2011).

2.13.2 Effect of methanol to oil ratio

The molar ratio of alcohol to oil is one of the most significant factors affecting the conversion efficiency yield of biodiesel (Ma and Hannah, 2009). Also, since the stoichiometric molar ratio of alcohol to oil for the transesterification is 3:1 and the reaction are reversible, higher molar ratios are required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride. In practice, to shift the reaction toward completion, the molar ratio should be higher than that of the stoichiometric ratio (Lee and Saka, 2010). Furthermore, to break the glycerin–fatty acid linkages during transesterification of triglycerides to biodiesel, excess methanol is required (Miao and Wu, 2006). Therefore, higher alcohol to oil molar ratios gives rise to greater alkyl ester conversion in a shorter time (Helwani *et al*., 2009). Moreover, increase in the amount of alcohol to oil increases biodiesel yield and biodiesel purity. Balat and Balat (2009) remarked that the key variables affecting transesterification are; reaction time, alcohol to oil molar ratios, reaction temperature and pressure, catalyst, water contents and free fatty acids levels in fats and oils. The authors noted that the universally accepted alcohols to glycerides molar ratios are 6:1–30:1. In addition, Behzadi and Farid (2009) reported that the overall transesterification reaction is characterized by three control stages: mass transfer, kinetic and equilibrium controlled. The slowest among these three stages is the mass transfer stage due to immiscibility of triglycerides and methanol (Halim *et al*., 2009). In another study, Chew and Bhatia (2008) noted that the choice of the molar ratio of alcohol to oil could significantly influence transesterification process. They reported that the process yield is increased with increase in the alcohol to oil molar ratio. Thus, methanol to oil molar ratio of 9:1 could provide the maximum yield of canola and corn oil.

The methanol to oil ratio in a catalytic based membrane was reported to be 6:1 (Shi *et al.*, 2010), 26:1 (Zhu *et al.*, 2010), 106:1 (Guerreiro *et al.*, 2009) and 254:1 (Guerreiro *et al.*, 2010). However, no clear explanation was given of the need for such a large amount of methanol to produce biodiesel. Regardless of the operational principle of the membrane, the conversion increased in proportion to the ratio of methanol to oil because the reaction would tend to be driven towards biodiesel production (Shi *et al.*, 2010).

2.13.3 Effect of reactant flow rate

There has been no detailed study on the effect of the reactant flow rate on biodiesel production in a membrane reactor. However, Dubé *et al*., (2007) and Baroutian *et al.*, (2011) in their study, observed a significant increase in the conversion of oil to FAME as the flow rate of reactants increased. The improvement of mixing intensity at higher flow rate or greater flow circulating velocity as explained by Baroutian *et al*., (2011) led to high yield of biodiesel because the reactants (oil/methanol) and catalyst were flowing in a turbulent flow regime (Vospernik *et al*., 2011). Mixing is also a crucial factor for the increase of the reaction rate in transesterification because oil is immiscible with methanol. Without mixing, the reaction only occurs at the interface between the layers of methanol and oil (Meher *et al*., 2006; Kumar *et al*., 2013). Concentration polarization is a common problem for membrane separation. This problem can be easily solved by increasing the reactant flow rate (Peng *et al*., 2007).

2.13.4 Effect of trans-membrane pressure (TMP)

Trans membrane pressure (TMP) is defined as the pressure difference between the feed side and the permeate side of the membrane (Nishimoto *et al.,* 2010). TMP is the driving force for membrane separation (TakhtRavanchi *et al*., 2008) and is normally kept constant throughout the process (Nishimoto *et al*., 2010). The TMP used in the production of biodiesel ranges between 37.9 and 173.4 kPa (Dubé *et al*., 2007; Cao *et al*., 2008a, 2008b). The permeate flux increases with higher TMP because a greater driving force is applied for separation (Gomes *et al*., 2010).

In biodiesel production via membrane reactor, TMP is positively affected by the concentration of unreacted oil in the emulsion within the reactor. If the residence time of the reaction is insufficient, the concentration of the unreacted oil in the reactor will increase (Falahati and Tremblay, 2012). Besides, TMP is correlated with the viscosity of the reaction mixture. This relation is clear when the glycerine-rich phase is recycled back to the reactor for methanol recovery. In other words, an increased content of glycerol in the reaction mixture would require higher TMP. However, the increase of TMP from increased glycerol content does not cause any negative effect in the membrane reactor (Cao *et al*., 2008b).

The TMP profiles in the membrane reactor can also act as an indicator to check the progress of the transesterification reaction. A sharp increase in the TMP indicates that transesterification is not occurring, and the oil has become a continuous phase within the membrane reactor. On the other hand, a constant and stable TMP profile for all operating times reveals that a sufficient amount of oil has been converted into FAME, allowing the continuous operation of the membrane reactor (Tremblay *et al.,* 2008).

2.13.5 Effect of membrane pore size and thickness

For a membrane reactor with separation based on the molecular size of the components, the selection of a membrane with a suitable pore size becomes extremely important in order to prevent oil droplets from passing through the membrane. It has been proven that no oil is found in the permeate stream when a membrane with a pore size between 0.05 – 1.4 µm is used to produce biodiesel. This separation occurs because the reported average size of the oil droplets falls in the range of 12 – 400 µm, which is much larger than the membrane pore size (Cao *et al*., 2008).

The thickness of the membrane is an additional vital factor that needs to be taken into consideration for the use of catalytic membranes in biodiesel production. Zhu *et al*. (2010) reported that the membrane thickness used in transesterification falls in the range of 0.04 – 0.26 mm.

2.14 ADVANTAGES OF CATALYTIC MEMBRANE REACTOR IN BIODIESEL PRODUCTION

The catalytic membrane reactor is a new technology for biodiesel production. This technology can offer an alternative to overcome the common limitations arising from conventional biodiesel production processes (Dubé *et al.*, 2007). The advantages of the catalytic membrane reactor for biodiesel production will be discussed in the following section.

2.14.1 Environmentally friendly process

The production of biodiesel using catalytic membrane reactor is undeniably an environmentally friendly process because of its low energy consumption. Transesterification in a catalytic membrane reactor is carried out under mild operating conditions. The highest reported reaction temperature in a membrane reactor was 70 °C (Dubé *et al.*, 2007), which is quite similar to the conventional homogeneous and heterogeneous transesterification of 65 °C but much lower than supercritical transesterification (Berchmans and Hirata, 2008). Research showed that among all the biodiesel production methods, supercritical transesterification requires the most extreme reaction temperature (240 – 340 °C) and reaction pressure (5.7 – 8.6 MPa). The reaction temperature and pressure (70 °C and 173.4 kPa) used in a membrane reactor are 5 and 50 times lower when compared to supercritical process respectively (Hawash *et al*., 2009).

Membrane reactor reduces the usage of solvents and chemicals that are harmful to the environment. The use of catalysts in the membrane reactor is 0.05 % for the basic catalyst (Tremblay *et al*., 2008) and 2 % for the acid catalyst (Dubé *et al*., 2007) which is lower when compared to the conventional method.

Although the operating parameters are similar to those of homogeneous transesterification, the problem of wastewater generation is eliminated when biodiesel is produced through membrane technology. Both acid and base catalyzed transesterification, require the washing process, which consists of two steps: neutralization and water washing (Atadashi *et al*., 2011).

In the production of biodiesel using membrane reactor, washing would not be needed to remove the catalyst in the permeate stream (Tremblay *et al*., 2008). Biodiesel is separated from the membrane as it is formed, eliminating the need for the washing step to remove free glycerol content from the FAME phase.

2.14.2 Lower investment cost

In the catalytic membrane reactor, both the separation and catalysis processes are combined in single unit operation (Vankelecom, 2012). The integration of these processes into a catalytic reactor is able to reduce the number of operating units, as well as the number of processing steps, thereby leading to a reduction in the size and complexity of the plant and a consequent reduction of the investment cost (Dittmeyer *et al*., 2008). One of the main factors contributing to the high production cost of biodiesel is the need for downstream processes, which include biodiesel separation and purification (Hasheminejad *et al*., 2011). The catalytically membrane has the advantage of not requiring decantation to separate the two phases obtained after transesterification (Gomes *et al*., 2011). In addition, it has the potential to simplify FAME, glycerol separation, and catalyst neutralization.

2.14.3 High process flexibility of feedstock conditions

The catalytic membrane reactor appears to be a suitable alternative to produce biodiesel from oil with high FFA content because it can be easily modified into an ‘acidic membrane’ by introducing SO_3H as a functional acid group into the polymer matrix. Furthermore, the water or moisture content found in oil sources can be separated by polymer membranes, such as PVA and PAN, during the pervaporation process (Chapman *et al.*, 2008), thereby preventing the water from hydrolyzing the produced FAME back to FFA. Therefore, cheaper feedstock such as non-edible oils, waste cooking oils and even unrefined crude oils with high FFA content can be used in biodiesel production (Hasheminejad *et al.*, 2011).

2.15 MEMBRANE LIFETIME AND FOULING IN BIODIESEL PRODUCTION

The life span of a membrane is shortened because of continuous contact with strong acid and base catalysts during operation. Therefore, it is vital to select a membrane with high resistance to degradation and corrosion. Carbon membranes are able to resist the harsh environment in the production of biodiesel when H_2SO_4 or NaOH is used as a catalyst. It has been reported that no tangible evidence of degradation of the carbon membrane was observed, even after 10 months of operation and contact with acid or base solution (Dubé *et al*., 2007). The blended PSSA/PVA (a kind of catalytically active membrane) showed a stable conversion of 80% after 5 repeated transesterification runs with 8 h of reaction time (Zhu *et al*., 2010). The polyethersulphone used in the biocatalytic membrane microreactor also showed good stability with no decay of its catalytic activity for at least 12 days of continuous operation (Machsun *et al*., 2010).

Fouling is one of the major challenges in membrane processes. Fouling of membrane can be attributed to the accumulation and deposition of particles in the feed onto the membrane surface and into the membrane pores (Pagliero *et al*., 2007). In biodiesel production, the agglomeration size of glycerol is influenced by the alcohol concentration in the emulsion. Increased alcohol concentration favors the formation of smaller glycerol agglomerates. This phenomenon probably arises because of the excess amount of alcohol used in the reaction that allows the glycerol and other alcohol soluble substances to pass through the membrane pores easily, causing pore plugging (Gomes *et al*., 2011). However, in the typical biodiesel production or refining process in which the alcohol concentration in the reaction mixture is lower, the serious fouling of the membrane that is caused by the accumulation of oil and other submicron particles on the inverted membrane surface was not observed (Cheng *et al.,* 2009; Wang *et al*., 2009). Unfortunately, there has not been much study on the fouling of catalytically active membranes, especially for the polymeric membranes used in biodiesel production. Fouling of the membrane can be reduced by increasing the temperature, regardless of the type of membrane used in biodiesel production. This phenomenon occurs because of the reduction in solution viscosity that is observed when the reaction temperature is increased (Pagliero *et al*., 2007).

2.16 LIMITATIONS IN MEMBRANE TECHNOLOGY FOR BIODIESEL PRODUCTION

Undeniably, membrane reactors can be considered an emerging technology for biodiesel production. In order to successfully develop and commercialize membrane reactors in the biodiesel industry, knowledge is required in three major fields: catalysis, membrane technology, and reactor engineering. However, the desired properties, such as the mechanical properties and surface morphology of the membrane, used in biodiesel production have not been fully studied. (Guerreiro *et al*., 2010; Shi *et al*., 2010; Zhu *et al*., 2010). Therefore, the ability of the synthesized membrane to separate glycerol from the product stream needs to be researched. Additionally, the engineering aspects of the membrane reactor have been minimally studied because most researchers have only offered proof of concepts. Biodiesel production using membrane reactors is still running under non-optimal conditions. Therefore, it is a challenge to choose the best possible combination of catalyst and membrane. Optimization studies and modeling will be needed to advance the membrane reactor into commercial operation.

Although high biodiesel yield can be obtained via the catalytically membrane. The purification problem can be reduced by using inert catalytically active membranes created from ceramic membranes. In the flow configuration studied by Guerreiro *et al*., (2010); Sarkar *et al*., (2010) and Zhu *et al*., (2010), the carbon membranes face the problem of low mechanical strength. It has been reported that the tested polymer membranes break before a high conversion of biodiesel could be achieved (Guerreiro *et al*., 2010). Therefore, more attention is needed to select the appropriate membranes and operating conditions to avoid membrane failure.

2.17 BIODIESEL PROPERTIES AND QUALITY

2.17.1 Biodiesel Properties

There are some major differences between biodiesel and petroleum diesel with regards to chemical composition. This obviously gives biodiesel different behaviors. The nature of the feed used during biodiesel production affects the behavior and properties of the diesel produced. The following fuel properties are considered:

- Cetane number
- Flashpoint
- Lubricity
- Sulphur content
- Cold filter plugging point
- Cloud point
- Pour point

The Cetane Number (CN): this is the propensity of any fuel to kindle after it has been fed into the engine component. According to current specification, it is required to maintain a CN of above 40 and most refiners make diesel with numbers ranging from 40 to 45. The CN for biodiesel falls within 46 to 60 but is influenced by the feedstock used (Biodiesel Education, 2004). This also reduces delay during ignition and makes the combustion ability of the engine better (Biodiesel Education, 2004). There are a few methods for measuring CN, which is a measurement of cetane index. Some use ASTM D4737, while some use ASTM D976. The first is calculated based on density and recovery temperatures of 10, 50 and 90 % while the latter only relates it to density and 50% recovery temperature.

Flash Point (FP): This can be defined as the lowest temperature after which the vapor over the fuel can ignite. Petroleum diesel is innately safe as they have an FP temperature ranging between 50 and 80 ^{o}C. The flash points for biodiesel are over 160 ^{o}C, which reduces the fire hazard related to their transportation or storage. This makes them better than petroleum fuels in terms of ease of use, storage and transportation (Biodiesel Education, 2004). There are various methods for the determination of FP's of liquids available in many standards, which include ASTM D93 and IP34.

Lubricity: This can be defined as the extent to which a lubricant can reduce friction. It has been said that it is difficult to measure material lubricity even though it can be obtained by a laboratory test. When the friction is low, it implies that the lubricity is high (Friedrich, 2003). It is also vital to note that reduction in fuel sulfur content according to recent regulations have decreased fuel lubricity. Biodiesel has good lubricity as quality blends of biodiesel have shown that the mixture improved greatly in relation to lubricity (Biodiesel Education, 2004). Lubricity for diesel can be measured by using ASTM D6078.

Sulfur content: Based on the current global sulfur regulation, sulfur levels are required to be less than 50 ppm from the beginning of 2005 (SAPIA, 2006). South African refiners are currently aligning their operations to meet this regulation not later than 2018. Biodiesel is free of sulfur particularly when made from pure vegetable oil. Biodiesel generated from waste vegetable oil may have low sulfur content. This needs to be checked to ensure that the quality is acceptable (Mittelbach and Remschmidt, 2005). This can be measured using ASTM D5453.

Pour Point (PP): This can be defined as the lowest temperature, which a fuel sample can be cooled to, while retaining its properties. In the mid-1960s, attention focused on developing laboratory bench-scale tests independent of CP or PP to predict minimum operability temperatures for diesel fuels. In Western Europe, this work resulted in the development of the CFPP test method. This method (ASTM standard D6371) calls for cooling the oil sample at a specified rate and drawing it under vacuum through a wire mesh filter screen. CFPP is then defined as the lowest temperature at which 20 ml of oil safely passes through the filter within the 60s. Guy (2008) recommends to blend biodiesel with petroleum diesel and to also blend it with antigen additives.

Heating Value: This is sometimes called the heat of combustion represented by HG. This is also dependent on the nature of the feedstock. Comparing petroleum diesel to biodiesel, petroleum diesel contains more HG than biodiesel even though it is less dense than biodiesel.

According to Mittelbach and Remschmidt (2005), the HG of petroleum diesel is 13% more than that of biodiesel. For an equal injection volume, automobiles using biodiesel have less power and force. Multi-fuel automobile utilizes motors that can detect the nature of the fuel and spontaneously switch the injection parameter (Mittelbach and Remschmidt, 2005). If biodiesel is used, consumption is high as there is an increase in injection capacity. The described behavior of biodiesel is specific to pure biodiesel. When biodiesel is blended with petroleum diesel as B5 or B10, the behavior of the petroleum diesel will not change.

Table 2.4 shows the characteristics of petroleum diesel and biodiesel from different PVO sources (Mittelbach and Remschmidt, 2005).

Table 2.4: Properties of Petroleum Diesel and Biodiesel

		Fossil Diesel	**Biodiesel from Soyabean oil**	**Biodiesel from Palm oil**	**Biodiesel from Canola oil**	**Biodiesel from Sunflower oil**
Density	Kg/m^3 (T in ^{o}C.)	835 (15)	884 (25)	867 (15)	888 (15)	880 (25)
Kinematic Viscosity	Mm^2/s at 38^{o}C)	2.7	3.05-4.08	4.3 – 6.3	3.5 - 5	4.20 – 4.40
Cloud point	^{o}C	-15	-2 to 2	13 to 16	-3 to 1	0 to 3
Pour point	^{o}C	-33	-3 to -1	-	-15 to -9	-3
CFFP	^{o}C	-18	-2	9 to 10	-19 to -8	-3
Flash point	^{o}C	50-80	141-171	155 - 174	153 - 179	164 - 183
Heating value	MJ/Kg	42.7	39.8	41.3	40.07	39.71
Cetane number		47	50	52	56	53

2.18 BIODIESEL QUALITY AND STANDARDS

In order to market biodiesel properly, certain specifications from the quality point of view are required. These standards then act as guidelines during biodiesel production to monitor quality. These standards also serve as warranty to customers that the products they buy are of high quality and that they are protected against safety and other environmental regulations (Prankl, 2002).

Considering the varieties of feedstock that are used for producing biodiesel, it is very appropriate to pay close attention to these standards. Many biodiesel guidelines are presently in place in some countries like the EN14214 applicable in EU. In the United States, ASTM D6751 is used (Mittelbach and Remschmidt, 2005). In South Africa, the standard known as SANS 1935 is used (Manaka, 2006).

2.19 ECONOMIC VIABILITY OF BIODIESEL

Biodiesel is an attractive renewable energy resource. However, there are some challenges that face this vital resource. These challenges include the high cost and limited availability of biodiesel feedstock beside the cheaper prices of crude petroleum. There are various factors contributing to the cost of biodiesel. These factors include feedstock prices, plant's capacity, feedstock quality, processing technology, net energy balance nature of purification and its storage, etc. However, the two main factors are the cost of feedstock and the production cost. It has been found that the cost of feedstock accounts for more than half of the total cost of biodiesel fuel (Yusuf *et al.*, 2016). Therefore, selecting the best feedstock is vital to ensure low biodiesel cost. Conversely, non-edible oils as a feedstock for biodiesel can reduce this cost. In terms of production cost, there are also two aspects, which are, the transesterification process cost, and the by-product (glycerol) recovery. The continuous transesterification process is a choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high-quality glycerol is another way to lower biodiesel production cost. Therefore, biodiesel plant must have its own glycerol recovery facility (Carraretto *et al.*, 2004; Sharma *et al.*, 2008; Murugesan *et al.*, 2009; Balat and Balat, 2010; Knothe, 2010 and Ahmad *et al*., 2011).

According to IEA (2014), biodiesel produced with current technology in OECD countries are still two to three times more expensive than gasoline and diesel. Moreover, a review of many economic feasibility studies around the world shows that biodiesel usually costs over US $0.5 per liter compared to the US $0.35 per liter for normal diesel. Currently, biodiesel cost is 1.5 – 3 times higher than the fossil diesel cost in developed countries (Yusuf *et al.*, 2016). Biodiesel is thus currently not economically feasible, and more research and technological development are needed in this area of research. Supporting policies such as tax credits are important to promote biodiesel research and make their prices competitive with other conventional sources of energy (Agarwal, 2007; Sharma *et al*., 2008; Demirbas, 2009 and Balat, 2011).

2.20 FUTURE OF BIODIESEL

Acceptance of Kyoto protocol and clean development mechanism (CDM) will lead to more biodiesel production around the world. For instance, it is anticipated that this policy will lead to a total biofuel demand in EU of around 19.5 and 30.3 million tons in 2012 and 2020 respectively (Mekhilef, *et al*., 2011). Biodiesel production is expanding rapidly around the world, driven by energy security and other environmental concerns. Given geographic disparities between demand and supply potential, and supply cost, expanded trade in biodiesel appears to make sense. The global potential of biodiesel production is very unclear, but in the end, it could be a substantial percentage of transport fuel demand. Currently, biodiesel can be more effective if used as a complement to other energy sources (Singh and Singh, 2010).

With the increase in global human population, more land will be needed to produce food for human consumption. Thus, the insufficient lands could increase the production cost of biodiesel plants. This problem already exists in Asia where vegetable oil prices are relatively high. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel production. Therefore, non-edible oil, genetically engineered plants, and microalgae feedstock can be the proper solutions for this problem and can ensure the sustainability of biodiesel production in the future (Sharma *et al*., 2008).

2.21 DESIGN OF EXPERIMENT (DOE)

Design of experiment (DOE) is a systematic procedure carried out under controlled conditions in order to obtain unknown effects, to test or establish a hypothesis or to illustrate a known effect. DOE is also known as Designed Experiments or Experimental Design; where all of the terms are considered to have the same meaning (Montgomery, 2009).

The engineering perspective on the use of experimentation is to reduce time in design or develop new products and processes, improve performance of existing processes, improve reliability and performance of products, achieve product and process robustness, perform evaluation of materials, design alternatives, setting component and system tolerances, etc. (PennState, 2015).

The DOE has been used to efficiently carry out experiments and analysis of results. The main use of DOE is to determine simultaneously the individual and interactive effects of input factors that affect the output results in any design.

An experiment has inputs and factors, some of which can be controlled and others cannot be controlled. The selection of factors affecting the output is of vital importance. Figure 2.8 is a presentation of a model of the process or system. The objectives of conducting the experiment on the system in Figure 2.8 may include the following (Montgomery, 2009):

- Determining which variables are most influential on the response *y*.
- Determining where to set the influential *x* so that *y* is usually near the nominal value.
- Determining where to set the influential *x* so that variability in *y* is small.
- Determining where to set the influential *x* so that the effects of the uncontrollable variables $Z_{1,}$ $Z_{2\ldots}$ Z_q are minimized.

The selection of an experimental design mostly depends on the objectives of the experiment and factors to be investigated.

Comparative objective: The primary goal of the experiment is to make a conclusion about the important factor or several factors under investigation in the presence of and/or in-spite of the existence of the other factors. The question of interest is whether that factor is "significant", (i.e., whether there is a significant change in the response for different levels of that factor), then is a comparative problem and a comparative design solution needed.

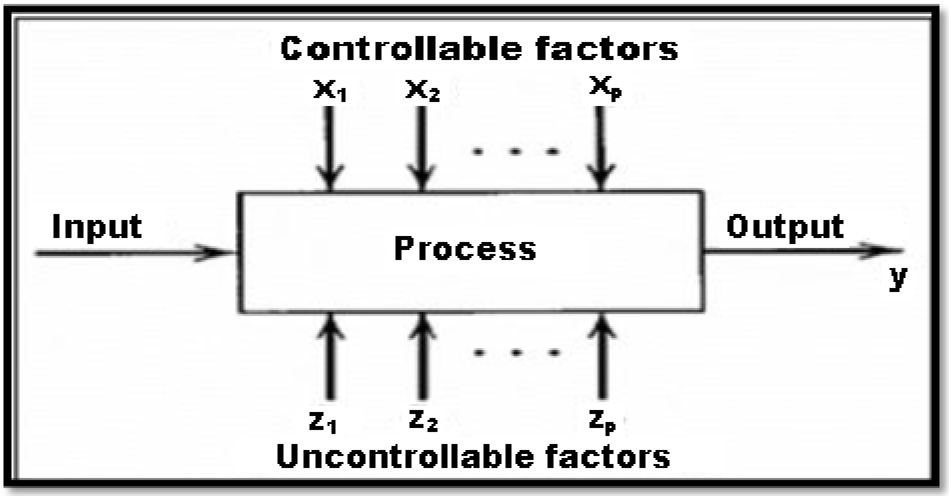


Figure 2.8: A general model of system variables (Montgomery, 2009)

Screening objective: The primary purpose of the experiment is to select or screen out the few important main effects from the many less important ones. These screening designs are also termed main effects designs.

Response Surface (method) objective: The experiment is designed to allow researchers to estimate interaction and even quadratic effects, and therefore gives an idea of the (local) shape of the response surface being investigated. For this reason, they are termed response surface method (RSM) designs. RSM designs are used to:

- Find improved or optimal process settings
- Troubleshoot process problems and weak points
- Make a product or process more robust against external and non-controllable influences. "Robust" means relatively insensitive to these influences.

Optimizing responses when factors are proportions of a mixture objective: If factors are proportions of a mixture and the "best" proportions of the factors are so as to maximize (or minimize) a response, then a mixture design is required.

Optimal fitting of a regression model objective: To model a response as a mathematical function (either known or empirical) of a few continuous factors and desire a "good" model parameter estimates (i.e., unbiased and minimum variance), then a regression design is needed.

2.21.1 OFAT Design

The most commonly used DOE is the one-factor-at-a-time design. This design involves varying one factor while keeping other factors constant. It can be used for the screening stage as well as the optimization stage of an experiment. The objective of OFAT is to provide information about individual variables and to optimize the process as the experiment proceeds (Qu and Wu, 2005).

The OFAT design carries a number of advantages reported in literature. Qu and Wu (2005) reported that OFAT design provided a faster identification of the influence of a given factor on the system and allows more flexibility than orthogonal fractional factorial designs (OFFD). The OFAT design also allows the rapid identification of maxima, minima boundaries in an experiment (Friedman and Savage, 1947; Czitrom, 1999).

The use of OFAT is being discouraged and many authors prefer the factorial design due to the following reasons (Czitrom, 1999; Montgomery, 2005; Wahid and Nadir, 2013):

- The OFAT designs do not show interactions between the variables.
- The prediction of the response in the factor space is improved in factorial designs.
- The lack of randomization can lead to biased conclusions.

However, the OFAT design is less complex and requires less training for the readers to understand the experimental outcomes (McDaniel and Ankenman, 2000; Qu and Wu, 2005).

2.21.2 Factorial Design

The approach deals with several factors in which all factors are varied simultaneously; therefore, it reduces the number of experiments to be performed. The design takes into account the interactions between factors that may affect the yield or response. The factorial design can be classified into two categories, which are full factorial designs and fractional designs (Montgomery, 2009). A common factorial design is with all input factors set at two levels each. The levels are called ‘high’ and ‘low’ or ‘+1’ and ‘-1’ respectively. A full factorial design is the one with all possible combinations of all the input factors. A full factorial design with k (2) number of factors and N (2) levels is represented as N^k (2^2) and with three factors at two levels is 2^3. Therefore, full factorial is not suitable for a high number of factors because it requires a large number of runs or experiments, which is not economical and feasible see Table 2.5. The number of runs does not take into account the centre points in a two level factorial, and replicates on two and three level factorials.

Table 2.5: Number of Runs for a Two Level (N^k) and Three Level Full Factorial

Number of Factors (k)	Two level factorial	Three level Factorial
	Number of Runs	Number of Runs
2	4	9
3	8	27
4	16	81
5	32	243
6	64	729
7	128	2187

A full factorial design is then deemed unsuitable when the numbers of factors are equals or greater than five. A solution to a large number of runs of the full factorial design is to carefully select a fraction of a full factorial in order to reduce the number of runs. When a fraction of a full factorial is considered, it is then referred to as a fractional factorial design and it is expressed as N^{k-p}, where:

N is the number of levels of each factor investigated,
K is the number of factors investigated and,
p describes the size of the fraction of the full factorial used.

In general, p represent the fraction used for instance ½ is p = 1, ¼ is p = 2 and 1/8 is p = 4.

The regression model statement for a simple 2 level factorial design is as follows:

$$y_i = \beta_0 + \beta_1 Z_{1i} + \beta_2 Z_2 i + \beta_3 Z_{1i} Z_{2i} + \varepsilon_i \qquad \text{(Equation 2.7)}$$

Where:

y_i = Output/Response for the ith unit.

β_0 = Coefficient for the intercept

β_1 = Mean difference on factor 1

β_2 = Mean difference on factor 2

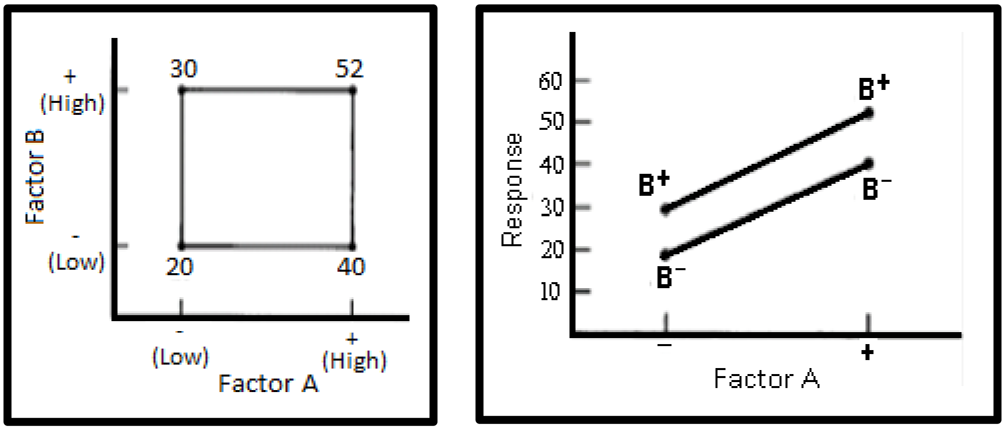
β_3 = Interaction of factor 1 and 2

Z_{1i} = Dummy variable for factor 1

Z_{2i} = Dummy variable for factor 2

ε_i = residual for the ith unit.

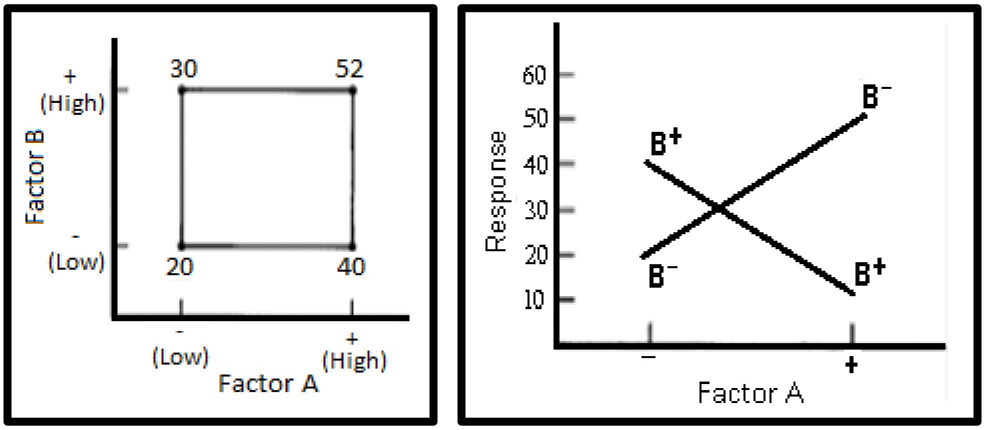
The factorial design is used to decide which of these factors is important and thereafter, decide what level of the factors gives the optimal response (finding the optimal level of the important factors).



(i) (ii)

Figure 2.9: A two-factor factorial experiment (i) with the response (y) showed at the corners (ii) without interaction (Montgomery, 2009).

Figure 2.9 (i) showed the response on factor A and B, which suggest that there is no interaction between the factors in Figure 2.9 (ii).



(i) (ii)

Figure 2.10: A two-factor factorial experiment (i) with the response (y) showed at the corners (ii) with interaction (Montgomery, 2009).

On the other hand, Figure 2.10 showed that there is an interaction between factors.

2.21.3 Response Surface Methodology Design

Many have described the response surface methodology (RSM) as a method that involves a group of mathematical and statistical practices in the development of the most functional relationship between a response (y) and control variables (x_i) (Khuri and Mukhopadhyay, 2010). The relationship between the response and control variables can be estimated using a low-degree polynomial model of the form (Khuri and Mukhopadhyay, 2010):

$$y = \beta\, f'(x) + \varepsilon \qquad \text{(Equation 2.8)}$$

Where:

y = Response of interest
x = Control variables/factors
f'(x) = Vector function consists of powers and cross-products of powers of x.
β = Constant coefficient term
ε = Represent the noise or error observed in the response (y).

This model is considered to establish a relationship to be used to predict response values for the control variables, to determine the significance of the factor whose level is represented by *x*, and to determine the optimum settings of *x* that result in the maximum (or minimum) response over a certain region of interest (Khuri and Mukhopadhyay, 2010).

The main goal of using RSM is for process optimization fitted on a three-dimensional response surface showing the expected response as a function of control variables (Montgomery, 2009). The first step in most RSM problems is the screening of the variables in order to select the few important main effects from the many less important variables (Khuri and Mukhopadhyay, 2010). Therefore, the response can be well modeled by a linear function of the independent variables using the function in the first order model as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_k x_k + \varepsilon \qquad \text{(Equation 2.9)}$$

This model is similar to the model Equation 2.7, which also shows the interaction of the variables. If the model ignores the cross products or interaction component that gives an indication of the curvature of the response surface that has to be fitted in RSM, the model becomes equation 2.9, which is called the steepest ascent model (Montgomery, 2012). First order model, which is called the steepest ascent model, shows the hill at which the new variables range. Further investigation is conducted in order to find where the optimum lies. This is illustrated in Figure 2.11.

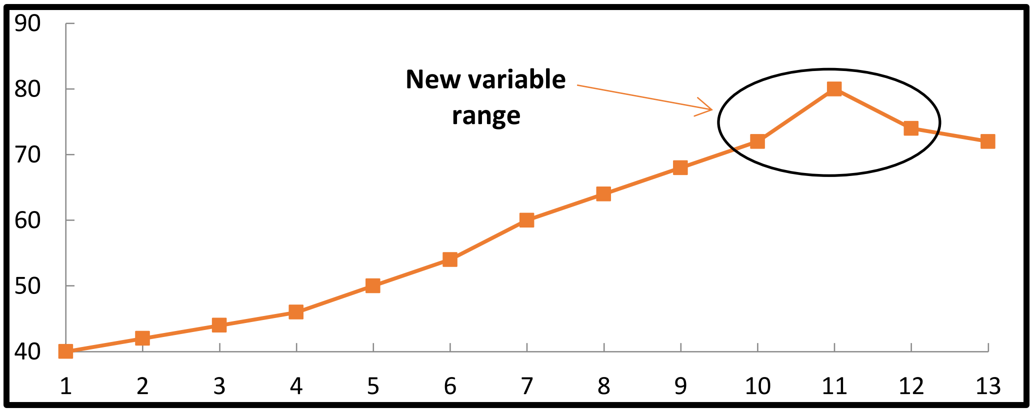


Figure 2.11: Response along the path of steepest ascent (Montgomery, 2012).

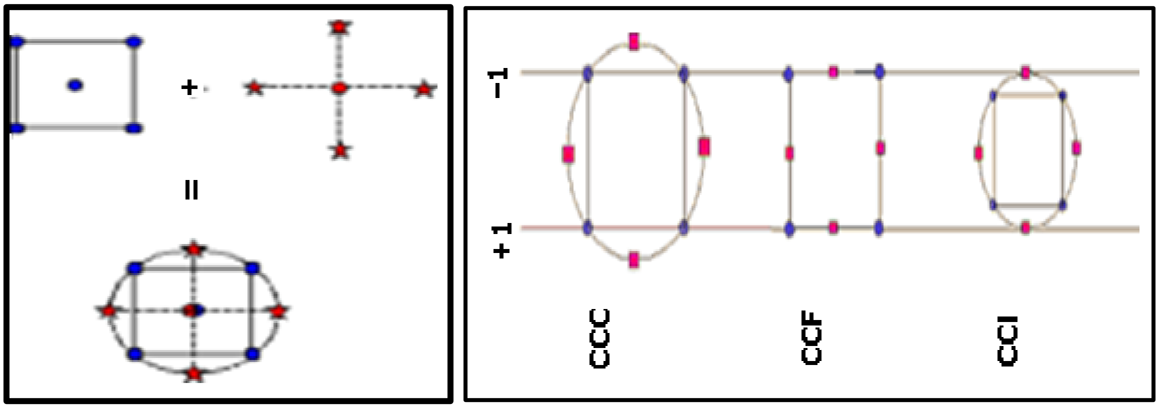
The choice of experimental design to generate a second order polynomial, which incorporates curvature to approximate the response in the RSM, is generally as follows:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \varepsilon \qquad \text{(Equation 2.10)}$$

The second order model contains the linear terms, cross product terms and second order terms as demonstrated in Equation 2.10. The second order polynomial model requires aresponse surface design that has more runs than the first order designs. This is accomplished by adding center points to the first order design (N^k). These response surface designs include the central composite design (CCD), the Box-Behnken design (BBD) and the Doehlert designs (DD) (Montgomery, 2012).

2.21.4 The Central Composite Design (CCD)

Central composite design contains an entrenched factorial or fractional factorial design with center points that is augmented with a group of 'star points' that allow estimation of curvature as illustrated in Figure 2.12 (a). This simply means that the CCD has five levels per factor (-α, -1, 0, +1 and +α). The star points represent new extreme values (low and high) for each factor in the design. There are three types of CCD that can be used when selecting a design, which are Circumscribed (CCC), Face-Centered (CCF) and Inscribed (CCI) as shown in Figure 2.12 (b). It can be designed in two ways, which is orthogonal block where the model terms and block effects can be estimated independently and to minimize the variation in the regression coefficients. The second way is the rotatability design where rotable design provides constant prediction variance at all points that are equidistant from the design center (Montgomery *et al.*, 2012).



(a) (b)

Figure 2.12: Central Composite Design (a) Generation of a CCD, (b) Illustrative representation of where the star points are placed for the 3 types of CCD.

CCD can be used to efficiently estimate first and second order terms and to model a response variable with curvature by adding center and axial points to a previously done factorial design.

2.21.5 Analysis of Design Model

The first analysis is considering the region of exploration for fitting the first-order model with the approximating function in Equation 2.9 for a well-modeled response. When the RSM shows a little curvature in the system for the first-order model to indicate the region of the optimum, a more elaborate model can be used. The more elaborate model is the second-order model in Equation 2.10 to perform an analysis to locate optimum.

