

**A STUDY OF BIODIESEL PRODUCTION FROM WASTE VEGETABLE OIL
USING EGGSHELL ASH AS A HETEROGENEOUS CATALYST**

by

NGOYA TSHIZANGA

Thesis submitted in fulfilment of the requirements for the degree of

Master of Technology: Chemical Engineering

in the Faculty of Engineering

at the Cape Peninsula University of Technology

Supervisor: Dr O.O. Oyekola

Co-supervisor: Dr Elizabeth Aransiola

Cape Town

October 2015

CPUT Copyright Information

The thesis may not be published either in part (in scholarly, scientific or technical journals), or as a whole (as a monograph), unless permission has been obtained from the university.

DECLARATION

I, Ngoya Tshizanga, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signature.....

Date.....

ABSTRACT

While biodiesel has the potential to resolve the energy crisis, its production is hampered by both feedstock and catalyst availability. The aim of this current study is to investigate the production of biodiesel from waste vegetable oil (WVO) as feedstock under heterogeneous catalysis, mediated by calcined eggshell ash. WVO, characterised by 9% free fatty acid (FFA) and 0.17wt% water content, was employed as feedstock in the biodiesel production via transesterification reaction. The composition of WVO was determined using Gas chromatography (GC) analysis. The eggshell was washed with distilled water to remove impurities, dried in an oven at 105°C, and then crushed into fine particle of 75µm, and finally, calcined in a muffle furnace at 800°C. The chemical properties of the catalyst were assessed as follows: 1) using X-ray diffraction (XRD) to determine the major component phase of the element; 2) using X-ray fluorescent (XRF) to determine the elemental composition of the eggshell ash; 3) using Brunauer Emmet Teller (BET) to define the structure, the surface area, pore volume and pore diameter of the eggshell ash; and 4) using SEM to show the morphology structure of the element. The XRD analysis performed on eggshell ash showed 86% CaO as a major component in the catalyst; the remaining 14% was composed of MgO, SiO₂, SO₃, P₂O₅, Na₂O, Al₂O₃, K₂O and Fe₂O₃, as obtained from XRF. The BET result of the catalyst prepared was characterised by large pore diameter (91.2 Å) and high surface area (30.7m²/g), allowing reactants to diffuse easily into the interior of the catalyst used.

The transesterification reaction was mediated by a base catalyst obtained from eggshell with WVO and methanol. The experiments were carried out using a reflux fitted system, with a three-necked flask immersed in a water bath. The mixture was then placed in a 500ml three-necked flask, fitted with an overhead stirrer to achieve a homogeneous mixture at a constant mixing speed of 600rpm and a reaction time of 5h30min.

Process optimisation was conducted using the following reaction conditions: reaction temperature (X_1), oil-to-methanol ratio (X_2) and catalyst loading (X_3). The ranges of process factors were chosen by considering the literature data based on the properties of the methanolysis reaction. The experiments were designed using Design Expert 9 software, and by applying 2³ full central composite design with six star points and six centre points. Response surface methodology (RSM) was used by employing central composite design (CCD) to evaluate the stability and variability of the process.

The result showed that at a 95% confidence level, all three factors affected the methyl ester yield. A second-order polynomial equation was developed to predict the response, which

was methyl ester as a function to its variables. RSM proved to be a suitable method for optimising the process. The optimum point was obtained at $65\pm 5^{\circ}\text{C}$ by employing 22.5:1 methanol-to-oil molar ratio, a 5h30min reaction time, and a 3.5wt% catalyst loading with a significant yield (91%) under optimal reaction conditions.

The reusability of the catalyst prepared was also investigated; CaO was recovered and reused for 10 cycles before any activity loss by 72% on the 18th reuse. The reaction followed a first order kinetics with a reaction constant $K = .197 \times 10^{-3} \text{ min}^{-1}$ and $\alpha = 0.61$. The biodiesel product was composed mainly of unsaturated oleic acid and had a viscosity of $4.5 \text{ mm}^2/\text{s}$, comparable to results obtained from the literature. The product characterisation was set to meet the requirements determined by the American Standard (ASTM D 6751) for biodiesel fuel.

ACKNOWLEDGEMENTS

It is a sincere pleasure to acknowledge those who assisted me, contributing to the accomplishment of this thesis:

- To the almighty God: thank you for giving me the breath, strength and ability to exercise my thinking and knowledge.
- To Dr O.O. Oyekola (CPUT Chemical Engineering) for his supervision: thank you so much for the opportunity you gave me to be part of your research field. This work could never be compiled without you. I am proud to have you as my supervisor.
- To Dr Elizabeth Aransiola and Mr Tafi Madzimbamuto: thank you for helping me with my data collection and analyses.
- To the University Research Fund (URF): many thanks for financial support on the biodiesel project.
- To my family: my special thanks go to my father for his encouragement and moral and financial support throughout my studies; to my mother, for being a guide and a helper throughout my challenges; and to my two daughters, Selecia and Samaya Mansurah, for giving me the reason to work hard and laugh at all time. You are such beautiful human beings.
- To Joelle, Sybillle, Rosine, Gervais and Franck Tshizanga: thank you so much for just being there for me and supporting me.
- To the Cape Peninsula University of Technology Chemical Engineering Department: grateful thanks for assistance with the experimental set-up and the laboratory availability.
- To my late brother, Francis Tshizanga: thanks for being an amazing brother.
- Lastly, to Abdel malik madina ahmat: thanks for just believing in me, for your support and love. I could not ask for more.

Dedicated to my late brother, Francis Tshizanga wa Tshizanga, for your tolerance and understanding. You inspired me throughout your existence.

PUBLICATION LIST

Conference Presentations

- N. Tshizanga, O.O. Oyekola and Elizabeth Aronsiola. *A Study on Biodiesel Production from Non-Edible and Waste Vegetable Oil using a Heterogeneous Catalyst from Natural Sources*. Paper presented at the postgraduate conference, Cape Town, November 5, 2013.
- N. Tshizanga, O.O. Oyekola, Elizabeth Aransiola. *Optimisation of Biodiesel Production from Waste Vegetable Oil and Egg Shell Ash: Application of Response Surface Methodology (RSM)*. Paper presented at the ICCT SAICHe Conference, Durban, July 27, 2014.

TABLE OF CONTENTS

DECLARATION	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	v
PUBLICATION LIST	vii
CHAPTER 1	2
INTRODUCTION	2
1.1 Background	2
1.2 Research questions	4
1.3 Research objectives and key questions	4
1.4 Research motivation and significance.....	4
1.5 Delineation of the research	5
CHAPTER 2	7
LITERATURE REVIEW	7
2.1 Biodiesel	8
2.1.1 Biodiesel production technologies.....	10
2.1.1.1 Transesterification	11
2.1.1.2 Esterification	14
2.1.2 Biodiesel feedstock.....	15
2.1.2.1 Waste vegetable oil	19
2.1.2.2 Alcohol.....	21
2.1.3 Factors affecting biodiesel production	22
2.1.3.1 Effect of temperature on biodiesel production.....	22
2.1.3.2 Effect of water content and free fatty acid.....	23
2.1.3.3 Molar ratio of alcohol-to-vegetable oil.....	24
2.1.3.4 Effect of catalyst.....	24
2.1.4 Catalysts in transesterification process	25
2.1.4.1 Homogeneous acid and base catalysts	26
2.1.4.2 Heterogeneous acid and base catalysts	27
2.1.4.3 Enzymatic catalysts.....	34

2.1.4.4	Reusability of catalyst	35
2.2	Physical and chemical properties of biodiesel	37
2.2.1	Acid number	37
2.2.2	Cetane number	37
2.2.3	Oxidation	38
2.2.4	Viscosity.....	38
2.2.5	Flash point.....	38
2.2.6	Cloud point	39
2.2.7	Pour point	39
2.2.8	Density	39
2.2.9	Free and total glycerol.....	39
2.3	Optimisation of biodiesel production	40
2.3.1	Response surface method (RSM)	41
2.3.1.1	Box-behnken design.....	41
2.3.1.2	Central composite design (CCD).....	42
2.4	Kinetics of biodiesel production.....	43
2.5	Summary.....	45
CHAPTER 3	47
MATERIALS AND METHODS	47
3.1	Feedstock	47
3.2	WVO Analyses.....	47
3.1.1	FFA characterisation.....	48
3.3	Catalyst Preparation	48
3.3.1	Catalyst characterisation.....	48
3.3.2	Catalyst reusability	49
3.4	Application of the response surface method (RSM)	49
3.5	Transesterification process	52
3.5.1	Equipment set-up	52
3.5.2	Experimental procedure	53
3.5.3	Crude biodiesel purification	53
3.6	Product estimation.....	54
3.7	Determination of kinetics	54
3.7.1	Constants	54

3.7.2 Rate law.....	55
3.8 American Society for Testing and Materials (ASTM) analysis	56
CHAPTER 4	59
RESULTS AND DISCUSSION.....	59
4.1 Characterisation of WVO	59
4.2 Catalyst characterisation	59
4.2.1 Catalyst composition.....	60
4.2.2 Catalyst structure, surface area, pore volume and pore diameter	60
4.2.3 Catalyst morphology	61
4.2.4 Catalyst major component phase	62
4.3 Biodiesel composition	63
4.4 Kinetics study on biodiesel.....	64
4.5 Effect of catalyst loading	65
4.6 Effect of temperature	66
4.7 Effect of oil-to-methanol molar ratio.....	67
4.8 Catalyst reusability	67
4.9 Statistical analysis from RSM.....	68
4.9.1 Interaction of catalyst and temperature	70
4.9.2 Interaction of oil/methanol ratio and temperature	71
4.9.3 Interaction of catalyst loading and oil-to-methanol ratio.....	72
4.9.4 Prediction of values from RSM	73
4.10 Properties of biodiesel using ASTM standard	74
4.11 Result summary.....	74
CHAPTER 5	77
CONCLUSION AND RECOMMENDATIONS.....	77
5.1 Conclusion.....	77
5.2 Recommendations	78
REFERENCES	80
APPENDICES.....	87
Appendix A: Experimental results obtained from calculation	88
Appendix B: Kinetics calculation	89

LIST OF FIGURES

Figure 2. 1: Transesterification reaction: (a) general equation; (b) three consecutive and reversible reactions	13
Figure 2. 2: Base-catalysed transesterification mechanism	13
Figure 2. 3: Acid-catalysed by a transesterification mechanism	13
Figure 2. 4: General cost breakdown for biodiesel production.....	18
Figure 2. 5: Classification of catalyst	25
Figure 2. 6: Profile of Box-behnken design at three levels	42
Figure 2. 7: Central composite design profile with three inputs	43
Figure 3.1: Calcination of eggshell to convert CaCO_3 to CaO	48
Figure 3.2: Experimental set-up	52
Figure 4.1: SEM image for calcined eggshell ash.....	62
Figure 4.2: XRD for calcined catalyst.....	63
Figure 4.3: Effect of catalyst loading	66
Figure 4.4: Effect of temperature on the yield.....	66
Figure 4.5: Effect of oil/meth molar ratio on the yield	67
Figure 4.6: Effect of reusability of catalyst.....	68
Figure 4.7: Response surface plot of combine catalyst loading and temperature	71
Figure 4.8: Response surface plot of combine oil/methanol ratio and temperature	72
Figure 4.9: Response surface plot of combine catalyst loading and oil/methanol ratio	73
Figure 4.10: Parity chart for the model employed. Plot of predicted vs. actual value.....	73