2.21.6 Model Adequacy checking for first-order regression

The relationship between the response and independent variables is assumed to be a purely algebraic relationship. The error term has zero mean with a constant variance σ^2 and errors are normally distributed. Therefore, the model adequacy cannot rely on the analysis of variance until the validity of these mentioned assumptions has been checked by the examination of residuals.

The definition of the residual is as follows:

$$e_i = y_i - \hat{y}_i, \qquad i = 1, 2, \ldots, n \qquad \text{(Equation 2.11)}$$

Where:

y_i = An observation

$\hat{y}_i$ = The corresponding fitted value.

The residuals have several important properties with zero mean, and their approximate average variance is estimated by:

$$\frac{\sum_{i=1}^{n}(e_i - \bar{e})^2}{n-p} = \frac{\sum_{i=1}^{n} e_i^{\,2}}{n-p} = \frac{SS_{Res}}{n-p} = MS_{Res} \qquad \text{(Equation 2.12)}$$

$n - p$ is degrees of freedom associated with them.

The model is adequate when the residuals are structureless, meaning that, there should be no obvious patterns. A more useful procedure is the use of a normal probability plot of the residuals. For a normal underlying error distribution, the plot resembles a straight line (Montgomery, 2012). Substantial departures from a straight line indicate that the distribution is not normal see illustration in Figure 2.13.

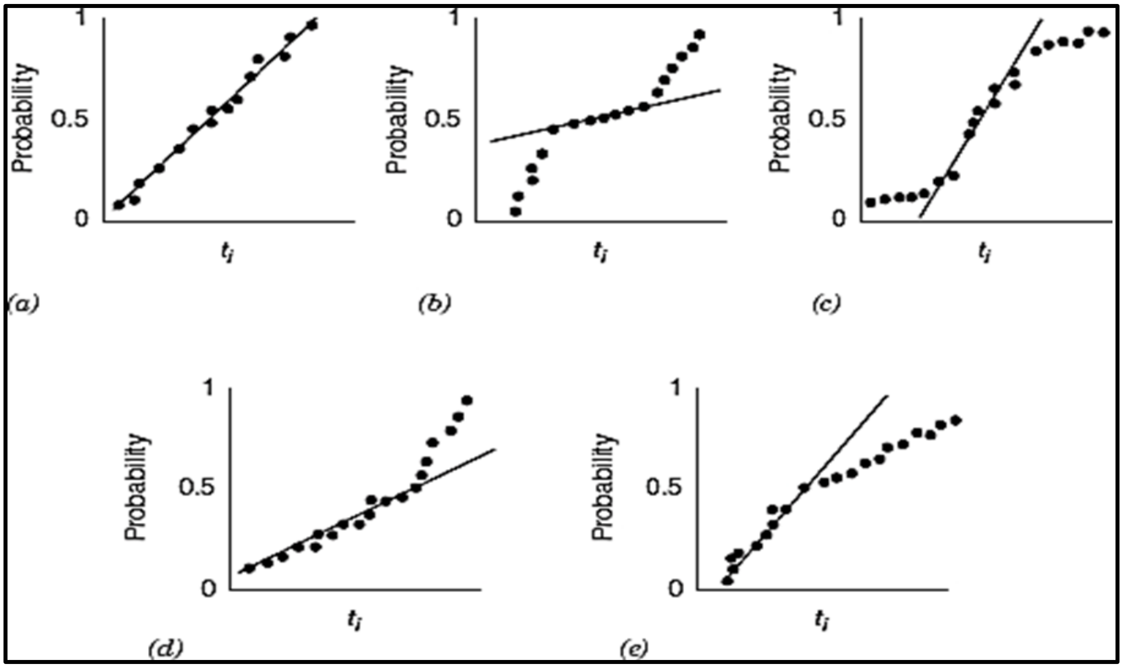


Figure 2.13: Normal probability plots: (a) ideal; (b) light-tailed distribution; (c) heavy-tailed distribution; (d) positive skew; (e) negative skew (Montgomery et al., 2012).

Observations that are outliers, or extreme values, which are separated in some fashion from the rest of the data are dealt with using scaled residuals. Methods of scaled residuals are standardized residuals, studentized residuals, PRESS Residuals and R-Student. An example of a normal probability plot of the external studentized residual is shown in Figure 2.14. The illustration in Figure 2.14 shows that the residuals do not lie exactly along the straight line. This is an indication that there may be outlier/s in the data, which is a problem with the normality assumptions.

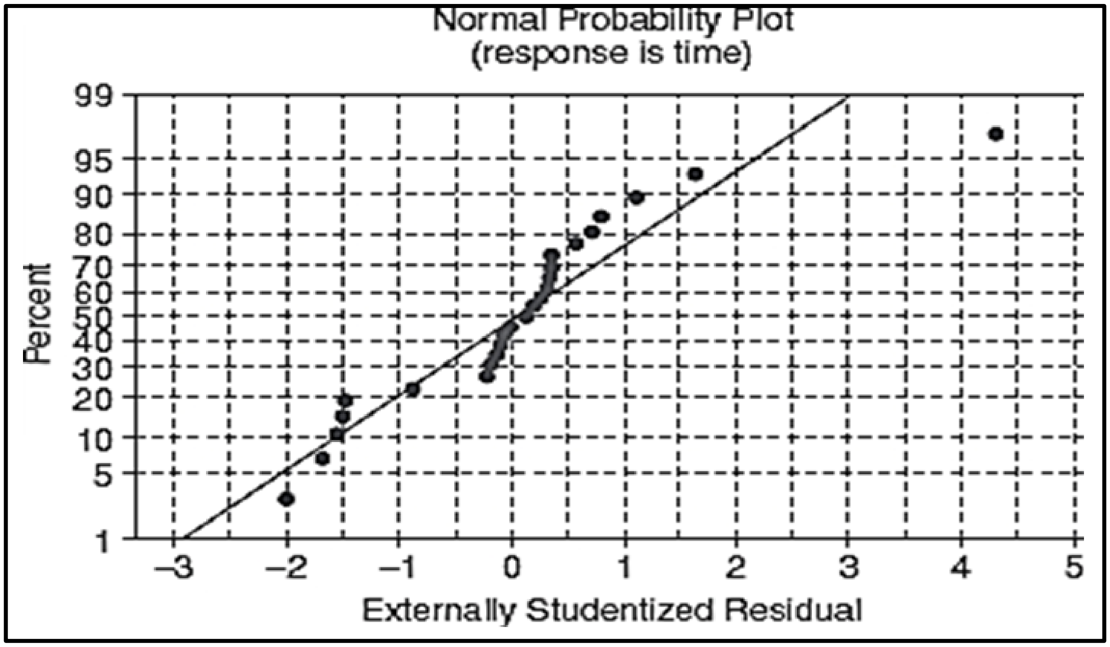


Figure 2.14: Normal probability plot of the externally studentized residuals for the delivery time data (Montgomery et al., 2012)

In order to detect several common types of model inadequacies, a plot of the externally studentized residuals t_i versus the corresponding fitted values $\hat{y}_i$ is used.

A model with no obvious defects follows a pattern of residual on Figure 2.15 (a). The plots of the patterns in Figure 2.15 (b), (c) and (d) show symptoms of model deficiencies, where the variance of the errors in Figures 2.15 (b) and (c) is not constant and in Figure 2.15 (d) is a nonlinear curve. Figure 2.15 (d) may mean that other regression variables are required in the model, for example, a squared term may be necessary and a transformation may be effective in this case (Montgomery *et al.,* 2012).

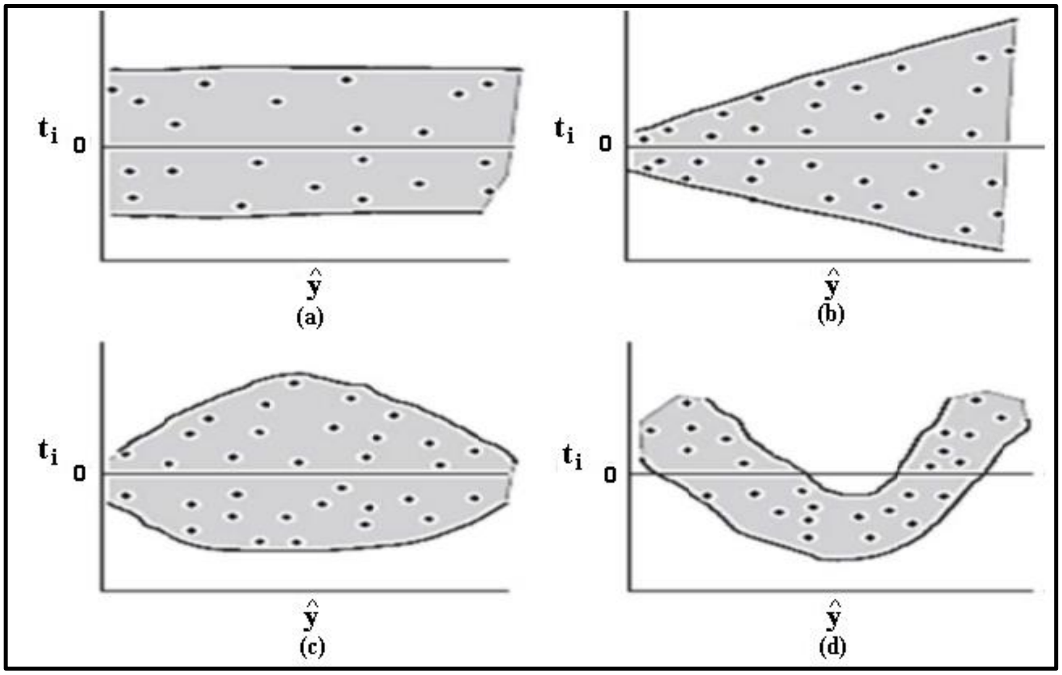


Figure 2.15: Patterns for residual plots: (a) satisfactory; (b) funnel; (c) double bow;(d) nonlinear (Montgomery et al., 2012).

Another potential violation of the basic regression assumptions is the presence of autocorrelation as seen in Figure 2.16. Autocorrelation is the correlation between model errors at different time periods.

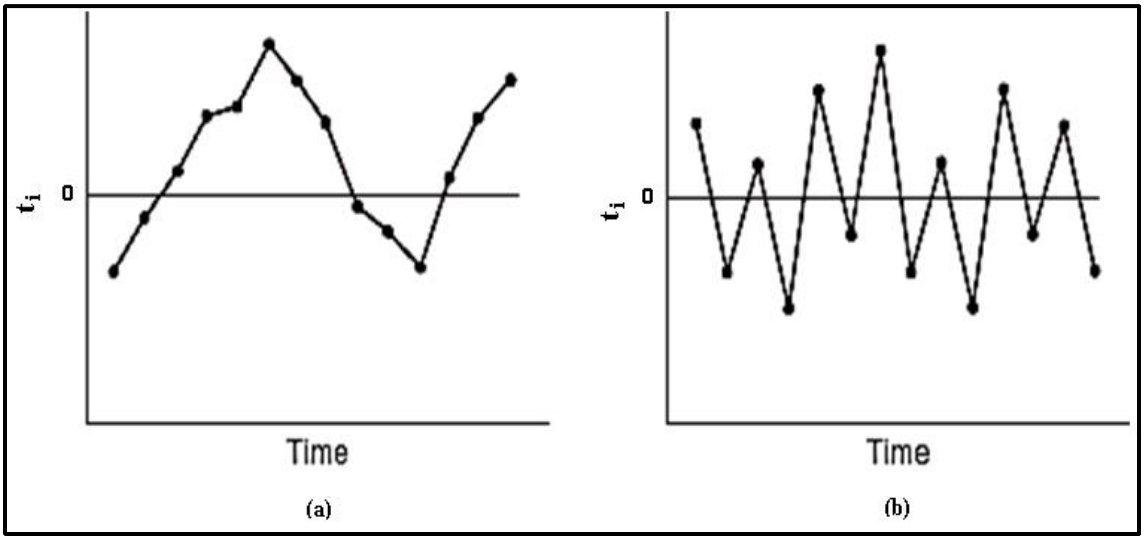


Figure 2.16: Prototype residual plots against time displaying autocorrelation in the errors: (a) positive autocorrelation; (b) negative autocorrelation (Montgomery et al., 2012).

2.21.7 Polynomial Regression Models in Two or More Variables

The regression function for fitting a second-order model such as Equation 2.10 is called response surface. Table 2.6 shows the analysis of variance for the Chemical Process example. The example in Table 2.6 indicates the lack of fit for the quadratic model shown by the large P_{value} ($P = 0.8120$) implying that the quadratic model is adequate.

The significance of regression is shown by the F_{value} (58.86) with a P_{value} of <0.0001 that signify that the quadratic model is significant and some of the coefficient parameters are nonzero. The R^2 and adjusted R^2 values for the model are satisfactory to fit the full quadratic model since there is no difference between the R^2 and adjusted R^2 values. The $R^2_{\text{prediction}}$ is calculated as shown in Equation 2.13 and it is an indication that the model can explain about 94 % of the variability in new data.

Table 2.6: Analysis of Variance for the Chemical Process Example (Montgomery et al., 2012).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_0	P Value
Regression **SS_R (β_1, β_2, β_0)** **SS_R (β_{11}, β_{22}, β_{12}, β_0, β_1, β_2)**	1733.6 (914.4) (819.2)	5 (2) (3)	346.71 (457.20) (273.10)	58.86	<0.0001
Residual **Lack of fit** **Pure error**	35.3 (8.5) (26.8)	6 (3) (3)	5.89 (2.83) (8.92)	0.3176	0.8120
Total	1768.9	11			
$R^2 = 0.9800$		$R^2_{\text{adj}} = 0.9800$			PRESS = 108.7

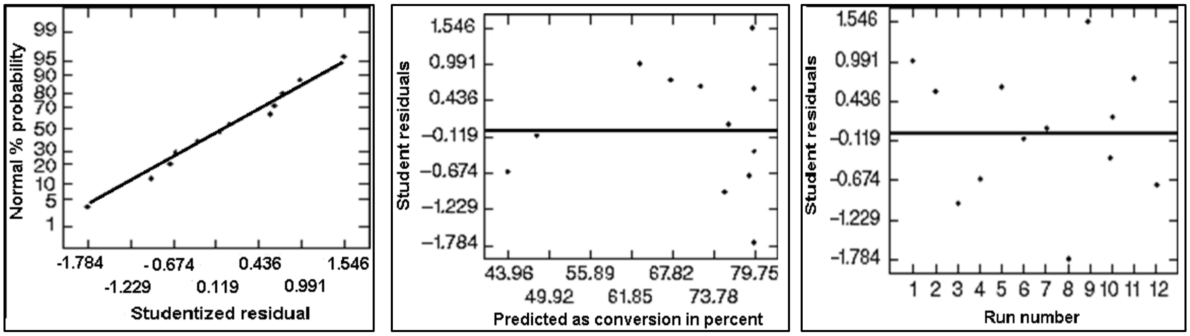
$$R^2_{prediction} = 1 - \frac{PRESS}{SS_T} = 1 - \frac{108.7}{1768.9} = 0.9385 \qquad \text{(Equation 2.13)}$$

The studentized residuals or the values of R-student are not large to indicate any potential problems with outliers as shown in Table 2.7 of the chemical process example.

Table 2.7: Observed Values, Predicted Values, Residuals, and Other Diagnostics for the Chemical Process Example (Montgomery et al., 2012)

Observed Value	Actual Value	Predicted Value	Residual	h_{ii}	Studentized Residual	Cook's D	R-Student
1	43.00	43.96	-0.96	0.625	-0.643	0.115	-0.609
2	78.00	79.11	-1.11	0.625	-0.745	0.154	-0.714
3	69.00	67.89	1.11	0.625	0.748	0.155	0.717
4	73.00	72.04	0.96	0.625	0.646	0.116	0.612
5	48.00	48.11	-0.11	0.625	-0.073	0.001	-0.067
6	76.00	75.90	0.10	0.625	-0.073	0.001	-0.067
7	65.00	63.54	1.46	0.625	0.982	0.268	0.979
8	74.00	75.46	-1.46	0.625	-0.985	0.269	-0.982
9	76.00	79.75	-3.75	0.250	-1.784	0.177	-2.377
10	79.00	79.75	-0.75	0.250	-0.357	0.007	-0.329
11	83.00	79.75	3.25	0.250	1.546	0.133	1.820
12	81.00	79.75	1.25	0.250	0.595	0.020	0.560

The plots in Figure 2.17 show no sign of model defect. The example in Figure 2.17 (a) and (b) show a horizontal line around the residuals of approximately zero, which suggests that the model fits the data well and the variances of the error terms are equal. The normal probability plot in Figure 2.17 (c) suggests that the error terms are normally distributed (Montgomery *et al*., 2012).



(a) **(b)** **(c)**

Figure 2.17:* *(a) Normal probability plot of the studentized residuals, (b) Studentized versus predicted conversion, (c) Studentized residuals run order (Montgomery et al., 2012).

A response surface and contour plots in figure 2.18 will then indicate the maximum response with its corresponding independent variables.

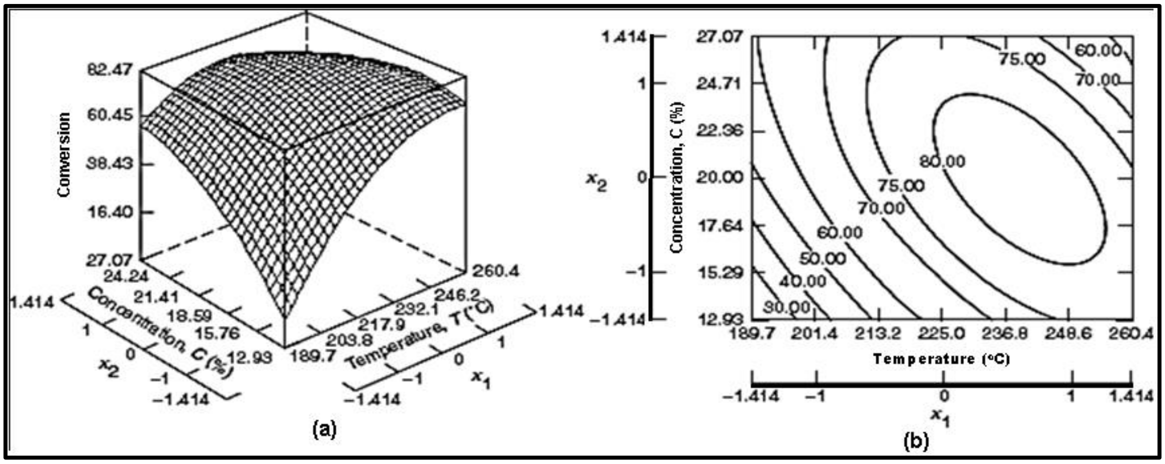


Figure 2.18: (a) Response Surface of predicted conversion, (b) Contour plot of predicted conversion (Montgomery et al., 2012).

The example of the response surface plot and contour plot indicate the maximum percent conversion at about 245 °C and 20 % concentration. The interest for using response surface and contour plot is in predicting the response (y) by estimating the mean response at a particular point in the process variable space.

2.22 SUMMARY

The challenge encountered by conventional biodiesel production processes have affected the viability of biodiesel as an economic and environmentally friendly alternative fuel. Homogeneous transesterification methods are still commonly used to commercially produce biodiesel, however, numerous environmental issues are associated with the high energy consumption, and the costly separation processes required for its operation has called for the search of innovative biodiesel production technologies.

This study is focused on using a packed bed membrane to produce and separate biodiesel from its byproducts. The use of heterogeneous catalytic method is currently being recognized as a promising technology in biodiesel production. Heterogeneous catalytic systems can ease the separation of biodiesel from the reaction mixture and allow the recovery and reuse of the catalyst, potentially leading to higher efficiency and lower production costs. In addition, the use of membrane as a reaction medium helps to eliminate the generation of wastewater.

The OFAT is the conventional method mostly used to carry out experiments. Although, there are other methods that have more advantages on the number of experiments conducted, showing interactions between the factors, and giving high precision and predictions over the design limits for all outputs of the system. The Central Composite design was selected for this study because of the reliability of predictions on the number of factors selected for the experiment.

CHAPTER 3: METHODOLOGY

3.1 INTRODUCTION

Transesterification is a chemical reaction used in converting vegetable oils to biodiesel. This process as explained in the literature involves vegetable oil reacting with alcohol such as methanol or ethanol in the presence of a catalyst to produce biodiesel and glycerol (Qiu *et al*., 2010). Oil extracted from soya bean seed was used as feedstock in this study because it is one of the oils approved by the government as a source material for the production of biofuel in South Africa. The acid value, iodine value and water mass fraction of the oil were measured. Methanol (99.8%) was selected due to its cost effectiveness and availability. Heterogeneous catalyst (CaO) was chosen for this study due to its recyclable nature, easily separated from the product, affordability, environmental friendly, and can be used in a continuous process without further purification. Activated carbon was employed as catalyst support because of its abundance in Kwazulu-natal, one of the provinces in South Africa.

Membrane separation technology was chosen for the separation process due to its ability to separate different components in a single process stream based on their molecular weight. In this process, reaction and separation took place within a single unit and therefore eliminates the need for a further purification step. Membrane reactors have the ability to selectively remove the product from the reaction mixture by allowing the liquid with lower molecular weight to pass through its pore while higher molecular weight liquids are prevented from passing. This method also allows for proper contact between the immiscible reactants and catalyst and as a result, a higher yield of the product is achieved (Westermann and Melin, 2009). South Africa like some other African countries suffers shortfall in water production and the use of membrane technology to produce biodiesel will help to conserve water, eliminate purification stage and make the environment free from pollution. This is a new innovation in the production of biodiesel and has more competitive price advantage by ensuring that further processing that adds to the production cost of biodiesel is totally eliminated.

Micro-porous TiO_2/Al_2O_3 membrane packed with potassium hydroxide catalyst supported on palm shell activated carbon was used to investigate the effects of reaction temperature, catalyst amount, and cross flow circulation velocity on the production of biodiesel in a packed bed membrane reactor. The result showed an optimum conversion of 94% biodiesel (Baroutian *et al.*, 2011).

The results above are very useful in providing a basis for the preliminary experiments.

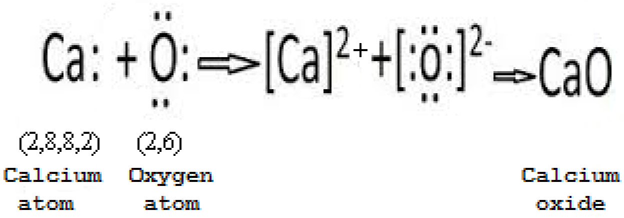
3.2 MATERIALS AND EXPERIMENTAL PROCEDURES

3.2.1 Preparation and characterization of the catalyst

The heterogeneous catalyst (CaO) was prepared using a method adapted from the literature (Baroutian et al., 2011). Pure calcium oxide (98.9%) and activated carbon were used as catalyst and catalyst support respectively. These were purchased from associated chemical enterprises, South Africa.

The activated carbon was screen to size range from 450 to 810 μm, washed with deionized water to remove impurities, and then put into an oven to dry at 100 ^{0}C for 24 hours, cooled in a desiccator and stored in a glass bottle. Activated carbon was added to the catalyst solution and then agitated in an orbital shaker at 180 rpm at a constant temperature of 25 ^{0}C for a period of 24 hours. The amount of adsorbed CaO was measured by the gravimetrical method. The total loading content of CaO was 40.50% by weight, based on the initial weight of activated carbon (Baroutian *et al.*, 2011).

In addition, the characteristics of the prepared supported catalyst were determined. Scanning electron micrographs (SEM) were obtained on an FEI Quanta 200 FESEM scanning electron microscope. The accelerating voltage was 20 kV. The SE and BSE detector were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K was carried out by ASAP 2020, Micromeritics. Before taking adsorption data, degassing at 120^0C and a residual pressure of 300 μmHg for 24 hours was performed using the degas port (Baroutian *et al*., 2011). Equation 3.1 shows the chemical structure of calcium oxide.



$$Ca: + \ddot{\underset{\cdot\cdot}{O}}: \Rightarrow [Ca]^{2+} + [:\ddot{\underset{\cdot\cdot}{O}}:]^{2-} \Rightarrow CaO$$

(Equation 3.1)

The SEM image of calcium oxide catalyst adhered to the surface of activated carbon, which represents particles in the range of 1 μm, is depicted in Figure 3.1. According to Guo *et al*. (2010), structures which are loosely attached and contain spaces of 1–5 μm between agglomerates, suggests that CaO/AC will exhibit an affinity to the entry of triglyceride and alcohol for the progression of transesterification.

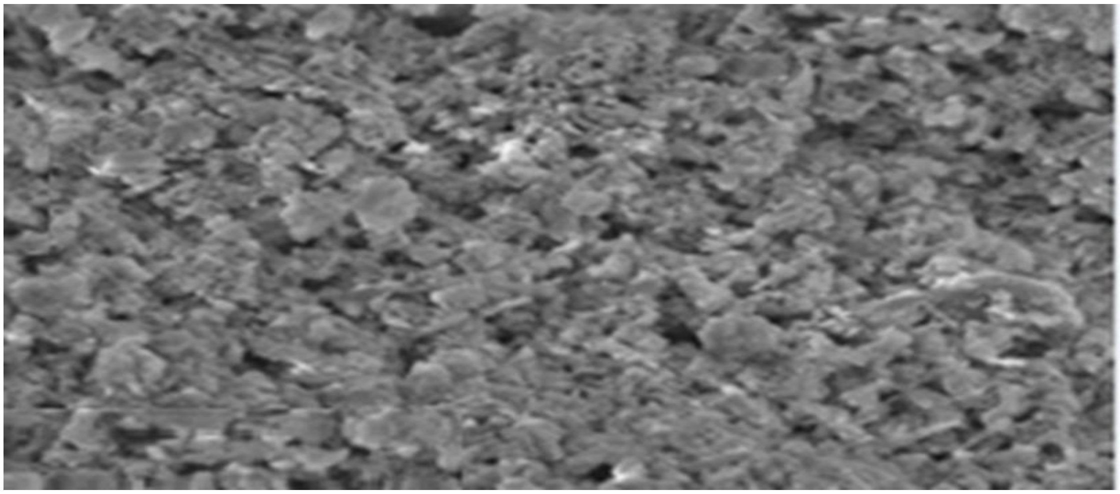
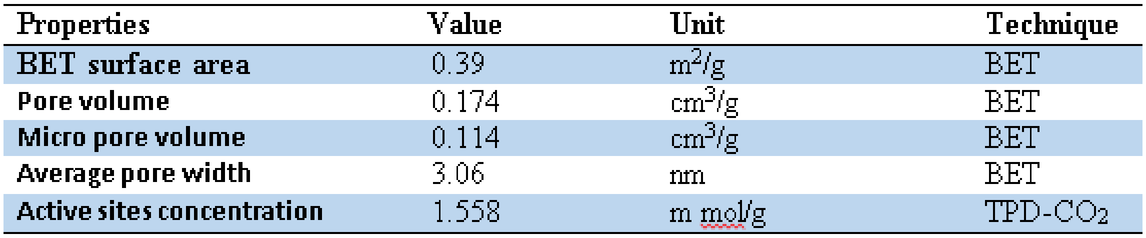


Figure 3.1: SEM image of calcium oxide supported on activated carbon (CaO/AC).

The BET surface area, pore volume, micropore volume, average pore width and active site concentration of the catalyst are presented in Table 3.1. A BET analysis was performed using N_2 gas. The BET analysis showed that the surface area of the CaO/AC was 0.39 m^2/g. A similar result was reported by Guo *et al.* (2010), using soybean oil as the feedstock.

Basicity of the catalyst was determined using temperature programmed desorption (TPD) method of CO_2 on Thermo Finnigan (TPDRO 1100) equipped with a thermal conductivity detector (TCD). Three hundred milligrams of the sample were treated at 300 ^oC for 1 h by passing helium at a flow rate of 20 ml/min. Then, the sample was saturated with carbon dioxide at a flow rate of 20 ml/min and at 100 ^oC for 1 h. Subsequently, the system was flushed with helium (20 ml/min) at 100 ^oC for 1 h to eliminate CO_2. Desorption was carried out from room temperature to 800 ^oC at a heating ramp of 5 ^oC /min (Baroutian *et al.*, 2011).

Table 3.1: CaO/AC catalyst characterization



Properties	Value	Unit	Technique
BET surface area	0.39	m^2/g	BET
Pore volume	0.174	cm^3/g	BET
Micro pore volume	0.114	cm^3/g	BET
Average pore width	3.06	nm	BET
Active sites concentration	1.558	m mol/g	TPD-CO_2

The significant reduction in BET surface area from virgin activated carbon (1.5 m^2/g) to the CaO/AC catalyst with 40 wt.% loading (0.39 m^2/g) indicates filling of CaO molecules into the activated carbon pores. CO_2 temperature programmed desorption (TPD) method was used to determine the basicity of catalyst and the result is presented in Table 3.1.

3.2.2 Experimental Apparatus, Setup, and Procedure

3.2.2.1 Apparatus

The lists of apparatus, equipments and materials used for the experiment are given below:

- Thermometer
- Magnetic stirrer

- Glassware (conical flasks, beakers)
- Retort stand for the conical bottom glass processor
- Calcium oxide nanoparticles
- Activated carbon
- Methanol
- Titration kit
- Weighing scale to measure CaO and methanol to accuracy
- Funnel
- Hotplate
- Spatula (for collecting CaO)
- Orbital shaker
- Oven

3.2.2.2 Overview of Experimental setup and preliminary runs

The experimental setup for the biodiesel production is shown in Figure 3.2. The setup consisted of 2 separate tanks for the reactants (oil and methanol). The dimensions (length, width and height), thickness and capacity of the tanks were 75mm×75mm×150mm, 10mm and 3 litres respectively.

The mixing tank where reactants were premixed in order to allow initial contact and homogenuity was used. The mixing tank has a variable speed stirrer specifically designed for viscous materials and a ventilated motor. The motor provides maximum constant torque throughout the entire speed range. The high level cast aluminum control box was integrated with the motor and has an on/off switch along with a speed control knob. The stirrer has a 12mm diameter x 110mm long aluminum support rod, 1.8 m long 3-wired grounded plug, and an 8mm diameter stirrer shaft having a stainless steel propeller. The electric motor drives the mechanical stirrer which mixes the process solution in the tank. The specification of the electric motor consisted of a speed range 30 to 3000 rpm, voltage 220VAC/230VAC, 50Hz, power input / output 50W / 35W and a maximum torque of 400 Nmm.

A tubular ceramic membrane (Atech Innovations Gmbh, Germany) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 1000 mm, 16 mm, 25.4 mm and 0.02 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m^2. A Watson marlow 313S peristaltic pump (Cole-Parmer Instrument, USA) was employed to feed the raw materials and to prepare circulation inside the system. The Chem-Durance chemical resistant pump tubing (ID = 44 mm, OD = 2.36 mm) was used. Pressure gauges controlled at 100 Kpa was used to monitored pressure of the system. To prepare reaction temperature a shell and tube heat exchanger equipped with a hot water circulator bath was used as a heat transfer medium. The reactant passes through the tube while being heated up to the desired temperature range (50 ^oC – 70 ^oC) by the hot water in the shell part of the heat exchanger. A coil type heater connected to a voltage regulator (0V - 200V) to obtain the desired temeprature range for the solution was employed. The coil wire material was made of stainless steel, its wire diameter was 8mm and coil width of 80mm. Its power rating, voltage and current were 2000W, 230V 50hz and 16A respectively.

Catalysts particles were packed inside the ceramic membrane and held in place using cloth screens attached to the upstream and downstream tubing. From the preliminary experiments conducted, it was observed that methanol and biodiesel molecules were able to pass through the membrane which can be attributed to their smaller molecular sizes while the glycerol and the unreacted oil were retained in the reaction medium. The operating principle of membrane reactor for biodiesel production is centred on emulsified droplet size and membrane pore size. Cao *et al*., (2006) reported that average size of the oil droplet and glycerol fall in the range of 12-400 μm, which is much larger than the membrane pore size used in biodiesel production.

Methanol is one of the essential reactants in the transesterification, it is necessary to recycle and return it to the process. For this purpose a simple and effective methanol recovery unit was employed. Methanol recovery unit, which is based on continuous distillation, consists of hot water bath, a three neck round bottom flask, a leibig condenser and a thermometer. The permeate stream containing biodiesel and methanol was collected in the three neck round bottom flask. The high temperature of the water bath leads to methanol evaporation which is then condensed and returned back to the system.

The biodiesel production equipment was successfully set up and was commissioned. The equipment was initially test run using water in order to detect any leakage. The equipment was then tested using the parameters required to carryout a biodiesel production before proceeding with the preliminary runs.

The preliminary runs provided the basis for this studies. It aimed at finding the optimum ranges of the experimental variables, the significant elements and as well as the best operating conditions for the research work. The preliminary experiments were conducted using the setup in Figure 3.2. in the laboratory.

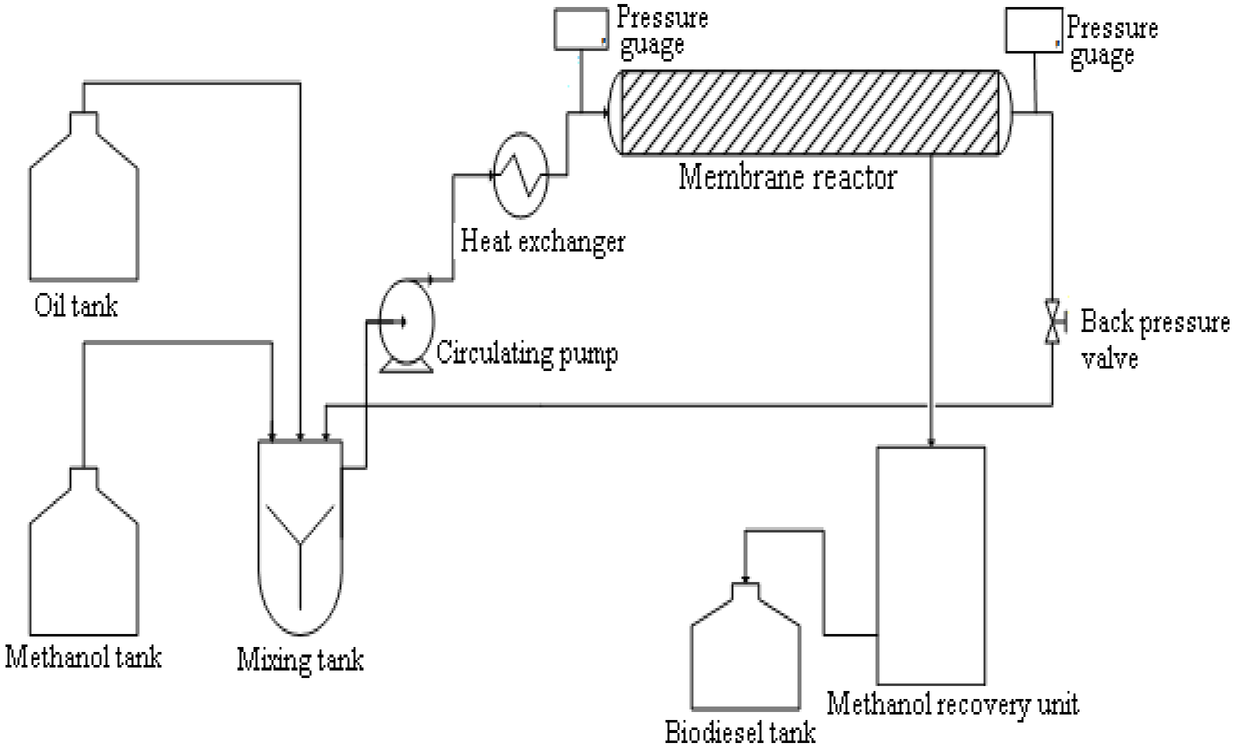


Figure 3.2: Laboratory scale experimental setup for biodiesel production.

3.2.2.3 Transesterification procedure in a packed bed membrane reactor

The procedures for the preliminary runs in the production of biodiesel on a laboratory scale are enumerated below:

- Pure soya bean oil was used for this experiment (Refer to section 3.1). For all experimental trials, same volume of soya bean oil was used throughout the study. The feedstock was preheated to eliminate any traces of water.
- The prepared catalyst (CaO/Activated carbon) was packed into the ceramic membrane and the two ends of the membrane were sealed with a cloth sieve.
- The feedstock and methanol dissolution were charged into the pre-mixing vessel to form the reaction mixture. The volume ratio of methanol to oil was varied from 3:1 to 12:1
- The oil/methanol mixture was heated to the desired reaction temperature using a shell and tube heat exchanger before the mixture goes into the membrane reactor. A thermometer was used to ensure the temperature of the mixture was up to theoretical specification. The Transmembrane Pressure inside the membrane was monitored by two pressure gauges and was controlled at 100Kpa in other to avoid compacting the boundary layer and decrease fouling.
- At the end of the transesterification stage, a complete separation of FAME-rich phase (permeate) from glycerol-rich phase (retentate) was achieved.
- After each run, the circulating pump and heat exchanger were switched off and the products were collected into a beaker. The excess alcohol was removed from the ester layer by evaporation and the produced biodiesel was analyzed. Subsequently, the system was fully drained, the catalyst was taken out and the system was flushed for 30 minutes with pure ethanol.

The operating standard of a membrane reactor for biodiesel production is based on the emulsified droplets size achieved; pore size of the membrane seems to be a critical factor in transesterification process using membrane reactors. Cao *et al*., (2006) reported that average size of the oil droplets ranges between 12-400 μm, which is much larger than the membrane pore size used in this experiment.

3.3 IDENTIFICATION OF VIABLE OPERATING LIMITS

The following elements were defined during the preliminary work:

(1) The optimum catalyst loading for the heterogeneous reaction

Calcium oxide (CaO) supported with activated carbon was used as heterogeneous catalyst. Defining the catalyst-loading limit in the membrane is a vital element in biodiesel production to avoid any side reaction with one of the reactants. Both materials were selected due to their abundance and low cost.

(2) *The upper and lower operating limits*

The upper and lower limits of the variables used in this experiment were determined to establish their significance. Specific experiments were carried out to know where the limit lies and literature studies assisted in providing the basis for this study in terms of the temperature used, molar ratio, flow rate and reaction time. The upper limit in this work was set by considering the impact; for example, raising the reaction temperature above the boiling point of methanol would consequently affect the yield of the product.

(3) *The significant factors and response*

The main response considered in this experiment was biodiesel yield. Four manipulated variables (temperature, flow rate, methanol/oil ratio and reaction time) were selected for the preliminary study.

3.4 EXPERIMENTAL DESIGN AND DATA ANALYSIS

The design of Experiment (DOE) provided an action plan for efficient experimental work. Inability to effectively select a suitable DOE might hinder the success of an experimental study. The results of the one factor at a time (OFAT) studies laid the foundation for the second phase of the DOE. The Centered Composite Design (CCD) was used in order to identify the curvatures with the addition of center-points and was used for optimization studies using the response surface methodology. The commercial software tool Design Expert version 10.0 was used for the statistical analysis of the experimental data.

CHAPTER 4: APPLICATION OF THE OFAT METHODOLOGY IN THE PRODUCTION OF BIODIESEL USING HETEROGENEOUS CATALYST

4.1 INTRODUCTION

The OFAT experimental method is the commonly used procedure for experimental design because it does not require extensive statistical knowledge to interpret the results obtained. In this study, Biodiesel was produced in a continous system using heterogeneous catalysis. Ceramic membrane acted as both the reactor and the separating medium. The performance of the ceramic membrane was evaluated in terms of selectivity, and critical variables that significantly influence the yield were identified.

4.2 EXPERIMENTAL TRIALS USING OFAT IN A SEMI BATCH SYSTEM

There are number of factors that affect the production of biodiesel; some variables are dependent while some are independent. In order to identify the best operating parameters that can be used later for optimization, preliminary experiments based on OFAT method were conducted.

4.2.1 Variables considered for Investigation:

The listed variables were investigated while following the procedure in section 3.2.2.3, in order to determine how these factors influence small-scale biodiesel systems for developing economies. They include:

- Temperature
- Reaction time
- Molar ratio of alcohol to oil
- Flow rate
- Concentration of catalyst

4.2.1.1 Effect of Temperature

The influence of temperature was investigated. Following the procedure in section 3.2.2.3, the trial was conducted by varying temperatures while other factors remained constant. The operating temperature range 50, 55, 60, 65, and 70 ^{o}C were considered. Experiments were initially conducted at temperatures below 50 ^{o}C but there was no significant influence on the yield. The highest temperature was 70 ^{o}C, as further increase showed declination of the product yield. As shown in Figure 4.1, increasing the reaction temperature favored the transesterification. However, raising the temperature above 65 ^{o}C, which is the boiling point of methanol, reduced the conversion rate due to the continuous boiling of methanol, and consequently leaves the reaction medium.

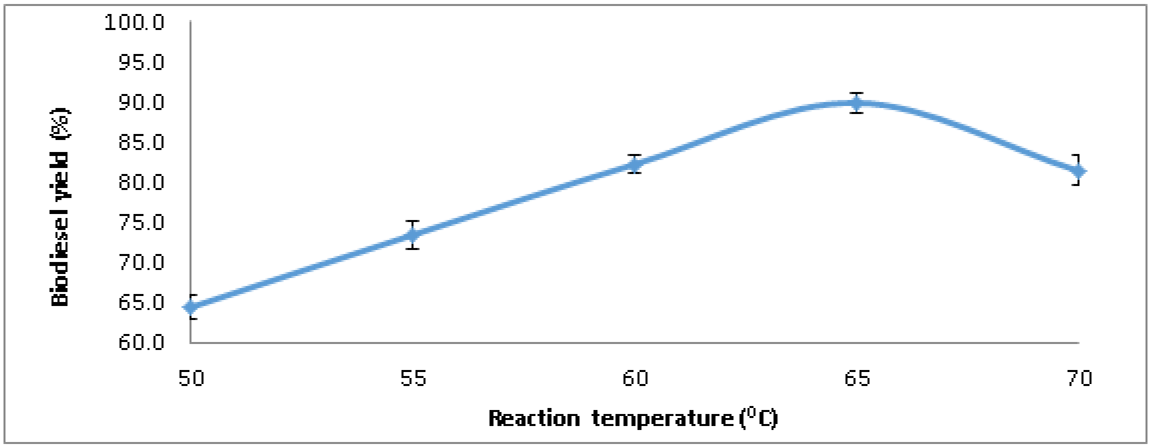


Figure 4.1: Influence of reaction temperature on biodiesel yield while flow rate(1000mL/min), reaction time (90 min), molar ratio (6:1) and catalyst concentration (3 g/L) were kept constant.

Therefore, the reaction at 65 ^{o}C is most appropriate. In summary, these results were in line with existing literature and affirmed a fundamental theory where higher reaction temperature favors higher biodiesel production (Baroutian *et al*., 2011).

The mean values of data were plotted in Figure 4.1, together with the standard error (standard deviation of the mean) in the form of error bars. The calculated standard errors for each ratio showed very small error and ranged between ±0.06 and ±0.20. Temperature of 70 ^{o}C showed the highest standard error of ±0.20 while temperature of 60 ^{o}C showed the lowest standard error of ±0.06. This small deviation indicates a high confidence of the mean values being close to the true value and therefore repeatability of the experiments is justified.

4.2.1.2 Effect of Reaction Time

The effect of reaction time on the production of biodiesel was investigated, results showed that time has a great effect on the process. This was considered as one of the key parameters, as incomplete reaction resulted in biodiesel yield with more contaminants (Mono and Diglycerides). A rule of thumb allowing the reaction to stay for not less than 60 minutes was used as a basis, to ensure quality biodiesel for the entire trial. This effect was studied ranging from 60 to 180 minutes using the same standard procedure (Baroutian *et al*., 2011). As shown in Figure 4.2, due to the heterogeneous reaction nature, there was no significant yield in the first 30 minutes of the reaction. The rate of conversion was slow in the first 60 minutes, however, the conversion increased rapidly as the time increased and the conversion reached a maximum of 93 % at a reaction time of 150 minutes. Increasing the time to 180 minutes shows no improvement in the conversion rate and the reduction in the yield was due to high emulsion of the mixture in the reacting. By comparison, Gajendra *et al*. (2011) reported a similar conversion of biodiesel at the same experimental condition.

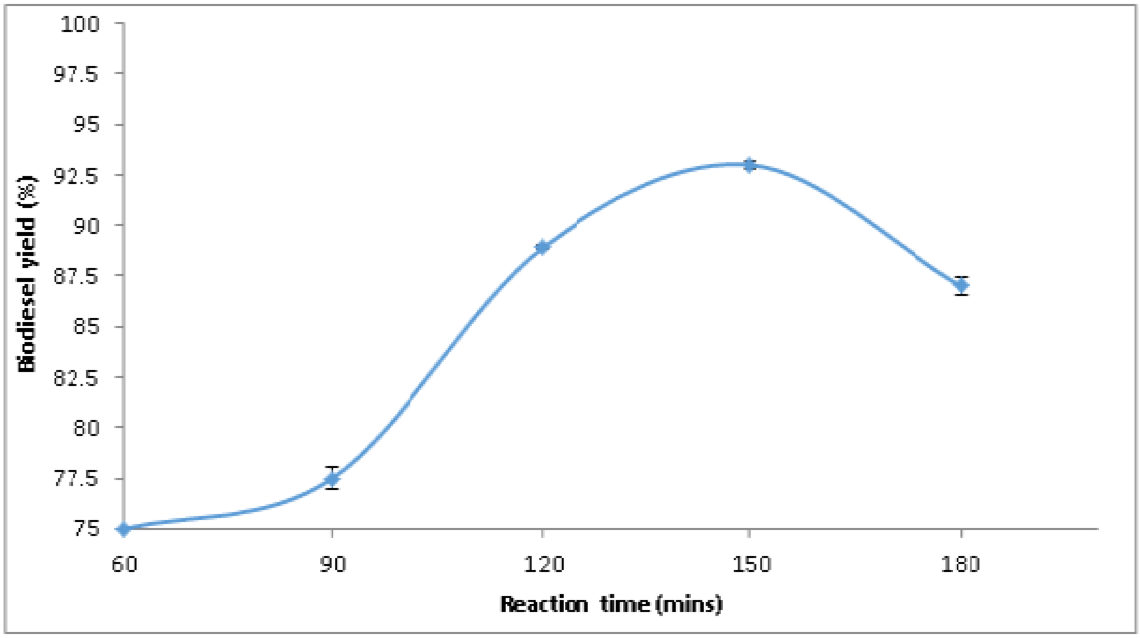


Figure 4.2: Influence of reaction time on biodiesel yield while flow rate (1000 mL/min), temperature (65 °C), molar ratio (6:1) and catalyst concentration (3 g/L) were kept constant

The mean values for the pair of data were plotted in Figure 4.2, together with the standard error (standard deviation of the mean) in the form of error bars. The calculated standard errors for each ratio showed very small error and ranged between ±0.06 and ±0.25. Reaction time of 90 minutes showed the highest standard error of ±0.25. This small deviation indicates a high confidence of the mean values being close to the true value and therefore repeatability of the experiments is justified.

4.2.1.3 Effect of Molar ratio of alcohol to oil

The molar ratio of methanol to oil ratio is one of the most significant variables that influence biodiesel yield. Based on stoichiometric ratio, transesterification process of triglyceride requires 3 moles of methanol and 1 mole of oil to yield three moles of fatty acid methyl ester and 1 mole of glycerol. However, because of the reversible nature of the reaction, an excess of the methanol is required to shift the equilibrium towards the product side. This behavior is based on the principles of thermodynamic equilibrium described by Le Chatelier principles.

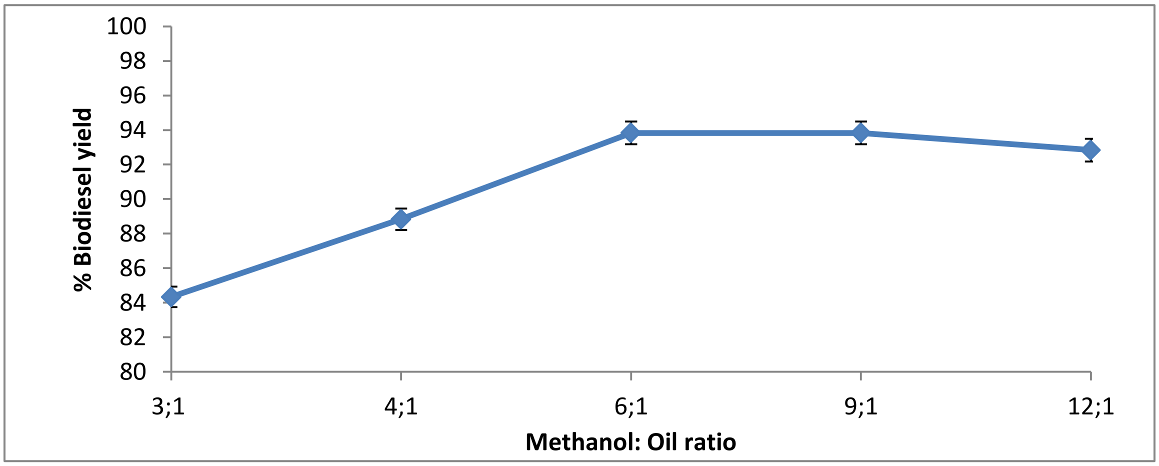


Figure 4.3: Influence of methanol: oil ratio on the production of Biodiesel while flow rate (1000 mL/min), reaction time (90 min), temperature (65 ^{O}C) and catalyst concentration (3 g/L) were kept constant.

As shown in Figure 4.3, a yield of 94% was attained at a methanol to oil ratio of 9:1. This indicates that there were more molecules of methanol in the reaction medium available to take part in the conversion, Dantas *et al*., (2011) also recorded similar result. However, there was a slight decline in FAME yield as the methanol to oil ratio increased to 12:1 and this might be due to the inhibiting oversaturation of methanol in the medium.

The mean values for the pair of data were plotted in Figure 4.3, together with the standard error (standard deviation of the mean) in the form of error bars. For this set of data, the result of the calculated standard error for each ratio was also small and ranged between ±0.07 and ±0.12. Molar ratios of 6:1 showed the highest standard error of ±0.12. This deviation is small and indicates a high confidence of the mean values being close to the true value.

4.2.1.4 Effect of Flow rate

Figure 4.4 shows the effect of flow rate on the biodiesel yield. The flow rate of oil and methanol mixture was varied from 900 mL to 1100 mL and an average of 85.7 % yield was obtained. It is possible to assume that increasing the flow rate has a positive effect on increasing biodiesel yield.

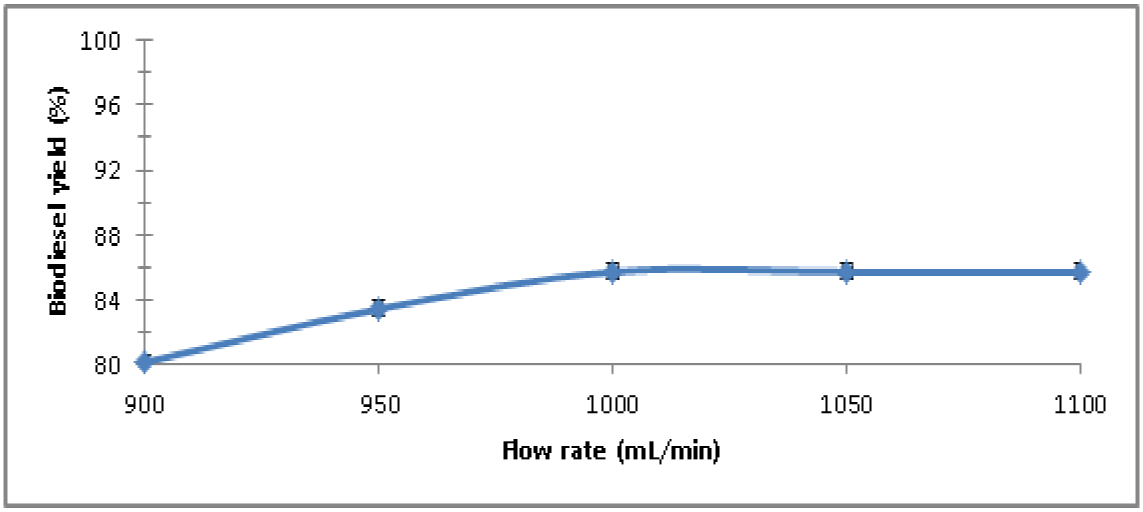


Figure 4.4: Influence of flow rate on biodiesel yield while molar ratio (6:1), reaction time (90 min), temperature (65 ^{0}C) and catalyst concentration (3 g/L) were kept constant

The mean values for the pair of data are plotted in figure 4.4, together with the standard error (standard deviation of the mean) in the form of error bars. The calculated standard errors for each ratio showed very small error and ranged between ±0.02 and ±0.17. This deviation is little and indicates a high confidence of the mean values being close to the true value.

4.2.1.5 Effect of Catalyst concentration

The concentration of catalyst plays an active part in the chemical process of biodiesel yield. Figure 4.5, shows that biodiesel yield increases with the increase in catalyst concentration from 0.5 g/L to 3 g/L. However, biodiesel yield decreased as the catalyst concentration further increased. This reduction in the biodiesel yield is due to soap formation in the presence of high amount of catalyst. In addition, this excess amount of catalyst increases the viscosity of reactants which also results in lowering the biodiesel yield. The transesterification is catalyzed by the basic sites generated on the surface of CaO/AC. The optimum catalyst concentration was determined to be 3 g/L of CaO catalyst with a biodiesel yield of 90.7%. Baroutian *et al*. (2011) also reported a similar result while using a solid supported catalyst (KOH/AC) to produce biodiesel.

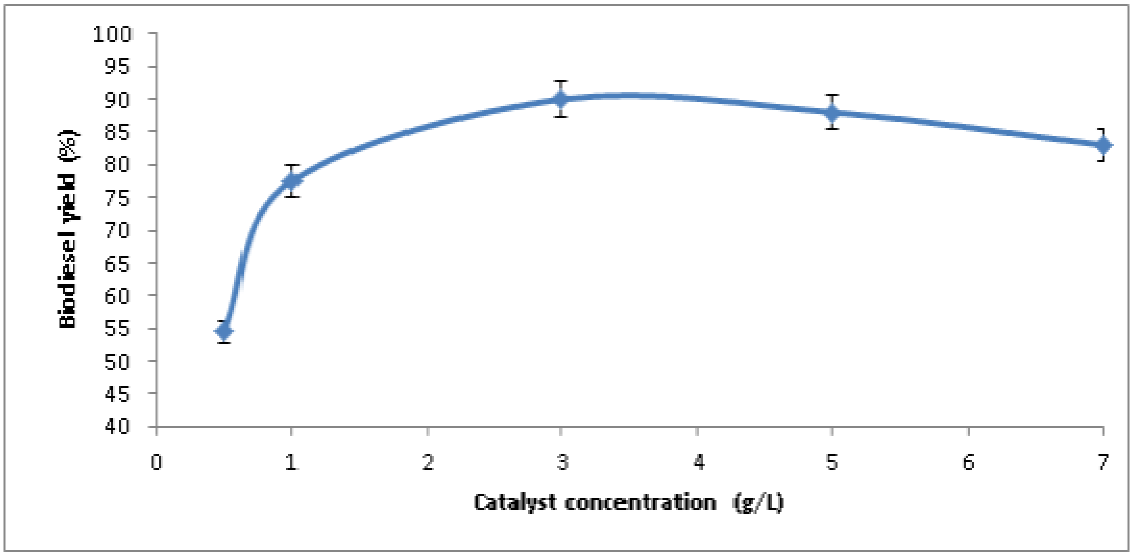


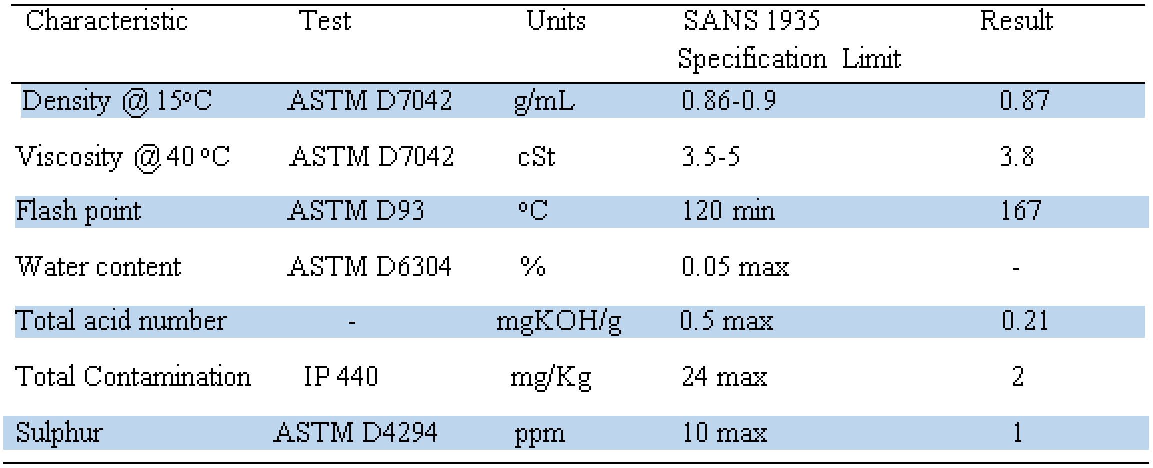
Figure 4.5: Influence of reaction time on biodiesel yield while flow rate (1000 mL/min), temperature (65 °C), molar ratio (6:1) and reaction time (90 mins) were kept constant

The mean values for the pair of data are plotted in Figure 4.5, together with the standard error (standard deviation of the mean) in the form of error bars. The calculated standard errors for each ratio showed very small error and ranged between ±0.03 and ±0.19. Catalyst concentration of 5 and 7 g/L showed the highest standard error of ±0.19. This minute deviation indicates a high confidence of the mean values being close to the true value and therefore justified the repeatability of the experiments.

4.3 CHARACTERIZATION OF THE BIODIESEL PRODUCED

The physical and chemical properties of the produced biodiesel were measured according to the test methods recommended by the American Society for testing and Materials (ASTM) and South African National Standard (SANS) as follows; viscosity at 40 ^{0}C, water content, density at 15 ^{0}C, total acid number, total contamination, Sulphur and flash point. The results of these characterizations are listed in Table 4.1.

Table 4.1: Characteristics of biodiesel produced from soybean oil in a membrane reactor



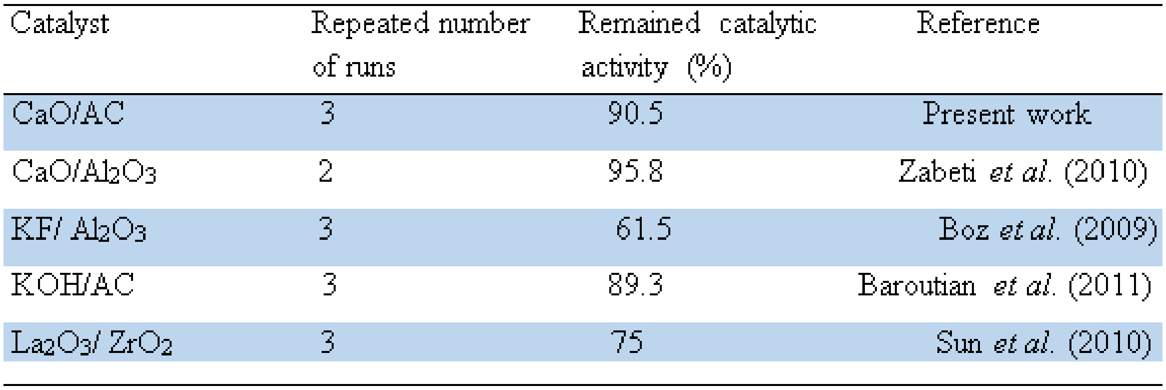
Characteristic	Test	Units	SANS 1935 Specification Limit	Result
Density @ 15°C	ASTM D7042	g/mL	0.86-0.9	0.87
Viscosity @ 40 °C	ASTM D7042	cSt	3.5-5	3.8
Flash point	ASTM D93	°C	120 min	167
Water content	ASTM D6304	%	0.05 max	-
Total acid number	-	mgKOH/g	0.5 max	0.21
Total Contamination	IP 440	mg/Kg	24 max	2
Sulphur	ASTM D4294	ppm	10 max	1

The results show that the biodiesel produced using membrane technology is within SANS 1935 standard specifications and American Society for testing and Materials (ASTM) biodiesel specification. Biodiesel properties are numerous, but the most important ones are those that have direct impact on the performance of the engine such as, viscosity because of its effect on the atomization of the fuel being injected into the engine combustion compartment, flash point which is much higher than diesel, density which is lesser than water and so on. All these properties help to increase the lifespan of the engine, give a better lubrication and complete combustion so that the engine can produce a higher energy output.

4.4 CATALYST REUTILIZATION

Reutilization of the CaO/AC catalyst in the transesterification of triglyceride under the optimal range conditions in the packed bed reactor was investigated. After each cycle, the used catalyst was taken out from the reactor and dried for reuse. The catalytic activity remains 90.5% of the fresh catalyst when the activated carbon supported catalyst was employed for the third time. It was calculated based on the conversion of oil to biodiesel under the optimum range. The decay in catalyst activity could be due to the leaching of active sites to the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of Ca^+ and CH_30^-. As shown in table 4.2, this value is within the range reported by other researchers (Zabeti *et al*. 2010, Baroutian *et al*. 2011).

Table 4.2: Comparison between catalyst supports



Catalyst	Repeated number of runs	Remained catalytic activity (%)	Reference
CaO/AC	3	90.5	Present work
CaO/Al_2O_3	2	95.8	Zabeti *et al.* (2010)
KF/ Al_2O_3	3	61.5	Boz *et al.* (2009)
KOH/AC	3	89.3	Baroutian *et al.* (2011)
La_2O_3/ ZrO_2	3	75	Sun *et al.* (2010)

4.5 SUMMARY

The experimental setup for this project was completely done and the membrane reactor exhibited a good performance in transesterification of high quality of biodiesel yield, and does not require any additional purification process. The effects of parameters including temperature, reaction time, catalyst concentration and flow rate were found significant. The optimum yield were between 90% - 94% within a reaction time of 60 – 180 minutes, methanol to oil ratio were 3:1 - 9:1 and temperature range were 60 ^{0}C - 70 ^{0}C. This yield is in line with what was recorded in the experiment conducted by Baroutian *et al.*, (2011). The characteristics of the product under these conditions were within the ASTM standard. However, further investigation still need to be carried out to establish the optimum yield for biodiesel within the optimum range of significant variables. The design of experiment proved to be a rational means to investigate the effect of independent variables and of their interactions on vegetable oils conversion for biodiesel production by heterogeneous catalytic transesterification. Response surface methodology is particularly convenient, allowing the determination of optimum set of experimental conditions, which minimize or maximize the response, as well as the changes in response surface produced by variation of independent variables and their mutual interactions.

CHAPTER 5: STATISTICAL ANALYSIS OPTIMISATION STUDIES USING RESPONSE SURFACE METHODOLOGY

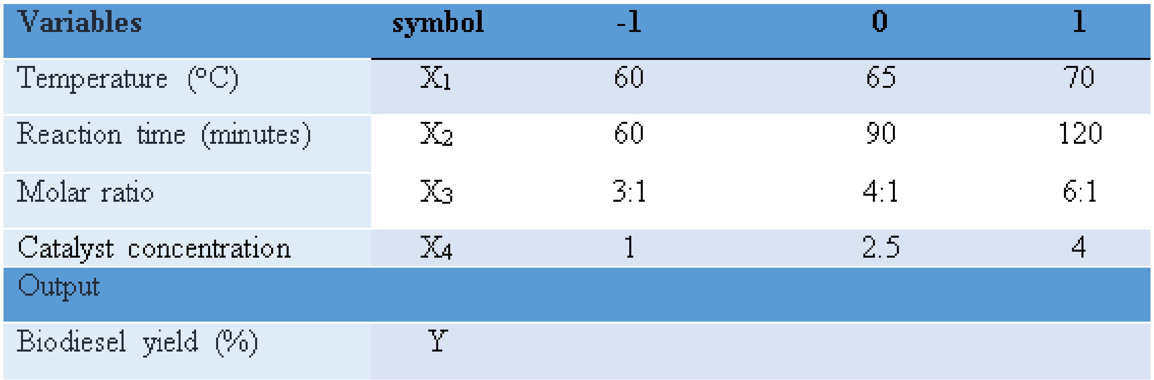
5.1 GENERAL INTRODUCTION

This chapter presents the application of CCD to optimize the biodiesel production in a packed bed membrane reactor. The laboratory experiments conducted according to the CCD matrix generated, Design Expert Software 10.0 was used to find optimum values for the independent variables in order to provide maximum output of the product.

5.2 DESIGN EVALUATION

The CCD was used to generate the experimental matrix and the model equations for the optimization of the biodiesel production. Four manipulated variables were varied at three levels: a high level, represented as (+1), a low level represented as (-1) a middle point (0). These four independent variables were represented as X_1, X_2, X_3 and X_4 with one output or dependent variable, which was biodiesel yield (Y) as illustrated in Table 5.1. The manipulated variables were selected based on their significance in the preliminary experiments.

Table 5.1: Manipulated variables, their CCD levels, and the output



Variables	**symbol**	**-1**	**0**	**1**
Temperature (°C)	X_1	60	65	70
Reaction time (minutes)	X_2	60	90	120
Molar ratio	X_3	3:1	4:1	6:1
Catalyst concentration	X_4	1	2.5	4
Output				
Biodiesel yield (%)	Y			

The experiments were conducted in a random order instead of the standard order to eliminate biases during the trials, and the analyses of the data were done at standard CCD run order as seen in Table 5.2 using the Design expert software.

Table 5.2: Experimental matrix results

Standard runs	Randomized runs	Coded factors				Response Y
		X_1	X_2	X_3	X_4	
1	**29**	-1	-1	-1	-1	62
2	**5**	1	-1	-1	-1	90
3	**14**	-1	1	-1	-1	60
4	**12**	-1	1	-1	-1	75
5	**13**	-1	-1	1	-1	49
6	**2**	1	-1	1	-1	66
7	**18**	-1	1	1	-1	55
8	**8**	1	1	1	-1	79
9	**24**	-1	-1	-1	1	84
10	**27**	1	-1	-1	1	92
11	**17**	-1	1	-1	1	89
12	**11**	1	1	-1	1	95
13	**6**	-1	-1	1	1	50
14	**10**	1	-1	1	1	60
15	**30**	-1	1	1	1	78
16	**3**	1	1	1	1	74
17	**25**	-2	0	0	0	50
18	**22**	2	0	0	0	60
19	**4**	0	-2	0	0	78
20	**15**	0	2	0	0	95
21	**23**	0	0	-2	0	65
22	**21**	0	0	2	0	48
23	**1**	0	0	0	-2	62
24	**9**	0	0	0	2	94
25	**20**	0	0	0	0	93
26	**7**	0	0	0	0	94
27	**26**	0	0	0	0	92
28	**28**	0	0	0	0	95
29	**19**	0	0	0	0	93
30	**16**	0	0	0	0	96

The quadratic equation model was selected for this experimental work. Before the analyses of the responses were carried out, the design model was evaluated to ensure that it is the right one for this experiment. The evaluation of a design was explained in detail in Chapter 2.

Table 5.3: The design model evaluation.

Factor	SE	VIF	Ri^2
A-Temperature	0.20	1.00	0.0000
B-Reaction time	0.20	1.00	0.0000
C-Molar ratio	0.20	1.00	0.0000
D-Catalyst amount	0.20	1.00	0.0000
AB	0.25	1.00	0.0000
AC	0.25	1.00	0.0000
AD	0.25	1.00	0.0000
BC	0.25	1.00	0.0000
BD	0.25	1.00	0.0000
CD	0.25	1.00	0.0000
A^2	0.19	1.05	0.0476
B^2	0.19	1.05	0.0476
C^2	0.19	1.05	0.0476
D^2	0.19	1.05	0.0476

The results in Table 5.3 showed that the model selected is suitable for the experimental data. The values of the variance inflation factor (VIF) for the entire model terms can be rounded up to 1. VIF measure the amount of multicollinearity in a set of multiple regression variables. The values of the VIF and Ri^2 indicate that all the factors in this model are independent of each other. The SE is the same for all the factors of the same category, which also showed that the model is suitable.

5.3 ANALYSIS USING THE CENTRAL COMPOSITE DESIGN

The ANOVA for Response Surface Quadratic model is shown in Table 5.4. The results show a large F-value of 24.05 and a P-value less than 0.05 indicating that the model was significant. The most significant model terms were indicated by F-values and P-values <0.05. The ANOVA table (table 5.4) showed that the four parameters of temperature, reaction time, molar ratio, catalyst amount and also interaction of temperature-catalyst amount, reaction time-molar ratio, reaction time-catalyst amount, molar ratio catalyst amount and quadratic terms of temperature, molar ratio, catalyst amount were significant based on the P-value smaller than 0.05. Due to the high P-values (more than 0.05), the interactions of temperature-reaction time, temperature-molar ratio and reaction time-catalyst amount and also quadratic terms of reaction time were found to be insignificant, and made removal of these terms very tempting. However, because removing these terms would reduce the lack of fit P-value below minimum desirable insignificant lack of fit of 0.1, they were untouched.

Table 5.4: ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	8183.89	14	584.56	24.05	< 0.0001	significant
X_1: A-Temperature	*2412.32*	*1*	*2412.32*	*99.26*	*<0.0001*	
X_2: B-Reaction time	*1199.92*	*1*	*1199.92*	*49.37*	*<0.0001*	
X_3: C-Molar ratio	*310.32*	*1*	*310.32*	*12.77*	*0.0028*	
X_4: D-Catalyst concentration	*933.75*	*1*	*933.75*	*38.42*	*< 0.0001*	
X_1X_2: AB	*31.08*	*1*	*31.08*	*1.28*	*0.2759*	
X_1X_3: AC	*6.63*	*1*	*6.63*	*0.27*	*0.6091*	
X_1X_4: AD	*253.61*	*1*	*253.61*	*10.44*	*0.0056*	
X_2X_3: BC	*303.63*	*1*	*303.63*	*12.49*	*0.0030*	
X_2X_4: BD	*145.81*	*1*	*145.81*	*6.00*	*0.0271*	
X_3X_4: CD	*222.76*	*1*	*222.76*	*9.17*	*0.0085*	
X_1^2: A^2	*2223.26*	*1*	*2223.26*	*91.48*	*< 0.0001*	
X_2^2: B^2	*61.97*	*1*	*61.97*	*2.55*	*0.1311*	
X_3^2: C^2	*643.77*	*1*	*643.77*	*26.49*	*0.0001*	
X_4^2: D^2	*361.05*	*1*	*361.05*	*14.86*	*0.0016*	
Residual	364.54	15	24.30			
Lack of Fit	*360.66*	*10*	*36.07*	*46.54*	*0.1533*	*Not significant*
Pure Error	*3.88*	*5*	*0.78*			
Cor Total	8548.43	29				

The term X_1 has the highest F-value and one of the lowest p>F value, meaning that the temperature has the largest effect on the biodiesel yield. It can also be seen that there is 15.33% chance that the LOF is due to noise which is an insignificant value, as LOF values greater than 0.05 (5%) are insignificant, showing that the model can fit any data.

The model equation for this response is expressed as:

$$Y = 94.75 + 5.18X_1 + 3.60X_2 - 7.07X_3 + 4.24X_4 + 1.39X_1X_2 - 0.64X_1X_3 - 3.98X_1X_4 + 4.36X_2X_3 + 3.02X_2X_4 - 3.73X_3X_4 - 9.38X_1^2 - 1.50X_2^2 - 9.00X_3^2 - 3.63X_4^2 \quad \text{(Equation 5.1)}$$

The data in Table 5.4 is not the only way to identify significant factors. The coefficients in the model equations also indicate the significant variables. The quadratic model used in calculating the conversion indicated that single parameters such as temperature, reaction time and catalyst amount had positive significant effect on the conversion of oil to biodiesel. Therefore, from Table 5.4 and Equation 5.1 it can be seen that the linear term of temperature (X_1) has the most significant impact among the single parameters. The fact that the coefficient for X_1 in Eq. 5.1 carries a positive sign shows that the increase in temperature increases the conversion of biodiesel.

It can also be seen that X_2X_3 is the most significant interaction term. This indicates that the biodiesel yield is positively influenced by the combination of the variation in both reaction time and molar ratio. The combination of variables X_1X_2 and X_2X_4 in this equation means that the biodiesel yield is boosted by the interaction between the reaction time-temperature and reaction time-catalyst amount. It is observed that the biodiesel yield is negatively affected by the interaction between temperature and the catalyst amount, even though these two factors individually increase the biodiesel conversion. The negative sign of the term X_1X_4 means that at higher temperature, methanol tends to leave the reaction medium due to the reaction temperature exceeding the boiling point of methanol, thus, biodiesel yield is reduced (Baroutian *et al.*, 2011).

The quadratic terms indicate the presence of curvatures. The negative signs in Eq. 5.1 reveal that the quadratic curves for X_1^2, X_2^2, X_3^2 and X_4^2 are concave. This means that biodiesel conversion increases with an increase in temperature, reaction time, molar ratio and catalyst concentration up to a maximum value beyond which the yield decreases with further increase of the four variables.

The suitability of the model was validated by evaluating the R-squared presented in Table 5.5. A high R^2 value is desirable and a reasonable agreement between adjusted R^2 and predicted R^2 is crucial (Ghafari *et al.* 2009). The difference between adjusted R^2 and predicted R^2 is less than 0.2.

Table 5.5: The R-Squared Results.

Std. Dev.	**4.93**	**R-Squared**	**0.9574**
Mean	75.94	**Adj R-Squared**	0.9176
C.V. %	6.49	**Pred R-Squared**	0.8861
PRESS	2083.00	**Adeq Precision**	14.726
-2 Log Likelihood	160.06	**BIC**	221.08
		AICc	224.34

Adequate precision (AP) is defined as a measure of the experimental signal to noise ratio (Anderson and Whitcomb 2005); an AP that exceeds 4 usually indicates that the model will give reasonable performance in prediction. The “Adeq Precision” for this study was 14.726. Therefore, the model was suitable to be used to navigate the design space.

Model validation is a very important step in model building sequence. Often the validation of a model seems to consist of nothing more than quoting the R^2 statistics from the fit (which measures the fraction of the total variability in the response that is accounted for by the model). However, there are other diagnostic tools for model validation such as predicted vs actual plot and residual analysis. These tools are based on graphical analysis. Graphical methods have an advantage over numerical methods for model validation because they readily illustrate a broad range of complex aspects of the relationship between the model and the data. Numerical methods for model validation tend to be narrowly focused on a particular aspect of the relationship between the model and the data and often try to compress the information into a single descriptive number or test result.

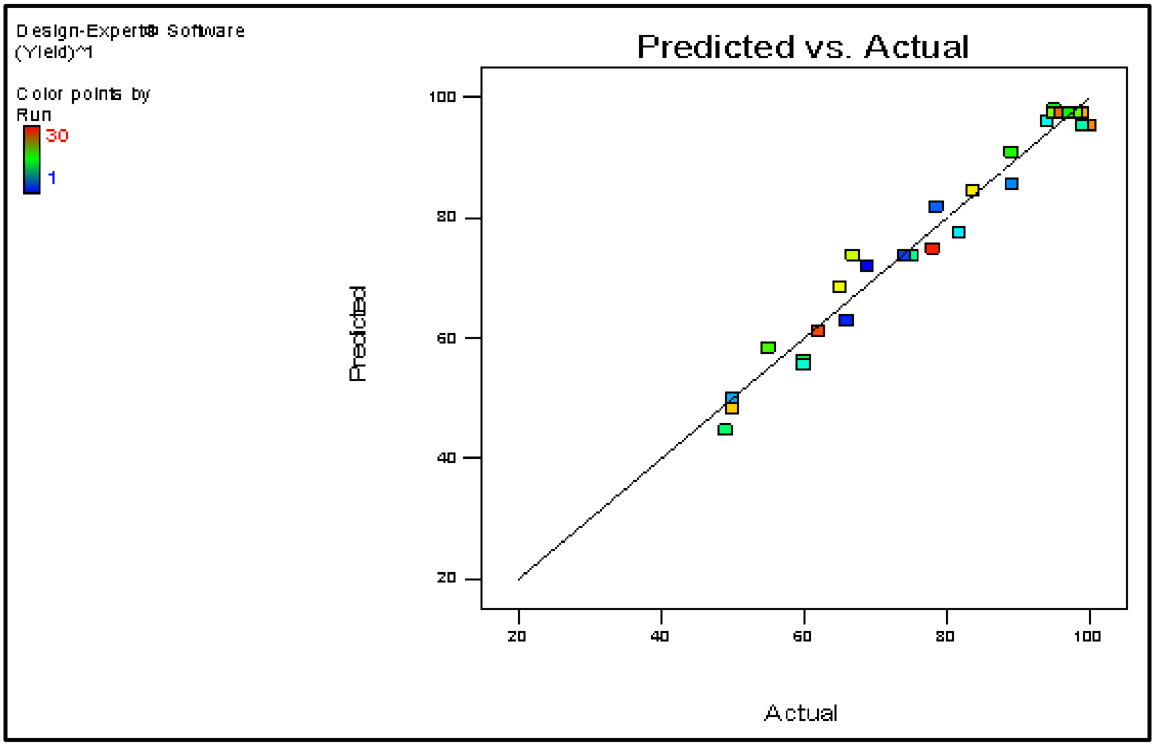


Figure 5.1: The biodiesel conversion predicted from model versus measured response.