LIST OF TABLES

Table 2.1: Opportunities and challenges associated with biodiesel production and use.....	10
Table 2.2: Biodiesel production technologies	11
Table 2.3: Examples of oil sources for biodiesel.....	15
Table 2.4: FFA range in different oil feedstock.....	16
Table 2.5: Common fatty acid in waste vegetable oil.....	17
Table 2.6: Price comparison from different feedstock	19
Table 2.7: General properties of WVO	20
Table 2.8: Biodiesel production from WVO	20
Table 2.9: Summary of reaction conditions and performance of different catalysts	31
Table 2.10: Opportunities and challenges of calcined CaO catalyst.....	32
Table 2.11: Use of CaO catalyst from natural sources in biodiesel production.....	33
Table 2.12: ASTM and EN specification for biodiesel	40
Table 3.1: Experimental range of independent variable (DOE)	50
Table 3.2: 2 ³ full CCD design of experiment with coded factors.....	51
Table 3.3: 2 ³ full CCD design of experiment with uncoded factors	51
Table 4.1: Waste vegetable oil characterisation obtained using GC	59
Table 4.2: Chemical composition of catalyst on a dry basis obtained using XRF.....	60
Table 4.3: Physicochemical properties of eggshell ash (CaO) using micromeritics physisorption and chemisorption analysers	61
Table 4.4: Fatty acid compositions of biodiesel using GC.....	63
Table 4.5: Full central composite design with experimental response value.....	64
Table 4.6: Biodiesel yield at different time.....	65
Table 4.7: Model summary statistics.....	69
Table 4.8: Sequential model sum of squares	69
Table 4.9: ASTM value obtained from analysis.....	74

GLOSSARY

ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American Society for Testing Materials
CCD	Central Composition Design
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GC	Gas chromatography
GPC	Gas performance chromatography
R²	Coefficient of determination
RSM	Response surface methodology
RPM	Revolution per minute
SEM	Scanning electron microscope
TG	Triglyceride
TLC	Thin layer chromatography
UV	Ultra violet light
VO	Vegetable oil
WVO	Waste vegetable oil
XRD	X-ray diffraction
XRF	X-ray fluorescence

TERMS AND DEFINITIONS

Acid number: an indication of acidity in the fuel

Ash content: a measure of the amount of inorganic matter (non-combustible matter) contained in the fuel

Biodiesel: a liquid fuel made up of fatty acid alkyl esters, fatty acid methyl esters (FAME), or long-chain mono alkyl esters

Biofuel: liquid or gaseous fuels from transport section

Cetane number: an indication on the fuel combustion

Cloud point: the temperature at which a cloud of wax crystal first appears in the oil when it is cooled

Pour point: the lowest temperature at which the oil sample can still be moved (Arjun *et al.*, 2008)

Density: a measurement of compactness of a substance

Experimental design: a specific set of experiments defined by a matrix composed by the different level combinations of variables studied

Factors or independent variables: experimental variables that can be changed independently of each other

Flash point: the temperature that indicates the overall flammability hazards in the presence of air (high flash points make for safe handling and storage of biodiesel)

Free and total glycerol: a measurement of the amount of unconverted or partially converted fats and by-product glycerol in the oil

Level of variables: different values of a variable at which the experiment must be carried out

Reflux: the process of boiling reactants while continually cooling the vapour, returning it back to the flask as a liquid (it heats a mixture for extended periods and at a certain temperatures)

Response or dependent variables: the measured values of the results from experiments

Transesterification: the process of producing biodiesel (these reactions are often catalysed by the addition of an acid or base catalyst)

Viscosity: a measure of internal fluid friction of fuel to flow

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

1.1 Background

The world is currently challenged with global warming and environmental pollution. The major sources of greenhouse gas emissions are fossil fuels (Abebe *et al.*, 2011; Atadashi *et al.*, 2011). Therefore, it is necessary to find alternative energy sources that are renewable, economically feasible and friendly to the environment. In addition, the depletion in petroleum worldwide has also stimulated the search for alternative sources (Minima & Saka, 2006; Atadashi *et al.*, 2011).

Biodiesel holds great potential as an alternative fuel. Characterised by the aforementioned properties, it has become the focus of many investigations with respect to the greenhouse gas emission and the environmental crisis. It is a biodegradable and non-toxic fuel and a carbon monoxide emission reducer that can be recycled by photosynthesis. This minimises the impact of biodiesel combustion on the greenhouse effect (Krawczyk, 1996; Korbitz, 1999; Agarwal & Das, 2001; Minima & Saka, 2006; Brito *et al.*, 2007; Kyong-Hwan *et al.*, 2008, Atadashi *et al.*, 2011). Moreover, biodiesel has the advantage of good fuel properties such as good lubricity, better quality exhaust gas emissions, sulphur free, carbon neutral and less emission of carbon dioxide in the atmosphere, a cetane number and cloud point which depend heavily on the feedstock and a high flash point (~150°C) which makes it volatile and easy to handle (Zhang *et al.*, 2003; Morais *et al.*, 2010; Kouzu *et al.*, 2012; Yaakob *et al.*, 2013; Glisic *et al.*, 2014). Nevertheless, the challenges associated with the development of alternative fuels continue to attract intensive investigations (Yagiz *et al.*, 2007; Kotwal *et al.*, 2009).

The conventional approach of biodiesel production is *transesterification*, using oil and alcohol in the presence of a catalyst with glycerol as a by-product of the reaction (Zhang *et al.*, 2003; Demirbas, 2005; Atadashi *et al.*, 2011; Boey *et al.*, 2011). Product quality is dependent on the type and amount of catalyst, type of oil feedstock, alcohol-to-oil ratio, FFA and water content in the oil and operating conditions such as agitation speed and temperature (Clark *et al.*, 2013).

Several studies concerning biodiesel production have focused on the use of vegetable oil or animal fat as feedstock in the presence of a catalyst (Zhang *et al.*, 2003; Demirba, 2005).

Edible oils are considered as first generation biodiesel feedstock (Atabani *et al.*, 2013). However, due to the competition with food availability or discharge of waste in the environment, there is presently a shift towards the use of waste vegetable oil (WVO) and non-edible oils as feedstock as these are considered low grade feedstock in biodiesel production (Zhang *et al.*, 2003). The oils used as feedstock in the production of biodiesel have attracted much attention since they are renewable and readily available (Yagiz *et al.*, 2007). Biodiesel, made from low-grade vegetable oils such as WVO and non-edible oils (jatropha, karanja and mahua) with high concentrations of free fatty acid (FFA), is more viable than petroleum-based products with respect to cost reduction and greenhouse gas emission reduction (Shu *et al.*, 2007; Wang *et al.*, 2011). While biodiesel production using WVO has been thoroughly reported in the literature, there are major drawbacks, particularly the presence of impurities and the high amounts of free fatty acid characterising this feedstock (Lam *et al.*, 2010).

Most catalysts used in biodiesel production are acids or bases (homogeneous or heterogeneous) associated with differing advantages and disadvantages due to their properties. Rates of reactions mediated by base catalysts are higher than the acid catalysed reactions in the production of biodiesel and are active in transesterification at temperatures around boiling point of methanol - 65 °C (Kouzu *et al.*, 2012). Previous reports have shown that heterogeneous catalysts, especially base catalysts, are effective options and are associated with high performance in the production of biodiesel from oil with high free fatty acids due to their ability to absorb water contained in the waste vegetable oil (Semwal *et al.*, 2007). Further, there is no formation of soap as a result of the free fatty acid content. Heterogeneous catalysts can also be easily removed from the reaction mixture, and subsequently reused (Yagiz *et al.*, 2007; Vyas *et al.*, 2010). Heterogeneous catalysts still suffer from serious mass transfer limitation problems that result in the formation of three phases together with oil and alcohol. These catalysts require high temperatures to achieve high conversion and need more time to reach optimum biodiesel yield (Mbaraka & Shanks, 2006; Semwal *et al.*, 2011).

Recent studies have been conducted on the use of ash from waste eggshell as heterogeneous catalysts for biodiesel production (Chakraborty *et al.*, 2010). Heterogeneous base catalysts of alkaline earth metal oxides have been investigated for biodiesel production (Khemthong *et al.*, 2012). It has been shown that the derived CaO contained in ash from waste materials is a potential heterogeneous catalyst. This new orientation for biodiesel production is eco-friendly and economical (Khemthong *et al.*, 2012).

Against this background, the aim of this research is to investigate biodiesel production from waste vegetable oil (WVO) using heterogeneous catalyst produced from eggshell, thereby producing value added product from waste materials.

1.2 Research questions

The primary research questions to be explored by this study are as follows:

- Is the use of ash from eggshell effective in biodiesel production?
- How does WVO with high FFA affect biodiesel yield?
- What are the optimum parameters required for biodiesel production via heterogeneous catalysis?

1.3 Research objectives and key questions

This study will focus on the production of biodiesel using waste vegetable oil (WVO) as feedstock in the presence of heterogeneous catalysts via transesterification. The following will be specifically investigated:

- to synthesise and characterise heterogeneous catalysts from eggshell;
- to investigate the production of biodiesel reaction kinetics using WVO as feedstock and eggshell ash as catalyst, as a function of agitation rate, temperature and catalyst loading; and
- to optimise biodiesel production by investigating interaction effects among process variables (temperature, oil-to-methanol molar ratio and catalyst loading).

1.4 Research motivation and significance

Due to increases in food prices, the use of waste materials has attracted a great deal of attention in the production of biodiesel. Feedstock cost plays a critical role in determining the competitiveness of biodiesel. Disposal of waste vegetable oil has been reported as challenging. The production of catalysts is typically expensive due to the number and amount of chemicals involved in the process. These conventional catalysts, being chemicals, are also not environmentally friendly. Employing readily available wastes is a potential alternative to reduce the production cost of biodiesel. The production of eggshell ash as

heterogeneous catalysts and sourcing a feedstock from waste vegetable oil, if effective, will be environmentally friendly. Further, investigating the effect of operating parameters will enhance in-depth understanding of this process.

1.5 Delineation of the research

This current study investigates biodiesel production from waste vegetable oil with a high FFA, the potential of a heterogeneous catalyst from eggshell ash and the optimisation of the reaction conditions using response surface method (RSM). Different criteria and operation parameters, including reaction kinetics and the effect of WVO with high FFA, will be investigated. However, the effect of water composition of the WVO and an economic analysis of biodiesel production will not be covered in the current study.

CHAPTER 2

LITERATURE REVIEW

CHAPTER 2

LITERATURE REVIEW

The energy crisis of the 1970s led to vigorous investigations pertaining to the use of biodiesel as an alternative fuel (Canakci *et al.*, 2001; Demirbas, 2005). Most of the biodiesel employed has been produced from vegetable oils or animal fats in the presence of chemical homogeneous or heterogeneous catalyst (Atadashi *et al.*, 2011). There are more than 350 oil-bearing crops — including sunflower, safflower, soybean, cottonseed, castor, palm, rapeseed and peanut oils — which are considered potential feedstock for biodiesel production. However, only some are suitably used due to their specific productivity and local climate (Demirba, 2005; Torres *et al.*, 2013).