The Actual by Predicted plot provides a visual assessment of model fit that reflects variation due to random effects. It plots the actual values against the predicted values. In Figure 5.1, the actual values versus the predicted values for conversion of the soya bean oil to biodiesel in the packed bed membrane reactor were plotted. The values were close to the 45-degree line and this indicates a strong correlation between the model's predictions and its actual results.

Normal plot of residuals estimates the experimental error obtained by subtracting the actual responses from the predicted responses. The predicted response is calculated from the chosen model, after all the unknown model parameters have been estimated from the experimental data. Examining residuals is a key part of all statistical modelling because it provides useful information about how well the model fits the data.

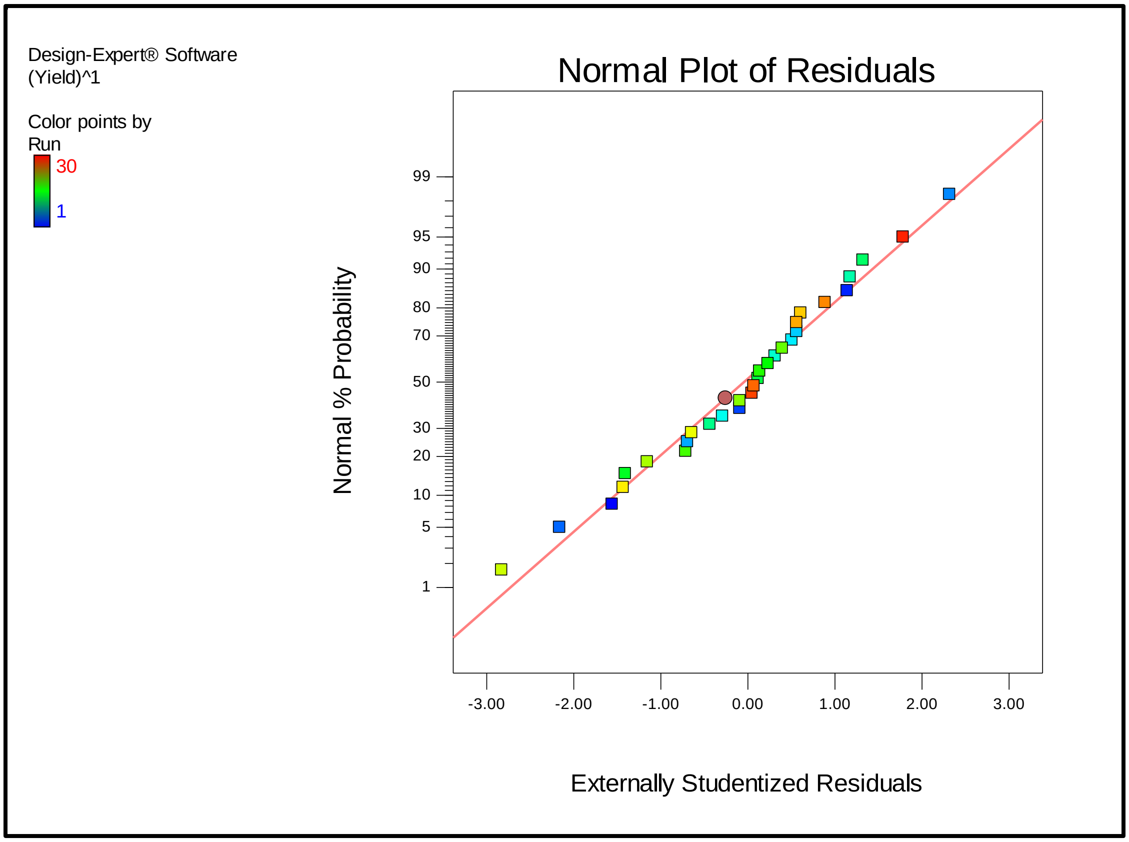


Figure 5.2: Normal plot of residuals.

In general, the residuals should be randomly distributed with no obvious patterns and unusual values. The normal plot (Fig. 5.2) shows that the set of data used for this experiment is normally distributed because the pattern approximates a straight line and there are no outliers. This implies that the model fits the experimental data.

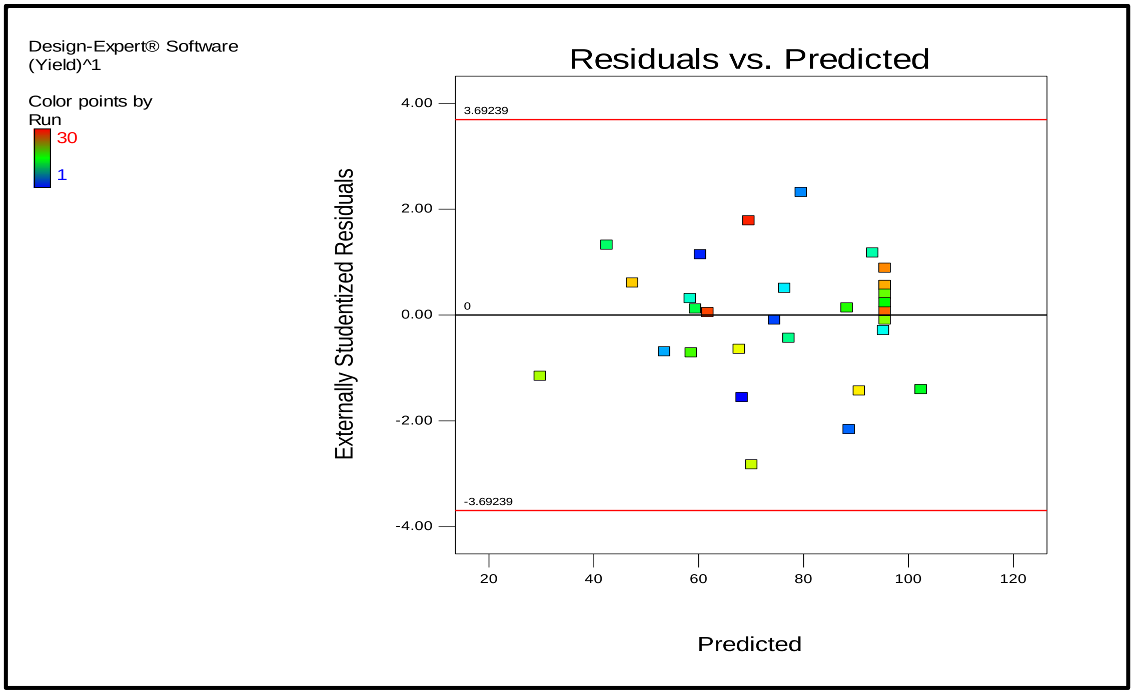


Figure 5.3: Residuals vs predicted values.

From Figure 5.3, it can be seen that the data points are scattered randomly without forming a pattern and this validates the assumption that the residuals are constant.

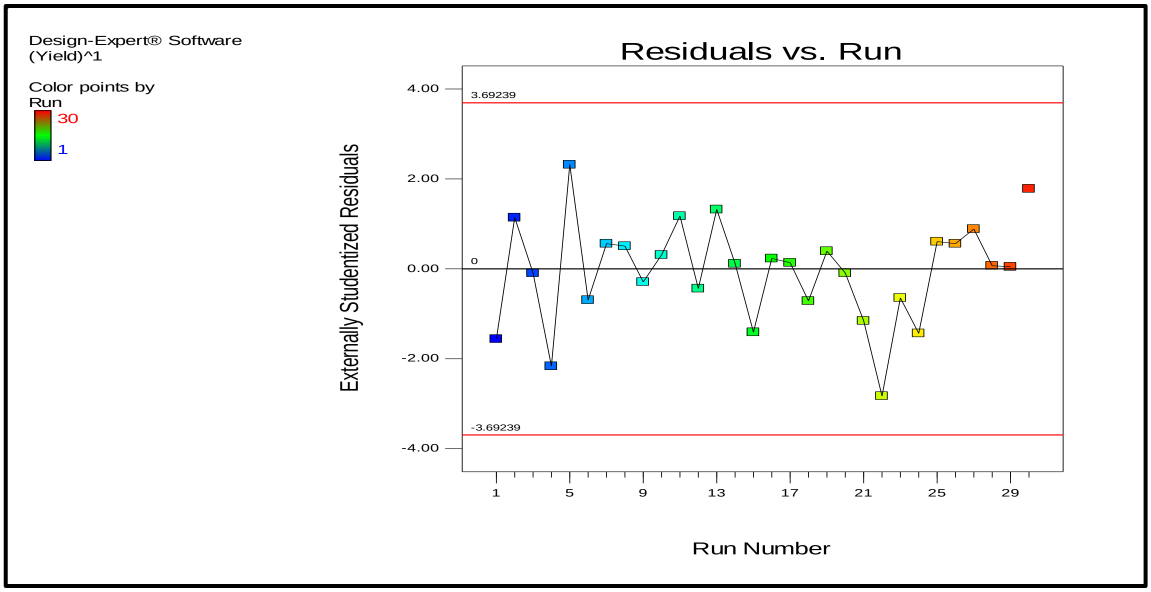


Figure 5.4: Residuals vs run number

The use of the residuals versus run plot is used to verify the assumption that the residuals are independent from one another. In Figure 5.4, independent residuals show no trends or patterns when displayed in run order and the points are randomly around the centerline therefore, validating the independence of the residual.

5.4. EFFECTS OF PROCESS PARAMETERS

The quadratic model (Eq. 5.1) to calculate conversion indicates that temperature, reaction time and catalyst amount have positive effects on the conversion of the soya bean oil to biodiesel in the packed bed membrane reactor. The 3D response surface plots showing the effect of temperature, reaction time, molar ratio, catalyst concentration and their interactions on methyl ester yield are shown in Figs. 5.5 – 5.8. The response surface methodology was used to study the interaction between the independent variables and to determine the optimum level of each parameter for maximum response.

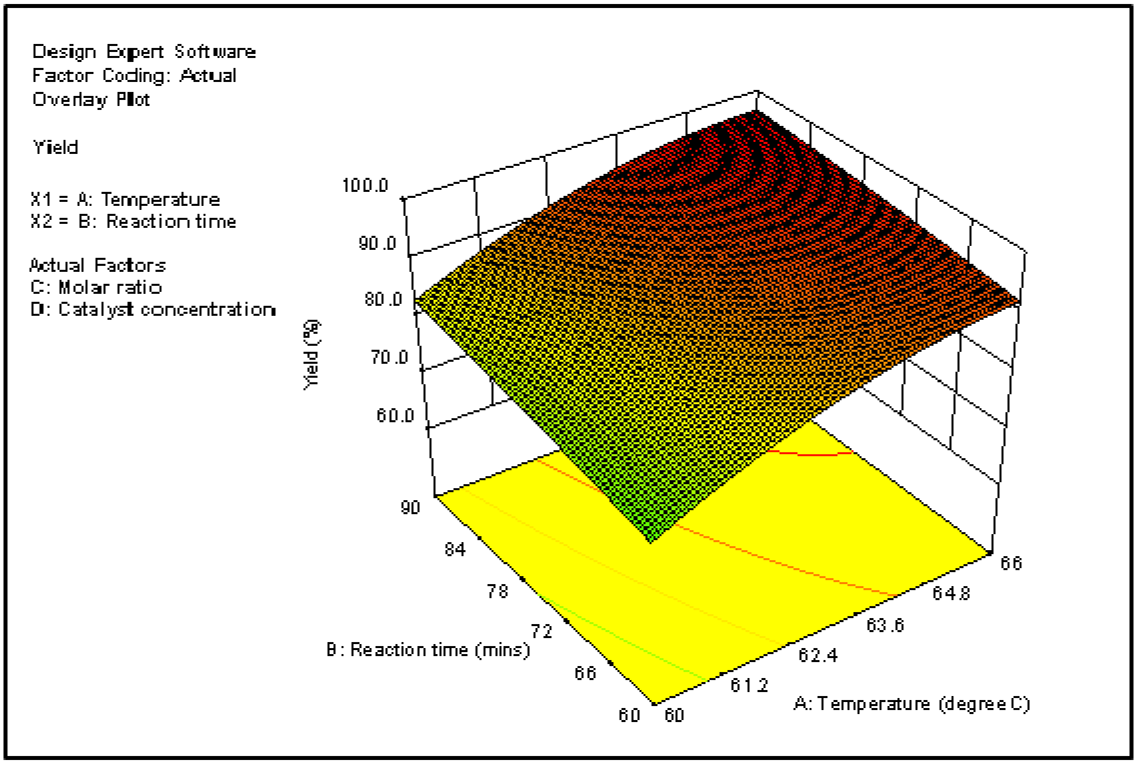


Figure 5.5: Response surface 3D plot of predicted biodiesel yields versus reaction time and temperature

Three-dimensional surface plot of the predicted soya bean oil conversion to biodiesel in the packed bed membrane reactor is shown in Figure 5.5. The figure demonstrates that conversion of oil to biodiesel increased as the reaction temperature and reaction time increased. This may be due to reduction of viscosity of the oil on increasing the temperature, which resulted in better mixing of oil with alcohol and faster separation of glycerol from biodiesel. This result is in agreement with those reported in the literature where higher reaction temperature and initial mixing of the immiscible reactants cause a higher production of biodiesel (Zabeti *et al.*, 2010 and Alamu *et al.*, 2007).

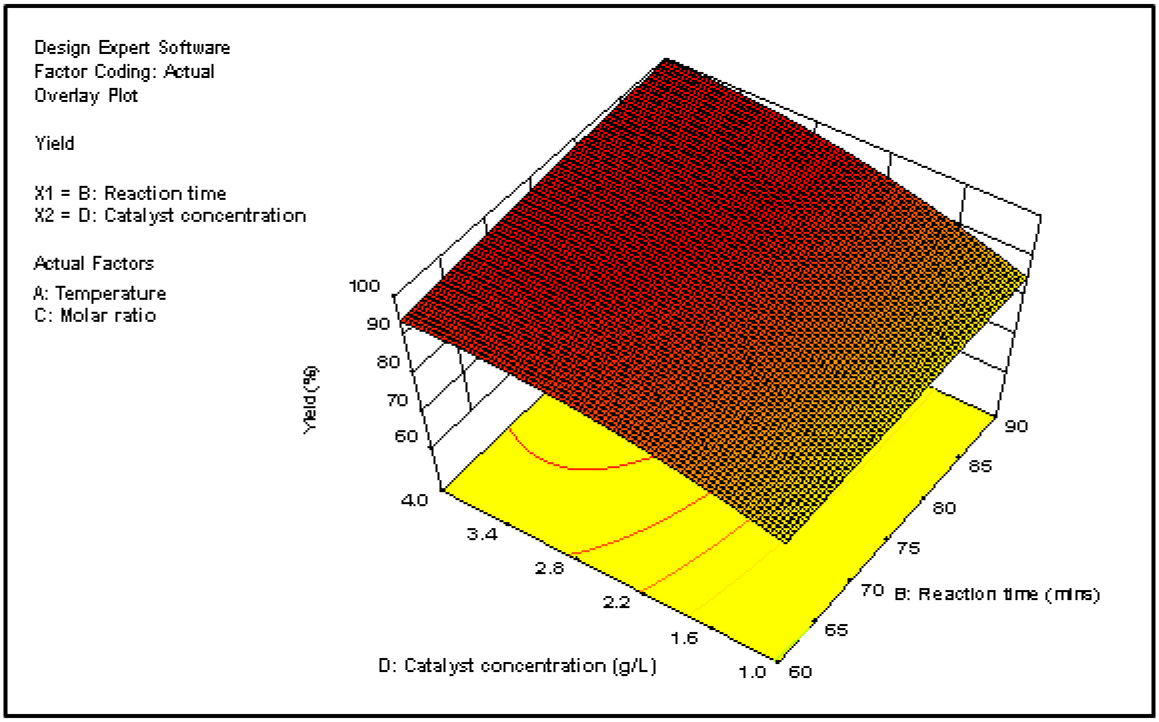


Figure 5.6: Response surface plot of predicted yields versus reaction time and catalyst concentration.

Figure 5.6 exhibits the effect of the catalyst concentration and reaction time. The FAME yield increased with increasing catalyst concentration and reaction time. Then, there was a slight decrease when the reaction period was too long due to the influence of the reversible reaction in transesterification (Samart *et al.*, 2009). The 3D response curve reveals that there is a significant interaction effect between the catalyst concentration and reaction time on the FAME yield.

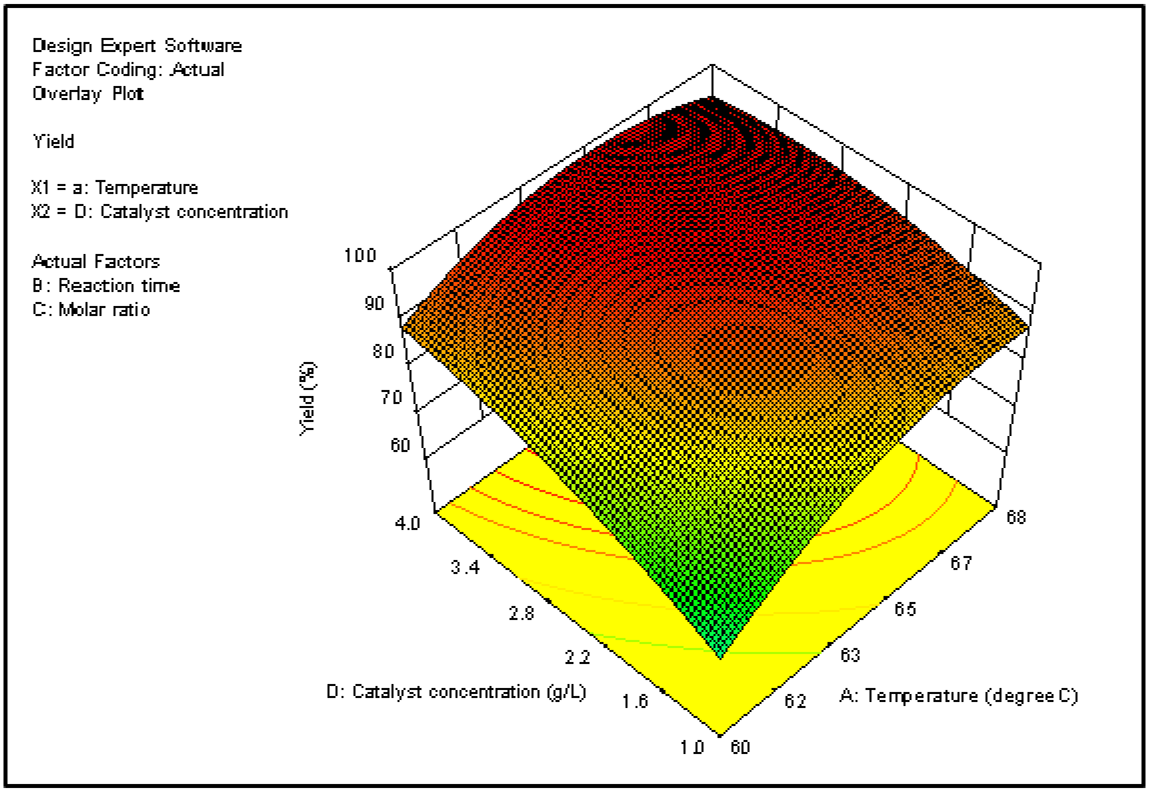


Figure 5.7: ***Response surface 3D plot of predicted biodiesel yields versus temperature and catalyst concentration***

Figure 5.7 shows the 3D response surface plot of predicted yield versus temperature and catalyst concentration. The figure demonstrates that conversion of feedstock to biodiesel increases as the reaction temperature and catalyst amount increases. However, at higher catalyst amount a reduction can be seen in the yield due to the catalyst concentration having a negative effect on the biodiesel produced. The decrease in yield at higher amounts of the catalyst can be attributed to the soap formation during the transesterification.

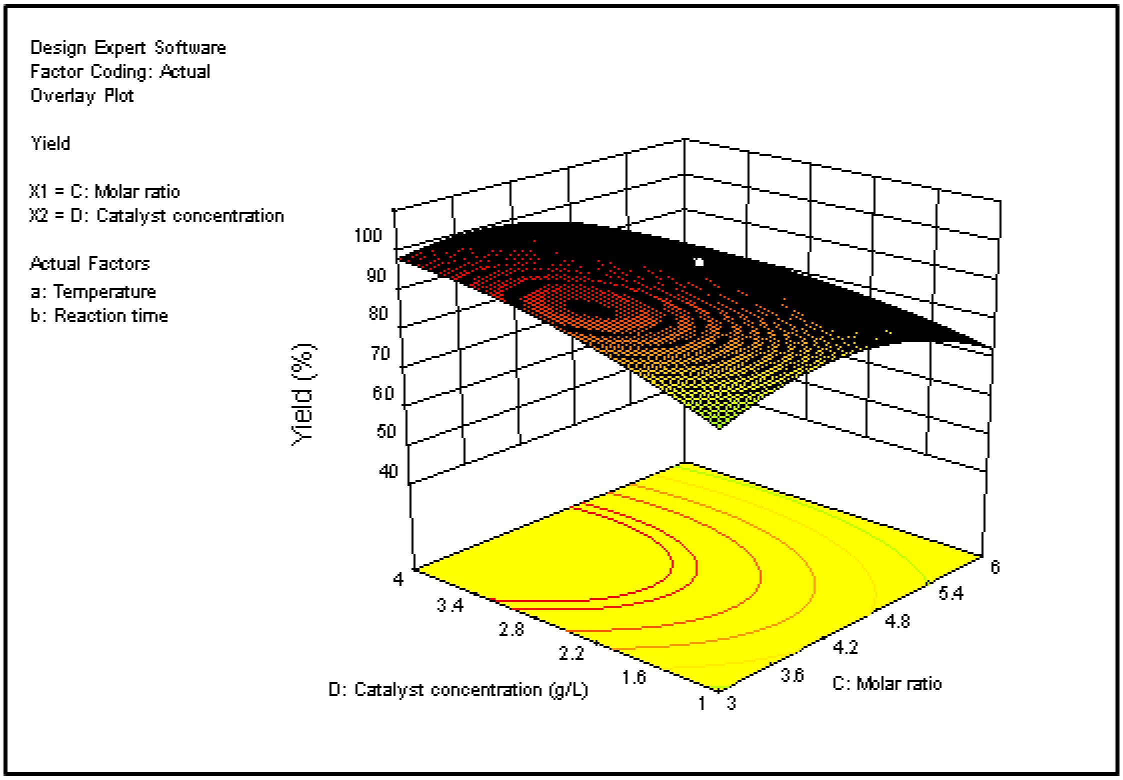


Figure 5.8: Response surface 3D plot of predicted biodiesel yields versus molar ratio and catalyst concentration

Figure 5.8 shows the 3D response surface plot of predicted yield versus molar ratio and catalyst concentration. The FAME yield increases slightly with the increasing methanol-to-oil molar ratio and catalyst concentration. Afterwards, the yield start to decrease as the molar ratio increases. In general, a high molar ratio results in a higher rate of methyl ester formation and ensures completion of the reaction. However, overloading of methanol would inactivate the catalyst and reversed the reaction since transesterification is a reversible reaction (Wan Omar and Saidina Amin, 2011).The 3D response curve under this condition indicates no significant interaction effect between methanol-to-oil molar ratio and catalyst concentration on the FAME yield.

5.5 OPTIMIZATION

The optimization process was done to find the values of the manipulated variables that would provide optimum biodiesel yield while taking into account all input parameters, by generating an overlay plot. The data on the overlay plot were computed using the generated model equation in order to find an optimum region for all variables.

The constraints shown in table 5.6 were defined to generate the optimum region using Design expert software:

(1) The target for the catalyst concentration was set to 3 g/L in order to avoid side reaction with the reactants, which could lead to soap formation.

(2) The temperature was set in range of 60 ^{o}C to 70 ^{o}C. This is because of the boiling point of methanol. Extending the temperature range above the maximum for this experiment will cause methanol to evaporate.

(3) The molar ratio was set in the range 3:1 to 6:1. Based on the stoichiometric ratio, 3 moles of methanol to 1 mole of oil is required to produce methyl ester. However, because of the reversible nature of the reaction, an excess of the methanol is needed to drive the reaction to product side.

(4) In industry, time is an important factor. The aim was to achieve maximum production of biodiesel in a short period. Therefore, range 60 minutes to 120 minutes was the selected reaction time for the optimization.

Based on the defined boundaries, optimization of the process was carried out.

Table 5.6: Numerical optimization results and constraints for the factors/response.

Parameter	**Goal**	**Experimental region**	
		Lower	Upper
Temperature (^{o}C)	In range	60	70
Reaction time (min)	In range	60	120
Catalyst concentration (g/L)	target	-	3
Molar ratio	In range	3:1	6:1
Yield (%)	Maximize		

The plot in Figure 5.9 identifies the optimum value for the response within the range of input parameters specified. The suggested optimum ester yield was 97.7% in 90 minutes at 65 ^{o}C, 3 g/L catalyst concentration and 4.5:1 molar ratio of alcohol to oil.

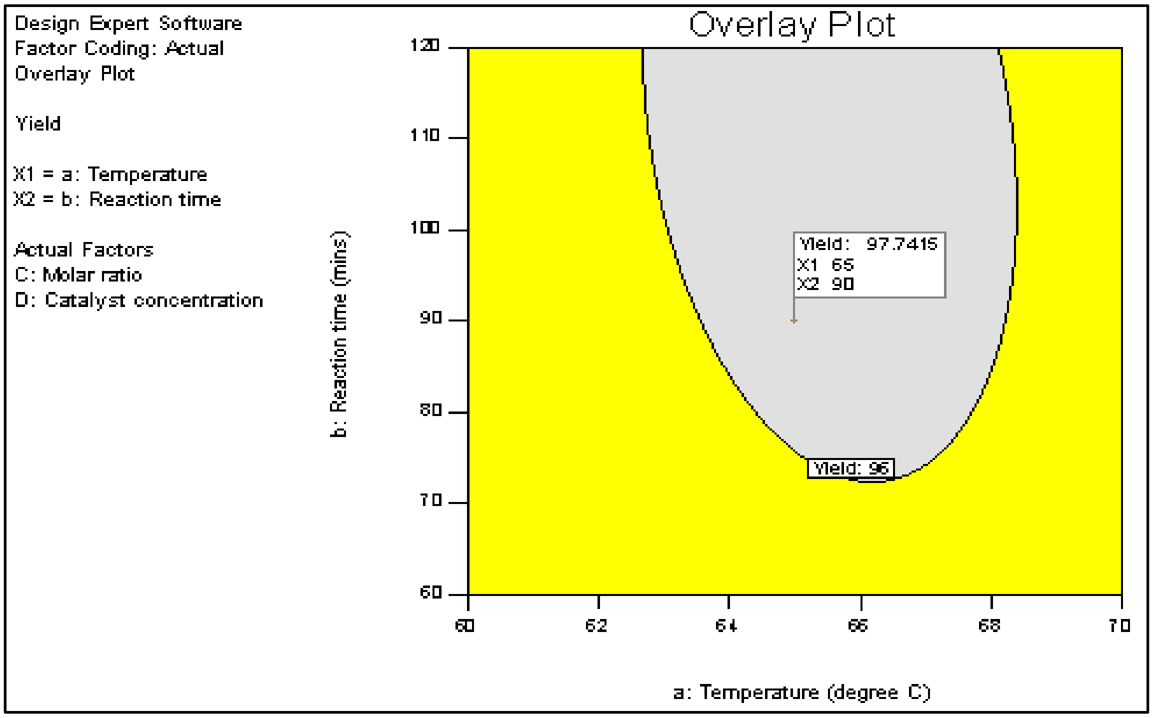


Figure 5.9: Overlay plot for the prediction of biodiesel production using membrane reactor

The results for the optimum values of the independent variables with the maximum yield are tabulated in Table 5.7 for Central Composite Design. These values were deduced from the overlay plot.

Table 5.7: The result of optimum values.

Parameter	Units	Code	CCD Theoretical value
Yield	%	Y	97.7
Temperature	^oC	X_1	65
Reaction time	min	X_2	90
Molar ratio		X_3	4.5:1
Catalyst concentration	g/L	X_4	3

5.6 VERIFICATION OF THE DESIGN MODELS

The validity of the predicted model was examined by performing verification experiment at these optimum synthesized conditions. The experiments conducted were repeated three times and the average yield is then presented in Table 5.8 alongside with the predicted model values.

Table 5.8: Verification of the design models

Parameter	Units	Code	CCD	
			Theoretical value	Experimental value
Yield	%	Y	97.7	96.9
Temperature	^oC	X_1	65	65
Reaction time	min	X_2	90	90
Molar ratio		X_3	4.5:1	4.5:1
Catalyst conc.	g/L	X_4	3	3

The predicted conversion value of 97.7% was approximately equal to the average observed value of 96.9%. Therefore, the experimental (obtained) value showed acceptable agreement with the predicted values. The errors values between the predicted and the observed results were less than 1% FAME conversion, indicating that the regression model was satisfactory.

5.7 SUMMARY

In this chapter, the Central Composite Design method was used to design the order of the experimental runs, in other to study interaction between variables and to statistically analyse the data obtained. This was done to find optimum conditions for the production of biodiesel in a packed bed membrane reactor.

The model equation and RSM graphs for the response were generated using experimental data. The model passed the evaluation test showing that it fit the experimental data and was significant. Based on the model equation, all the independent variables had positive influence on the yield. For each variable, the yield of biodiesel increased to a maximum point beyond which there was no significance in the yield.

The optimization process was carried out within the boundaries of optimum region of the independent variables using an overlay plot. Theoretical optimum values were generated with a maximum response and these data where verified by conducting further experiments using the theoretical optimum values.

CHAPTER 6: CONCLUSION AND RECOMMENDATIONS

The need for alternative energy sources across the world is increasing as nonrenewable resources are being depleted. For this reason, different renewable energy sources are being studied and investigated. Biodiesel produced by the transesterification of vegetable oils is gaining considerable importance as a renewable fuel.

Because biodiesel is still being produced using the conventional method, there are limitations that characterized this production method, such as water utilization for purification leading to waste water generation, separation and purification problems associated with homogenous catalysis. These challenges do not make biodiesel competitive to fossil fuel. Therefore, there is a need to research a robust, efficient systems and method to overcome the numerous problems associated with conventional method and make biodiesel more competitive.

The use of heterogeneous catalysis (calcium oxide) supported by activated carbon in a membrane reactor proved to be a remedy to the limitation of conventional method and ease the process of biodiesel production. This type of catalyst was chosen due to its low cost and availability. The activated carbon provided a good surface area to the catalyst and allowed proper contact between the oil and methanol.

The main aim of this study was to produce biodiesel from vegetable oils using heterogeneous catalysts in a ceramic membrane. The specific objectives of this work were: (1) To evaluate the performance of supported CaO used as heterogeneous catalyst in a membrane reactor for the production of biodiesel. (2) To evaluate the efficiency of the membrane in terms of selectivity. (3) To evaluate the influence of temperature, methanol/oil ratio, catalyst concentration and reaction time on biodiesel yield using an appropriate experimental design tool to establish the optimum conditions for biodiesel yield.

Preliminary experiments were carried out using the OFAT design in order to screen the parameters and identify the optimum ranges for the optimisation studies. CaO/AC heterogeneous catalyst was successfully used in the transesterification reaction of soya bean oil into FAME. The experimental results showed that CaO/AC had excellent activity and stability during transesterification. The catalyst was used three times, and no apparent activity loss was observed. Therefore, the use of CaO/AC as a solid catalyst is efficient and does not require additional separation process, thus eliminating the purification step.

Results from the preliminary experiments indicated that the effects of parameters including temperature, reaction time, molar ratio and catalyst concentration were significant. The optimum yield ranged between 90 % - 94 % within a reaction time of 60 – 180 minutes, methanol to oil ratio 3:1 - 9:1 and temperature range of 60 ^{o}C - 70 ^{o}C at 3 g/L of catalyst. This yield is in line with the result recorded in the experiment conducted by Baroutian *et al*., (2011). The important variables selected based on the results from the OFAT experiments were further investigated to establish the optimum yield for biodiesel within the optimum range of significant variables.

The ceramic membrane with the pore size of 0.02 μm was very suitable for this reaction and separation process due to its high flux and the good quality of the permeate. This new method of biodiesel production showed the advantage of no water usage in the process as compared to the conventional method, which required 8 litres of water to purify 1 litre of biodiesel. This leads to wastewater being generated and consequently creates a causal effect of polluting the environment. The water usage in the conventional method was quantified during an experiment conducted in laboratory. The characteristics of the product under these conditions were within the ASTM and SANS 1935 standards.

The Response surface methodology based on Central Composite design (CCD) was used to analyze the data and generate model equations for the response variables. The overlay plot provided the optimum region for the response based on the results computed from the model equation. The surface and contour plots were effectively used in determining the optimum factor combinations for the maximum yield. OFAT could not readily identify nor quantify the interaction between the factors. Furthermore, experimental verification carried out on the design also confirms the validity of the model.

Overall, it can be deduced that the membrane reactor served as a good medium for the production of biodiesel, because it does not require utilization of water in the process, thereby eliminating wastewater generation and reduction in production cost, and more importantly, it is an environmentally friendly process.

Further study need to be conducted on the fouling effects and stability of the membrane for the production of biodiesel.

REFERENCES

Agarwal, A.K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog Energy Combust Science,* 33 (3):233–271.

Ahmad, A.L., Mat, N.H., Yasin, C.J.C. and Derek, J.K. 2011. Lim Microalgae as a sustainable energy source for biodiesel production: a review. *Renewable Sustainable Energy Review*, 15 (1):584–593

ASTM standard D6751. Standard specification for biodiesel fuel (B100) blend stock for distillate fuels. ASTM, West Conshohocken, PA.

ASTM standard D975. Standard specification for diesel fuel oils. ASTM, West Conshohocken, PA.

ASTM Standard specification for biodiesel fuel (B100) blend stock for distillate fuels. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D6751-08; 2008a.

ASTM Standard specifications for diesel fuel oil, biodiesel blend (B6 to B20). In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D7467-08a; 2008b.

ASTM Standard specification for diesel fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D975-08a; 2008c.

ASTM Standard specification for fuel oils. In: Annual Book of ASTM Standards, ASTM International, West Conshohocken, Method D396-08b; 2008d.

Atabani, A., Silitonga, A., Badruddin, I.A., Mahlia, T., Masjuki, H. and Mekhilef, S. 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable Sustainable Energy Review*, 16: 2070-2093.

Atadashi, I.M., Aroua, M.K. and Abdul, A.A. 2011. Biodiesel separation and purification: a review. *Renewable Energy,* 36: 437–43.

Ataya, F., Dubé, M.A. and Ternan, M. 2006. Single-phase and two-phase base-catalysed transesterification of canola oil to fatty acid methyl esters at ambient conditions. *Industrial Engineering Chemical Resource*, 45:5411–7.

Azam, M.M., Waris, A. and Nahar, N.M. 2005. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass and Bioenergy*, 29(4):293–302.

Azócar L., Ciudad G., Heipieper H.J., Muñoz R. and Navia R. 2010. Improving fatty acid methyl ester production yield in a lipase-catalysed process using waste frying oils as feedstock. *Journal Bioscience Bioengineering,* 109:609–614.

Balat, M. 2011. Potential alternatives to edible oils for biodiesel production – a review of current work. *Energy Convers Manage,* 52 (2):1479–1492.

Balat, M. and Balat, H. 2010. Progress in biodiesel processing. *Applied Energy,* 87(6): 1815–1835.

Balat, M., and Balat, H. 2009. A critical review of biodiesel as a vehicular fuel. *Energy Convers. Manage*ment, 49:2727–2741.

Banković-Ilić, I.B., Stamenković, O.S. and Veljković, V.B. 2012. Biodiesel production from non-edible plant oils. *Renew Sustainable Energy Review,* 16(6):3621–47.

Barnard, T.M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M. and Wilhite, B.A. 2011. Continuous-flow preparation of biodiesel using microwave heating. *Energy Fuel*, 21:1777–81.

Baroutian, S., Aroua, M.K., Raman, A.A.A. and Sulaiman, N.M.N. 2011. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. *Bioresource Technology*, 102:1095–1102.

Behzadi, S. and Farid, M.M. 2009. Production of biodiesel using a continuous gas–liquid reactor. *Bioresource Technology,* 100:683–689.

Berchmans, H.J. and Hirata, S. 2008. Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresource Technololgy*; 99:1716–21.

Biodiesel. 2014 World Market Outlook and Forecast up to 2018, Merchant Research and Consulting, Ltd. 2014.

Böddeker, K.W. 2008. Liquid separations with membranes. Berlin: Springer-Verlag Berlin Heidelberg; 34.

British Petroleum (BP) statistical review of world energy (June 2013) http://www.bp.com/content/dam/bp/pdf/statisticalreview/statistical_review_of_world_energy_2013.pdf [cited 14.03.17]

British Petroleum (BP), Statistical review of world energy, 2009. Retrieved 10th February, 2017: from; http://www.bp.com/liveassets/bp_internet/globalbpstatistical_energy_review_2008/STAGING/local_assets/9_downloads/statistical_review_of_world_energy_full_report_9.pdf

Buonomenna, M.G., Choi, S.H. and Drioli, E. 2010. Catalysis in polymeric membrane reactors: the membrane role. *Asia Pacific Journal Chemical Engineering*, 5:26–34.

Campanelli, P., Banchero, M. and Manna L. 2010. Synthesis of biodiesel from edible, nonedible and waste cooking oils via supercritical methyl acetate transesterification. *Fuel*. 89:3675–82.

Canakci, M., and Sanli, H. 2010. Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal Industrial Microbiology Biotechnology*, 35 (5):431–441.

Cao, P., Dubé, M.A. and Tremblay, A.Y. 2008. High-purity fatty acid methyl ester production from canola, soybean, palm, and yellow grease lipids by means of a membrane reactor. *Biomass Bioenergy*, 32:1028–36.

Cao, P., Dubé, M.A. and Tremblay, A.Y. 2008b. Methanol recycling in the production of biodiesel in a membrane reactor. *Fuel*, 87:825–33.