Due to our increasing global population and the resultant food crisis, there has been a shift towards the use of waste vegetable oil in the production of biodiesel. While hopeful, the use of homogeneous catalyst and waste vegetable oil in biodiesel production has shown several drawbacks: equipment corrosion, formation of soap and consumption of catalyst (Shu *et al.*, 2010). Presently, there are several heterogeneous-based catalysts available for biodiesel production from feedstock characterised with high FFA content. However, the use of base catalysts is not a viable option due to mass transfer limitation, high reaction temperatures and long reaction times (Shu *et al.*, 2010). A number of studies on feedstock with elevated FFA levels and heterogeneous catalysts, including waste shell, have been reported (Shu *et al.*, 2010). This particular heterogeneous catalyst (waste shell) is hydrophilic and can be easily removed from the reaction mixture by filtration without any loss of catalyst; if the oil has high FFA content and more water, acid catalysed transesterification is suitable (Kapilan *et al.*, 2009).

There are a few methods for the production of biodiesel, but the most commonly relied upon method is *transesterification* (Zhang *et al.*, 2003; Zanzi *et al.*, 2011). The high cost of biodiesel is the major obstacle in process commercialisation (Encinar *et al.*, 2007). But the use of waste oil to produce biodiesel is a sensible option for cost reduction, as WVO is estimated to be about half the price of virgin oil (Kulkarni & Dalai, 2006; Birla *et al.*, 2012).

2.1 Biodiesel

Biodiesel has recently increased in attractiveness because of its production from renewable sources (Di-Serio *et al.*, 2005). Biodiesel is composed of 14-24 carbon chains ($C_{14}-C_{24}$) and can be formulated as $C_{15-25} H_{28-48} O_2$ (Yusuf *et al.*, 2011). To produce high quality biodiesel at low cost, researchers are using various processes such as the batch process, supercritical alcohol process, microwave irradiation methods and ultrasounds for carrying out transesterification reactions by decreasing the reaction time, amount of alcohol, amount of catalyst and reaction temperature (Ejikeme *et al.*, 2010; Vyas *et al.*, 2010; Talebian-kiakalaieh *et al.*, 2013). These processes are explained as follows:

- *Batch process*: The process allows production of biodiesel continuously, semi-continuously, and in batch-mode, this process drastically reduces production time and increases production volume. This process typically requires intricate process controls and online monitoring of product quality and has the effect of increasing glycerol product in the ester phase (Talebian-kiakalaieh *et al.*, 2013).
- *Supercritical alcohol process*: Transesterification in supercritical conditions are completed in minutes. This process has no interphase mass transfer to limit the reaction rate and alcohol is not only a reactant but also an acid catalyst. The disadvantage of this process, though, is its high cost of apparatus due to the high temperature and pressure, neither of which is viable in the large scale practice in industry (Vyas *et al.*, 2010).
- *Microwave irradiation*: The use of this process offers various advantages of a short reaction time, a low methanol-to-oil molar ratio, a drastic reduction in the quantity of by-product and energy consumption, and improvement in the product yield. The most significant limitation of this process, though, is the penetration depth of microwave radiation into the absorbing material (Vyas *et al.*, 2010).
- *Ultrasound*: This process uses sound to compress and stretch the molecular spacing of the medium through which it passes. This process is known for its multiple advantages such as an increase in chemical reaction speed and yield, short reaction time and lower energy consumption than the conventional mechanical stirring method. The emulsification caused by the cavitation bubbles is the most significant limitation of this process (Thompson *et al.*, 1999; Deshmane *et al.*, 2013).

Biodiesel is used in many countries: American countries (United State of America, Brazil); European countries (France, Italy, Germany); and Asian countries (Indonesia, Malaysia). A high percentage of biodiesel, nearly 85%, comes from European countries, with the annual

production increasing from 15 000 barrel per day in 2000 to 289 000 in 2008 in European countries (Atabani *et al.*, 2012). The cost of biodiesel fuel depends on feedstock type, geographic area and variability in seasonal crop production. The cost of biodiesel fuel is 1.5-3 times higher than the fossil diesel cost in developed countries (Yusuf *et al.*, 2011).

Currently there are four main concentrations in volume of biodiesel used in the market (Yusuf *et al.*, 2011):

- *Pure B100*: this is the pure biodiesel obtained after purification with a concentration of 100% biodiesel, very rare on the market;
- *Blends (B20-B30)*: fuel with a concentration of 20-30% biodiesel, the most common on the market;
- *Additive B5*: fuel with a concentration of 5% biodiesel, not requiring any engine modification; and
- *Lubricity-additive B2*: fuel with a concentration of 2% biodiesel.

Generally, biodiesel is composed of five main saturated and unsaturated methyl esters, depending on the type of oil used: 1) methyl palmitate $C_{17}H_{34}O_2$; 2) methyl stearate $C_{19}H_{36}O_2$; 3) methyl oleate $C_{19}H_{34}O_2$, 4) methyl linoleate $C_{19}H_{30}O_2$; and 5) methyl linolenate $C_{19}H_{30}O_2$ (Herbinet *et al.*, 2008; Grana *et al.*, 2012). Biodiesels with high levels of methyl oleate (mono unsaturated fatty acid) have excellent characteristics in ignition quality, fuel stability and flow properties at low temperatures (Ong *et al.*, 2013). Various studies on the characterisation properties of biodiesel have suggested that the presence of fatty acid composition interferes with the fuel properties and quality of biodiesel such as cold flow properties (pour point and cloud point), cetane number and oxidation stability (Yusuf *et al.*, 2011; Ong *et al.*, 2013). Generally, saturated chains increase cloud point, cetane number and stability of methyl ester due to the absence of double bond (Ong *et al.*, 2013).

Biodiesel has demonstrated a number of promising characteristics and applications; its application is, however, challenged by some constraints (Table 2.1).

Table 2.1: Opportunities and challenges associated with biodiesel production and use (Yusuf *et al.*, 2011)

Advantages (opportunities)	Disadvantages (challenges)
Reduces the environmental effect of waste products	Higher oxidation stability than petroleum diesel
Free from sulphur and aroma content and reduces air toxicity	Lower volatility causing a deposit in the engine
Reduces net carbon dioxide emission by 78%	12% lower energy content than diesel
Biodegradable, renewable, economical feasible, with high lubricity	Higher nitrogen-oxides (NO _x) emission, higher price, higher viscosity
Miscible, insoluble in water, safe storage, inflammable	
Compatible with existing engine model	

2.1.1 Biodiesel production technologies

There are four primary ways of producing biodiesel from vegetable oils and animal fat (Demirbas, 2005; Arjun *et al.*, 2008; Zhang *et al.*, 2010; Atabani *et al.*, 2012):

- *Direct use and blending* (dilution) with diesel fuel: mainly vegetable oil is diluted with diesel to reduce the viscosity and improve the performance of engines;
- *Micro-emulsion* (supercritical) with a solvent such as methanol, ethanol or other alcohols;
- *Thermal cracking* (pyrolysis) by means of heat or by heat with the aid of catalyst: this method is a thermal decomposition of organic matter in the absence of oxygen and presence of catalyst; and
- *Transesterification*, also called *alcoholysis*, with short chain alcohols in the presence of catalyst: mixture of oil, catalyst and alcohol with the objective of reducing the viscosity of oil and producing high quality biodiesel. This is the most commonly used method and is regarded as the best method among all others, due to its economic feasibility and simplicity (Vyas *et al.*, 2010; Endalew *et al.*, 2011; Atadashi *et al.*, 2011; Lin *et al.*, 2011; Atabani *et al.*, 2012).

Atabani *et al.* (2011) conducted a comparison between different biodiesel production approaches highlighting their merits and demerits (Table 2.2).

Table 2.2: Biodiesel production technologies (adapted from Atabani *et al.*, 2012)

Methods	Advantages	Disadvantages
Direct or blending	Simple process	High viscosity, bad volatility, bad stability
Pyrolysis	Fuel properties closer to diesel, simple process, no pollution	High temperature required, high cost equipment, low purity
Micro-emulsion	Short reaction time, high conversion, good adaptability	High temperature and pressure required, high equipment cost, high energy consumption.
Transesterification	High conversion, suitable for industrialised product, efficiency, low cost, simple	Low FFA and water content when using homogeneous and heterogeneous based catalyst, neutralisation and washing step for pollutant products with soap formation when using homogeneous acid catalyst

2.1.1.1 Transesterification

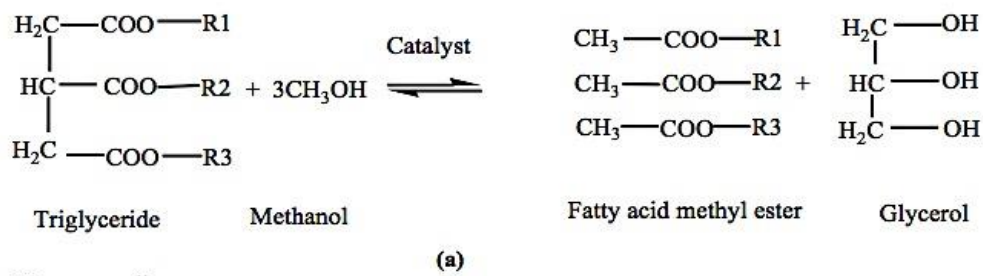
Biodiesel fuels are usually produced via a *transesterification process* (Fukuda *et al.*, 2001; Vincente *et al.*, 2007; Sharma *et al.*, 2008; Yang *et al.*, 2013), a direct method used from vegetable oil or animal fat in the presence of acid, base or enzyme catalyst (Figure 2.1) (Demirbas, 2005; Yagiz *et al.*, 2007; Vincente *et al.*, 2007; Aderim & Hameed, 2009; Asakuma *et al.*, 2009; Lee *et al.*, 2009; Oletoye & Hamed, 2011).

Transesterification was employed as early as 1846 using castor oil through ethanolysis, a process later initiated in South Africa in 1979 (Demirbas, 2005). The process is the reaction of fat/oil (triglycerides) with an alcohol to form alkyl esters (biodiesel) and crude glycerol (Figure 2.1a). This reaction does not proceed in the absence of catalysts or supercritical conditions (Sharma *et al.*, 2008; Ejikeme *et al.*, 2010; Vyas *et al.*, 2010; Tariq *et al.*, 2012). The reaction is reversible, making it difficult to obtain 100% conversion (Oletoye *et al.*, 2011; Tariq *et al.*, 2012; Pathak, 2015). The transesterification process consists of three

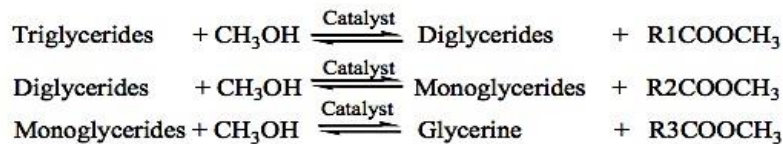
consecutive steps of reversible reactions, yielding one molecule of ester at each step (Sharma *et al.*, 2008; Tariq *et al.*, 2012). Firstly the conversion of triglycerides (TG) to diglycerides (DG) occurs, followed by the conversion of diglycerides to monoglycerides (MG) and finally, monoglycerides to glycerol (Figure 2.1b) (Sharma *et al.*, 2008; Ejikeme *et al.*, 2010; Tariq *et al.*, 2012).