Caro J. 2008. Catalysis in Micro-structured membrane reactors with nano-designed membranes. *Chinese Journal Catalysis*, 29:1169–77.

Carraretto, C., Macor, A., Mirandola, A., Stoppato, A. and Tonon, S. 2004. Biodiesel as alternative fuel: experimental analysis and energetic evaluations. *Energy Conversion Management*, 29 (12–15):2195–2211.

Chapman, P.D., Oliveira, T., Livingston, A.G. and Li, K. 2008. Membranes for the dehydration of solvents by pervaporation. *Journal of Membrane Science*; 318:5-37.

Chen, H., Peng, B., Wang, D. and Wang, J. 2010. Biodiesel production by the transesterification of cotton seed oil by solid acid catalysts. *Front Chemical Engineering Chinese*, 1:11–5.

Cheng, L.H., Cheng, Y.F., Yen, S.Y. and Chen, J. 2009. Ultrafiltration of triglyceride from biodiesel using the phase diagram of oil–FAME–MeOH. *Journal of Membrane Science*; 330:156–65.

Chew, T.L. and Bhatia, S. 2008. Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. *Bioresource Technology*, 99:7911–7922.

Chouhan, A.P.S. and Sarmav, A.K. 2011. Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renewable Sustainable Energy Review*, 15 (9):4378–4399.

Conservation ADoE. How can I dispose of used cooking oils and fats? Retrieved 13th March, 2017, fromhttp://www.dec.state.ak.us/eh/docs/fss/cooking.pdf.

Cvengros, J. and Cvengrosova, Z. 2009. Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids. *Biomass Bioenergy*; 27:173–81.

Czitrom, V. 1999. One-factor-at-a-time versus designed experiments. The American statistician, 53 (2):126-131.

Da silva, F.N., Prata, A.S. and J.R. Teixera. 2003. Technical feasibility assessment of oleic sunflower methyl ester utilisation in Diesel bus engines. *Energy Conversion and management,* 44: 2857-2878.

Dantas, M. B., Albuquerque, A. R., Soledade, L. E. B., Queiroz, N., Maia, A. S., Santos, I. M. G., Souza, A. L., Cavalcanti, E. H. S., Barro, A. K. and Souza, A. G. 2011. Biodiesel from soybean oil, castor oil and their blends. Journal of Thermal Analysis and Calorimetry, 106, (2):607-611.

Demirbas A. 2008. New liquid biofuels from vegetable oils via catalytic pyrolysis. *Energy Education Science Technology,* 21:1-59.

Demirbas, A. 2008. Biodiesel – a realistic fuel alternative for diesel engines. Springer-Verlag London Limited.

Demirbas, A. 2009. Progress and recent trends in biodiesel fuels. *Energy Conversion Management,* 50(1):14–34.

Demirbas, T. and Demirbas, A.H. 2010. Bioenergy, green energy, Biomass and biofuels. *Energy Sources Part A,* 32:1067–1075.

Dittmeyer, R., Svajda, K. and Reif, M. 2008. A review of catalytic membrane layers for gas/liquid reactions. *Top Catalyst*, 29:3-27.

Dizge, N., Aydiner, C., Imer, D.Y., Bayramoglu, M., Tanriseven, A. and Keskinler B. 2009. Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. *Bioresource Technology*, 100:1983–91.

Drioli, E., Fontananova, E., Bonchio, M., Carraro, M., Gardan, M. and Scorrano, G. 2008. Catalytic membranes and membrane reactors: an integrated approach to catalytic process with a high efficiency and a low environmental impact. *Chinese Journal Catalysis*, 29:1152–8.

Dubé, M.A., Tremblay, A.Y. and Liu, J. 2007. Biodiesel production using a membrane reactor. *Bioresource Technology*, 98:639–47.

EN14214. Automotive fuels–fatty acid methyl esters (FAME) for diesel engines—requirements and test methods. Berlin, Germany: Beuth-Verlag.

Ertl, H., Knozinger, H., Schuth, F. and Weitkamp, J. 2008. Catalytic membrane reactors. *Handbook of heterogeneous catalysis*. Weinheim: Wiley-VCH; 2198–241.

Falahati, H. and Tremblay, A.Y. 2012. The effect of flux and residence time in the production of biodiesel from various feedstocks using a membrane reactor. *Fuel*, 91:126–33.

FAO. 2009. The state of food and agriculture 2009, FAO. Rome, Italy.

Fazal, M., A. Haseeb, A. and Masjuki, H. 2011. Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renewable Sustainable. Energy Review*, 15:1314-1324.

Friedman, M. and Savage, L. J. 1947. Planning experiments seeking maxima. New York and London: McGraw-Hill.

Friedrich, S. 2003. A worldwide review of the commercial production of Biodiesel. Renewable Sustainable Energy Review, 14 (8):4365–4377.

Fukuda, H., Kondo, A. and Noda, H. 2009. Biodiesel fuel production by transesterification of oils. *Journal Bioscience Bioengineering*, 92:405–416.

Gajendra, K., Dharmendra, K., Johari, P. and Singh, C.P. 2011. Enzymatic transesterification of Jatropha curcas oil assisted by ultrasonication. Ultrason Sonochem, 5 (18):923–927.

Gogate, P.R. and Kabadi, A.M. 2009. A review of applications of cavitation in biochemical engineering/biotechnology. *Biochemical Engineering Journal*, 44:60–72.

Gomes, M.C.S., Arroyo, P.A. and Pereira, N.C. 2011. Biodiesel production from degummed soybean oil and glycerol removal using ceramic membrane. *Journal of Membrane Science,* 378:453–61.

Gomes, M.C.S., Pereira, N.C., Barros, S.T.D. 2010. Separation of biodiesel and glycerol using ceramic membranes. *Journal of Membrane Science*, 352:271–6.

Guerreiro, L., Castanheiro, J.E., Fonseca, I.M., Martin-Aranda, R.M., Ramos, A.M. and Vital, J. 2009. Transesterification of soybean oil over sulfonic acid functionalised polymeric membranes. *Catalysis Today*, 118:166–71.

Guerreiro, L., Pereira, P.M., Fonseca, I.M., Martin-Aranda, R.M., Ramos, A.M. and Dias, J.M.L 2010. PVA embedded hydrotalcite membranes as basic catalysts for biodiesel synthesis by soybean oil methanolysis. *Catalysis Today,* 156:191–7.

Guo, F., Peng, Z., Dai, J. and Xui, Z. 2010. Calcined sodium silicate as solid base catalyst for biodiesel production. *Fuel Processing Technology,* 91 (3):322.

Halim, S.F.A., Kamaruddin, A.H. and Fernando, W.J.N. 2009. Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: Optimization using response surface methodology (RSM) and mass transfer studies. *Bioresource Technology*, 100:710–716.

Hama S., Tamalampudi S., Fukumizu T., Miura K., Yamaji H., Kondo A. and Fukuda, H. 2016. Lipase localization in Rhizopus oryzae cells immobilized within biomass support particles for use as whole-cell biocatalysts in biodiesel-fuel production. *Journal of Bioscience and Bioengineering,* 101:328–333.

Hasheminejad, M., Tabatabaei, M., Mansourpanah, Y., Far, M.K. and Javani, A. 2011. Upstream and downstream strategies to economize biodiesel production. *Bioresource Technology*, 102:461–8.

Hasna, A. M. 2015. Dimensions of sustainability. *Journal of Engineering for Sustainable Development*: *Energy, Environment and Health,* 2 (1): 47–57.

Hawash, S., Kamal, N., Zaher, F., Kenawi, O. and Diwani, G.E. 2009. Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. *Fuel*, 88:579–82.

Helwani, Z., Othman, M.R., Aziz, N., Fernando, W.J.N., and Kim, J. 2009. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Process Technology*, 1502–1514.

International Energy Agency (IEA). Biofuels for transport: an international perspective. Available from: http://www.iea.org/textbase/nppdf/free/2014/biodiuels2014.pdf [cited 14.03.17].

Jain, S. and Sharma, M.P. 2010. Prospects of biodiesel from Jatropha in India: a review. *Renewable Sustainable Energy Review*, 14 (2):763–771.

Jegannathan, K.R., Abang, S., Poncelet, D., Chan, E.S. and Ravindra, P. 2008. Production of biodiesel using immobilized lipase — a critical review. *Critical Review Biotechnology*, 28:253–64.

Kalu, E.E., Chen, K.S. and Gedris, T. 2011. Continuous-flow biodiesel production using slit-channel reactors. *Bioresource Technology*, 102: 4456–61.

Kansedo, J., Lee, K.T. and Bhatia, S. 2008. Feasibility of Palm Oil as the Feedstock for Biodiesel Production via Heterogeneous Transesterification. *Chemical Engineering and Technology*, 993-999.

Karmakar, A., Karmakar, S. and Mukherjee, S. 2010. Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, 101 (19):7201–7210.

Kelkar, M.A., Gogate, P.R. and Pandit, A.B. 2008. Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. *Ultrasonic Sonochemical*, 15:188–94.

Khuri, A. I. and Mukhopadhyay, S. 2010. Response surface methodology. Wiley Interdisciplinary.

Knothe, G. 2011. Historical perspectives on vegetable oil-based diesel fuels. *Industrial Oils*, 12:1103–1107.

Knothe, G., 2010. Biodiesel and renewable diesel: a comparison. *Prog Energy Combust Science*, 36 (3): 364–373.

Kulkarni, M.G., Gopinath, R., Meher, L.C. and Dalai, A.K. 2010. Solid acid catalysed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry,* 8: 1056–62.

Kumar N, Varun, and Chauhan S.R. 2013. Performance and emission characteristics of biodiesel from different origins: a review. *Renewable Sustainable Energy Review*, 21:633–58.

Lam, M.K., Lee, K.T. and Mohamed, A.R. 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. *Biotechnology Advance,* 28:500–18.

Lee, J.S., and Saka, S. 2010. Biodiesel production by heterogeneous catalysts and supercritical technologies. *Bioresource Technology*, 10:7191–7200.

Lee, S., Posarac, D. and Ellis, N. 2012. An experimental investigation of biodiesel synthesis from waste canola oil using supercritical methanol. *Fuel*, 91:229–37.

Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S. and Mingdong, D. 2011. Opportunities and challenges for biodiesel fuel. *Applied Energy*, 88 (4):1020–1031.

Lipnizki, F., Field, R.W. and Ten, P-K. 2009a. Pervaporation-based hybrid process: a review of process design, applications and economics. *Journal Membrane Science*, 153:183–210.

Liu, X., He, H., Wang, Y., Zhu, S. and Piao, X. 2008. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, 87:216–21.

Lotero, E., Liu, Y., Dora E., Lopez, K.S., Bruce, D.A. and Goodwin, J.G. 2005. Synthesis of Biodiesel via Acid Catalysis. *Industrial Engineering Chemical Res*ource, 44:5353-63.

Ma, F., and Hanna, M.A. 2009. Biodiesel production: a review. *Bioresource Technol*ogy, 70:1–15.

Machsun, A., Gozan, M., Nasikin, M., Setyahadi, S. and Yoo, Y. 2010. Membrane microreactor in biocatalytic transesterification of triolein for biodiesel production. *Biotechnology Bioprocess Engineering*, 15:911–6.

Marchetti, J.M., Miguel, V.U. and Errazu, A.F. 2007. Possible methods for biodiesel production. *Renewable Sustainable Energy Review*, 11:1300–11.

Masjuki, H.H. 2010. Biofuel engine: a new challenge. Inaugural lecture University of Malaya, Malaysia.

Mbaraka, I.K. and Shanks, B.H. 2006. Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. *Journal Am Oil Chemical Society*, 83:79–91.

McDaniel, W. R. and Ankenman, B. E. 2000. Comparing experimental design strategies for quality improvement with minimal changes to factor levels. *Quality and Reliability Engineering International*, 16: 355-362.

Meher, L.C., Sagar, D.V. and Naik, S.N. 2006. Technical aspects of biodiesel production by transesterification-a review. *Renewable Sustainable Energy Review*, 10:248–268.

Mekhilef, S., Siga, S. and Saidur, R. 2011. A review on palm oil biodiesel as a source of renewable fuel. *Renewable Sustainable Energy Review*,15(4):1937–49.

Meng, X., Chen, G. and Wang, Y. 2008. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. *Fuel Processing Technology*; 89:851–7.

Miao, X., and Wu, Q. 2006. Biodiesel production from heterotrophic microalgal oil. *Bioresource Technology*, 97:841–846.

Mittelbach, M. and Remschmidt, C., 2004. Biodiesel-The comprehensive handbook, First ed., Boersedruck, Ges.m.b.H, Austria.

Mofijur, M., Masjuki, H.H., Kalam, M.A., Hazrat, M.A., Liaquat, A.M. and Shahabuddin, M. 2012. Prospects of biodiesel from jatropha in Malaysia. *Renewable and Sustainable Energy* Reviews, 16:5007–5020.

Montgomery, D. C. 2005. Design and analysis of experiments. 6th ed. Hoboken: NJ: John Wiley & Sons, Inc.

Montgomery, D. C. 2009. Design and Analysis of Experiments. John Wiley & Sons, Inc.

Montgomery, D. C., Peck, E. A. and Vining, G. G. 2012. Introduction to Linear Regression Analysis. Fifth ed.

Murphy, D.J. 2003.Working to improve the oil palm crop. *Information,* 14 (11):670-671.

Murugesan, A., Umarani, C., Chinnusamy, T.R., Krishnan, M., Subramanian, R. and Neduzchezhain, N. 2009. Production and analysis of bio-diesel from non-edible oils – a review. *Renewable Sustainable Energy Review*, 13 (4):825–834.

Nishimoto, A., Yoshikawa, S. and Ookawara, S. 2010. A model for transport phenomena in a cross-flow ultrafiltration module with microchannels. *Membranes,* 1:13–24.

Nitske, W.R. and Wilson, C.M.1965: Rudolf Diesel: Pioneer of the Age of Power, University of Oklahoma Press, 318 (39): 280-282.

NREL, 2007. World Biofuels Assessment, Worldwide Biomass Potential: Technology characterizations: Golden, Colorado.

Oda, M., Kaieda, M., Hama, S., Yamaji, H., Kondo. A. and Izumoto, E. 2005. Facilitatory effect of immobilized lipase-producing Rhizopus oryzae cells on acyl migration in biodiesel-fuel production. *Biochemical Engineering Journal*, 23:45–51.

Ong, Y.T., Ahmad, A.L., Zein, S.H.S., Sudesh, K. and Tan, S.H. 2011. Poly(3-hydroxybutyrate)-functionalised multi-walled carbon nanotubes/chitosan green nanocomposite membranes and their application in pervaporation. *Separation Purification Technology*, 76:419–27.

Pagliero, C., Mattea, M., Ochoa, N. and Marchese, J. 2007. Fouling of polymeric membranes during degumming of crude sunflower and soybean oil. *Journal of Food Engineering*, 78:194–7.

Pal, A., Verma, A., Kachhwaha, S.S. and Maji, S. 2010. Biodiesel production through hydrodynamic cavitation and performance testing. *Renewable Energy*, 35:619–24.

Pantoja, S. S. 2013. Oxidative stability of biodiesels produced from vegetable oils having different degrees of unsaturation. Energy Conversion and Management, 74: 293-298.

Parawira, W. 2010. Biodiesel production from Jatropha curcas: a review. *Science Resource Essays*, 5 (14):1796–1808.

Pashley, A. Biodiesel Output Seen by Oil World Rising to 24.7 Million Tons. http://www.bloomberg.com/news/2013-09-03/biodiesel-output-seen-by-oil-world-rising-to-24-7-million-tons.html (retrieved 20 March 2017).

Patil, P.D. and Deng, S. 2009. Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88(7):1302-1306.

Peng, F., Hu, C. and Jiang, Z. 2007. Novel poly (vinyl alcohol)/carbon nanotube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures. *Journal of Membrane Science*, 297: 236 – 42.

PennState. 2015. Design of Experiments. Available: https://onlinecourse.science.psu.edu/stat503/node/5 (Accessed February 2017)

Phan, A.N., and Phan, T.M. 2008. Biodiesel production from waste cooking oils. *Fuel*, 87:3490–6.

Phan, A.N., Harvey, A.P. and Rawcliffe, M. 2011.Continuous screening of base-catalysed biodiesel production using new designs of mesoscale oscillatory baffled reactors. *Fuel Processing Technology*, 92:1560–7.

Pinnarat, T. and Savage, P.E. 2008. Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions. *Industrial Engineering Chemical Resource*, 47:6801–8.

Pryde, E.H. 1984. Vegetable oils as fuel alternatives. *Journal Am Oil Chemical Society,* 61:1609–1610.

Qiu, Z., Zhao, L and Weatherley, L. 2010. Process intensification technologies in continuous biodiesel production. *Chemical Engineering Processing*, 49:323–30.

Qu, X. and Wu, C. F. J. 2005. One-factor-at-a-time designs of resolution. *Journal of statistical planning and inference*, 131 (2): 407-416.

Quesada-Medina, J. and Olivares-Carrillo, P. 2011. Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. *The Journal of Supercritical Fluids*, 56:56–63.

Roth, L. and K. Kormann. 2000. Olpflanzen-Pflanzenol. Fette. Wachse. Fettsauren. Botanik. Inhaitsstoffe. Analtik. Landsberg: ecomed.

Sahoo, P.K., Das, L.M., Babu, M.K.G. and Naik, S.N. 2007. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. *Fuel*, 86:448–54.

Saka, S., Isayama, Y., Ilham, Z. and Jiayu, X. 2010. New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol. *Fuel*, 89:1442–6.

Saleh, J., Tremblay, A.Y. and Dubé, M.A. 2010. Glycerol removal from biodiesel using membrane separation technology. *Fuel,* 89:2260–6.

Samart, C., Sreetongkittikul, P. and Sookman, C. 2009. Heterogeneous catalysis of transesterification of soybean oil using KI/mesoporous silica. *Fuel Process Technology*, 90:922–5.

Sanchez Marcano, J.G. and Tsotsis, T.T. 2012. The coupling of the membrane separation process witha catalytic reaction. *Catalytic Membranes and Membrane Reactor*, Weinheim: Wiley-VCH., 5-14.

Sanz Requena, J.F., Guimaraes, A.C., Quirós Alpera, S., Relea Gangas, E., HernandezNavarro, S., Navas Gracia, L.M., Martin-Gil, J. and Fresneda Cuesta, H. 2010. Life Cycle Assessment (LCA) of the biofuel production process from sunflower oil, rapeseed oil and soybean oil. *Fuel Processing Technology,* In Press, Corrected Proof.

Sarkar, B., Sridhar, S., Saravanan, K. and Kale, V. 2010. Preparation of fatty acid methyl ester through temperature gradient driven pervaporation process. *Journal of Chemical Engineering,* 162:609–15.

Shao, P. and Huang, R.Y.M. 2007. Polymeric membrane pervaporation. *Journal Membrane Science*, 287:162–79.

Sharma, Y.C., Singh, B. and Upadhyay, S.N. 2008. Advancements in development and characterization of biodiesel: a review. *Fuel*, 87 (12):2355–2373.

Shi, W., He, B., Ding, J., Li, J., Yan, F. and Liang, X. 2010. Preparation and characterization of the organic–inorganic hybrid membrane for biodiesel production. *Bioresource Technology*, 101:1501–5.

Shuit, S.H., Lee, K.T., Kamaruddin, A.H. and Yusup, S. 2010. Reactive extraction and in situ esterification of Jatropha curcas L. seeds for the production of biodiesel. *Fuel*, 89, 527–30.

Silitonga, A., Atabani, A., Mahlia, T., Masjuki, H., Badruddin, I.A. and Mekhilef, S. 2011. A review on prospect of Jatrophacurcas for biodiesel in Indonesia. *Renewable Sustainable Energy Review*, 15, 3733-3756.

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

South African Bureau of Standards, 2006. Chemical and Mining Standards, Personal communication via email,

Srivastava, A. and Prasad, R. 2000. Triglycerides-based diesel fuels. *Renewable Sustainable Energy Review*, 4 (2):111–133

Syers, J.K., Wood, D. and Thongbai, P. 2007. The proceedings of the international technical workshop on the feasibility of non-edible oil seed crops for biofuel production. Chiang Rai, Thailand: Mae Fah Luang University.

Tai-Shung NC. 2010. Development and purification of biodiesel. *Separation Purification Technology*, 20:377–81.

TakhtRavanchi, M., Kaghazchi, T. and Kargari, A. 2008. Immobilized liquid membrane for propylene-propane separation. World Acad *Science Engineering Technology*, 79–81.

Tan, K.T., Lee, K.T. and Mohamed, A.R. 2010. Effects of free fatty acids, water content and cosolvent on biodiesel production by supercritical methanol reaction. *The Journal of Supercritical Fluids*; 53:88–91.

Tremblay, A.Y., Cao, P. and Dubé, M.A. 2008. Biodiesel production using ultralow catalyst concentrations. *Energy Fuel*, 22:2748–55.

Vankelecom, I.F.J. 2012. Polymeric membranes in catalytic reactors. *Chemical Review*, 102:3779–810.

Vellguth, G. 1983. Performance of vegetable oils and their monoesters as fuels for diesel engines. SAE paper no: 831358.

Vospernik, M., Pintar, A., Bercic, G., Batista, J. and Levec, J. 2011. Potentials of ceramic membranes as catalytic three-phase reactors. *Chemical Engineering Resource,* 82:659–66.

Wahid, Z. and Nadir, N. 2013. Improvement of one factor at a time through design of experiments. *World applied sciences journal* (Mathematical applications in engineering), 21: 56-61.

Wan Omar, W. N. N. and Saidina Amin, N. A. 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and Bioenergy, 35 (3):1329–1338.

Wang, J., Chen, K., Wu, J., Wang, P., Huang, S. and Chen, C. 2012. Production of biodiesel through transesterification of soybean oil using lithium ortho silicate solid catalyst, *Fuel Processing Technology,* 104:167–173.

Wang, Y., Wang, X., Liu, Y., Ou, S., Tan, Y. and Tang, S. 2009. Refining of biodiesel by ceramic membrane separation. *Fuel Process Technology*, 90:422–7.

Wen, Z., Yu, X., Tu, S-T., Yan, J. and Dahlquist, E. 2009. Intensification of biodiesel synthesis using zigzag micro-channel reactors. *Bioresource Technology,* 100:3054–60.

Westermann, T. and Melin, T. 2009. Flow-through catalytic membrane reactors—principles and applications. *Chemical Engineering Processing*, 48:17–28.

Xiao, Y., Gao, L.J., Xiao, G.M., Fu, B.S. and Niu, L. 2012. Experimental and modeling study of continuous catalytic transesterification to biodiesel in a bench-scale fixed-bed reactor. *Industrial Engineering Chemical Resource*, 51:11860–5.

Xie, W. and Li, H. 2011. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. *Journal Molecular Catalysis A: Chem.*, 255:1–9.

Yee, K.F., Tan, K.T., Abdullah, A.Z. and Lee, K.T., 2009. Life cycle assessment of palm biodiesel: revealing facts and benefits for sustainability. *Applied Energy*, 86:189–96.

Yin, J.Z., Xiao, M. and Song, J.B. 2008. Biodiesel from soybean oil in supercritical methanol with co-solvent. *Energy Conversion Management*, 49:908–12.

Yusuf, N.N.A.N., Kamarudin, S.K. and Yaakub, Z. 2016. Overview on the current trends in biodiesel production. *Energy Conversion Management*, 52 (7):2741–2751.

Zabeti, M., WanDaud, W. M. A. and Aroua, M. K. 2009. Optimization of the activity of CaO/Al_2O_3 catalyst for biodiesel production using response surface methodology. *Applied Catalysis* A, 366:154–159.

Zhang, Y., Dubé, M., McLean, D. and Kates, M. 2013. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology,* 90: 229–240.

Zheng, M., Skelton, R.L. and Mackley, M.R. 2007. Biodiesel reaction screening using oscillatory flow meso reactors. *Process Saf Environment Prot*., 85:365–71.

Zhou, H., Lu, H. and Liang, B. 2006. Solubility of multicomponent systems in the biodiesel production by transesterification of Jatropha curcas l. oil with methanol. *Journal Chemical Engineering Data*, 51:1130–5.

Zhu, M., He, B., Shi, W., Feng, Y., Ding, J. and Li, J. 2010. Preparation and characterization of PSSA/PVA catalytic membrane for biodiesel production. *Fuel*, 89:299–304.

APPENDIX A: PRELIMINARY EXPERIMENTS

Sample calculations

1) <u>Mass of methanol required at a 6:1 methanol to oil molar ratio</u>

mm_{SO} = 879.40 g/mol

Basis: mass of feed oil, M= 400g

$$n_{feed} = \frac{M}{mm} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (A-1)$$

Where: n_{feed} is the number of moles in the source oil

M is the mass of oil in g

mm is the molar mass

Therefore: $n = \frac{400}{879.4} = 0.454\ mol$

Molar ratio = 6: 1 therefore:

$n_{methanol} = 6\ x\ 0.454 = 2.724\ mol$

$mm_{methanol}$ = 32.04 g/mol

Mass of methanol required, $M = n\ x\ mm \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (A - 2)$

$$= 2.724\ x\ 32.04$$

$$= \mathbf{87.3\ g}$$

2) <u>% yield of biodiesel produced</u>

Feed oil mass = 400 g

Mass of biodiesel = 376.8 g

$$\%\ yield = \frac{mass\ of\ biodiesel\ produced}{mass\ of\ source\ oil}\ x\ 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (A - 3)$$

Therefore:

$$\%\ yield = \frac{376.8}{400}\ x\ 100 = \mathbf{94}\ \%$$

A-1. EXPERIMENTAL DATA FOR OPTIMUM RANGE

A-1.1 Raw data for Semi-batch reactor process

Table A-1.1: The effect of reaction time on biodiesel yield from soybean Oil.

Reaction time	**Mass of methanol (g)**	**Mass of oil (g)**	**Yield (g)**			**% Yield (g/g)**			**Average % Yield**
			1st	**2nd**	**3rd**	**1st**	**2nd**	**3rd**	
60	87.4	400	300.0	299.6	300.4	75.0	74.9	75.1	75.0
90	87.4	400	308.0	310.8	311.2	77.0	77.7	77.8	77.5
120	87.4	400	355.6	355.2	356.0	88.9	88.8	89.0	88.9
150	87.4	400	372.4	371.6	372.0	93.1	92.9	93.0	93.0
180	87.4	400	347.6	348.0	348.4	86.9	87.0	87.1	87.0

Table A-1.2: The effect of temperature on biodiesel yield from soybean Oil.

Temperature (°C)	**Mass of methanol (g)**	**Mass of oil (g)**	**Yield (g)**			**% Yield (g/g)**			**Average % Yield**
			1st	**2nd**	**3rd**	**1st**	**2nd**	**3rd**	
50	87.4	400	256.4	258.0	256.8	64.1	64.5	64.2	64.3
55	87.4	400	294.0	293.6	291.6	73.5	73.4	72.9	73.3
60	87.4	400	328.0	328.0	328.8	82.0	82.0	82.2	82.1
65	87.4	400	360.0	358.8	360.0	90.0	89.7	90.0	89.8
70	87.4	400	323.6	325.2	326.4	80.9	81.3	81.6	81.3

Table A-1.3: The effect of flow rate on biodiesel yield from soybean Oil.

Flowrate (g/min)	Mass of methanol (g)	Mass of oil (g)	Yield (g)			% Yield (g/g)			Average % Yield
			1st	2nd	3rd	1st	2nd	3rd	
900	87.4	400	320.4	320.4	320.4	80.1	80.1	80.1	80.1
950	87.4	400	333.2	333.2	332.8	83.3	83.3	83.2	83.3
1000	87.4	400	342.4	342.8	342.8	85.6	85.7	85.7	85.7
1050	87.4	400	342.8	342.4	342.8	85.7	85.6	85.7	85.7
1100	87.4	400	342.8	342.8	342.8	85.7	85.7	85.7	85.7

Table A-1.4: The effect of methanol/oil ratio on biodiesel yield from soybean Oil.

Methanol/oil ratio	Mass of methanol (g)	Mass of oil (g)	Yield (g)			% Yield (g/g)			Average % Yield
			1st	2nd	3rd	1st	2nd	3rd	
3:1	43.7	400	337.2	336.4	337.2	84.3	84.1	84.3	84.2
4:1	58.3	400	356.0	355.6	356.8	89.0	88.9	89.2	89.0
6:1	87.4	400	375.2	376.8	376.0	93.8	94.2	94.0	94.0
9:1	131.2	400	376.0	376.4	376.0	94.0	94.1	94.0	94.0
12:1	174.9	400	371.2	372.0	372.0	92.8	93.0	93.0	92.9

Table A-1.5: The effect of catalyst concentration on biodiesel yield from soybean Oil

Concentration (wt/wt)	Mass of methanol (g)	Mass of oil (g)	Yield (g)			% Yield (g/g)			Average % Yield
			1st	2nd	3rd	1st	2nd	3rd	
0.5	87.4	400	218	217.6	217.6	54.5	54.4	54.4	54.4
1	87.4	400	309.2	310	310	77.3	77.5	77.5	77.4
3	87.4	400	360	360	360.4	90	90	90.1	90.0
5	87.4	400	350.4	351.2	351.6	87.6	87.8	87.9	87.8
7	87.4	400	332	333.2	332.4	83	83.3	83.1	83.1

A-2: Raw data for Continuous reaction process

Table A-2.1: The effect of temperature in a continous biodiesel production.

Temperature (°C)	Mass of methanol (g)	Mass of oil (g)	Yield (g)			% Yield (g/g)			Average % Yield
			1st	2nd	3rd	1st	2nd	3rd	
50	87.4	400	416.70	416.79	416.75	92.6	92.6	92.6	92.61
55	87.4	400	418.37	418.46	418.37	92.9	92.9	92.9	92.98
60	87.4	400	423.27	423.32	423.32	94.0	94.0	94.0	94.07
65	87.4	400	424.76	424.67	424.71	94.3	94.3	94.3	94.35
70	87.4	400	419.27	419.22	419.18	93.1	93.1	93.1	93.16

Table A-2.2: The effect of reaction time in a continous biodiesel production.

Reaction time (min)	**Mass of methanol (g)**	**Mass of oil (g)**	**Yield (g)**			**% Yield (g/g)**			**Average % Yield**
			1st	**2nd**	**3rd**	**1st**	**2nd**	**3rd**	
60	87.4	400	417.87	417.87	417.87	92.86	92.86	92.86	92.86
75	87.4	400	421.56	421.61	421.61	93.68	93.69	93.69	93.69
90	87.4	400	422.28	422.28	422.24	93.84	93.84	93.83	93.84
105	87.4	400	424.53	424.58	424.53	94.34	94.35	94.34	94.34
120	87.4	400	423.05	423.09	423.09	94.01	94.02	94.02	94.02

Table A-2.3: The effect of methanol/oil ratio in a continous biodiesel production.

Reaction time (min)	**Mass of methanol (g)**	**Mass of oil (g)**	**Yield (g)**			**% Yield (g/g)**			**Average % Yield**
			1st	**2nd**	**3rd**	**1st**	**2nd**	**3rd**	
3:1	43.7	400	300.0	299.6	300.4	75.0	74.9	75.1	75.0
4:1	58.3	400	308.0	310.8	311.2	77.0	77.7	77.8	77.5
6:1	87.4	400	355.6	355.2	356.0	88.9	88.8	89.0	88.9
9:1	131.2	400	372.4	371.6	372.0	93.1	92.9	93.0	93.0
12:1	174.9	400	347.6	348.0	348.4	86.9	87.0	87.1	87.0

APPENDIX B: STATISTICAL AND OPTIMIZATION STUDIES

B-1. RAW DATA FOR CENTRAL COMPOSITE DESIGN

Table B-1: Experimental data from the CCD

Standard runs	Randomized runs	Matrix				Repeat 1 Y_1 (%)	Repeat 2 Y_2 (%)	Repeat 3 Y_3 (%)	Average Y (%)
1	29	-1	-1	-1	-1	61	63	63	62
2	5	1	-1	-1	-1	90	91	90	90
3	14	-1	1	-1	-1	60	61	60	60
4	12	-1	1	-1	-1	74	75	75	75
5	13	-1	-1	1	-1	49	48	49	49
6	2	1	-1	1	-1	66	67	66	66
7	18	-1	1	1	-1	55	54	55	55
8	8	1	1	1	-1	79	79	78	79
9	24	-1	-1	-1	1	84	84	84	84
10	27	1	-1	-1	1	92	91	92	92
11	17	-1	1	-1	1	89	89	89	89
12	11	1	1	-1	1	95	95	94	95
13	6	-1	-1	1	1	50	50	49	50
14	10	1	-1	1	1	60	59	60	60
15	30	-1	1	1	1	78	78	79	78
16	3	1	1	1	1	74	74	74	74
17	25	-2	0	0	0	50	51	50	50
18	22	2	0	0	0	60	60	60	60
19	4	0	-2	0	0	78	77	79	78
20	15	0	2	0	0	95	95	95	95
21	23	0	0	-2	0	65	65	64	65
22	21	0	0	2	0	48	48	48	48
23	1	0	0	0	-2	62	62	61	62
24	9	0	0	0	2	93	94	94	94
25	20	0	0	0	0	93	92	93	93
26	7	0	0	0	0	94	94	94	94
27	26	0	0	0	0	92	93	93	92
28	28	0	0	0	0	95	95	95	95
29	19	0	0	0	0	92	93	93	93
30	16	0	0	0	0	96	96	95	96

B-2. EVALUATION OF THE DESIGN

Standard errors (SE) must be the same for each type of coefficient. The ideal VIF is 1. VIFs values greater than 10 indicate that the coefficients are poorly estimated due to multicollinearity. Ideally, the value of the Ri^2 should be 0. High values of Ri^2 show that terms are correlated with each other, which can lead to poor predictions and erroneous models. Table B-2 shows that the model chosen does not contain correlated terms.

Table B-2.1: Evaluation of the chosen design.

Factor	**SE**	**VIF**	**Ri^2**
A	0.20	1.00	0.0000
B	0.20	1.00	0.0000
C	0.20	1.00	0.0000
D	0.20	1.00	0.0000
AB	0.25	1.00	0.0000
AC	0.25	1.00	0.0000
AD	0.25	1.00	0.0000
BC	0.25	1.00	0.0000
BD	0.25	1.00	0.0000
CD	0.25	1.00	0.0000
A^2	0.19	1.05	0.0476
B^2	0.19	1.05	0.0476
C^2	0.19	1.05	0.0476
D^2	0.19	1.05	0.0476

Table B-2.2: Diagnostics Case Statistics on the Central Composite Design

Run order	Actual value	Predicted value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Cook's Distance	Influence on Fitted Value DFFITS	Standard order
1	62.00	67.75	-5.75	0.583	-1.803	-1.968	0.303	-2.329[1]	23
2	66.00	66.63	-0.63	0.583	-0.196	-0.190	0.004	-0.224	6
3	74.00	76.79	-2.79	0.583	-0.875	-0.868	0.072	-1.027	16
4	78.00	81.58	-3.58	0.583	-1.124	-1.134	0.118	-1.342	19
5	90.00	83.29	6.71	0.583	2.104	2.421	0.413	2.864[1]	2
6	50.00	53.79	-3.79	0.583	-1.189	-1.207	0.132	-1.428	13
7	95.00	94.83	0.17	0.167	0.037	0.036	0.000	0.016	26
8	79.00	73.79	5.21	0.583	1.633	1.740	0.249	2.059	8
9	94.00	92.75	1.25	0.583	0.392	0.381	0.014	0.450	24
10	60.00	57.63	2.37	0.583	0.745	0.733	0.052	0.868	14
11	95.00	90.96	4.04	0.583	1.267	1.296	0.150	1.533	12
12	75.00	72.96	2.04	0.583	0.640	0.627	0.038	0.742	4
13	49.00	46.79	2.21	0.583	0.693	0.680	0.045	0.805	5
14	60.00	56.13	3.87	0.583	1.215	1.236	0.138	1.463	3
15	95.00	95.92	-0.92	0.583	-0.287	-0.278	0.008	-0.329	20
16	96.00	94.83	1.17	0.167	0.259	0.250	0.001	0.112	30
17	89.00	90.13	-1.13	0.583	-0.353	-0.342	0.012	-0.405	11
18	55.00	59.46	-4.46	0.583	-1.398	-1.448	0.182	-1.714	7
19	93.00	94.83	-1.83	0.167	-0.407	-0.395	0.002	-0.177	29
20	95.00	94.83	0.17	0.167	0.037	0.036	0.000	0.016	25
21	48.00	44.58	3.42	0.583	1.071	1.077	0.107	1.274	22
22	60.00	67.58	-7.58	0.583	-2.378	-2.911	0.528	-3.444[1]	18
23	65.00	72.92	-7.92	0.583	-2.483	-3.125	0.575	-3.697[1]	21
24	84.00	82.96	1.04	0.583	0.327	0.317	0.010	0.375	9
25	50.00	46.92	3.08	0.583	0.967	0.965	0.087	1.141	17
26	95.00	94.83	0.17	0.167	0.037	0.036	0.000	0.016	27
27	92.00	89.29	2.71	0.583	0.849	0.841	0.067	0.995	10
28	95.00	94.83	0.17	0.167	0.037	0.036	0.000	0.016	28
29	62.00	60.96	1.04	0.583	0.327	0.317	0.010	0.375	1
30	78.00	78.46	-0.46	0.583	-0.144	-0.139	0.002	-0.164	15

Box-Cox Power Transformation

Constant K	95% Cl low	95% Cl High	Best Lambda	Rec. Transform
0.000	-1.76	1.73	-0.20	None

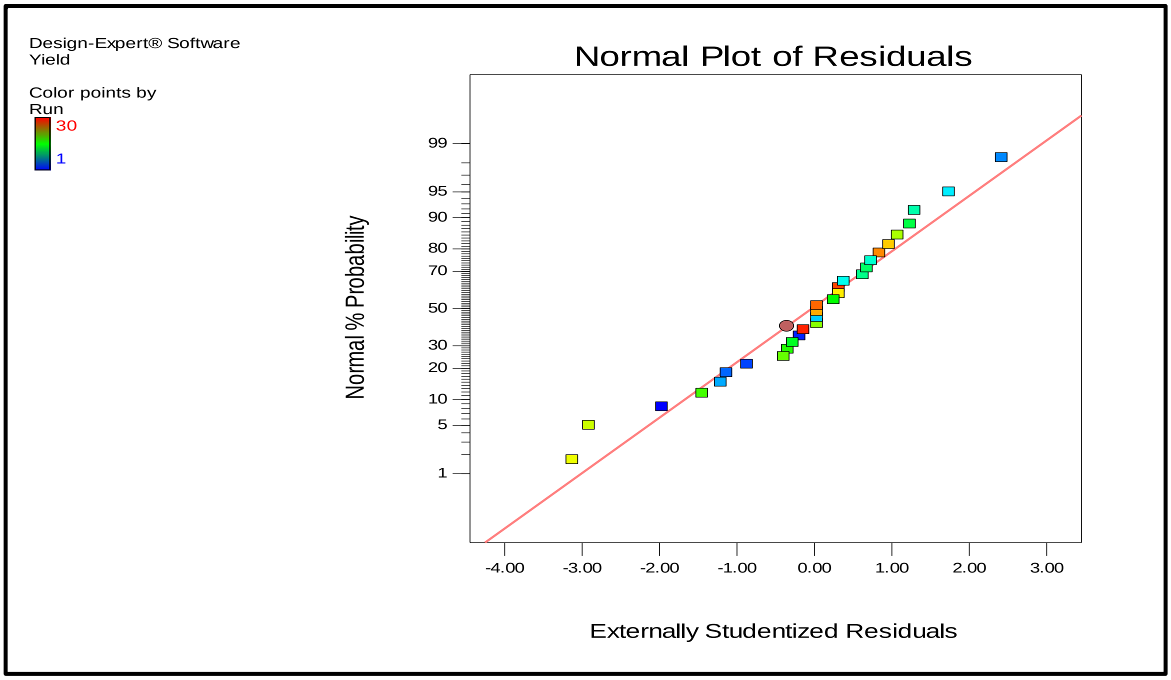


Figure B-2.1: Normal Probability plot of the Studentized Residuals of the Biodiesel production

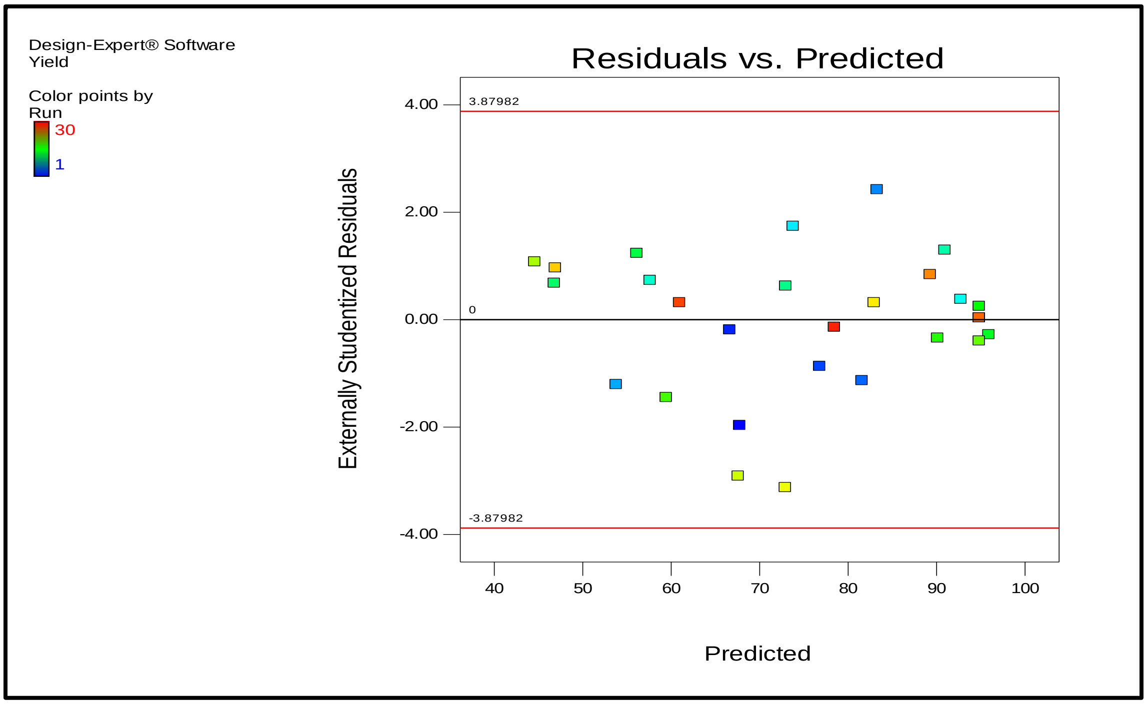


Figure B-2.2: Residuals vs the Predicted values.

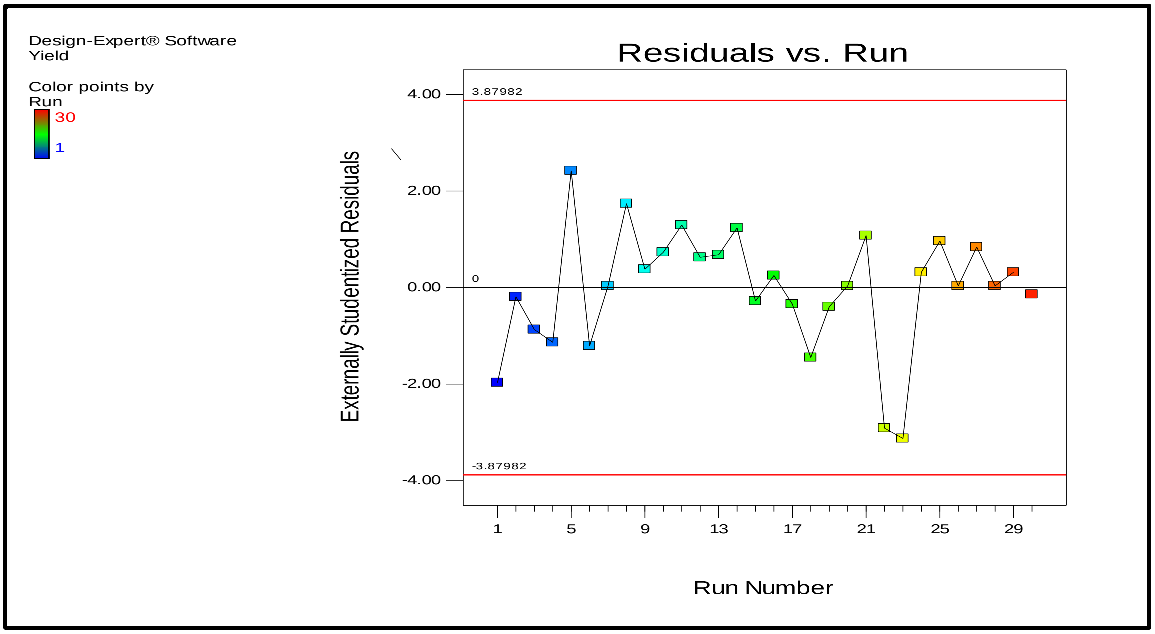


Figure B-2.3: Residuals vs Run Order

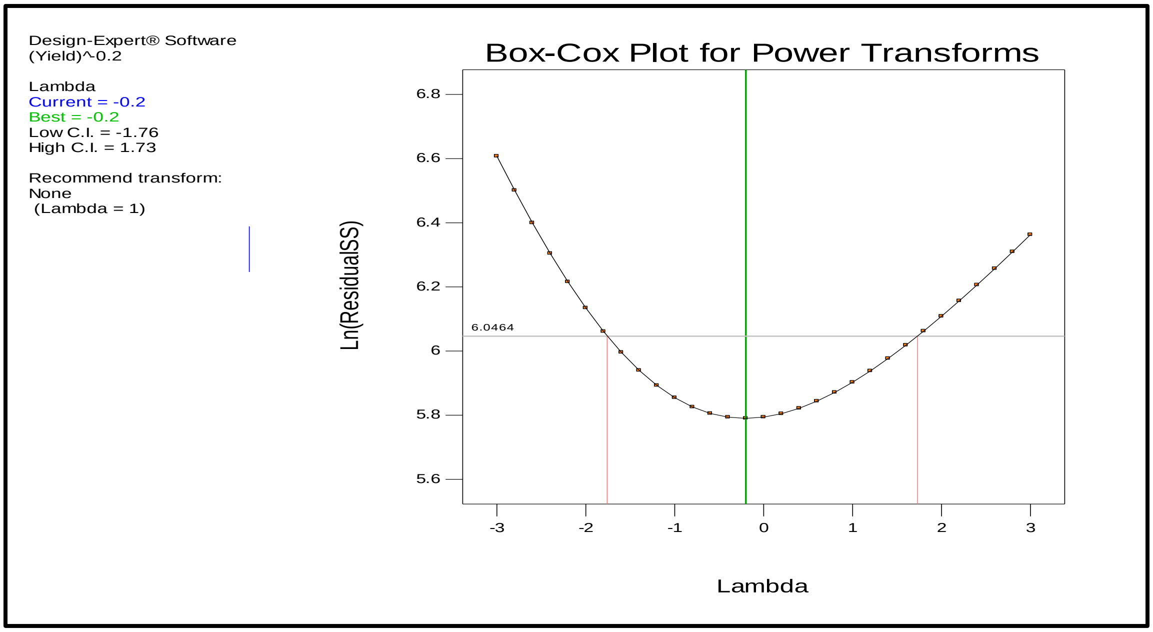


Figure B-2.4: Box-Cox Plot Power Transforms.

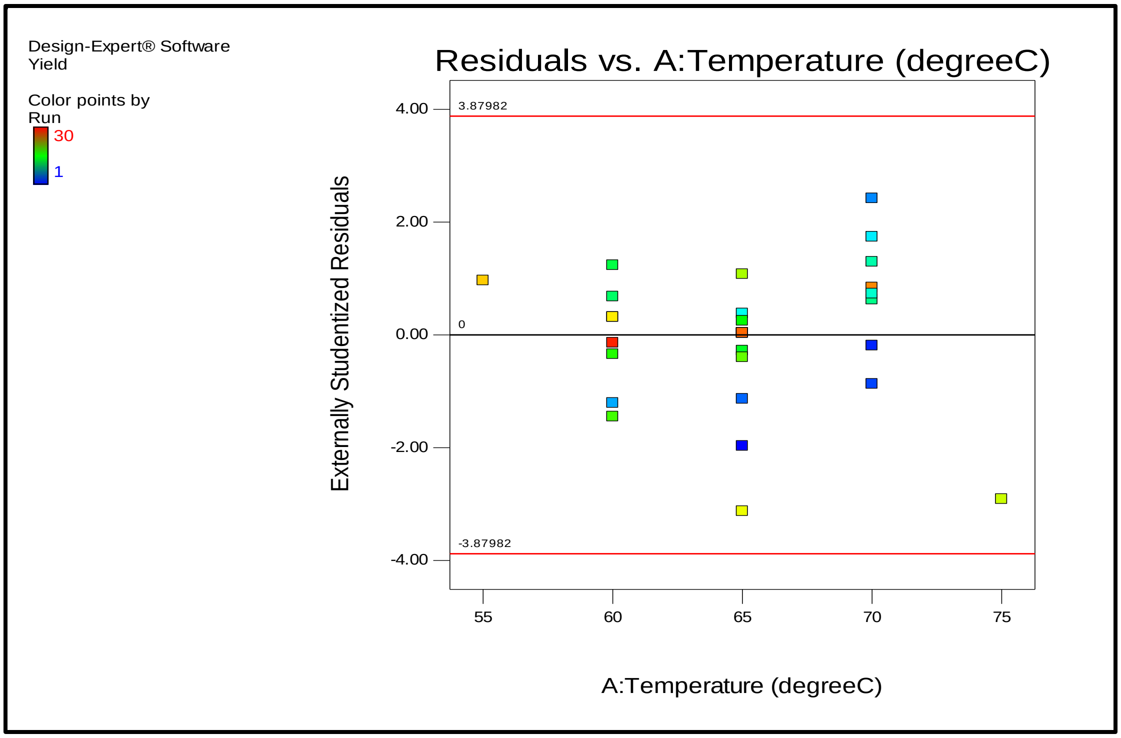


Figure B-2.5: Plot of Residuals vs Temperature (degree C).

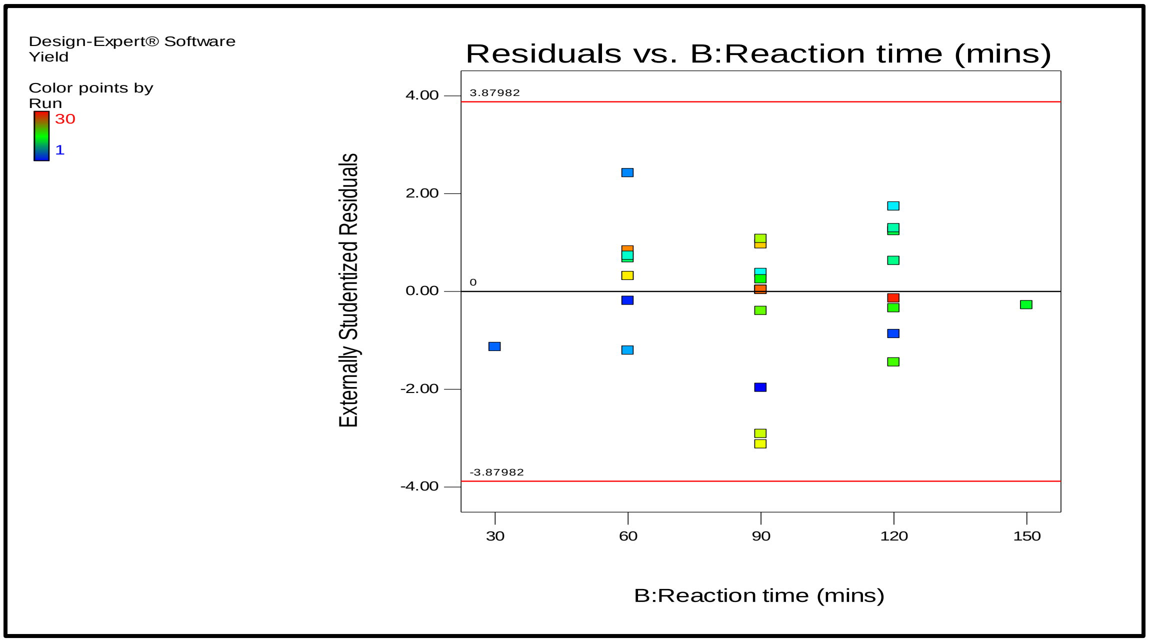


Figure B-2.6: Plot of Residuals vs Reaction time (mins).

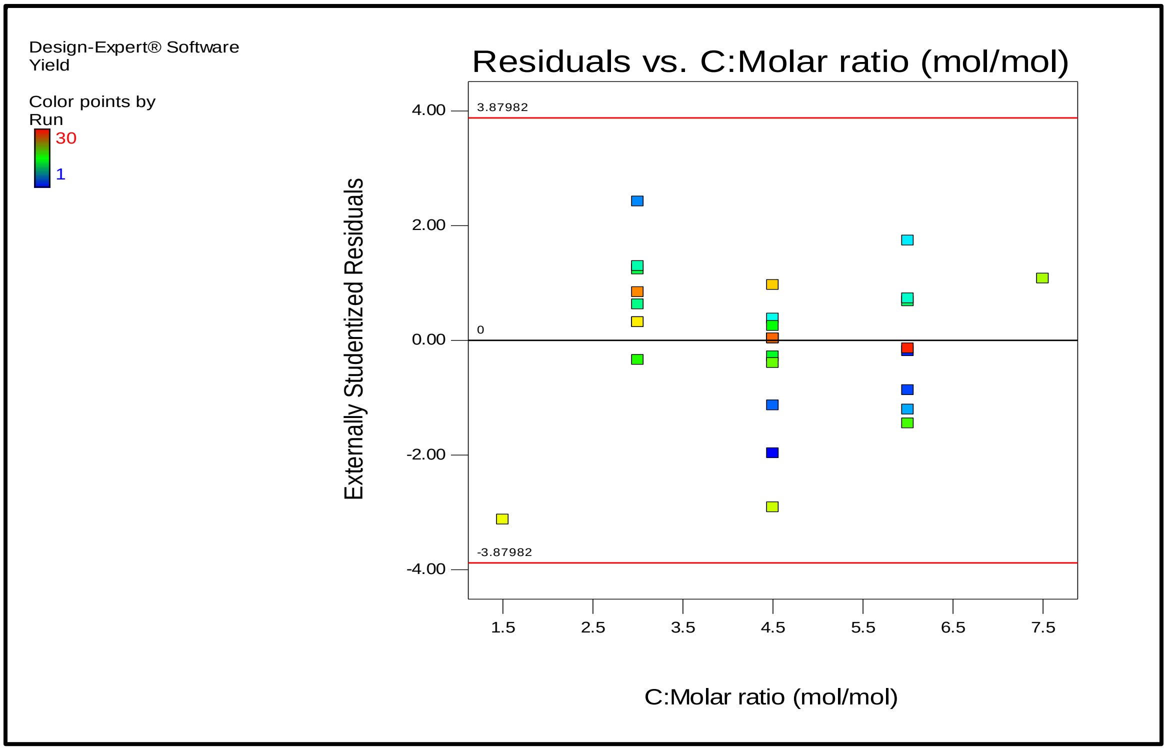


Figure B-2.7: Plot of Residuals vs Molar ratio (mol/mol).

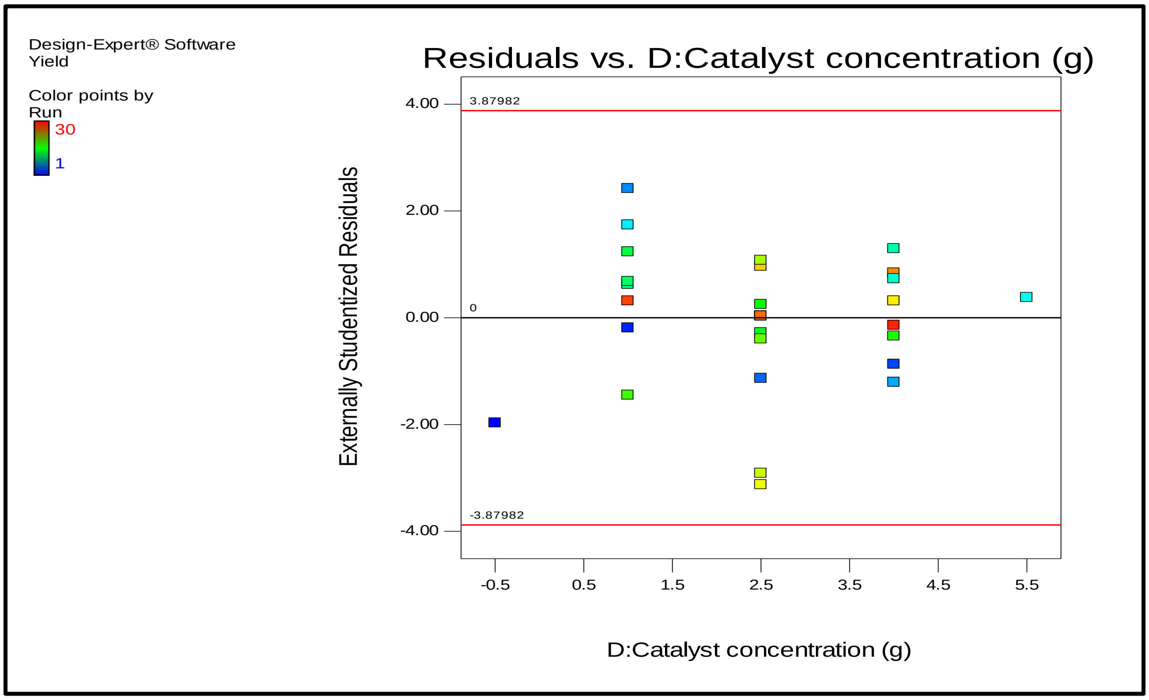


Figure B-2.8: Plot of Residuals vs Catalyst concentration (g).

Table B-2.3: Optimization Report of Constrains and Solutions on the CCD

Constraints						
Name	**Goal**	**Lower Limit**	**Upper Limit**	**Lower Weight**	**Upper Weight**	**Importance**
A:Temperature	is in range	60	70	1	1	3
B:Reaction time	is in range	60	120	1	1	3
C:Molar ratio	is in range	3	6	1	1	3
D:Catalyst concentration	is in range	1	4	1	1	3
Yield	maximize	48	96	1	1	3

Solutions							
Number	**Temperature**	**Reaction time**	**Molar ratio**	**Catalyst concentration**	**Yield**	**Desirability**	
1	66.479	90.000	4.290	2.500	96.381	1.000	Selected
2	67.127	90.000	4.239	2.500	96.336	1.000	
3	67.125	90.000	3.620	2.500	96.538	1.000	
4	65.978	90.000	4.223	2.500	96.508	1.000	
5	67.140	90.000	3.857	2.500	96.817	1.000	
6	66.474	90.000	4.385	2.500	96.044	1.000	
7	66.058	90.000	4.174	2.500	96.648	1.000	
8	67.365	90.000	4.168	2.500	96.367	1.000	
9	66.111	90.000	3.470	2.500	96.225	1.000	
10	66.351	90.000	4.290	2.500	96.383	1.000	
11	68.054	90.000	3.800	2.500	96.003	1.000	
12	66.937	90.000	3.816	2.500	96.889	1.000	
13	66.949	90.000	3.497	2.500	96.285	1.000	
14	67.688	90.000	4.142	2.500	96.153	1.000	
15	65.086	90.000	3.647	2.500	96.037	1.000	
16	65.439	90.000	4.228	2.500	96.213	1.000	
17	65.368	90.000	3.625	2.500	96.251	1.000	
18	66.246	90.000	3.669	2.500	96.779	1.000	
19	65.023	90.000	3.756	2.500	96.152	1.000	
20	65.290	90.000	4.246	2.500	96.047	1.000	
21	65.533	90.000	4.318	2.500	96.011	1.000	
22	68.031	90.000	3.777	2.500	96.014	1.000	
23	65.821	90.000	4.226	2.500	96.441	1.000	
24	66.883	90.000	4.045	2.500	96.836	1.000	
25	64.921	90.000	4.092	2.500	96.006	1.000	
26	67.999	90.000	3.945	2.500	96.076	1.000	
27	66.834	90.000	4.240	2.500	96.460	1.000	
28	67.474	90.000	3.864	2.500	96.602	1.000	
29	66.190	90.000	3.836	2.500	96.965	1.000	
30	67.612	90.000	4.194	2.500	96.103	1.000	
31	64.865	90.000	4.044	2.500	96.002	1.000	
32	65.120	90.000	3.688	2.500	96.150	1.000	

Solutions						
Number	**Temperature**	**Reaction time**	**Molar ratio**	**Catalyst concentration**	**Yield**	**Desirability**
33	66.194	90.000	4.339	2.500	96.202	1.000
34	66.009	90.000	3.481	2.500	96.227	1.000
35	67.863	90.000	4.022	2.500	96.167	1.000
36	66.685	90.000	4.333	2.500	96.208	1.000
37	67.329	90.000	4.070	2.500	96.574	1.000
38	66.895	90.000	4.304	2.500	96.244	1.000
39	65.080	90.000	4.069	2.500	96.207	1.000
40	66.974	90.000	4.296	2.500	96.237	1.000
41	65.739	90.000	3.507	2.500	96.188	1.000
42	65.934	90.000	4.208	2.500	96.530	1.000
43	66.593	90.000	3.416	2.500	96.077	1.000
44	65.677	90.000	4.290	2.500	96.188	1.000
45	65.617	90.000	3.618	2.500	96.420	1.000
46	65.919	90.000	4.256	2.500	96.399	1.000
47	64.962	90.000	3.794	2.500	96.127	1.000
48	65.430	90.000	3.783	2.500	96.559	1.000
49	65.921	90.000	3.940	2.500	96.896	1.000
50	64.954	90.000	3.860	2.500	96.163	1.000
51	66.498	90.000	3.399	2.500	96.014	1.000
52	66.316	90.000	3.437	2.500	96.150	1.000
53	66.961	90.000	4.344	2.500	96.077	1.000
54	67.772	90.000	3.659	2.500	96.139	1.000
55	67.021	90.000	4.346	2.500	96.045	1.000
56	65.968	90.000	3.781	2.500	96.863	1.000
57	65.314	90.000	3.572	2.500	96.075	1.000
58	65.278	90.000	4.074	2.500	96.385	1.000
59	65.687	90.000	4.104	2.500	96.629	1.000
60	66.642	90.000	3.652	2.500	96.753	1.000
61	66.082	90.000	4.121	2.500	96.759	1.000
62	67.184	90.000	4.303	2.500	96.106	1.000
63	67.195	90.000	4.194	2.500	96.416	1.000
64	67.270	90.000	4.168	2.500	96.430	1.000
65	67.258	90.000	3.751	2.500	96.678	1.000
66	65.376	90.000	4.138	2.500	96.364	1.000
67	67.313	90.000	4.016	2.500	96.652	1.000
68	67.525	90.000	3.577	2.500	96.184	1.000
69	67.472	90.000	4.145	2.500	96.335	1.000
70	66.078	90.000	4.137	2.500	96.728	1.000
71	65.201	90.000	4.157	2.500	96.179	1.000
72	67.938	90.000	4.050	2.500	96.048	1.000
73	65.189	90.000	3.628	2.500	96.099	1.000
74	67.829	90.000	4.143	2.500	96.009	1.000
75	67.433	90.000	4.260	2.500	96.072	1.000
76	65.892	90.000	4.290	2.500	96.288	1.000
77	65.719	90.000	3.814	2.500	96.776	1.000

Solutions						
Number	**Temperature**	**Reaction time**	**Molar ratio**	**Catalyst concentration**	**Yield**	**Desirability**
78	67.011	90.000	3.434	2.500	96.048	1.000
79	66.408	90.000	4.338	2.500	96.221	1.000
80	67.085	90.000	3.506	2.500	96.258	1.000
81	66.379	90.000	4.185	2.500	96.670	1.000
82	65.275	90.000	4.048	2.500	96.415	1.000
83	66.520	90.000	4.168	2.500	96.704	1.000
84	67.819	90.000	3.693	2.500	96.150	1.000
85	65.092	90.000	3.720	2.500	96.176	1.000
86	67.631	90.000	3.579	2.500	96.101	1.000
87	66.692	90.000	3.911	2.500	96.979	1.000
88	65.289	90.000	4.141	2.500	96.288	1.000
89	65.609	90.000	4.263	2.500	96.229	1.000
90	67.503	90.000	3.561	2.500	96.161	1.000
91	67.165	90.000	3.511	2.500	96.234	1.000
92	68.042	90.000	3.985	2.501	96.000	1.000
93	64.998	90.000	4.073	2.506	96.144	0.999
94	64.990	90.119	3.678	2.500	96.000	0.999
95	67.994	90.000	3.744	2.493	96.000	0.999
96	66.078	90.160	3.412	2.500	96.000	0.998
97	64.644	90.000	3.855	2.542	96.000	0.991
98	69.410	90.000	4.605	2.500	91.503	0.968
99	70.000	90.000	4.402	2.501	91.073	0.964
100	65.455	91.943	3.011	2.500	93.358	0.960

APPENDIX C: VERIFICATION OF THE OPTIMUM VALUES OF THE FACTORS

TableC-1.1: CCD Run 1

Table C-1.1 CCD Run 1			
Parameter	**Units**	**Code**	**Experimental value**
Yield	%	Y	97.0
Temperature	^oC	X_1	65
Reaction time	min	X_2	90
Molar ratio		X_3	4.5:1
Catalyst concentration	g/L	X_4	3

Table C-1.2: CCD Run 2

Table C-1.2 CCD Run 2			
Parameter	**Units**	**Code**	**Experimental value**
Yield	%	Y	96.9
Temperature	^oC	X_1	65
Reaction time	min	X_2	90
Molar ratio		X_3	4.5:1
Catalyst concentration	g/L	X_4	3

Table C-1.3: CCD Run 3

Table C-1.3 CCD Run 3			
Parameter	**Units**	**Code**	**Experimental value**
Yield	%	Y	96.9
Temperature	^oC	X_1	65
Reaction time	min	X_2	90
Molar ratio		X_3	4.5:1
Catalyst concentration	g/L	X_4	3

APPENDIX D: RESEARCH OUTPUTS

D-1: CONFERENCE SERIES PUBLICATION

- Olagunju O.A. and Musonge, P. 2017. Production of Biodiesel Using a Membrane Reactor to Minimize Separation Cost. IOP Conference Series: Earth Environmental Science. 78 012019.

IOP Conference Series: Earth and Environmental Science

Production of Biodiesel Using a Membrane Reactor to Minimize Separation Cost

To cite this article: O A Olagunju and P Musonge 2017 *IOP Conf. Ser.: Earth Environ. Sci.* **78** 012019

IOP Conf. Series: Earth and Environmental Science **78** (2017) 012019 doi:10.1088/1755-1315/78/1/012019

Production of Biodiesel Using a Membrane Reactor to Minimize Separation Cost

O A Olagunju[1] and P Musonge[1]

Department of Chemical Engineering, Durban University of Technology, South Africa, 4000
E-mail: gilbert4life2004@yahoo.com, paulm@dut.ac.za

Abstract. This study investigates the performance of a packed bed membrane reactor in the transesterification process of triglycerides to methyl ester using soyabean oil as feedstock. A TiO_2/Al_2O_3 ceramic microporous membrane was selected due to its chemical inert nature and thermal stability to selectively remove the product from the reaction medium. CaO impregnated on the surface of activated carbon was packed into the membrane and acted as catalyst. The synthesized catalyst had a total loading of 40.50 % and was characterized by XRD and temperature-programmed desorption of CO_2 (CO_2-TPD). The crude biodiesel produced was micro-filtered by the ceramic membrane with a pore size of 0.02 μm to retain the unreacted oil and free glycerol, at the transmembrane pressure of 100 KPa. The best condition was achieved with a temperature of 65 ^{o}C, methanol/oil molar ratio of 6:1 for 150 minutes, which resulted in the highest FAME yield of 94 %. Methyl ester produced met the ASTM D6751 and SANS 1935 specifications. The product obtained was mainly composed of methyl esters. Glycerol was not detected in the product stream due to the ability of the membrane to retain the glycerol and the unreacted oil in the medium, which solved the issue of glycerol separation from biodiesel.

1. Introduction

The continuous exploration of sustainable energy resources has become a global challenge. Biofuel has been identified as one of the most favorable renewable energy sources with great potentials to solve issues relating to global fossil fuel addiction. Biofuels are sustainable, biodegradable and environmentally friendly. Currently, biodiesel is gaining considerable recognition as a sustainable renewable energy source because it is renewable, non-toxic and eco-friendly [1]-[3].

This biofuel has several benefits over conventional fossil fuels, and some of them include cleaner engine emissions, renewability, and better lubricating properties, which makes it a good alternative fuel [4]. Biodiesel can be produced from various sources such as vegetable oil (canola, soybean and sunflower oil), non-edible oils (Jatropha curcas, rapeseed oil) and used vegetable oil [5]-[8].

Biodiesel is mostly produced in the conventional way using homogeneous base catalysts such as sodium hydroxide or potassium hydroxide. Acid homogeneous catalysts have also been used but the rate of reaction is slow compared to the base catalyzed reaction. Homogeneous processes have many shortcomings such as further separation of the catalyst from the reaction mixture, generation of large amounts of wastewater during the separation and purification of the product, and formation of soap due to the reaction of the alcohol with the free fatty acid present in the reaction medium [9]. Baroutian *et al.* [10] stated that biodiesel produced using KOH as the catalyst generated a high yield of the product but an additional process such as purification of product and treatment of wastewater generated was further needed. Previous research conducted by Saleh *et al.* [11] showed that for each litre of biodiesel produced, about 10 litres of wastewater is generated and the treatment invariably increased the cost of production.

Biodiesel may be regarded as a suitable sustainable energy with many advantages but still seems less attractive due to its cost as compared to fossil fuel. In other to make biodiesel more competitive and attractive to users a better approach which eliminates the various challenges associated with its production such as immiscibility of reactants, separation of the product, further purification of product and wastewater generation has to be provided. One of such approaches involves the use of membrane separation technology to explore some of the challenges encountered by using homogeneous transesterification.

Membrane separation technology has been extensively used in wastewater purification by various researchers because of its ability to carry out the separation of different components in a single process stream based on their molecular weight. In this process, reaction and separation take place within a single unit and therefore eliminates the need for a further purification step. Membrane reactors have the ability to selectively remove the product from the reaction mixture by allowing the component with lower molecular weight to pass through its pores while higher molecular weight components are rejected. This method also allows for proper contact between the immiscible reactants and catalyst and as a result, a higher yield of the product can be achieved [12].

South Africa is known to be a water scarce country and the use of membrane technology to produce biodiesel will help to conserve water for other purposes as it will eliminate the use of water for purifying the product and makes the environment free from pollution. Baroutian *et al.* [10] had previously explored this technology, using potassium hydroxide as catalyst and palm oil as feedstock. However, the problem of membrane selectivity remains, which this study aims to address. Furthermore, a comparative study using a different feedstock and catalyst is essential for affirming this technology for the production of biodiesel.

In this study, a packed bed membrane reactor was used to produce FAME. The combination of heterogeneous alkali transesterification and triglyceride separation in the packed bed membrane reactor was employed. The advantage of this new process is in the simplification of the refining steps.

The ceramic membrane is a filter medium composed of inorganic oxides, which permeate liquids through pores and separate out solid matters by retention. Ceramics have high permeability, good separation i.e. sharp cut-off value and long lifetime. Ceramic membranes offer more advantages over the polymeric membranes and these include; high chemical resistance, high thermal stability, and high durability. The chemical stability makes possible, the utilization of chemically aggressive cleaning methods. Furthermore, the thermal stability enables the use of steam and high temperatures during its operation [10].

For this purpose, a tubular ceramic (TiO_2/Al_2O_3) membrane was used as reactor and separator because of its high thermal stability. The tubular membrane was packed with calcium oxide catalyst supported on activated carbon. Among the available supports [13] [14] activated carbon has proved to be highly effective as a catalyst support that can be used in the transesterification process. Activated carbon has a large surface area, inert carbon skeleton, good physical/thermal stability and it can be locally produced at low cost.

Thus, the objective of the present study is to evaluate the applicability of using a packed bed ceramic membrane reactor to separate biodiesel from the reaction medium by analyzing the permeate flux and the quality of the product obtained. The influence of process parameters on the performance of the reactor was also evaluated.

2. Experimental

2.1. Materials

Soybean oil was purchased from a local market. Methanol (99.8%) was supplied by Laboratory supplies co., South Africa. Pure calcium oxide (98.9%) was used as a catalyst for transesterification and was obtained from associated chemical enterprises, South Africa and the activated carbon granules used as the catalyst support in this study was purchased from the same company.

2.2. Reactor Setup

Figure 1 shows the experimental setup for the biodiesel production. A tubular ceramic membrane (Atech Innovations Gmbh, Germany) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 1000 mm, 16 mm, 25.4 mm and 0.02 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m^2. A Watson Marlow 313S peristaltic pump (Cole-Parmer Instrument, USA) was used to feed the reactants into the system. The Chem-Durance chemical resistant pump tubing with a size of 16 (ID = 44 mm, OD = 2.36 mm) was used because of its ability to withstand the operation temperature. A shell and tube heat exchanger equipped with a hot water circulating bath was used as the heat transfer medium. Pressure gauges and thermometers were used to monitor pressures and temperatures of the system. Catalysts particles were packed inside the ceramic membrane and held in place using cloth screens attached to the upstream and downstream tubing. It was observed from the preliminary experiment conducted, that methanol and biodiesel molecules were able to pass through the membrane, which can be attributed to their smaller molecular sizes lower than the pore size of the membrane while the glycerol and unreacted oil go into the recycling tank. This finding quite differs from the result of the study carried out by Baroutian *et al*. [10] who recorded that product, by-product and methanol were able to pass through the membrane, which means the filtrate containing FAME, and glycerol needs a further separation process for pure FAME to be obtained and this can take several hours to be accomplished. Although the pore size of the membrane used for this experiment was 0.02μm and may be the reason for the inability of glycerol to pass through.

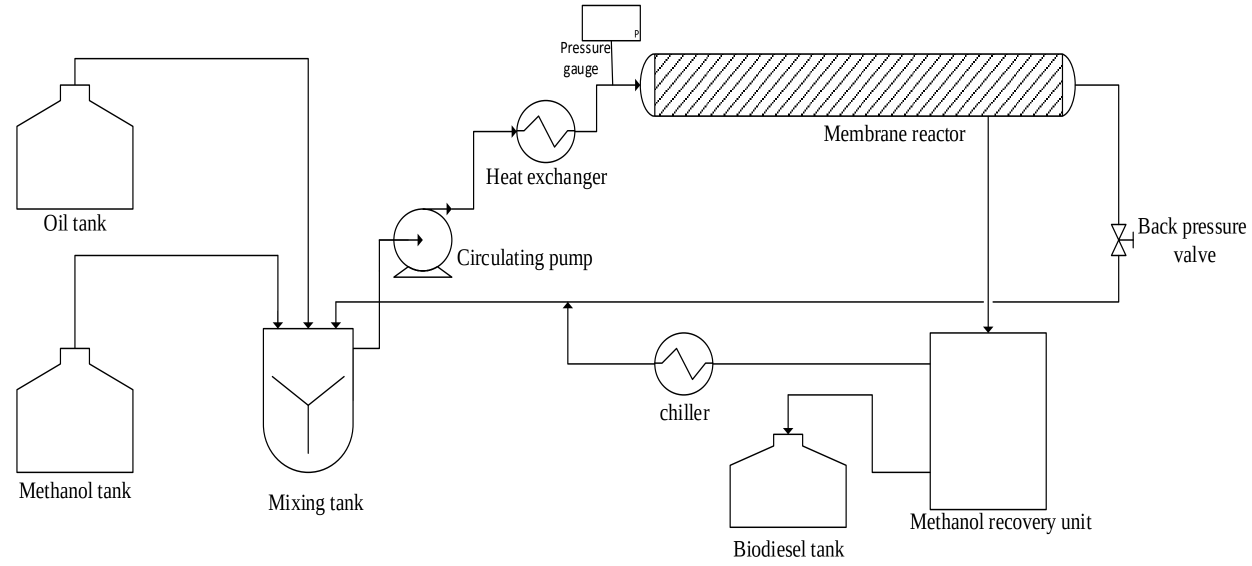


Figure 1. Schematic diagram of a membrane reactor for biodiesel production.

2.3. Catalyst Preparation and Characterization

The catalyst solution was prepared by dissolving the CaO in deionized water. Activated carbon was sieved to size range from 450 to 810 μm, washed with deionized water to remove fines and dirt, oven dried at 100 ^{0}C for a day, cooled in a desiccator and stored in glass bottles. Activated carbon was added to the catalyst solution and then agitated in an orbital shaker at 180 rpm at a constant temperature of 25 ^{0}C for 24 h. The amount of adsorbed CaO was measured by the gravimetrical method. The total loading content of CaO was 40.50 % by weight, based on the initial weight of activated carbon.