Different types of transesterification mechanisms have been reported by several researchers. The commonly used are *base-catalysed transesterification* and *acid-catalysed transesterification* (Knothe *et al.*, 2005; Sharma *et al.*, 2008; Ejikeme *et al.*, 2010; Tariq *et al.*, 2012; Pathak, 2015). Generally, the mechanism of the base-catalysed transesterification occurs in four steps (Ejikeme *et al.*, 2010). Firstly, the base catalyses the reaction by removing a proton from the alcohol, rendering it more nucleophilic (Figure 2.2). Secondly, a tetrahedral intermediate is generated by the nucleophilic attack of the alkoxil at the carbonyl group of the triglyceride (Figure 2.2). Thirdly, the alkyl ester and its corresponding anion of diglyceride are formed. And finally, the catalyst is deprotonated and regenerates the active species which reacts with a second molecule of the alcohol, starting another catalytic cycle (Figure 2.2).

Conversely, strong acids catalyse the reaction by donating a proton to the carbonyl group to make it more electrophilic (Figure 2.3). The protonation of the carbonyl group leads to the carbocation, which, after the nucleophilic attack of the alcohol, produces the tetrahedral intermediate. This in return eliminates alcohol to form ester and regenerate the catalyst H^+ (Figure 2.3) (Ejikeme *et al.*, 2010; Pathak, 2015). Excess alcohol is often used in the production of biodiesel to increase the yield of fatty acid alkyl esters (biodiesel) and allow phase separation from glycerol (Demirba, 2005; Banerjee & Chakraborty 2009; Ejikeme *et al.*, 2010; Kumar *et al.*, 2010; Oletoye *et al.*, 2011). The stoichiometric ratio of triglyceride to alcohol is three, and the reaction produces three moles of alkyl ester from one mole of triglyceride (Figure 2.1a) (Sharma *et al.*, 2008; Lee *et al.*, 2009). In practice, to have a maximum ester yield, the ratio should be slightly higher than the stoichiometric ratio (Sharma *et al.*, 2008). See Figures 2.1 – 2.3 below.



More generally,



Where, R₁, R₂, and R₃ are the alkyl group

(b)

Figure 2. 1: Transesterification reaction: (a) general equation; (b) three consecutive and reversible reactions (adapted from Tariq *et al.*, 2012)

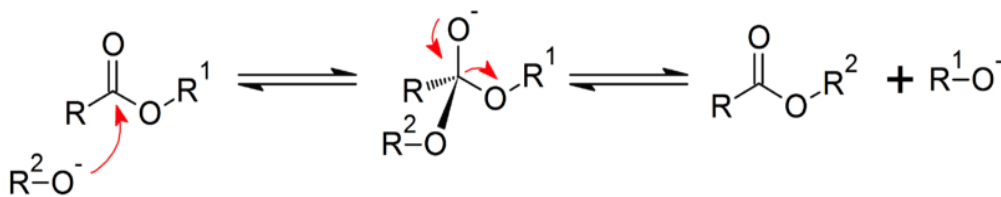


Figure 2. 2: Base-catalysed transesterification mechanism (adapted from Ejikeme *et al.*, 2010)

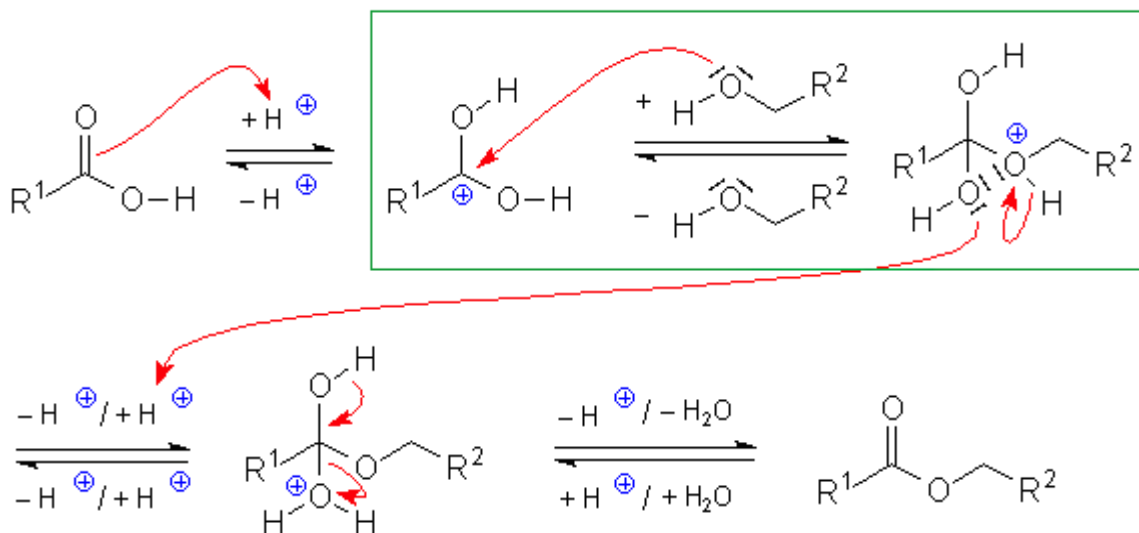


Figure 2. 3: Acid-catalysed by a transesterification mechanism (Ejikeme *et al.*, 2010; Pathak, 2015)

Methanol is the most commonly used alcohol in the transesterification process because of its low cost and high reaction rate (Zhang *et al.*, 2003; Demirba, 2005; Sharma *et al.*, 2008; Lee *et al.*, 2009; Borges & Diaz, 2012). However, ethanol is a preferred alcohol in the transesterification process because it can be derived from agricultural products, it is renewable, and it is biologically less objectionable in the environment (Demirba, 2005). The purpose of the transesterification process is to lower the viscosity of the oil, to reduce the density and to increase the volatility of the biodiesel product (Brito *et al.*, 2007; Vyas *et al.*, 2010). This process of using methanol, ethanol, propanol and butanol has proven to be a promising process of biodiesel production (Brito *et al.*, 2007).

The transesterification reaction is affected by various parameters including the following (Demirbas, 2005; Atabani *et al.*, 2012):

- reaction temperature and time;
- water content and free fatty acid content;
- type of alcohol and molar ratio of alcohol-to-vegetable oil;
- choice of catalyst and catalyst concentration; and
- rate of mixing, intensity and stirring mode.

Of the above mentioned, choice of catalyst is the first step for designing a transesterification process (Lee *et al.*, 2009).

2.1.1.2 Esterification

Esterification is a pre-treatment process or a sub-category of the transesterification process when low quality oil or fat is used as feedstock (Vyas *et al.*, 2010; Borges & Diaz, 2012; Kay & Suhaimi-Yasir, 2012).

Esterification is conventionally a homogeneous acid-catalysed reaction which precedes slowly in the presence of strong acids — sulphuric acid(H_2SO_4); fluoric acid (HF); hydrochloric acid (HCl); phosphoric acid(H_3PO_4); p-toluene sulphonic acid and organic sulphonic acid — and the use of these homogeneous acids causes equipment corrosion (Vyas *et al.*, 2010; Borges & Diaz, 2012). Several heterogeneous acid catalysts have been used in the FFA esterification: zirconium oxide, titanium oxide, tin oxide, sulphonic ion-exchangeresin, sulphonic modified mesostructure silica and sulphonate carbon-based catalysts. A high reaction temperature (80-250°C) is also required for FFA esterification (Borges & Diaz, 2012).

2.1.2 Biodiesel feedstock

Feedstock for biodiesel production may be categorised as *liquid feedstock* (animal fat, edible oil and non-edible oil) and *alcohol feedstock* (methanol, ethanol and propanol) (Issariyakul *et al.*, 2014) and should fulfil two requirements: low production cost and large production scale (Atabani *et al.*, 2012). More than 350 oil crops are known; however, not all are suitable for biodiesel production (Zhang *et al.*, 2010). Examples of sources of oil regarded as potential feedstock for biodiesel production are shown in Table 2.3. These can be divided into four categories as follows (Zhang *et al.*, 2010; Atabani *et al.*, 2012):

- *Edible vegetable oil* (first generation feedstock): this contains less FFA and does not need pre-treatment method but causes threat to food availability.
- *Non-edible vegetable oil* (second generation feedstock): this oil type is not suitable for human food consumption and contains higher FFA (2%-50%) than waste or recycled oil and its use usually causes threat of deforestation.
- *Waste or recycled oil* (second generation feedstock): this contains high FFA (2%-40%) depending on the use of oil and may need pre-treatment when used with homogeneous catalysts to avoid soap formation and water production.
- *Animal fats*: this oil type is expensive and not often used in the production of biodiesel.

Table 2.3: Examples of oil sources for biodiesel (adapted from Atabani *et al.*, 2012)

Edible oils	Non-edible oils	Animal fats	Other sources
Corn	Mahua, Jatropha	Pork lard	Bacteria
Coconut	Pongamia, cumaru	Beef tallow	Algae (cyanobacteria)
Canola	Camelina, Cotton seed	Poultry fat	Microalgae (chlorellavulgaries)
Peanut	Karanja or honge	Fish oil	Tarpenes
Palm kernel	Cynara cardunculus	Chicken fat	Poplar
Sunflower	Abutilon muticum		Switch grass
Sesam	Neem, Jojoba		Miscanthes
Barley	Passion seed		Latexes
Rice bran oil	Moringa, Tobacco seed		fungi
Safflower	Rubber seed tree		
Rapeseed	Salmon oil, Tall		
Soybean	Coffee ground		

Each feedstock source has a specific composition of fatty acids (Table 2.4) depending on the use of the oil and the chemical features of FFA which are described by the carbon number and unsaturation degree (Table 2.5) (Lee *et al.*, 2009). Oils and fats are composed primarily of triglycerides. *Triglycerides* consist of a glycerin backbone with fatty acid radicals attached in place of the hydroxyl (Figure 2.1). The relative amounts of the different fatty acid radicals determine the properties of the specific triglyceride (Canakci *et al.*, 2001; Kim *et al.*, 2004; Semwal *et al.*, 2011).

Table 2.4: FFA range in different oil feedstocks (adapted from Lin *et al.*, 2011)

Oil types	FFA range (%)
Crude oil	0.3-0.7
Refined oil	0.05
Restaurant waste grease	2-7
Animal	5-30
Waste oil	3-25
Trap grease	40-100

Most waste oils contain 10-25% FFA which cannot be converted to biodiesel via transesterification (Canakci *et al.*, 2001; Kyong-Hwan *et al.*, 2008). FFA composition both reduces catalyst effectiveness and decreases the production yield (Demirbas, 2005). Therefore, waste vegetable oil needs to be treated before the transesterification process in order to reduce the acidity and eliminate other debris; otherwise they may adversely affect the biodiesel yield.

The pre-treatment of WVO will depend on the FFA content (Table 2.4). If the FFA is less than 2.5% it can be treated with a homogeneous alkali catalyst such as NaOH (Kyong-Hwan, 2008), but if higher than 2.5% it can be treated with H₂SO₄ or other acids.

More than 90% of FFAs are composed of 16-18 carbon chains. There are two kinds of free fatty acids found in WVO containing 12 to 22 carbons: 1) saturated fatty acids containing a single carbon bond, and 2) unsaturated fatty acids containing one or more carbon-to-carbon double bonds which are polarised (Table 2.5). Common fatty acids in biodiesel are as follows: stearic acids, palmitic acids, linolenic acid and oleic acid (Lee *et al.*, 2009; Talebian-kiakalaieh *et al.*, 2013). Oleic acid is the most common type of FFA found in oils due to its structure (Shu *et al.*, 2010). The differing levels of saturation can affect some biodiesel fuel properties such as cloud point, cold filter plug point and pour point.

Table 2.5: Common fatty acid in waste vegetable oil (adapted from Santonri *et al.*, 2012)

Name	Systematic name	Structure
<u>Unsaturated fatty acid</u>		
Capronic acid	Hexanoic acid	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$
Caprilic acid	Octanoic acid	$\text{CH}_3(\text{CH}_2)_8\text{COOH}$
Lauric acid	Dodecanoic acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic acid	Tetradecanoic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic acid	Hexadecanoic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic acid	Octadecanoic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Arachidic acid	Eicosanoic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
<u>Saturated fatty acid</u>		
Caproic acid	9-Decenoic acid	$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{COOH}$
Palmitoleic acid	9-hexadecenoic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Oleic acid	Cis-9-Octadecenoic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic acid	9,12-octadecadienoic acid	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$
Linolenic acid	6,9,12-Octadecatrienoic acid	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{COOH}$
Arachidonic acid	5,8,11,14-Eicosatetraenoic acid	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_4(\text{CH}_2)_2\text{COOH}$

According to Murayama (1994), Luis *et al.*, (2009) and Lim and Teong (2010), 75% of biodiesel production costs correspond to the cost of raw vegetable oil. Conventionally, high quality and mostly non-refined virgin oils — soybean, sunflower, olive, palm, fish, canola, cottonseed, peanut and linseed — are used (Parawira 2009; Agarwal *et al.*, 2012; Talebian-Kiakalaieh *et al.*, 2013; Christopher *et al.*, 2014). Biodiesel production costs are approximately 1.5 times higher than compared to diesel (Agarwal *et al.*, 2012) due to the increase in the price of agricultural raw materials (Figure 2.4).

The remaining costs can be delineated as follow: 12% chemical feedstock (methanol and catalysts), 2% energy (preparation of catalyst, transesterification process), and 11% for general overhead, direct labour and depreciation (Figure 2.4). A previous study has estimated that biodiesel production costs range between \$1.50 and \$2.50 per gallon, depending on the feedstock used in the production process (Lew *et al.*, 2014). Therefore, a clear and effective way to lower the cost of biodiesel production is to use cheap non-edible vegetable oils, animal fats, yellow grease and waste oils as raw materials (Christopher *et al.*, 2014). Cost of production is a major obstacle in biodiesel commercialisation (Atadashi *et al.*, 2013).

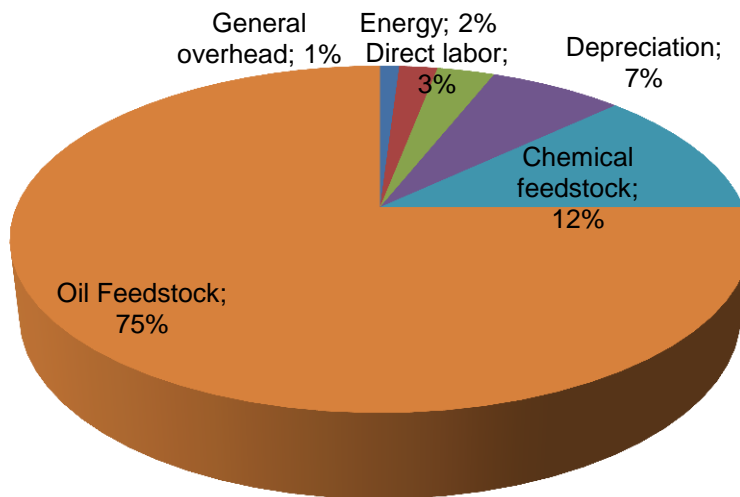


Figure 2. 4: General cost breakdown for biodiesel production (adapted from Lim & Teong, 2010)

Currently, 95% of all biodiesel is produced from edible oil. Sunflower is mostly used (84%), followed by palm oil (13%), soybean and other edible oils (2%) (Lim & Teong, 2010). The use of virgin vegetable oils and animal fat poses a threat to human food consumption and environmental problems such as deforestation, and is not feasible on a long-term basis because of the growing gap between demand and supply of oil (Atabani *et al.*, 2012). In order to comply with food industry regulations, the utilisation of non-edible and waste vegetable oils should be exploited.

While non-edible oils are good alternatives due to their non-competition with food consumption, they may not be sufficiently available to satisfy the global energy demand (Atabani *et al.*, 2012). Consequently, waste vegetable oil (WVO) is a promising supplementary alternative feedstock as it is economical, non-edible, and reduces the cost of waste product disposal (Zhang *et al.*, 2003; Luis *et al.*, 2009; Issariyakul *et al.*, 2014).

In view of the above challenges, the majority of studies have focused on non-edible oils or waste oil as low quality feedstock for biodiesel production, including algae, castor, rubber, Pongamia Pinnata, soapstock (by-product of vegetable oil refinery), microalgae, jatropha oil and grease oil (Shu *et al.*, 2010; Marchetti, 2012; Talebian-kiakalaieh *et al.*, 2013).

Price is certainly an important parameter to consider in the choice of biodiesel feedstock (Issariyakul *et al.*, 2014). The price of WVO is considered, on an average, two to three times cheaper than virgin vegetable oil (Agarwal *et al.*, 2012; Talebian-kiakalaieh *et al.*, 2013). The

cost of WVO decreases as FFA content increases. Table 2.6 shows that the price of WVO is twice as low as that of palm oil, soybean and rapeseed; it thus follows that the use of WVO as feedstock has the potential advantages of ready availability and reduction in feedstock costs.

Table 2.6: Price comparison from different feedstock (adapted from Lim &Teong, 2010)

Feedstock	Price of crude feedstock (USD/tons)	Price of biodiesel (USD/tons)
Rapeseed	815-829	940-965
Animal tallow	245	500
Palm oil	610	720-750
Soybean	735	880-805
WVO	360	600
Jatropha	N/A	400-500

2.1.2.1 Waste vegetable oil

WVO properties differ across the globe (Yaakob *et al.*, 2013). They are collected from large-scale food processing industries, households and service facilities. American and European countries (United State of America, Brazil, France and Italy, for example) produce 10-15 million gallons of WVO per day (Glisic *et al.*, 2014). An increase in food consumption has increased the production of WVO (household and industrial sources) in larger amounts and wider availability (Agarwal *et al.*, 2012; Issariyakul *et al.*, 2014), leading to the environmental crisis of the escalating challenge of waste disposal (Torres *et al.*, 2013). When used vegetable oil undergoes various physical and chemical changes, some undesirable and unknown compounds are formed. The compounds formed during frying increase the molecular mass and reduce the volatility of oil. These constitute a menace when discharged untreated into the environment (Luis *et al.*, 2009).

Using WVO as an alternative feedstock has the potential to alleviate this environmental issue associated with disposal (Canakci *et al.*, 2001; Sharma *et al.*, 2008; Agarwal *et al.*, 2012). Other advantages of the use of waste oil over edible vegetable oil include availability, composition of a higher proportion of saturated fatty acids and renewability of better oxidation stability (Sharma *et al.*, 2008; Agarwal *et al.*, 2012). The problem associated with WVO, however, is that it usually contains impurities and large amounts of FFA that cannot be converted directly to biodiesel using alkaline catalysts (Canakci *et al.*, 2001; Demirba,

2005; Kyong-Hwan *et al.*, 2008). WVO has approximately 350 times more impurities than virgin oils (Marchetti, 2012) and has a high acid number (Zhao *et al.*, 2013). Hence, the use of WVO will likely require some pre-treatments (e.g. steam injection, column chromatography, neutralisation and vacuum filter) (Talebian-kiakalaieh *et al.*, 2013).

WVO is characterised by low volatility and high viscosity, both of which can negatively influence the conversion efficiency. The high viscosity of WVO is due to the presence of different impurities (solid particles and sulphur content) (Marchetti, 2012; Hamamre *et al.*, 2014). According to the ASTM, the viscosity of WVO should range between 1.9-6mm²/s (Table 2.7) (Hamamre *et al.*, 2014).

Table 2.7: General properties of WVO (adapted from Birla *et al.*, 2012)

Properties	Values
Density (kg/m ³)	896-950
Viscosity (cSt) at 40°C	29-40
Acid value (mg of KOH/g of oil)	1.5-2
Free fatty acid (%)	0.1-0.25

Birla *et al.* (2012) used waste oil with CaO from snail shell as catalysts. The biodiesel production process was characterised by a 99.58% conversion with a yield of 87.28% at 60°C with 8.45:1 methanol-to-oil ratio and 2wt% catalyst concentration within 7h. Wang *et al.* (2007) achieved 97.02% yield of biodiesel from waste oil of high acid value (75.92 ± 0.036mgKOH/g) with two-step catalysis (esterification followed by transesterification). Furthermore, Omar *et al.* (2011) used waste cooking palm oil with Sr/ZrO₂ catalyst in biodiesel production obtaining a 79.7% yield within 87min, 2.7wt% and 29:1 methanol-to-oil ratio at 115.5°C (Table 2.8).

Table 2.8: Biodiesel production from WVO

Reaction conditions	Catalyst	Yield (%)	Conversion (%)	References
60C, 8.45:1 meth/oil ratio, 2wt% catalyst concentration, 7h	CaO from snail shell	87.28	99.58	Birla <i>et al.</i> , 2012
60C, 8.45:1 meth/oil ratio, 2wt% catalyst concentration, 7h	Ca	97.02	-	Wang <i>et al.</i> , 2007

Table 2.8: Cont.

115.5C, 29:1 meth/oil ratio, 2.7wt% catalyst concentration, 87min	Sr/ZrO ₂	79.7	-	Omar <i>et al.</i> , 2011
---	---------------------	------	---	---------------------------

2.1.2.2 Alcohol

Alcohol is one of the starting materials in the production of biodiesel (Demirbas, 2005; Yusuf *et al.*, 2011; Li-Wang *et al.*, 2013). Alcohol is used in transesterification in order to shift the reaction equilibrium to the product right side, and excess alcohol is usually adopted in biodiesel production to ensure that the oil is completely converted to biodiesel in a short period of time (Demirbas, 2005; Tang *et al.*, 2013). A 98% conversion can be achieved at 6:1 alcohol-to-oil ratio for an alkali-catalysed reaction (Issariyakul *et al.*, 2014). When too much alcohol is used, the polarity of the reaction mixture is increased, increasing the solubility of glycerol back into the ester phase, causing reverse reaction between glycerol and ester which results in ester yield being reduced (Issariyakul *et al.*, 2014).

There are different types of alcohol used in biodiesel production: methanol, ethanol, butanol, propanol and amyl alcohol. The type of alcohol used in transesterification affects the reaction performance (Mittelbach & Remschmidt, 2005; Yusuf *et al.*, 2011; Issariyakul *et al.*, 2014). Generally, the alcohols employed in transesterification of biodiesel production are methanol and ethanol, selected according to their cost and properties (Velickovie *et al.*, 2012; Marchetti, 2012). However methanol, which is normally obtained from mineral oil, is the most commonly used alcohol in transesterification due to its economic benefit, low viscosity and lower molecular weight (32.04g/mol). It requires less reaction time and has high performance (Zhang *et al.*, 2003; Demirba, 2005; Lee *et al.*, 2009; Guerrero *et al.*, 2011; Borges & Diaz, 2012; Torres *et al.*, 2013; Issariyakul *et al.*, 2014). Methanol is currently produced from non-renewable fossil sources such as natural gas. Furthermore, it has low solubility and immiscibility which is referred to as *mass transfer limitation* (Issariyakul *et al.*, 2014). The price of methanol varies with the crude oil price. The price varies between \$1.00 and \$1.90 USD per gallon. Some researchers have used methyl acetate as a replacement of methanol, producing triacetin as a by-product instead of glycerol mostly in the presence of an enzyme or under supercritical conditions (Casas *et al.*, 2011). This solvent, though, is not frequently used with natural or chemical catalyst. Therefore, methanol becomes a suitable alcohol in the transesterification process (Guerrero *et al.*, 2011).