In addition, the characteristics of the prepared supported catalyst were determined. Scanning electron micrographs (SEM) were obtained on an FEI Quanta 200 FESEM scanning electron microscope. The accelerating voltage was 20 kV. The SE and BSE detectors were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K was carried out by ASAP 2020, Micromeritics. Prior to taking adsorption data, degassing at 120 ^{0}C and a residual pressure of 300 μmHg for 24 hours was performed using the degassing port.

2.4. Transesterification in the Packed Bed Membrane Reactor

Soybean oil and methanol were charged into the mixing tank separately. The volume ratio of oil to methanol was varied between 3:1 to 12:1 and the catalyst was packed into the membrane reactor. Methanol was charged continuously into the reactor using the circulating pump according to Olagunju and Musonge [15] and heat exchanger was started up to heat the reactants. Subsequently, the reactor was filled with the reactant. The pressure inside the membrane was monitored by two pressure gauges and was controlled at 100Kpa. The permeate stream containing biodiesel and methanol was collected in the beaker. After each run, the circulating pump and heat exchanger were switched off. Thereafter, the system was fully drained, the catalysts were taken out and the system was flushed for 30 min with methanol and then drained. Biodiesel yield in the present experiment was calculated by using the following equation (1):

$$\text{Biodiesel conversion (\%)} = (\text{Mass of the biodiesel} / \text{Mass of the oil used}) * 100\% \qquad (1)$$

3. Results and Discussion

3.1. Catalyst Properties

The SEM analysis of calcium oxide catalyst supported on activated carbon (CaO/AC) showed a good dispersion of calcium oxide on the surface of activated carbon as shown in Figure 2. Based on this result, after loading the catalyst, activated carbon retained its structure and the calcium species were found vastly distributed upon the surface of the support.

Table 1. Characterisation of CaO/AC catalyst

Characteristic	Value	Units	Technique
BET surface area	240.51	m^2/g	BET
Pore volume	0.152	cm^3/g	BET
Micro pore volume	0.121	cm^3/g	BET
Average pore width	2.87	nm	BET
Active sites concentration	1.436	mmol/g	TPD-CO_2

Surface area, pore volume and pore width of the supported catalyst on activated carbon are presented in Table 1. The significant reduction in BET surface area from virgin activated carbon (1425 m^2 /g) to the CaO/AC catalyst with 40.50 wt. % loading (240.51 m^2 /g) indicates filling of calcium oxide molecules into the activated carbon pores. CO_2 temperature programmed desorption (TPD) method was used to determine the basicity of the catalyst.

3.2. Selection of Suitable Membrane for Separation

In order to achieve the suitability of membrane selection, it is important to estimate the size of the dispersed oil droplets in the continuous alcohol phase. The minimum particle size in the oil-methanol emulsion can be estimated from the work of DeRoussel *et al*. [16]. According to previous studies, the average drop size for the unreacted oil was 44 microns with a lower and upper size limit of 12 and 400 microns, respectively [16]. The membrane pore size selected in this study is 0.02 microns, which was able to trap the unreacted oil within the membrane.

The retention of free glycerol and unreacted oil in the reaction medium micro-filtrated by the 0.02 μm membrane was over 99%, which met the standard for biodiesel. The content of impurities was 2 mg/kg and was better than the results of water washing process, so this membrane pore size was selected as a suitable one for the biodiesel refining.

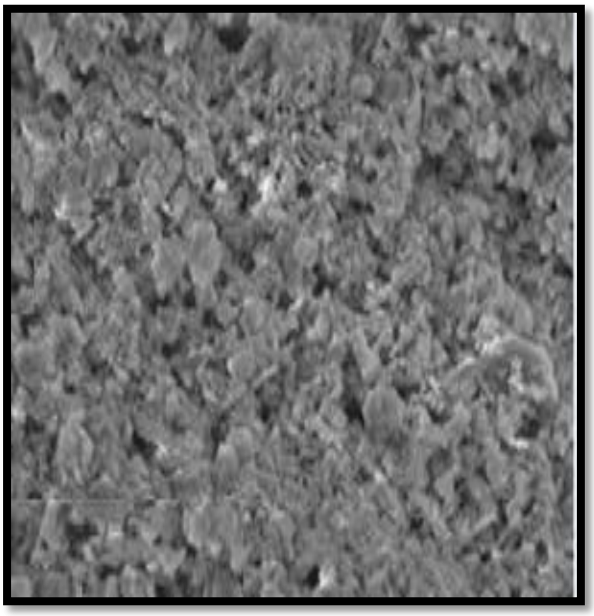


Figure 2. SEM image of calcium oxide supported on activated carbon (CaO/AC).

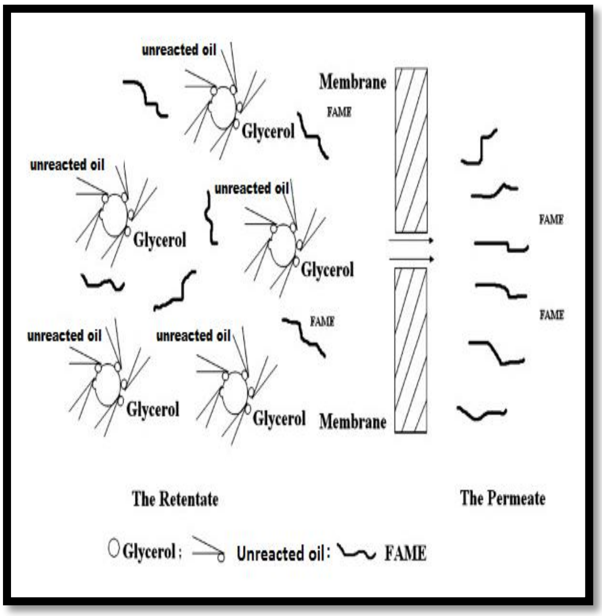


Figure 3. Cross-filtration of crude biodiesel by membrane separation.

The presence of minor residual soap and free glycerol in the biodiesel can cause a serious engine problem and hazardous emissions [17]. Although the South African biodiesel standard (SANS 1935) does not set a direct property for the soap in the final product, the limitation of the content of contaminants in the biodiesel makes a strict rule for the soap content in the refined biodiesel so as to meet the limitation of free glycerol content of less than 0.02 (wt %)

The principle of membrane separation of unreacted oil and free glycerol is depicted in Figure 3. Due to the immiscibility of free glycerol and biodiesel and surface activity of soap, the unreacted oil existed in the form of reversed micelle, which was very similar to the form of phospholipids in the hexane micelle whose size was larger than a single solute molecule [18]. The free glycerol existed in form of droplets suspended in the reaction medium. The hydrophilic end of unreacted oil bond to the free glycerol droplets, while the hydrophobic ones immersed into the crude biodiesel.

3.3. Separation of the Permeate Stream

When the experiments were carried out, the permeate from the membrane reactor percolated as a clear, amber, homogeneous solution. As the solution began to reach room temperature, the permeate separated into two phases with a clear boundary. The absence of particles in the permeate enhanced the separation process. GC analysis revealed that the homogeneous samples were those with the lowest percentage of FAME.

Table 2. Composition of the lower and upper layer for permeate samples taken at 30 and 90 minutes from the beginning of permeation

Phase	FAME (wt. %)	Glycerol (wt. %)	Methanol (wt. %)	Calculated Density (g/mL)
Lower (30 min)	85.5	0	14.5	0.863
Upper (30 min)	19.5	0	80.5	0.828
Lower (90 min)	93.4	0	6.6	0.861
Upper (90 min)	15.6	0	84.4	0.825

Table 2 shows the composition of the different phases. The lower phase in both of these samples was the FAME-rich phase, with an average mass composition of 85.5% after 30 minutes and 93.4% after 90 minutes from the start of permeation (run with membrane pore size 0.02 micron and 300 g oil injection). All samples of the FAME-rich phase taken throughout the run had non-detectable levels of glycerol using GC. In the results, the upper phase was found to be the methanol-rich phase containing no glycerol. This indicates that the amount of FAME in the FAME-rich phase was such that its density was greater than the density of the methanol-rich phase. One important finding was that the location of the FAME-rich phase and methanol-rich phase changed due to no glycerol content. The recycling of the methanol-rich phase is of interest, in order to maximize its usage.

The above observations indicate that the methanol-rich phase of the de-phased permeates can be recycled to the reactor in order to decrease the overall methanol: oil molar ratio. In order to reach a commercial methanol to oil molar ratio of 6:1, it is entirely practical to cool the permeate to allow for phase separation and recycle the methanol-rich phase to the reactor. According to a previous study carried out by Olagunju and Musonge [15], methanol: oil mole ratios of 3:1, 6:1, 9:1 and 12:1 were used and the best condition was achieved with a temperature of 65 °C, methanol/oil molar ratio of 6:1 for 150 minutes, which resulted in the highest FAME yield of 94 %. These operating parameters and yield served as basis for this current experiment study.

At the completion of the runs, the membrane reactor retentate was observed to contain a stable interfacial emulsion similar to that obtained in a batch reactor run under identical process conditions. The conventional method requires several hours to achieve complete separation of the FAME-rich and methanol/glycerine-rich phases. This is because emulsions from the oil or soaps produced during the reaction process may act as emulsifiers or dispersants to prevent phase separation. The situation in a batch reactor would even be worse when using high free fatty acid feedstock. In that case, a significant reduction in biodiesel yield would result. The membrane is thus performing an additional purification function by retaining emulsions within the reactor. The membrane reactor was also tested as a batch reactor without pressurizing the system. The entire content in the reactor was then transferred into a separating funnel and effective separation was completed after 5 hours.

3.4. FAME Characterization

Physical and chemical properties of the produced biodiesel were measured according to the test methods recommended by the American Society for testing and Materials (ASTM). The results of these characterizations are listed in Table 3.

Table 3. Characteristics of FAME produced from soya bean oil using membrane reactor

Characteristic	Test	Units	SANS 1935 Specification Limit	Result
Density @ 15°C	ASTM D7042	g/mL	0.86-0.9	0.87
Viscosity @ 40 °C	ASTM D7042	cSt	3.5-5	3.8
Flash point	ASTM D93	°C	120 min	167
Water content	ASTM D6304	%	0.05 max	-
Total acid number	-	mgKOH/g	0.5 max	0.21
Total Contamination	IP 440	mg/Kg	24 max	2
Sulphur	ASTM D4294	ppm	10 max	1

The results show that the FAME produced using membrane technology is within ASTM standard specifications and biodiesel specification. Biodiesel properties are numerous but the most important properties are those that have direct impact on the performance of the engine such as viscosity, flash point, density and so on. All these properties help to increase the lifespan of the engine, give a better lubrication and complete combustion so that the engine can produce a higher energy output.

4. Conclusion

The experimental setup for this project was constructed and the membrane reactor exhibited a good performance in the transesterification of the high quality of biodiesel yield, which does not require any additional purification process. The following conclusions could be drawn from the study:

(1) The ceramic membrane with the pore size of 0.02 μm was very suitable for this reaction and separation process due to its high flux and the good quality of the permeate.

(2) This new method of biodiesel production showed the advantage of no water usage in the process as compared to the conventional water washing that leads to wastewater being generated and consequently leading to environmental pollution requiring additional treatment.

(3) The characteristics of the product under these conditions were within the ASTM standard.

5. Reference

[1] Jiang J J and Tan C S 2012 Biodiesel production from coconut oil in supercritical methanol in the presence of co-solvent *J. Taiwan Inst. Chem. Eng.* 43 102–7

[2] Manh D V, Chen Y H, Chang C C, Chang M C and Chang C Y 2011 Biodiesel production from tung oil and blended oil via ultrasonic transesterification process *J.Taiwan Inst. Chem. Eng.* 42 640–44

[3] Zhou C, Wang C, Wang W, Wu Y, Yu F, Chi R and Zhang J 2010 Continuous production of biodiesel from soybean oil using supercritical methanol in a vertical tubular reactor: I. Phase holdup and distribution of intermediate product along the axial direction *Chin. J. Chem. Eng.* 18 626–9

[4] Gan M, Pan D, Ma L, Yue E and Hong J 2009 The kinetics of the esterification of free fatty acids in waste cooking oil using $Fe_2 (SO_4)_3$/C catalyst *Chin. J. Chem. Eng.* 17 83–7

[5] Alcantara A, Amores J, Canoira L, Fidalgo E, Franco M J and Navarro A 2000 Catalytic production of biodiesel from soybean oil used frying oil and tallow. *Biomass and Bioenergy* 18 515–27

[6] Leung D and Guo Y 2006 Transesterification of neat and used frying oil: optimization for biodiesel production *Fuel Processing Technol.* 87 883–90

[7] Mittelbach M and Remschmidt C 2004 *Biodiesel-The comprehensive handbook,* First ed., Boersedruck, Ges.m.b.H, (Austria)

[8] Wang Z M, Lee J S, Park J Y, Wu C Z and Yuan Z H 2007 Novel biodiesel production technology from soybean soap stock. *Korean J. Chem. Eng.* 24 1027–30

[9] Sharma Y C and Singh B 2010 Development of biodiesel: current scenario *Renewable and Sust. Energy Rev.* 13 1646-51

[10] Baroutian S, Aroua M K, Raman A A A and Sulaiman N M N 2011 A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst *Bioresource technol.* 102 1095–1102

[11] Saleh J, Tremblay AY and Dubé M A 2010 Glycerol removal from biodiesel using membrane separation technology *Fuel* 89 2260–6

[12] Westermann T and Melin T 2009 Flow-through catalytic membrane reactors principles and applications *Chem. Eng. Process.* 48 17–28

[13] Xie W and Huang X 2006 Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst *Catal. Lett.* 107 53–59

[14] Zabeti M, WanDaud W M A and Aroua M K 2009 Optimization of the activity of CaO/Al_2O_3 catalyst for biodiesel production using response surface methodology *Appl.Catal. A* 366 154-9

[15] Olagunju O A and Musonge P 2015 The performance of a packed bed membrane reactor for the production of biodiesel 2nd Intl., Conf., on Composites, Biocomposites & Nanocomposites 28-30 October 2015 Durban University of Technology, South Africa

[16] DeRoussel P, Khakhar D V and Ottino J M 2001 Mixing of viscous immiscible liquids. Part 2: over emulsification interpretation and use *Chem. Eng.* 56 5531

[17] Plank C and Lorbeer E 1995 Simultaneous determination of glycerol and mono- di- and triglycerides in vegetable oil methyl esters by capillary gas chromatography *J. Chromatogra. A* 697 461–8

[18] Lin L, Rhee K C and Koseoglu S S 1997 Bench-scale membrane degumming of crude vegetable oil: process optimization *J. Membr. Sci.* 134 101–8

Acknowledgements
The financial support from the Institute of Wastewater treatment, Durban University of Technology, South Africa is highly acknowledged.

D-2: CONFERENCE

- Olagunju, O.A and Musonge, P. The performance of a packed bed membrane reactor for the production of biodiesel. 2nd International Conference on Composites, Biocomposites & Nanocomposites, Durban University of Technology, South Africa, 28-30 October 2015.

[illegible]

G.A Olagunju[a*], P. Musonge[a]

[a] Department of Chemical Engineering, Durban University of Technology, South Africa, 4000

gilbert4life2004@yahoo.com, paulm@dut.ac.za

[illegible]

ABSTRACT

This work investigated the performance of a packed bed membrane reactor in the transesterification process of triglycerides to methyl ester using soyabean oil as feedstock. A SiO_2/Al_2O_3 ceramic microporous membrane was selected due to its chemical inert nature and thermal stability to selectively remove the product from the reaction medium. CaO impregnated unto the surface of an activated carbon was packed into the membrane and acted as catalyst.

Operating variables such as temperature, reaction time and flow rate were investigated. The result indicated that premixing the reactants at a temperature of 50^0C facilitated proper contact and accelerated rate of reaction. The maximum yield was 94% during a transesterification of 150 minutes at 65^0C

The performance of the membrane reactor in terms of selectivity, FAME conversion and catalyst retention were compared with the performance of a similar membrane reactor. This allows one to critically analyse the mechanisms through which the operating variables enhances the performance of the membrane reactor.

□□□□ □□□□: ceramic membrane, transesterification, triglycerides, FAME, methyl ester

□□□□□□□□□C□□□□□

The continuous exploration of sustainable energy resources has becomes a global challenge. Biofuel have been identified as one of the most favourable renewable energy sources with great potentials to solve issues relating to global fossil fuel addiction. Biofuels are sustainable, biodegradable and environmental friendly. Currently biodiesel is gaining considerable recognition as a sustainable renewable energy source because it is renewable, non-toxic and eco-friendly (□iang and □an 2012□Manh *et al.*, 2011□□hou *et al.*, 2010).

This biofuel has several benefits over conventional fossil fuels, and some of them include cleaner engine emission, renewability and better lubricating properties, which makes it a good alternative fuel (□an et al., 2009). Biodiesel can be produced from various sources such as vegetable oil (canola, soybean and sunflower oil), non-edible oils (Jatrophacurcas, rapeseed oil) and used vegetable oil (□eung and □uo

2006□ □ang et al., 2007□Alcantra et al., 2000□Mittelbach and Remschmidt, 2004).

Biodiesel is mostly produced in the conventional way using homogeneous base catalysts such as sodium hydroxide or potassium hydroxide. Acid homogeneous catalysts have also been used but the rate of reaction is slow compared to the base catalysed reaction. Homogeneous processes have a lot of shortcomings such as further separation of the catalyst from the reaction mixture, generation of large amounts of wastewater during the separation and purification of the product, and formation of soap due to the reaction of the alcohol with the free fatty acid present in the reaction medium (Sharma and Singh, 2010). Baroutian *et al*. (2011) stated that biodiesel produced using □□□ as the catalyst generated high yield of the product but an additional process such as purification of product and treatment of wastewater generated was further needed, which invariably increased the cost of production.

Heterogeneous catalysis has shown to be a more favourable substitute for biodiesel production from vegetable oils and fat. Heterogeneous catalysis and their activities for transesterification have been studied in recent years (□an *et al*., 2010). Unlike homogeneous catalysis, heterogeneous catalyst is recyclable and can be reused severally with better separation of the end products.

Many researchers have successfully reported the use of heterogeneous catalysis in the production of biodiesel and some of them include: metal hydroxides (□alai *et al*., 2006), metal complexes (Abreu *et al*., 2003), metal oxides such as calcium oxide (□ranados *et al*., 2007), magnesium oxide (□ ang and □ang, 2007), zirconium oxide (□iputti et al., 2006), zeolites, hydrotalcites and supported catalysts (□ie and □uang, 2006). Among the listed catalyst, calcium oxide has attracted much attention due to its basic strength, low solubility in methanol and can be produced from cheap sources. □□pe□ *et al.* (2007) studied the catalytic activity of CaO for biodiesel production from sunflower oil and 94% conversion was reported. Also, □oosu□ *et al.* (2010) reported a yield of 94% using CaO as catalyst while producing biodiesel from palm oil. However, most of these methods were carried out using the conventional batch system and one of the major complications associated with heterogeneous catalysis in this type of system, is the formation of three phases with alcohol and oil which leads to diffusion limitations thus lowering the rate of the reaction (Mbara□a and Shan□s, 2006).

Biodiesel production might be regarded as a suitable sustainable energy with a lot of advantages but still seems less attractive and costlier as compared to fossil fuel and this can be attributed to high cost of production. In other to make biodiesel more competitive and attractive to users a better approach which eliminates all the various challenges associated with its production such as immiscibility of reactants, separation of product, further purification of product and wastewater generation has to provided. This method involves the use of membrane separation technology to exploit the various challenges encountered by using homogenous transesterification.

Membrane separation technology has been extensively used in wastewater purification by various researchers because of its ability to carry out separation of different components in a single process stream based on their molecular weight. In this process, reaction and separation take place within a single unit and therefore eliminates the need for a further purification step. Membrane reactors have the ability to selectively remove the product from the reaction mixture by allowing the component with lower molecular weight to pass through its pore while higher molecular weight components are restricted. This method also allows for proper contact between the immiscible reactants and catalyst and as a result, higher yield of the product can be achieved (Westermann and Melin, 2009). South Africa is known to be a water scarce country and the use of membrane technology to produce biodiesel will help to conserve water for other purposes, eliminate its use for purifying the product and makes the environment free from pollution. This technology had been previously explored by Baroutian *et al*. (2011) using potassium hydroxide as catalyst and palm oil as feedstock. However, there is still a problem of membrane selectivity which this study tends to address. Furthermore, a comparative study using a different feedstock and catalyst is essential for affirming this technology for the production of biodiesel.

In this work, a packed bed membrane reactor was used to produce methyl esters biodiesel. The combination of heterogeneous alkali transesterification and triglyceride separation in the packed bed membrane reactor will be employed.

Ceramic membrane is a filter medium composed of inorganic oxides which permeate liquids through pores and separate out solid matters by retention. Ceramic have high permeability, good separation i.e. sharp cut-off value and long lifetime. Ceramic membrane offer more advantages over polymeric membrane and this includes: high chemical resistance, high thermal stability and high durability. The chemical stability makes possible, the utilization of chemically aggressive cleaning methods. Furthermore the thermal stability enables the use of steam and high temperature during its operation (Baroutian *et al*., 2011)

For this purpose a tubular ceramic (TiO_2/Al_2O_3) membrane will be used as reactor and separator because of its high thermal stability and it will be filled with calcium oxide catalyst supported on activated carbon. Among the available supports (Zabeti et al., 2009; Xie and Huang, 2006) activated carbon has proved to be highly effective as a catalyst support that can be used in transesterification process.

Activated carbon has a large surface area, inert carbon skeleton, good physical/thermal stability and it can be locally produced at low cost.

[illegible]

[illegible]

Soybean oil was purchased from a local market. Methanol (99.8%) was supplied by Laboratory supplies co., South Africa. Pure calcium oxide (98.9%) was used as a catalyst for transesterification and was obtained from associated chemical enterprises, South Africa and the activated carbon granules used in this work was purchased from the same company.

[illegible]

Fig. 1 shows the experimental setup for the biodiesel production. A tubular ceramic membrane (Atech Innovations Gmbh, Germany) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 1000 mm, 16 mm, 25.4 mm and 0.02 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m^2. A Watson marlow 313S peristaltic pump (Cole-Parmer Instrument, USA) was employed to feed the raw materials and to prepare circulation inside the system. The Chem-Durance chemical resistant pump tubing with a size of 16 ([illegible] [illegible]44 mm, [illegible] [illegible]2.36 mm) was used. To prepare reaction temperature a shell and tube heat exchanger equipped with a hot water circulator bath was used. Pressure and temperature of the system were monitored by pressure gauges and thermometer. Catalysts particles were packed inside the ceramic membrane and held in place using cloth screens attached to the upstream and downstream tubing. From the preliminary experiment conducted, it was observed that methanol and biodiesel molecules were able to pass through the membrane which can be attributed to their smaller molecular sizes while the glycerol and unreacted oil goes into the recycling tank. This finding quite differs from the result of the study carried out by Baroutian *et al*., (2011) who recorded that product, by-product and methanol were able to pass through the membrane which means the filtrate containing biodiesel and glycerol needs further separation process for pure biodiesel to be collected and this can take several hours to be accomplished. Although the pore size of the membrane used for this experiment was 0.02μm and might be the reason for inability of glycerol to pass through.

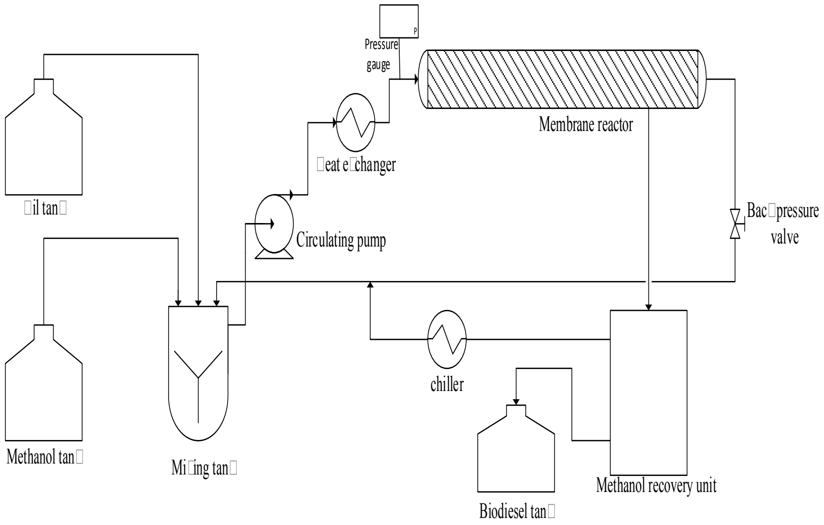


Figure 1: Schematic diagram of membrane reactor for biodiesel production.

Catalyst preparation and characterization

The catalyst solution was prepared by dissolving the CaO in deionized water. Activated carbon was sieved to size range from 450 to 810 µm, washed with deionized water to remove fines and dirt, oven dried at 100^0C for a day, cooled in a desiccator and stored in glass containers. Activated carbon was added into the catalyst solution and then agitated in an orbital shaker at 180 rpm at constant temperature of 25^0C for 24 h. The amount of adsorbed CaO was measured by gravimetrical method. The total loading content of CaO was 40.50% by weight, based on the initial weight of activated carbon.

In addition, the characteristics of the prepared supported catalyst were determined. Scanning electron micrographs (SEM) were obtained on a FEI Quanta 200 FESEM scanning electron microscope. The accelerating voltage was 20 kV. The SE and BSE detector were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K was carried out by ASAP 2020, Micromeritics. Before taking adsorption data, degassing at 120^{0}C and a residual pressure of 300 μmHg for 24 hours was performed using the degas port.

Transesterification in the packed bed membrane reactor

Soybean oil and methanol were charged into the mixing tank separately. The volume ratio of oil to methanol was 1:6 and the catalyst was also packed into the membrane reactor. Methanol was charged continuously into the reactor using the circulating pump according to Baroutian et al., (2011) and heat exchanger was started up to heat the reactants. Subsequently the reactor was filled with reactant. Pressure inside the membrane was monitored by two pressure gauges and was controlled at 100 kpa. The permeate stream containing biodiesel and methanol were collected in the beaker. After 1 hour of reaction time, the circulating pump and heat exchanger were switched off and the products were collected into a beaker. The excess alcohol was removed from the ester layer by evaporation and the produced biodiesel were sent for analysis. After each run, the system was fully drained, the catalysts were taken out and the system was flushed for 30 min with pure ethanol and then drained after each run. Biodiesel yield in the present experiment was calculated by using the following:

[illegible]

[illegible]

[illegible]

The SEM analysis of calcium oxide catalyst supported on activated carbon (CaO/AC) showed a good dispersion of calcium oxide on the surface of activated carbon as shown in Fig. 5. Based on this result, after loading catalyst, activated carbon retained its structure that was important for catalysis and therefore the calcium species were found vastly distributed upon the surface of the support.

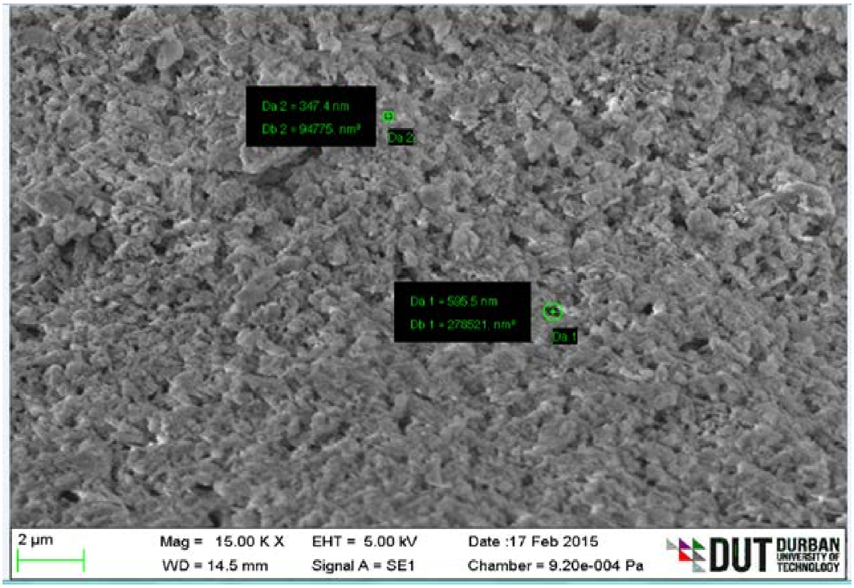


Fig 5: SEM image of calcium oxide supported on activated carbon (CaO/AC)

[illegible]

[illegible]

As shown in Fig. 6 (a), increasing the reaction temperature favoured the transesterification. However, raising the temperature above 65^{o}C which is the boiling point of methanol drops the conversion rate due to the continuous boiling of methanol which consequently leaves the reaction medium. Therefore, the reaction at 65^{o}C is appropriate. These results correspond with those reported in the literature where higher reaction temperature favours higher biodiesel production (Baroutian et al., 2011).

[illegible]

As shown in Fig. 6 (b), due to the heterogeneous reaction nature, there was no significant yield in the first 30 minutes of the reaction. The rate of conversion was slow in the first 60 minutes, however, the conversion increased rapidly as the time increased and the conversion reached a maximum of 90% when the reaction time was 150 minutes. Increasing the time beyond 150 minutes shows little improvement in the conversion rate. By comparison, □a□endra et al. (2010) report 93% conversion of biodiesel at the same experimental condition.

[illegible] r[illegible]

Figure 6 (c) shows the effect of flow rate on the biodiesel yield. The flow rate of oil and methanol mixture was varied from 900mL to 1100mL and an average of 85.7% yield was obtained. It is possible to assume that increasing the flow rate has a positive effect on increasing biodiesel yield.

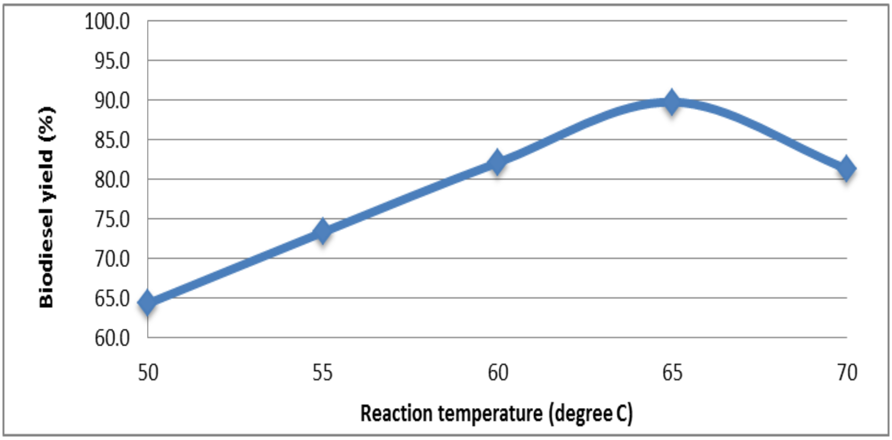


Fig. 6 (a) Influence of reaction temperature on biodiesel yield

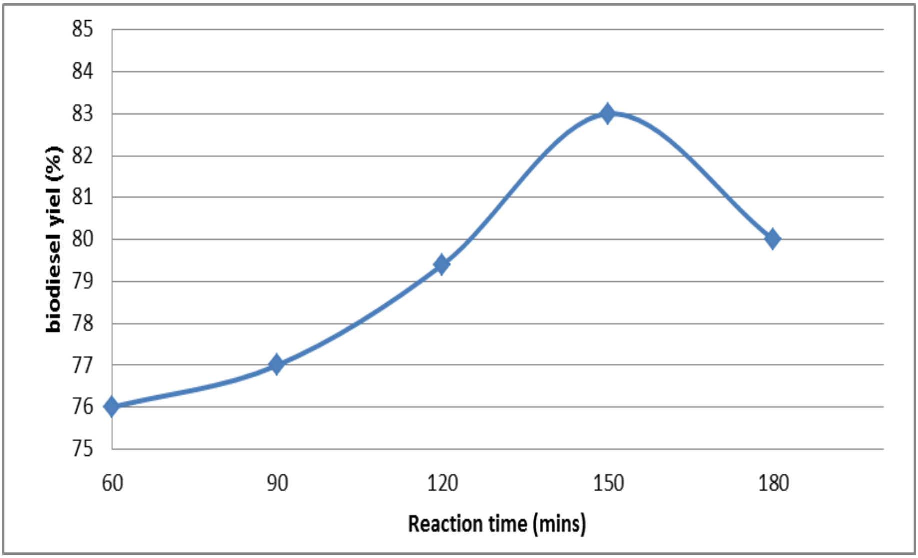


Fig. 6 (b) Influence of reaction time on biodiesel yield

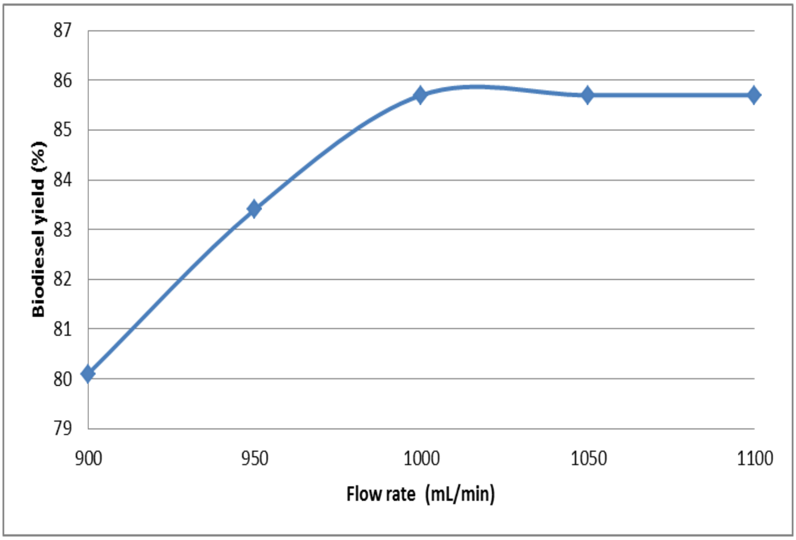
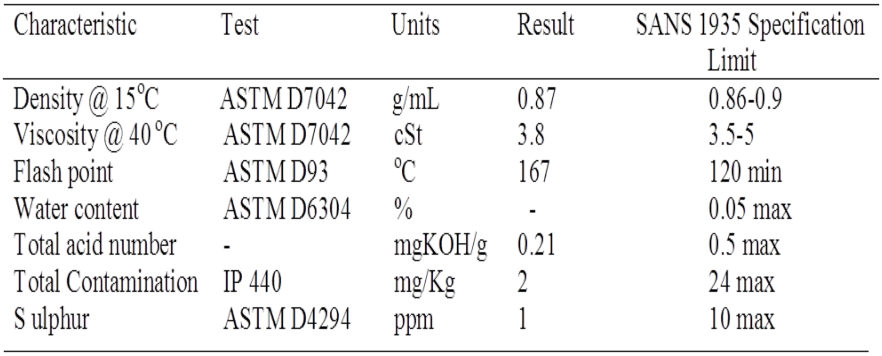


Fig. 6 (c) Influence of flow rate on biodiesel yield

[illegible]

Physical and chemical properties of the produced biodiesel were measured according to the test methods recommended by the American Society for testing and Materials (ASTM) as follows viscosity at 40^{0}C (ASTM D7042), water content (ASTM D6304), density at 15^{0}C (ASTM 7042), total acid number, total contamination ([illegible] 440), Sulphur (ASTM D4294), flash point (ASTM D93). The results of these characterizations are listed in Table 1. It can be seen from the table that the biodiesel produced using membrane technology is within ASTM standard specifications.

Table 1: Characteristics of biodiesel produced from soya bean oil using membrane reactor



Characteristic	Test	Units	Result	SANS 1935 Specification Limit
Density @ 15°C	ASTM D7042	g/mL	0.87	0.86-0.9
Viscosity @ 40 °C	ASTM D7042	cSt	3.8	3.5-5
Flash point	ASTM D93	°C	167	120 min
Water content	ASTM D6304	%	-	0.05 max
Total acid number	-	mgKOH/g	0.21	0.5 max
Total Contamination	IP 440	mg/Kg	2	24 max
Sulphur	ASTM D4294	ppm	1	10 max

Biodiesel properties are numerous but the most important once are those that have direct impact on the performance of the engine such as viscosity because of its effect on the atomization of the fuel being injected into the engine combustion compartment, flash point which is much higher than diesel, density which is lesser than water and so on. All these properties help to increase the life span of the engine, give a better lubrication and complete combustion so that the engine can produce a higher energy output.

CONCLUSION

The membrane reactor exhibited a good performance in transesterification of high quality of biodiesel yield which does not require any additional purification process. Also, it was observed that membrane was able to retain the glycerol due to its higher molecular weight from passing through its pore but allowed methanol and biodiesel to flow through. This is an exhibition of good performance which helps to safe cost and time required if further processes are to take place. The effects of parameters including temperature, reaction time and flow rate were found significant. The highest yield of 94% was obtained at 65^0C reaction temperature, reaction time of 150 minutes and flow rate of 900mL/min. This yield is in line with what was recorded in the experiment conducted by Baroutian et al., (2011). The characteristics of the product under these conditions were within the ASTM standard.

REFERENCES

[1] Abreu, F.R., Lima, D.G., Hamu, E.H., Einloft, S., Rubim, J.C. and Suarez, P.A.Z., 2003. New metal catalysts for soybean oil transesterification. J. Am. Oil Chem. Soc. 80: 601– 604.

[2] Alcantara, A., Amores, J., Canoira, L., Fidalgo, E., Franco, M.J. and Navarro, A., 2000. Catalytic production of biodiesel from soybean oil used frying oil and tallow. Biomass and Bio energy: 18. 515–527.

[3] Baroutian, S., Aroua, M.K., Raman, A.A.A. and Sulaiman, N.M.N., 2011. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bio resource Technology. 102: 1095–1102.

□4□ □alai, A.□., □ul□arni, M.□. and Meher, □.C., 2006. Biodiesel productions from vegetable oils using heterogeneous catalysts and their applications as lubricity additives. □EEE□C Climate Change Technology Conference, E□CCCC art 4057358.

□5□□an, M., □an, □., Ma, □., □ue, E. and □ong, □, 2009. The kinetics of the esterification of free fatty acids in waste cooking oil using Fe2 (S□4)3□C catalyst: Chin. □ Chem. Eng.17, 83–87.

□6□□ranados, M.□., □oves, M.□.□., Alonso, □.M.R., Mariscal, F.C., □alisteo, R., Moreno□ost, □, Santamar□a, □□.□. and Fierro., 2007. Biodiesel from sunflower oil by using activated calcium oxide: Applied Catalysis. B, Environmental 73: 317–326.

□7□□iang, □□ and □an, C.S., 2012. Biodiesel production from coconut oil in supercritical methanol in the presence of co solvent: □ Taiwan Inst. Chem. Eng. 43, 102–107.

□8□ □itputti, □, □itiyanan, B., Rangsunvigit, □, Bunya□iat, □., Attanatho, □. and □envanitpan□a□ul, □, 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem. Eng. □ 116: 61–66.

□9□□eung, □. and □uo, □., 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Processing Technology. 87:883–890.

□10□□□pe□, □.E.,Suwanna□arn, □., Bruce, □. A. and □oodwin □r., □. □., 2007. Esterification and transesterification on tung stated □irconia: effect of calcination temperature. □ournal of Catalysis. 247 (1), 43□50.

□11□Manh, □.□., Chen, □.□., Chang, C.C., Chang, M.C. and Chang, C.□., 2011. Biodiesel production from □ung oil and blended oil via ultrasonic transesterification process: □. □aiwan □nst. Chem. Eng. 42, 640–644.

□12□Mbara□a, □□. and Shan□s, B.□., 2006. Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. □A□CS. □ournal of the American □il Chemists□Society 83. 79–91.

□13□ Mittelbach, M. and Remschmidt, C., 2004. Biodiesel□□he comprehensive handboo□, First ed., Boersedruc□, □es.m.b.□, Austria.

□14□ Sharma, □.C. and Singh, B., 2010, □evelopment of biodiesel: current scenario, Renewable and Sustainable Energy Reviews, 13. 1646□1651.

□15□□ ang, □. and □ang, □., 2007. □ransesterification of soybean oil with nano□Mg□ or not in supercritical and subcritical methanol. Fuel 86, 328–333.

□16□ □ ang, □.M., □ee, □.S., □ar□, □.□., □ u, C.□. and □uan, □.□., 2007. □ovel biodiesel production technology from soybean soap stoc□. □orean □ournal of Chemical Engineering: 24, 1027–1030.

□17□ □ estermann, □. and Melin, □., 2009. Flow□through catalytic membrane reactors□ principles and applications. Chem. Eng. □rocess. 48, 17–28.

□18□ □ie, □ . and □uang, □., 2006. Synthesis of biodiesel from soybean oil using heterogeneous □F□□n□ catalyst. Catal. □ett. 107: 53–59.

□19□ □an, S., □iMaggio, C., Mohan, S., □im, M., Salley, S.□. and Simon, □g □□., 2010. Advancements in heterogeneous catalysis for biodiesel synthesis. □op Catal. 53: 721□36.

□20□ □oosu□, B., □domsap, □.,□uttasawat, B. and □rasae, □., 2010. □mproving transesterification activity of Ca□ with hydration techni□ue. Bio resource □echnology, 101 (10), 3784□3786.

□21□□abeti, M., □ an□aud, □ . M. A. and Aroua, M. □., 2009. □ptimi□ation of the activity of Ca□□Al2□3 catalyst for biodiesel production using response surface methodology. Appl. Catal., A 366: 154–159.

□22□ □hou, C., □ ang, C., □ ang, □ ., □ u, □., □u, F., Chi, R. and □hang, □., 2010. Continuous production of biodiesel from soybean oil using supercritical methanol in a vertical tubular reactor: □

phase holdup and distribution of intermediate product along the axial direction. Chin. J. Chem. Eng.18, 626–629.

D-3: JOURNAL PUBLICATION (SUBMITTED FOR REVIEW)

- Olagunju, O.A. and Musonge, P. 2017. Optimization of soybean oil biodiesel production by using response surface methodology. South African Journal of Chemical Engineering.

Optimization of soybean oil biodiesel production by using response surface methodology

O.A Olagunju, **P. Musonge**

Department of Chemical Engineering, Durban University of Technology, South Africa, 4000

gilbert4life2004@yahoo.com, paulm@dut.ac.za

ABSTRACT

The response surface methodology (RSM) based on central composite design was used to determine the optimal conditions for the biodiesel production from soybean oil. Four process variables were assessed (2^4 experimental design). A total of 30 experiments was designed and conducted to study the effect of temperature, reaction time, methanol to oil molar ratio and catalyst concentration (calcium oxide supported on activated carbon). The optimum condition was obtained at 3 g/L catalyst concentration, 65 ^{0}C temperature, 4.5:1 methanol to oil molar ratio and 90 minutes reaction time. At this optimum condition, the FAME yield was 96.9 %, which is well within the yield of 97.7 % as predicted by the model. Experimental verification was carried out on the design and it confirms the validity of the model. The biodiesel produced was characterized and the fuel properties such as kinematic viscosity, density, flash point, copper corrosion, calorific value, cloud point, pour point, ash content and carbon residue were determined. Methyl ester produced met the ASTM D6751 and SANS 1935 standards.

Keywords: Soybean oil, Biodiesel, Response surface methodology, Central composite design, Fuel properties.

INTRODUCTION

Fossil fuels are getting exhausted all over the world and this is caused by the continuous increase in demand of these products. Many countries in the world are in search of alternative sources of fuel for their energy need. Among the various renewable energy sources, biodiesel is considered as an alternative to diesel fuel because it is a renewable source that under goes complete combustion. It is also biodegradable, non-toxic and emits less CO particulates as compared to conventional diesel (Yoosuk *et al*., 2010; Kafuku *et al*., 2010). Biodiesel can be produced from various sources like vegetable oils, greases, and animal fats. It is chemically known as fatty acid alkyl ester. Biodiesel can be produced by the transesterification of triglycerides with alcohol (commonly methanol) in the presence of a catalyst (base, acid and enzyme) (Dussan *et al*., 2010; TuThanh *et al*., 2010).

Primarily, the production of biodiesel has been by the conventional method. This involves the reaction of vegetable oil or animal fat with an alcohol (methanol) in the presence of homogeneous basic catalysts (primarily sodium hydroxide or potassium hydroxide). Using a basic catalyst such as NaOH or KOH has a lot of disadvantages such as soap formation, difficulty in recovering which leads to downstream wastewater treatment and hence, increasing the cost of biodiesel production. The total cost of producing biodiesel using homogenous catalyst is not sufficiently competitive enough compared to fuel produced from crude oil. Therefore, there is need to consider an alternative process, which eliminates the various problems associated with homogenous transesterification problems leading to safer, cheaper, and more environment-friendly operation.

The combination of heterogeneous catalysis and membrane technology is an alternative process that can be used to overcome the challenges encountered by the homogenous process. In the heterogeneous process, the catalyst can be easily separated from the product and be reused. There is also an integration of reaction and separation into a single process, thereby reducing separation cost and recycle requirement, resulting in higher conversion (Olagunju and Musonge, 2017).

Studying the optimization process is crucial for maximising the production of biodiesel. Conservatively, the optimization of biodiesel production process was achieved with the variation of one factor at a time and the response is a function of a single parameter which is time consuming and excessive in cost (Olagunju and Musonge 2017). This technique does not include interactive effects among the variables and it does not depict the complete effect of the parameters on the process (Olagunju and Musonge 2017).

However, the use of response surface methodology (RSM) technique in multivariable system offers a research strategy to study the interaction of the parameters using statistical methods.

The experimental model of biodiesel synthesis which is developed using response surface methodology is able to simulate the reaction under various transesterification conditions with good error estimation. This is helpful when mass production of the biodiesel is needed.

Rashid *et al.* (2009) used RSM to optimize the process parameters in base catalytic methanolysis of sunflower seed oil for biodiesel production. In another study, Bojan *et al.* (2011) applied the same method for biodiesel production from high free fatty acid J. curcas oil. Response surface methodology was also applied to optimize transesterification conditions for biodiesel production using acid oil and jajoba oil (Bouaid *et al.*, 2007; Chen *et al.*, 2008). In the present study, efforts were made to optimize the process condition for transesterification reaction to increase the yield of biodiesel from soybean oil in a membrane reactor. The influence of the variables such as temperature, reaction time, molar ratio and catalyst concentration, on transesterification was studied. The quality tests of the fatty acid methyl ester produced was also reported.

EXPERIMENTAL

Materials

Soybean oil was purchased from a local market. Methanol (99.8%) was supplied by Laboratory supplies co., South Africa. Pure calcium oxide (98.9%) was used as a catalyst for transesterification and was obtained from Associated Chemical enterprises, South Africa and the activated carbon granules used as the catalyst support in this study was purchased from the same company.

Transesterification in the packed bed membrane reactor

Figure 1 shows the experimental setup. Soybean oil and methanol were charged into the mixing tank separately. The volume ratio of oil to methanol was varied from 3:1 to 6:1

and the catalyst was packed into the membrane reactor. Methanol was charged continuously into the reactor using the circulating pump according to Olagunju and Musonge (2015) and heat exchanger was started up to heat the reactants. Subsequently, the reactor was filled with the reactant.

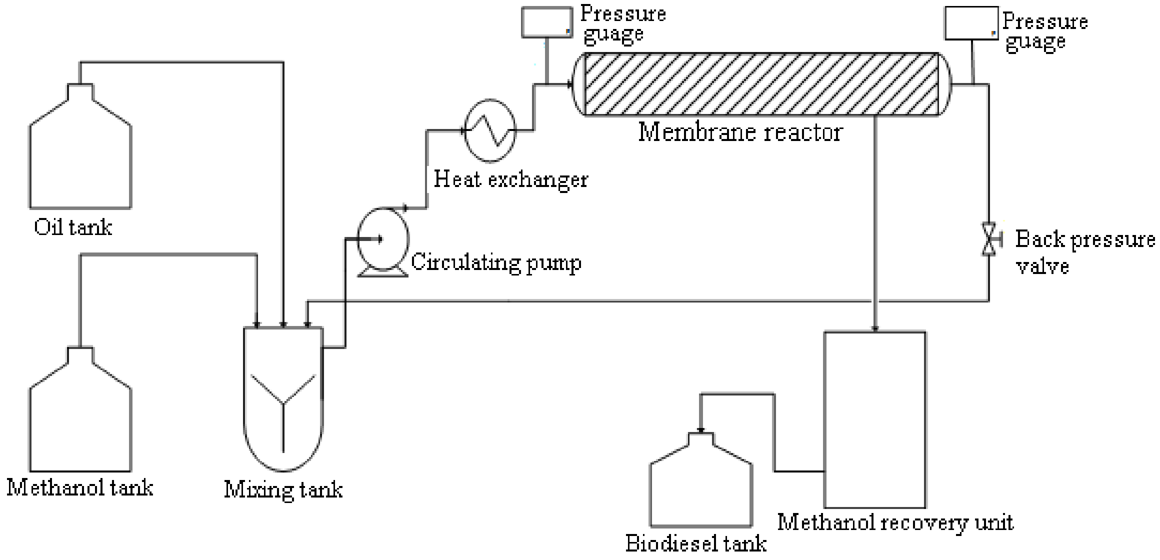


Figure 1: Laboratory scale experimental setup for biodiesel production.

The pressure in the membrane reactor was monitored by two pressure gauges and was controlled at 100Kpa. The permeate stream containing biodiesel and methanol was collected in the beaker. After each run, the circulating pump and heat exchanger were switched off. Thereafter, the system was fully drained; the catalysts were taken out and dried. The system was flushed for 30 min with methanol. Biodiesel yield in the present experiment was calculated by using the following equation (1):

$$\text{Biodiesel conversion (\%)} = (\text{Mass of the biodiesel} / \text{Mass of the oil used}) * 100\% \qquad (1)$$

Experimental design

A preliminary study to determine the optimum range of significant variables was previously carried out. The optimum yield was between 90% - 94% within a reaction time of 60 – 180 minutes, methanol to oil ratio 3:1 - 6:1, catalyst concentration 1 - 4 g/L.

and temperature range of 60 ^{0}C - 70 ^{0}C (Olagunju and Musonge 2015). This result set the base for the optimization process of biodiesel production in the current study.

The effects of four transesterification variables on the yield of soybean oil methyl esters were evaluated using response surface methodology based on central composite design (CCD) with four factors varied at three levels: a high level, represented as (+1), a low level represented as (-1) and a middle point (0) consisting of 30 experiments. The design variables were temperature (X_1, ^{o}C), reaction time (X_2, min), molar ratio (X_3) and catalyst concentration ($X_{4,}$ g/L) while the response variable was biodiesel yield (Y, %). The range and the levels of the independent variables chosen for the present study are presented in Table 1. Each experiment was performed in triplicates and the average yield of biodiesel was taken as the response variable Y.

Table 1 – Experimental range and values for RSM

Variables	**symbol**	**-1**	**0**	**1**
Temperature (^{o}C)	X_1	60	65	70
Reaction time(minutes)	X_2	60	90	120
Molar ratio	X_3	3:1	4:1	6:1
Catalyst concentration	X_4	1	2.5	4
Output				
Biodiesel yield (%)	Y			

Statistical analysis (ANOVA)

The polynomial equation raised to the order of two was then assigned to the obtained data by a multiple regression protocol. Thus complying an empirical model which gives the nature between responses measured to the independent variables of the experiment. The empirical regression model equation for a four factor system was taken as:

$$\mathbf{Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 + \alpha_{12} X_1 X_2 + \alpha_{13} X_1 X_3 + \alpha_{14} X_1 X_4 + \alpha_{23} X_2 X_3 + \alpha_{24} X_2 X_4 + \alpha_{34} X_3 X_4 + \alpha_{11} X_1^2 + \alpha_{22} X_2^2 + \alpha_{33} X_3^2 + \alpha_{44} X_4^2} \quad \mathbf{(2)}$$

where Y is the predicted response, α_0 is the intercept, α_1, α_2, α_3, α_4 are linear coefficients, α_{11}, α_{22}, α_{33}, α_{44} are squared coefficients, and α_{12}, α_{13}, α_{14}, α_{23}, α_{24}, α_{34} are interaction coefficients and X_1 represented temperature (^oC) , X_2 was reaction time (min), X_3 was molar ratio and X_4 was catalyst concentration. The response of the CCD design was fitted with a second order polynomial equation. Statistical analysis of the data was performed by Design-Expert version 10.0 (Stat Ease, Inc., Minneapolis, USA) to evaluate the analysis of variance (ANOVA), the F value within the level of 95% and p value of <0.05. The optimum values of the selected variables were obtained by analysing the response surfaces and solving the regression equation. The fitted polynomial equation was expressed in the form of three-dimensional response surface plots to illustrate the main interactive effects of the independent variables.

RESULTS AND DISCUSSION

Response surface methodology

A central composite design was employed in this study to develop an experimental matrix for the reaction variables; temperature, reaction time, methanol:oil ratio and catalyst concentration. Table 2 shows the experimental matrix for 30 randomized runs.

The biodiesel yield varied from 48% to 96%. The application of the advanced multiple regression analysis was employed to obtain the polynomial equation with the coefficient of full regression model equation and their statistical significance was determined. The equation of the significant terms obtained from the model in its coded form is as follows:

$$Y = 94.75 + 5.18X_1 + 3.60X_2 - 7.07X_3 + 4.24X_4 + 1.39X_1X_2 - 0.64X_1X_3 - 3.98X_1X_4 + 4.36X_2X_3 + 3.02X_2X_4 - 3.73X_3X_4 - 9.38X_1^2 - 1.50X_2^2 - 9.00X_3^2 - 3.63X_4^2 \qquad (2)$$

Table 2: Experimental matrix results

Standard runs	Randomized runs	Coded factors				Response Y
		X_1	X_2	X_3	X_4	
1	**29**	-1	-1	-1	-1	62
2	**5**	1	-1	-1	-1	90
3	**14**	-1	1	-1	-1	60
4	**12**	-1	1	-1	-1	75
5	**13**	-1	-1	1	-1	49
6	**2**	1	-1	1	-1	66
7	**18**	-1	1	1	-1	55
8	**8**	1	1	1	-1	79
9	**24**	-1	-1	-1	1	84
10	**27**	1	-1	-1	1	92
11	**17**	-1	1	-1	1	89
12	**11**	1	1	-1	1	95
13	**6**	-1	-1	1	1	50
14	**10**	1	-1	1	1	60
15	**30**	-1	1	1	1	78
16	**3**	1	1	1	1	74
17	**25**	-2	0	0	0	50
18	**22**	2	0	0	0	60
19	**4**	0	-2	0	0	78
20	**15**	0	2	0	0	95
21	**23**	0	0	-2	0	65
22	**21**	0	0	2	0	48
23	**1**	0	0	0	-2	62
24	**9**	0	0	0	2	94
25	**20**	0	0	0	0	93
26	**7**	0	0	0	0	94
27	**26**	0	0	0	0	92
28	**28**	0	0	0	0	95
29	**19**	0	0	0	0	93
30	**16**	0	0	0	0	96

Where Y is biodiesel yield and X_1, X_2, X_3 and X_4 are the coded forms of temperature (^oC), reaction time (min), methanol:oil ratio, catalyst concentration (g/L) respectively. From the equation, the coefficient with one factor signifies the effect of individual form while the coefficient which has two factors and second order form signifies the interaction between themselves and other variables. The suffix symbols positive or negative (+/−) signifies the synergy and negative effects, where the positive stands for synergistic effect and the negative stands for negative effect (Joshi *et al.*, 2008). Then the model was analysed by using analysis of variance (ANOVA) to obtain the fitness of the model. The study of this model variation is presented in Table 3.

Table 3: ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	8183.89	14	584.56	24.05	< 0.0001	significant
X_1: *A-Temperature*	*2412.32*	*1*	*2412.32*	*99.26*	*<0.0001*	
X_2: *B-Reaction time*	*1199.92*	*1*	*1199.92*	*49.37*	*<0.0001*	
X_3: *C-Molar ratio*	*310.32*	*1*	*310.32*	*12.77*	*0.0028*	
X_4: *D-Catalyst concentration*	*933.75*	*1*	*933.75*	*38.42*	*< 0.0001*	
X_1X_2: *AB*	*31.08*	*1*	*31.08*	*1.28*	*0.2759*	
X_1X_3: *AC*	*6.63*	*1*	*6.63*	*0.27*	*0.6091*	
X_1X_4: *AD*	*253.61*	*1*	*253.61*	*10.44*	*0.0056*	
X_2X_3: *BC*	*303.63*	*1*	*303.63*	*12.49*	*0.0030*	
X_2X_4: *BD*	*145.81*	*1*	*145.81*	*6.00*	*0.0271*	
X_3X_4: *CD*	*222.76*	*1*	*222.76*	*9.17*	*0.0085*	
X_1^2: A^2	*2223.26*	*1*	*2223.26*	*91.48*	*< 0.0001*	
X_2^2: B^2	*61.97*	*1*	*61.97*	*2.55*	*0.1311*	
X_3^2: C^2	*643.77*	*1*	*643.77*	*26.49*	*0.0001*	
X_4^2: D^2	*361.05*	*1*	*361.05*	*14.86*	*0.0016*	
Residual	364.54	15	24.30			
Lack of Fit	*360.66*	*10*	*36.07*	*46.54*	*0.1533*	*Not significant*
Pure Error	*3.88*	*5*	*0.78*			
Cor Total	8548.43	29				

The statistical analysis of the regression equation by ANOVA showed that the R^2 value (multiple correlation coefficient) was 0.9574 (R^2 value >0.75 indicates fitness of the model). The obtained value presents the total variation of the data evaluated by our model and it is capable of explaining 95.74% of the total variation in the experimental observed parameters and their mutual interactions. The theoretical values of adj R^2 and the pred R^2 were 0.9176 and 0.8861 respectively, the difference between adjusted R^2 and predicted R^2 is less than 0.2 which signifies reliability of the model.

The scale of R^2 ranges from 0 to 1.0 and a value closer to 1.0 signifies the model fitness. Adequate precision (AP) is defined as a measure of the experimental signal to noise ratio (Baroutian *et al.*, 2011); an AP that exceeds 4 usually indicates that the model will give reasonable performance in prediction. The adequate precision value of the model is 14.726 which confirms the model's flexibility and reliability (Yuan *et al.*, 2008). The model F value of 24.05 indicates that the model is significant. The p value of the model was <0.0001 ($p < 0.05$) which is significant and the lack of fit model was found to be insignificant. The small value of p shows mutual interaction between the variables and indicates the importance of those variables in the model. (Noordin *et al.*, 2014). Thus, according to p value (value less than 0.05 indicates the significance level) obtained in this study, we found that the X_1, X_2, X_3, X_4, X_1X_4, X_2X_3, X_2X_4, X_3X_4, X_1^2, X_3^2 and X_4^2 were significant.

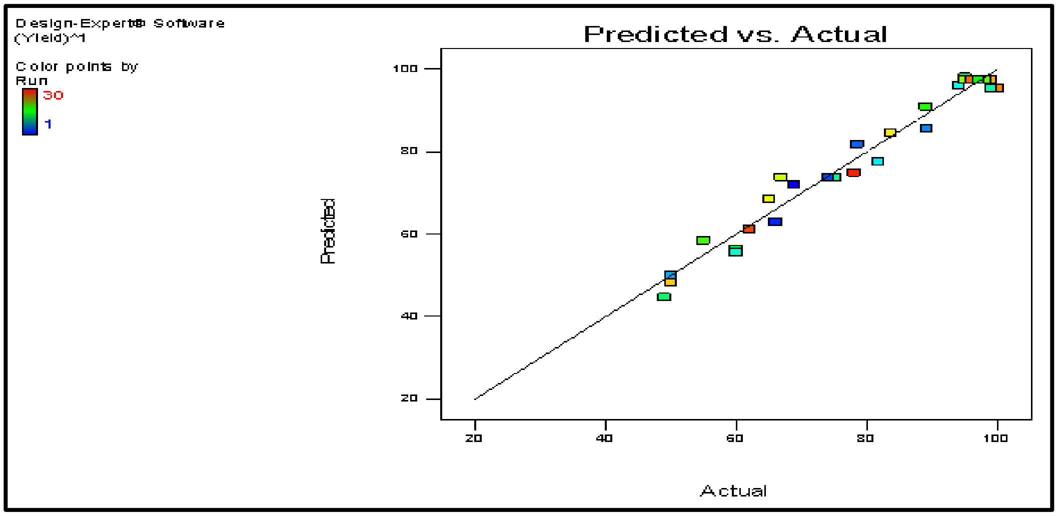


Figure 2: The biodiesel conversion predicted from model versus actual yield.

Fig. 2 shows the actual values and the predicted values for the conversion of soybean oil to biodiesel in the packed bed membrane reactor, with a high value of coefficient of determination ($R^2 = 0.9574$). The values were close to the 45-degree line and this indicates a strong correlation between the model prediction and its actual result.

The surface plots in three dimensions represent the graphical interface about the regression equation of reaction variables. Fig. 3 – Fig. 6 represents the 3D surface plots of predicted biodiesel yield. These plots illustrate the interaction between two independent variable on single dependent parameter i.e., biodiesel yield. The plots are drawn with the aid of the regression equation and represent the interactions of each independent variable on the response variables.

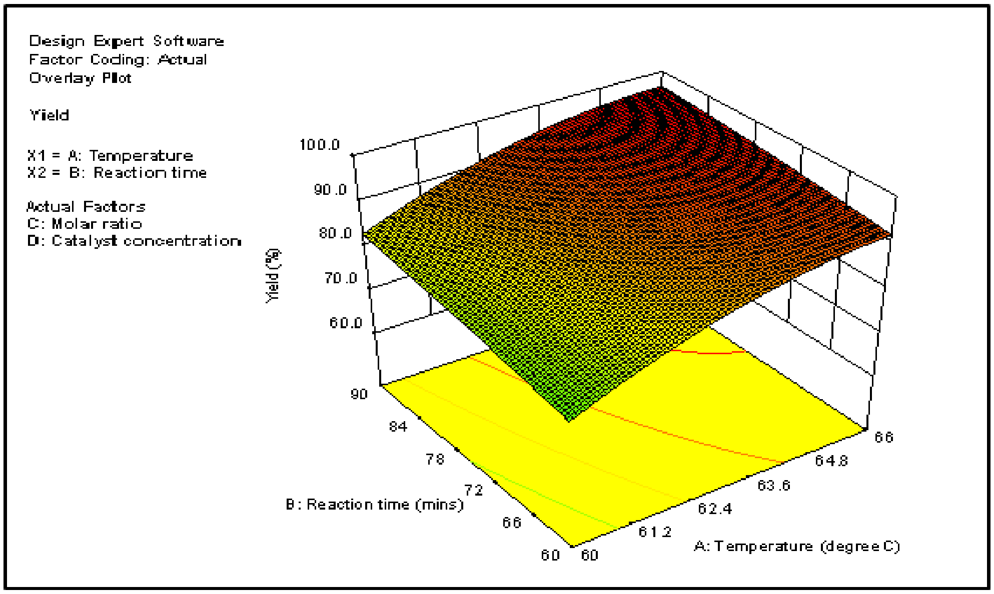


Figure 3: ***Response surface 3D plot of predicted biodiesel yields versus reaction time and temperature***

Fig. 3 represents the interaction between temperature (°C) and reaction time (min), the variation in the biodiesel yield is depicted well in the plot; i.e. the biodiesel yield increases significantly by increasing both temperature and reaction time at 4.4:1 molar ratio and 2.8 % catalyst concentration.

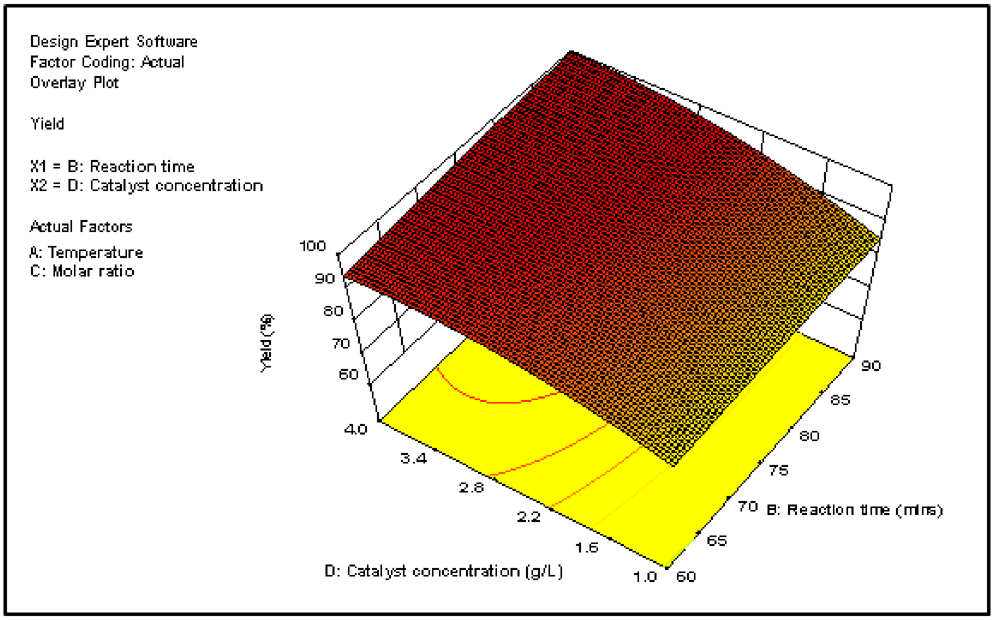


Figure 4: ***Response surface 3D plot of predicted biodiesel yields versus reaction time and catalyst concentration***

Fig. 4 shows the nature of reaction time and catalyst concentration on the biodiesel yield. There is a proportional increase in the biodiesel yield as the reaction time increases, whereas a slight increase can be seen when the catalyst concentration is increased at 3.4g/L.

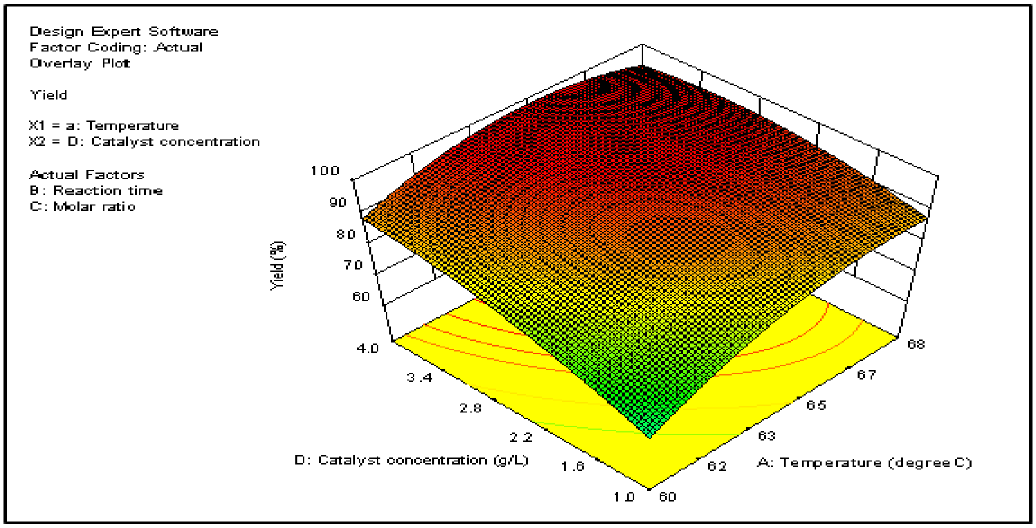


Figure 5: ***Response surface 3D plot of predicted biodiesel yields versus temperature and catalyst concentration***

Fig. 5 shows the mutual interaction between temperature and catalyst concentration on the biodiesel yield in which there is an increase in biodiesel yield for both increase in temperature and catalyst concentration at 90 min reaction time and 4.3:1 molar ratio. However, increase temperature above 65 ^{o}C led to the decrease in biodiesel yield and this could be as a result of methanol evaporating from the reaction medium.

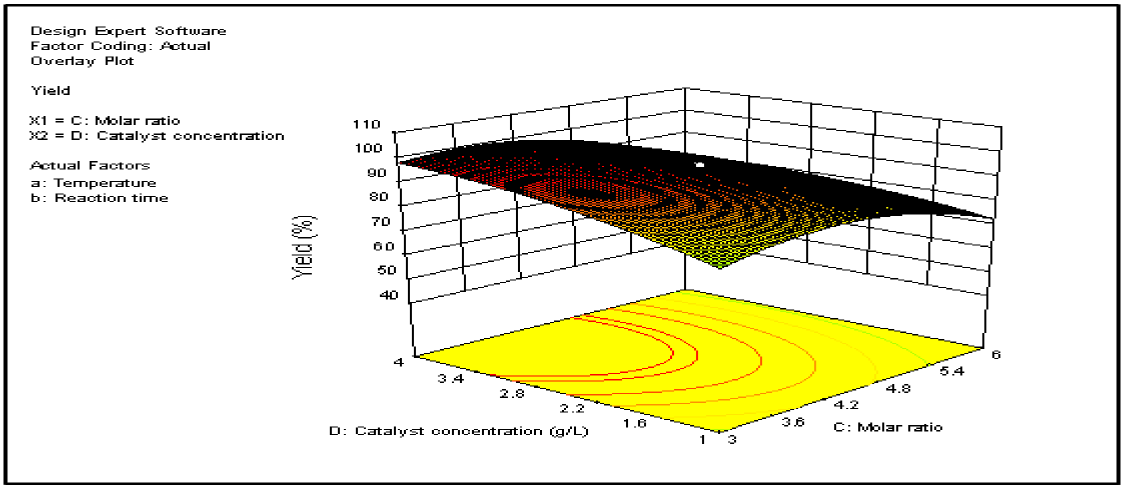


Figure 6: ***Response surface 3D plot of predicted biodiesel yields versus molar ratio and Catalyst concentration***

Fig. 6 depicts the 3D response surface plot of predicted yield versus molar ratio and catalyst concentration at reaction time 90 min. and temperature 65 ^{o}C. The biodiesel yield increases slightly with initial increase in methanol-to-oil molar ratio and catalyst concentration. However, yield start to decrease as the molar ratio increases further. In general, a high molar ratio results in a higher rate of methyl ester formation and ensures completion of the reaction. However, overloading of methanol would deactivate the catalyst and reversed the reaction since transesterification is a reversible reaction (Wan Omar and Saidina Amin, 2011).

Optimization

Based on the model obtained and input criteria, the production of soybean biodiesel in the packed bed membrane reactor was optimized. The main objective of this study was to maximize conversion of soybean oil to biodiesel. Table 4 shows the response and all reaction variables with respective high and low limit to satisfy the condition defined for the optimum yield. In order to evaluate the accuracy of the developed model a transesterification experiment was carried out under the optimum conditions, the experiment were carried out three times and the average was taken. The predicted conversion value was 97.7% while the average observed value was 96.9%. The experimental (obtained) value showed acceptable agreement with the predicted value. The error value between the predicted and the observed results was less than 1% FAME conversion, indicating that the regression model was satisfactory.

Table 4: Numerical optimization results and constrains for the factors/response.

Parameter	**Goal**	**Experimental region**	
		Lower	Upper
Temperature (^oC)	In range	60	70
Reaction time (min)	In range	60	120
Catalyst concentration (g/L)	target	-	3
Molar ratio	In range	3:1	6:1
Yield (%)	Maximize		

Biodiesel characterization

The physical and chemical properties of the produced biodiesel were measured according to the test methods recommended by the American Society for testing and Materials (ASTM) and South African National Standard (SANS) as follows; viscosity at 40 ^0C, water content, density at 15 ^0C, total acid number, total contamination, Sulphur and flash point. The results of these characterizations are listed in Table 5.

The results show that the biodiesel produced using membrane technology is within the South African Bureau of Standards (SANS 1935) standard specifications and American Society for testing and Materials (ASTM D6751) biodiesel specification.

Table 5: Characteristics of biodiesel produced from soybean oil in a membrane reactor

Characteristic	Test	Units	SANS 1935 Specification Limit	Result
Density @ 15°C	ASTM D7042	g/mL	0.86-0.9	0.87
Viscosity @ 40 °C	ASTM D7042	cSt	3.5-5	3.8
Flash point	ASTM D93	°C	120 min	167
Water content	ASTM D6304	%	0.05 max	-
Total acid number	-	mgKOH/g	0.5 max	0.21
Total Contamination	IP 440	mg/Kg	24 max	2
Sulphur	ASTM D4294	ppm	10 max	1

Biodiesel properties are numerous but the most important ones are those that have direct impact on the performance of the engine such as viscosity because of its effect on the atomization of the fuel being injected into the engine combustion compartment, flash point which is much higher than diesel, density which is lesser than water and so on. All these properties help to increase the lifespan of the engine, give a better lubrication and complete combustion so that the engine can produce a higher energy output.

CONCLUSION

In this study, experiments using RSM to determine the optimum reaction conditions for the production of biodiesel from soybean oil in a membrane reactor was carried out. High quality biodiesel was produced without the need to wash and purify. The effects of parameters including temperature, reaction time, molar ratio and catalyst concentration were found significant. The highest conversion of 96.9 % was obtained at 65 °C temperature, 90 min. reaction time, 4.5:1 molar ratio and 3 g/L catalyst concentration. The characteristics of the product under the optimum condition were within the ASTM standard and SANS standard. This study therefore showed that the use of a membrane for biodiesel production conserved water for other purposes; eliminate purification step and wastewater generation thereby reducing the cost of biodiesel production.

ACKNOWLEDGEMENTS

The financial support from the Institute of Wastewater treatment, Durban University of Technology, South Africa is highly acknowledged.

REFERENCES

Baroutian, S., Aroua, M.K., Raman, A.A.A. and Sulaiman, N.M.N. 2011. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. *Bioresource Technology.* 102: 1095–1102.

Bojan, S.G., Chelladurai, S. and Durairaj, S.K. 2011. Response surface methodology for optimization of biodiesel production from high FFA Jatrophacurcas oil. *International Journal of Green Energy*. 8(6): 607–617.

Bouaid, A., Bajo, L., Martinez, M. and Aracil, J. 2007. Optimization of biodiesel production from jajoba oil Trans. *Inst. Chemical Engineering*. 85:378–382.

Chen, X., Du, W. and Liu, D. 2008. Response surface optimization of biocatalytic biodiesel production with acid oil. *Biochemical Engineering Journal*. 40:423–429.

Dussan, K.J., Cardona, C.A., Giraldo, O.H., Gutierrez, L.F. and Perez, V.H. 2010. Analysis of a reactive extraction process for biodiesel production using a lipase immobilized on magnetic nanostructures. *Bioresource Technology*. 101:9542–9549.

Joshi, A., Pund, S., Nivsarkar, M., Vasu, K. and Shishoo, C. 2008. Dissolution test for site-specific release isoniazid pellets in USP apparatus 3 (reciprocating cylinder): optimization using response surface methodology. *Eur. J. Pharm. Biopharm*. 69 (2): 769–775.

Kafuku, G., Lam, M.K., Kansedo, J., Lee, K.T. and Mbarawa, M. 2010. Heterogeneous catalyzed biodiesel production from Moringaoleifera oil. *Fuel Processing Technology*. 91: 1525–1529.

Noordin, M.Y., Venkatesh, V.C., Sharif, S., Elting, S. and Abdullah, A. 2014. Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 1045 steel. *Journal of Material Processing Technology*. 145 (1): 46–58.

Olagunju, O. A. and Musonge, P. 2015. The performance of a packed bed membrane reactor for the production of biodiesel 2nd Intl., Conf., on Composites, Biocomposites & Nanocomposites 28-30 October 2015 Durban University of Technology, South Africa.

Olagunju, O. A. and Musonge, P. 2017. Production of biodiesel using a membrane reactor to minimize separation cost. *Earth Environment science.* IOP Conference series. 78: 012019.

Rashid, U., Anwar, F. and Arif, M. 2009. Optimization of basecatalytic methanolysis of sunflower (*Helianthus annuus*) seed oil for biodiesel production by response surface methodology. *Industrial Engineering Chemical Resource*. 48:1719–1726.

TuThanh, L., Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y. and Bandow, H. 2010. Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process. *Bioresource Technology*. 101:639–645.

Wan Omar, W. N. N. and Saidina Amin, N. A. 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and Bioenergy*. 35(3): 1329–1338.

Yoosuk, B., Krasae, P., Puttasawat, B., Udomsap, P., Viriya-empikul, N. and Faungnawakiji, K. 2010. Magnesia modified with strontium as a solid base catalyst for transesterification of palm olein. *Chemical Engineering Journal*. 162:58–66.

Yuan, P., Liu, J., Zeng, G., Shi, J., Tong, J. and Huang, G. 2008. Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. *Renewable Energy*. 33 (7):1678–1684.

.