Ethanol is an alternative source that is produced from renewable sources, as 60% of current world ethanol production is from sugar crop feedstock (Yusuf *et al.*, 2011; Torres *et al.*, 2013). Ethanol is less toxic because it can be easily produced from renewable sources by fermentation (Yusuf *et al.*, 2011). The disadvantage of ethanol, however, is its low reactivity of ethoxide as compared to methanol (Issariyakul *et al.*, 2014). Moreover, ethanol is more complicated to recover from the process, making the separation and purification of ethyl ester more difficult. This requires more energy and longer reaction time. The performance of the ethyl ester produced is less as compared to methyl ester; thus, it is not cost effective (Guerrero *et al.*, 2011; Yusuf *et al.*, 2011).

The cost of ethanol is dependent on its raw material (sugar cane, elephant grass, orange peels and beer broth, for example) and varies in the range \$2.00 - \$2.58 USD per gallon (Ziolkowska, 2014).

2.1.3 Factors affecting biodiesel production

The production of biodiesel is mainly affected by the reaction temperature, the type of catalyst (homogeneous or heterogeneous, acid or base), methanol-to-oil molar ratio, rate of the transesterification process and impurity content (usually free fatty acids and water) (Ong *et al.*, 2013). These are discussed in the subsequent sections:

2.1.3.1 Effect of temperature on biodiesel production

Temperature is a crucial parameter as it influences the reaction rate and yield of biodiesel during transesterification (Kotwal *et al.*, 2009; Babajide *et al.*, 2010). Transesterification can occur at different temperatures depending on the oil used (Meher *et al.*, 2006; Babajide *et al.*, 2010). The reaction temperature must be less than the boiling point of alcohol in order to ensure minimum vaporisation (Tariq *et al.*, 2012). The conversion of FFA and biodiesel production increases with increasing temperatures (Shu *et al.*, 2010; Babajide *et al.*, 2010). In order to favour the methanol nucleophilic attack on triglyceride, a high temperature is needed (Shu *et al.*, 2010). Brito *et al.* (2007) used a temperature range of 200-476°C for biodiesel production with WVO, discovering that the viscosity of the product diminished with an increased temperature. Babajide *et al.* (2010) showed that the conversion of sunflower using KNO_3 fly ash at temperatures of 200°C and 160°C resulted in conversions of 89.34% and 87.12% respectively. Omar and Amin (2011) employed a temperature higher than the methanol boiling point 115.5°C for biodiesel with waste cooking palm oil using Sr/ZrO₂, and

79.7% yield was obtained. High reaction temperatures reduced mass transfer limitation resulting in higher methyl ester yield and FFA conversion (Omar & Amin, 2011). The temperature ranges most often employed, as reported in the literature, are between 25°C and 150°C for a homogeneous catalyst, and between 40°C and 200°C for a heterogeneous catalyst (Endalew *et al.*, 2011; Issariyakul *et al.*, 2014).

2.1.3.2 Effect of water content and free fatty acid

FFA determines the viability of the oil for the transesterification process (Tariq *et al.*, 2012). Water can prevent the conversion of FFA to esters from reaching completion (Canakci *et al.*, 2001; Kim *et al.*, 2012). Addition of water, as little as 0.1wt%, might lead to the reduction in the yield of methyl ester. During a transesterification reaction, the presence of water causes more negative effects than FFA (Ma *et al.*, 1999; Peng *et al.*, 2011; Atadashi *et al.*, 2012). When the feedstock contains high percentages of FFA or water, the alkali catalysts (homogeneous catalyst) react with the FFA to form soap and the water can hydrolyse the triglycerides into diglycerides, forming more FFA (Borges & Diaz, 2012). Soap formation consumes the catalyst, decreases the ester (biodiesel) yield and also prevents glycerol separation from biodiesel (Canakci *et al.*, 2001).

The percentage of FFA can be reduced by conducting esterification prior to the transesterification process. The level of FFA in waste oil is often greater than 2wt% (Brito *et al.*, 2007). Previous studies have suggested that feedstock FFA content prior to transesterification should be 0.5-1% (Fenge *et al.*, 1945; Nye & Southwell, 1984; Mittelbach *et al.*, 1992; Ma *et al.*, 1999). FFA plays an important role in some critical parameters of biodiesel such as the cetane number, oxidation stability and cold flow properties (Ramos *et al.*, 2009). Despite these challenges, heterogeneous catalysts have proven to mediate the transesterification of oil with FFA content of 6-15% without any pre-treatment (Singh *et al.*, 2010). A 90% yield of biodiesel was obtained from waste palm oil containing 6.6-6.8% FFA using CaO (Boey *et al.*, 2011). Hassani *et al.* (2013) used waste cooking oil with high FFA (9.85%) via a two-step esterification-transesterification process, with a maximum conversion of 87% observed under optimum conditions (6:1 methanol-to-oil molar ratio, 1% KOH catalyst concentration and 65°C).

To decrease the FFA content to 0.5wt% and to improve the properties of WVO, several pre-treatment methods have been suggested:

- reaction in supercritical alcohol;

- reaction with enzyme; and
- pre-treatment with esterification reaction.

Of these, esterification reaction has been found to be more efficient and cost effective.

2.1.3.3 Molar ratio of alcohol-to-vegetable oil

Molar ratio, associated with the type of catalyst used, is one of the most important variables affecting the yield of biodiesel (Ma & Hanna, 1999; Srivastava & Prasad, 2000; Demirba, 2005; Hu *et al.*, 2011; Silva *et al.*, 2011; Birla *et al.*, 2012; Khemthong *et al.*, 2012). The yield of biodiesel increases with increasing molar ratio of alcohol/oil during the process (Demirbas, 2005). The stoichiometric molar ratio of methanol-to-oil is 3:1, helping to drive the reaction toward completion and gain more products (Hu *et al.*, 2011). Excessive molar ratio of alcohol-to-oil interferes with the separation of glycerol because there is an increase in solubility of the mixture; therefore, the ideal alcohol-to-oil ratio has to be established empirically (Demirbas, 2005; Meher *et al.*, 2006). Vegetable oil and WVO can be transesterified between 1:6 and 1:40 oil/alcohol molar ratio (Demirbas, 2005). Khemthong *et al.* (2012) showed that the most suitable molar ratio was found to be in the range of 1:15 and 1:25 in the production of biodiesel using eggshell ash (CaO) as heterogeneous catalyst. Beyond this range, the yield decreased. Birla *et al.* (2012) and Shu *et al.* (2010) also demonstrated that the conversion of biodiesel is directly proportional to the oil/alcohol molar ratio.

An optimum alcohol-to-oil ratio varies with the oil quality and type used (Issariyakul *et al.*, 2014). The overloading of methanol would inactivate the catalyst and consequently favour the backward reaction of transesterification process (Omar & Amin, 2011).

2.1.3.4 Effect of catalyst

Selection of catalyst depends on a number of factors: the type of feedstock (edible or non-edible oil), operation condition (temperature and pressure), required catalytic activity (high surface area), and its cost and availability (Chouhan *et al.*, 2011). The transesterification reaction is strongly dependent on the weight of the catalyst, which in turn affects the yield. An adequate increase in catalyst concentration results in an increase in the number of its active sites and thereby an increase in the yield of methyl ester (Omar & Amin, 2011). Excessive catalyst loading leads to high slurry viscosity and consequent poor reaction mixtures (Taufiq-yap *et al.*, 2014).

2.1.4 Catalysts in transesterification process

Catalysts play a significant role in the transesterification reaction. Catalyst types and concentrations are very important for achieving an optimal process (Argawal *et al.*, 2012; Issariyakul *et al.*, 2014). Catalysts are usually used in the production of biodiesel to improve the reaction rate and yield (Tariq *et al.*, 2012). Catalytic activity is a function of its specific surface area, base strength and base site concentration. In general, a good catalyst must have several qualities (i.e. not be deactivated by water, be stable, be activated at low temperature and have high selectivity) (Smith & Notheisz, 2006; Di-Serio *et al.*, 2008; Rafaat *et al.*, 2010).

The selection of a catalyst depends on the amount of FFA in the feedstock while using WVO (Singh & Samar, 2011; Issariyakul *et al.*, 2014). To achieve biodiesel that is economically feasible, the development of active and cheap catalysts for effective transesterification of different kinds of feedstock is absolutely necessary (Atadashi *et al.*, 2013).

There are three different types of catalysts that can be employed in the transesterification process of biodiesel: acid catalysts, base catalysts and biocatalyst (Figure 2.5) (Pathak, 2015).

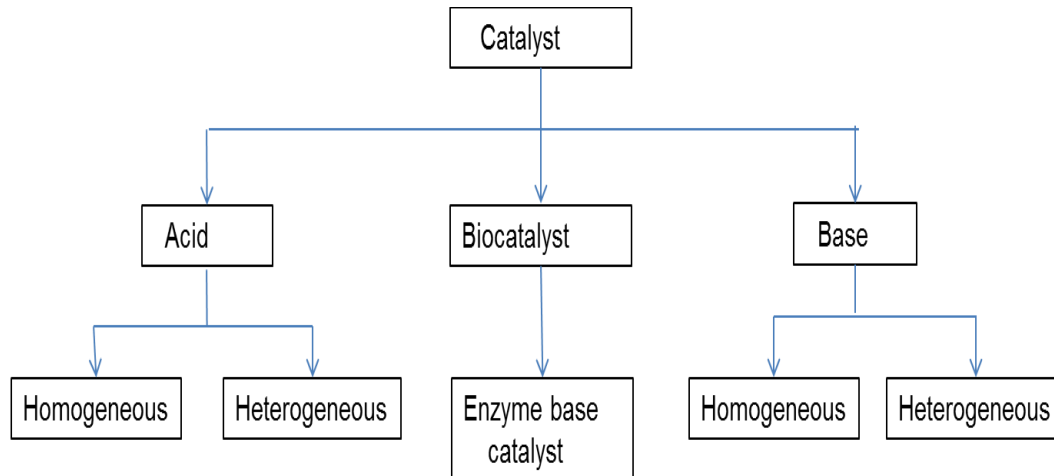


Figure 2. 5: Classification of catalyst (adapted from Pathak, 2015)

Recently, there have been significant advancements in biodiesel production from homogeneous catalysts to heterogeneous catalysts due to their high performance in the production quality and efficiency (Atadashi *et al.*, 2012; Pathak, 2015).

2.1.4.1 Homogeneous acid and base catalysts

Homogeneous catalysts are conventionally used in commercial biodiesel production processes. The homogeneously-catalysed process often offers a reaction yield higher than 97% in short period of time (10min-2h) with a reaction temperature between 25°C and 70°C (Endalew *et al.*, 2011; Issariyakul *et al.*, 2014). Homogeneous catalysts are catalysts that exist in the same phase as the reactants and are limited to quality of the feedstock being anhydrous and acid value lower than 1mg of KOH/g of oil in the transesterification process (Issariyakul *et al.*, 2014; Chouhan *et al.*, 2011). These catalysts can either be acidic (H_2SO_4 , HCl, H_3PO_4 etc) or alkaline (NaOH, KOH, CH_3ONa , CH_3OK). They are associated with a number of disadvantages including the formation of soap during biodiesel processes with FFA higher than 0.5%, corrosion of the equipment, high energy consumption resulting in an increase in capital equipment cost, difficult separation of glycerol from methyl ester which leads to formation of emulsion, and increases in viscosity (Endalew *et al.*, 2011; Atadashi *et al.*, 2012). Others disadvantages include consumption of catalyst with water content higher than 0.3% resulting in low reaction yield, difficult recovery of glycerol due to the solubility of catalyst, the need for excessive methanol, long reaction time, high temperature requirement, high catalyst loading and catalyst toxicity (Ghoreishi *et al.*, 2012; Talebian-kiakalaieh *et al.*, 2013; Deshmane & Adewuyi, 2013; Christopher *et al.*, 2014). Metal alkoxides (CH_3ONa and CH_3OK) are more active even at lower molar concentration but they are more expensive than alkaline metal hydroxide (NaOH and KOH); thus their low price makes them preferable as catalysts as they can render a high conversion of oil simply by increasing the catalyst concentration (Atadashi *et al.*, 2012).

The most commonly used homogeneous catalysts are basic catalysts, as they are 4000 times faster than homogeneous acid catalysts (Ma *et al.*, 1999; Vyas *et al.*, 2010; Atadashi *et al.*, 2012; Deshmane & Adewuyi, 2013; Xie *et al.*, 2013). These catalysts require high quality feedstock and give high conversions of TG at short reaction times. However, these have been shown to be sensitive to water and FFA content in feedstock, leading to soap formation, reduction of catalysts, and performance and separation problems (Atadashi *et al.*, 2013; Christopher *et al.*, 2014). During homogeneously-catalysed transesterification the glycerol produced is of low quality and requires distillation for purification (Chouhan *et al.*, 2011).

Homogeneous acid catalysts such as H_2SO_4 can be used to transesterify oil with high FFA and water content; however, the process is slower than reactions mediated by homogeneous basic catalysts. This is less attractive for industrial purposes but can be used

in the esterification step, which converts FFA to TG. Marchetti (2012) and Zhang *et al.* (2003) showed biodiesel production from waste oil characterised by an acid concentration of 1.5-3.5mol%, with excess methanol in the presence of H₂SO₄, at a high molar ratio of 50:1, and a temperature of 80°C. A 97% conversion was reached at a reaction time of 10h.

The ability of a homogeneous acid catalyst to act as an esterification reagent and play a solvent role in the process can mediate esterification and transesterification processes to occur in a single stage (Talebian-kiakalaieh *et al.*, 2013). Studies have shown that two-stage transesterification is more advantageous: no acid waste treatment, low equipment cost, and easy recovery of catalyst as compared to the limitation of a single step process (Vyas *et al.*, 2010; Talebian-kiakalaieh *et al.*, 2013).

Generally, the choice of homogeneous catalysts is due to their higher kinetic reaction rate, low cost and short reaction time. Nevertheless, because of high-energy consumption, high cost of refined feedstock and difficulties associated with the use of homogeneous catalysts, there is a shift toward heterogeneous catalysts (Vyas *et al.*, 2010; Rezaei *et al.*, 2013).

2.1.4.2 Heterogeneous acid and base catalysts

Heterogeneous catalysts are usually in a solid phase in the reaction mixture, are insensitive to FFA and are characterised by a number of advantages as compared to the homogeneous catalysts: several washing steps can be eliminated, the separation process is easy to handle, the cost is low, they are environmentally friendly, the catalyst can be reused, they have less toxicity, they have high catalytic activity, and there is a reduction of production costs. However, heterogeneous catalysts have limitations as well, specifically related to catalytic structure and properties (Lee *et al.*, 2009).

The reaction conditions of heterogeneous catalysis are intensified to define reaction rates by increasing reaction temperature (100-250°C), catalyst amount (3-10wt%) and methanol/oil molar ratio (10:1-25:1) (Lee *et al.*, 2009). These conditions, which can be cost and energy intensive (Christopher *et al.*, 2014), are also associated with mass transfer limitations leading to the formation of three phases mixture (catalyst, oil and alcohol) (Talebian-kiakalaieh *et al.*, 2013).

Most catalysts used in biodiesel production are acidic or basic with different advantages and disadvantages due to their properties (Atadashi *et al.*, 2012). Previous reports have shown that heterogeneous catalysts, especially alkaline alternatives, can be reused and have a high performance to produce biodiesel from oil with high FFA because of their ability to

absorb water contained in the WVO (Semwal *et al.*, 2007; Rezaei *et al.*, 2013; Talebian-kiakalaieh *et al.*, 2013). High content of FFA accelerates the basic catalyst deactivation during the transesterification process (Borges & Diaz, 2012). Contrary to the use of homogeneous catalyst, Leung *et al.* (2012) stated that heterogeneous catalysts are suitable in transesterification of high FFA feedstock because of their easy separation from the mixture and reusability. Nevertheless, the reaction proceeds at slower rate due to the reaction mixture which constitutes a three-phase system. Heterogeneous catalysts have been proven to be economically feasible and achieve good conversion (~98%) as compared to homogeneous catalysts (Marchetti, 2012).

I. Heterogeneous acid catalysts

Presently, heterogeneous acid catalysts are replacing homogeneous acid catalysts due to their insensitivity toward FFA and the easy removal of the catalyst from the mixture without any loss in catalytic activity (Shu *et al.*, 2010). Relative to heterogeneous base-catalysed process, acid-catalysed reactions require a longer reaction time, a high reaction temperature and a high alcohol/oil molar ratio resulting in lower biodiesel yield (Di-Serio *et al.*, 2005; Bankovic-illic *et al.*, 2014; Christopher *et al.*, 2014). Acid catalysts have lower catalytic activity; hence, higher reaction temperatures (~200°C) and higher reaction times (8-20h) required. *Catalyst leaching*, a phenomenon associated with heterogeneous acid-catalysed transesterification, results in an extra purification step and generation of waste solvent, thereby escalating the biodiesel production cost (Issariyakul *et al.*, 2014).

Acid catalysts can mediate both esterification and transesterification processes simultaneously and have better results for oil with FFA greater than 2% (Shu *et al.*, 2010; Endalew *et al.*, 2011; Chouhan *et al.*, 2011; Talebian-kiakalaieh *et al.*, 2013). Furthermore, they can produce a large number of salt interactions likely to cause corrosion of equipment.

There are several reports about the use of heterogeneous acid catalysts including zeolite, La/zeolite beta, Zs(Zn(C₁₈H₃₅O₂)₂), and Fe-Zn (Brito *et al.*, 2007; Shu *et al.*, 2010; Canakci *et al.*, 2011; Carrero *et al.*, 2010; Yogesh *et al.*, 2011; Issariyakul *et al.*, 2014). An identified advantage of the use of acid catalyst is its hydrophobicity; hence, it can tolerate water content in the feedstock up to 20% without significant loss in catalytic activity (Issariyakul *et al.*, 2014).

Recent studies have been conducted concerning the use of zeolite as a heterogeneous acid catalyst for biodiesel production (Brito *et al.*, 2007; Singh & Sharma, 2011; Yogesh *et al.*,

2011). Zeolites are microporous crystalline solids with well-defined structures, usually containing silicon, aluminium and oxygen bonded together (Chung *et al.*, 2008). Zeolites are more suitable transesterification catalysts to synthesise biodiesel as compared to other chemical catalysts due to the following qualities: high thermal stability, regenerability, no toxicity, no corrosion, no environmental pollution, high size selectivity and high concentration of active acid site (Shu *et al.*, 2007). Zeolites are either naturally occurring or synthesised from chemicals. There is potential to generate zeolites from natural sources and wastes such as coal fly ash, animal bones and palm kernel shells (Yagiz *et al.*, 2007). Their elemental compositions of calcium carbonate, silicates, aluminium and magnesium provide a good basis for their use in the production of biodiesel (Singh & Sharma, 2011).

Zeolites as catalysts have an acidic characteristic and shape selectivity (Carrero *et al.*, 2010; Canakci *et al.*, 2011; Singh & Sharma, 2011; Yogesh *et al.*, 2011). The strength and pore structure of acidic zeolites is responsible for their catalytic activity in FFA removal (Chung *et al.*, 2008). In view of this, Oletoye *et al.* (2011) studied transesterification of biodiesel as heterogeneous catalyst, finding that eggshell, a solid waste, can be used as low cost catalyst after modification with magnesium and potassium nitrate for biodiesel production, as a yield of 95% at 8:1 alcohol/oil molar ratio was obtained.

The ability of heterogeneous acid catalysts to act as an esterification reagent can mediate esterification and transesterification processes to occur in single stage (Talebian-Kiakalaieh *et al.*, 2013). Further development in heterogeneous acid catalysts is required, especially in terms of ester yield, acid value of the product and catalyst leaching (Issariyakul *et al.*, 2014).

II. Heterogeneous base catalysts (metal oxide)

Presently, there are several heterogeneous-base catalysts available for biodiesel production. These include CaO, CaZrO₃, Al₂O₃-SnO, Li/MgO, Al₂O₃/KI, KOH/Al₂O₃, KOH/Nay and alumina/silicate supported K₂CO₃ (Shu *et al.*, 2010).

Base-catalysed transesterification is associated with faster rates and greater yield as compared to the acid-catalysed processes (Christopher *et al.*, 2014). These catalysts are classified into six categories according to Hattori's classification for solid base catalyst: 1) single metal oxide, 2) mixed metal oxide, 3) supported alkali, 4) alkaline earth metals, 5) hydroxalicates and 6) organic base solids. The most commonly used are single metal oxides (Lee *et al.*, 2009).

Reaction rates in single metal oxides depend directly on the basicity of the oxide, especially of the strong base site. There are a variety of single metal oxides — including magnesium oxide (MgO), calcium oxide (CaO) and strontium oxide (SrO) — that have been employed as catalysts for the transesterification of biodiesel (Supper *et al.*, 1999; Sharma *et al.*, 2011). Liu *et al.* (2008) used SrO metal oxide as a catalyst for transesterification of soybean oil after calcination of SrCO₃ at 1200°C for 5h. A 95% yield was obtained at 65°C, 3wt% catalyst and 12:1 molar ratio methanol-to-alcohol.

From the economic and ecological point of view, CaO is the most popular and promising metal oxide applied for biodiesel synthesis due to its low cost, excellent catalytic properties, high basic strength ($H_{-}=26.5$), minor toxicity, and low environmental impact due to its low solubility in methanol and high availability (Table 2.10) (Suppes *et al.*, 2001; Liu *et al.*, 2008; Lee *et al.*, 2009; Navajas *et al.*, 2012; Deshmane & Adewuyi, 2013; Rezaei *et al.*, 2013; Tang *et al.*, 2013). The use of CaO as a heterogeneous catalyst has been around for many years as it can be produced from numerous sources: chicken eggshell, mollusk shell, bones, golden apple snail shell, mussel shell, oyster shell, meretrix venus shell and mud crab shell (Boey *et al.*, 2011; Jazie *et al.*, 2013).

i. Eggshell and calcium oxide

The first information pertaining to the use of CaO as catalyst with rapeseed oil in the production of biodiesel was reported by Peterson and Scarrah in 1984 (Boey *et al.*, 2011). Rezaei *et al.* (2013) used waste mussel shell to produce biodiesel after calcination at 1050°C. The catalyst was found to be effective, resulting in a 98% yield, at a temperature of 60°C, a 24:1 molar ratio methanol-to-oil and 12wt% catalyst loading. Viriya-Empikul *et al.* (2009) calcined waste shells of egg, golden apple snail, and Venus meretrix at 800°C to produce CaO catalysts for biodiesel using palm oil. The results showed that all catalysts gave high biodiesel production, as > 90% yields were obtained in 2h.

Liu *et al.* (2011) used calcined river snail shell as catalyst with soybean oil. A 98% yield was obtained at 65°C, 3wt% catalyst loading at 9:1 methanol molar ratio within 3h. When further transesterification work on CaO was conducted by Boro *et al.* (2011) using a solid oxide catalyst derived from waste shell of *Turbinilla Striatula* with mustard oil, a 93.3% yield was achieved at 65±5°C by employing 3wt% catalyst with 9:1 methanol-to-oil ratio within 6h.

Catalyst activity of CaO can be improved by employing thermal activation treatment and washing such as calcination to remove the surface carbonate and hydroxyl group (Chouhan *et al.*, 2011). Activities of various catalysts are summarised in Table 2.9.

Table 2.9: Summary of reaction conditions and performance of various catalysts

Catalyst type	Feedstock	Reaction conditions	Yield (%)	References
Homogeneous Acid: H₂SO₄	Waste oil	50:1; 80°C; 1.5-3.5mol%; 10hrs	97	Zhang <i>et al.</i> , (2003)
Heterogeneous acid: Zeolite	Palm oil	8:1	95	Oletoye <i>et al.</i> , (2011)
Heterogeneous base: CaO	Palm olein	2h; 8:1	>90	Viriya-Empikul, (2009)
CaO	Soybean	65°C; 3wt%; 9:1, 3-6hr	98	Liu <i>et al.</i> , (2011) Boro <i>et al.</i> , (2011)
CaO from snail shell	Waste vegetable oil	60°C; 8.45:1; 2wt%; 7h	87.28	Birla <i>et al.</i> , (2012)
CaO	Waste vegetable oil	60°C; 8.45:1; 2wt%; 7h	97.02	Wang <i>et al.</i> , (2007)
Sr/ZrO₂	Waste cooking palm oil	115.5°C; 29:1; 2.7wt%, 87min	79.7	Omar <i>et al.</i> , (2011)

In this present work, chicken eggshell was chosen as source of CaO catalyst due to its ready availability.

Recent studies employed eggshell to produce solid oxide (CaO) as a low cost catalyst and it has proven to be a good source of CaO (Singh *et al.*, 2011; Jazie *et al.*, 2013). This process not only provided an opportunity to use the eggshell, but also added value to the waste generated due to its eco-friendly characteristic and availability (Boro *et al.*, 2011; Khemtong *et al.*, 2011). CaO has been reported to produce FAME as high as 98% yield during the first cycle of reaction (Endalew *et al.*, 2011).

Eggshells, which constitute about 10-11% of the total weight of the whole egg, are composed of approximately 85-95% calcium carbonate (CaCO₃), weighing 5.5 grams of mass, and the remaining 5% contains calcium phosphate (0.3%), magnesium carbonate (0.3%), and soluble and insoluble proteins (Lechtanski 2000; Nakano *et al.*, 2003; Butcher *et*

al., 2004; Gunasekaran *et al.*, 2009; Jazie *et al.*, 2013). Calcium oxide (CaO) is a basic anhydride, allowing it to have good catalytic activity that can react easily with water.

Calcium oxide cannot be found naturally on earth, as it is made from calcination of calcium carbonate at a high temperature. Calcination of limestone to produce lime has been practised since antiquity by cultures all around the world. Usually, calcination of CaCO₃ takes place at 500–600°C. However, using higher temperatures (>700°C at atmospheric pressure) has proven to enhance the performance of the catalyst and lead to a complete decomposition of CaCO₃, as shown in Equation 2.1 (Wei *et al.*, 2009; Sharma *et al.*, 2010; Birla *et al.*, 2012; Navajas *et al.*, 2012; Rezaei *et al.*, 2013):



The production of CaO from CaCO₃ might increase the cost of catalyst preparation on industrial scale (Chakraborty *et al.*, 2010).

Table 2.10: Opportunities and challenges of calcined CaO catalyst

Advantages (Opportunities)	Disadvantages (Challenges)
Environmentally friendly	High catalyst preparation cost
Contributes to rural development	Non-available on commercial scale
Renewable	Requires more alcohol for transesterification
High catalytic activity	
Reusable	
Feedstock availability	

Singh *et al.* (2011) reported that CaO derived from waste eggshell was an effective catalyst for transesterification with soybean oil; a 97-98% biodiesel yield was obtained at 65°C with alcohol/oil ratio 9:1. Other researchers such as Viriya-Empikul *et al.* (2010) used eggshell ash with palm oil: a 95% yield was reached within 2h at 12:1 methanol/oil ratio. The high yield was due to the high surface area exhibited by the eggshell catalyst. Oletoye *et al.* (2011) studied transesterification of biodiesel from palm oil using eggshell as a heterogeneous catalyst, with results revealing that eggshell can be utilised as a low cost heterogeneous catalyst after modification with magnesium and potassium nitrate for biodiesel production. A yield of 95% at 8:1 alcohol/oil molar ratio was obtained. Furthermore, Khemthong *et al.* (2011) demonstrated that CaO as catalyst from eggshell and waste bones in biodiesel production with palm olein oil resulted in a yield >90%. In yet another study,

Navajas *et al.* (2012) used CaO from chicken eggshell to catalyse the transesterification of oil under reaction conditions of 5h, a molar ratio of 24:1 and methanol/oil at 60°C with 4% catalyst loading: a 90% yield was obtained.

Huaping *et al.* (2006) used non-edible *Jatropha curcas* oil with chemical CaO as a base catalyst, with a relative lower methanol/oil ratio of 9:1, catalyst loading 1.5 wt%, at a reaction temperature of 70 °C. A FAME yield of 94% was obtained. Wei *et al.* (2009) utilised chicken eggshell calcined at 1000°C: a 95% yield was observed at 65°C, 9:1 methanol/oil molar ratio, with catalyst loading of 3wt% at 3h. This study confirmed what Sharma *et al.* (2010) observed by using chicken eggshell ash with karaja oil: at a molar ratio of 9:1 methanol-to-oil within 2h30min, a 95% yield was obtained. Jazie *et al.* (2013) investigated eggshell calcined at 900°C to mediate rapeseed oil conversion. A 96% yield was obtained at 3wt% catalyst concentration, 9:1 molar ratio at 60°C, and a reaction time of 3h. Boey *et al.* (2011) reported that CaO-catalysed transesterification reaction using waste oil with high FFA between 6.6-6.8% yielded about 90%, as compared to NaOH and KOH with only 46% and 61% respectively. Tang *et al.* (2013) employed modified CaO to compare the yield of two different feedstock oil (soybean oil and rapeseed oil) under the same conditions (65°C, methanol-to-oil ratio of 15:1 and 5wt% catalyst concentration). A 99.5% biodiesel yield was observed when using soybean oil within 3h and rapeseed oil yielded 99.8% within 2h30min. Use of CaO from natural sources as heterogeneous catalysts are summarised in Table 2:11.

Table 2.11: Use of CaO catalyst from natural sources in biodiesel production

Sources	Feedstock	Reaction conditions	Yield (%)	References
Chicken eggshell	Soybean oil	65°C, 9:1 ratio	97-98%	Singh <i>et al.</i> , (2011)
River snail shell	Soybean oil	65°C, 3wt% catalyst loading, 9:1 ratio, 3h	98%	Liu <i>et al.</i> , (2011)
Turbinilla striatula shell	Mustard oil	65±5 °C, 3wt% catalyst loading, 9:1 ratio, 6h	93%	Boro <i>et al.</i> , (2011)
Golden apple snail, venus meretrix eggshell	Palm olein oil	12:1 ratio; 2h	90-95%	Viriya-Empikul <i>et al.</i> , (2010); Viriya-Empikul <i>et al.</i> , (2009)

Table 2.11: Cont

Chicken eggshell	Palm olein oil	8:1	90-95%	Oletoye <i>et al.</i> , (2011); Khemthong <i>et al.</i> , (2011)
Chicken eggshell	Waste vegetable oil	60°C, 5h, 24:1 ratio, 4% catalyst loading	90%	Navajas <i>et al.</i> , (2012)
Chicken eggshell	Rapeseed	60±5°C, 3wt% catalyst loading, 3hr, 9:1 ratio	95-96%	Wei <i>et al.</i> , (2009); Jazie <i>et al.</i> , (2013)
Chicken eggshell	Karaja oil	9:hr,1 ratio, 2.5, 3wt% catalyst loading, 65°C	95%	Sharma <i>et al.</i> , (2010)

The catalysis by CaO can produce a lower FAME yield than expected from its high triglyceride conversion due to the formation of $\text{Ca}(\text{OCH}_3)_2$ on the CaO surface (Lee *et al.*, 2009).

2.1.4.3 Enzymatic catalysts

Enzymatic catalysts possess properties of both homogeneous and heterogeneous catalysts. In recent years, enzymatic reactions using lipase have attracted growing attention due to its advantages over chemical catalysts: it has easy product recovery, environmental-friendly properties, high selectivity and a low alcohol-to-oil molar ratio (Vyas *et al.*, 2010; Zhao *et al.*, 2013). Enzyme catalysts tolerate FFA and water content, facilitating easy purification of biodiesel and glycerol (Zhao *et al.*, 2013). Enzyme catalysts are expensive, though, and biodiesel can be contaminated by residual enzymes. While enzymes can be easily deactivated, a long reaction time is required. These major drawbacks limit industrial application of enzymes in the production of biodiesel (Boey *et al.*, 2011; Endalew *et al.*, 2011; Zhao *et al.*, 2013). In order to minimise some of these limitations, immobilised enzymes are employed. These facilitate multiple uses and consequent cost reduction. However, the build-up of glycerol limits the number of their reusability (Vyas *et al.*, 2010).

2.1.4.4 Reusability of catalyst

Catalyst activity is a function of its surface area, base strength, surface morphology, chemical composition and base site concentration (Navajas *et al.*, 2012). The structure texture of a catalyst depends on the preparation method (Navajas *et al.*, 2012). Catalysts can be easily separated from reaction mixture by filtration or centrifugation and reused for several runs (Hu *et al.*, 2011). Reusability is of a great importance for industrial application, as this may contribute to the reduction of biodiesel production costs (Wan *et al.*, 2014).

The reusability of several catalysts has been studied intensively (Kouzou & Hidaka, 2012). Many heterogeneous catalysts can be reused several times (three-20 cycles) depending on their chemical properties. In studying the deactivation of catalysts, Liu *et al.* (2011) discovered that the SrO catalyst could be reused for 10 cycles before decreasing in activity by 90%. Likewise, Wan *et al.* (2014) demonstrated that MnCO₃/ZnO catalyst in subcritical methanol processes with soybean oil could be used for more than 17 cycles. The results indicated that TG conversion and FAME yield kept their values above 92% and 86% respectively without a regeneration process. Furthermore, Taufiq-yap *et al.* (2014) used solid mixed oxide CaO-La₂O₃ catalyst with *Jatropha curcas* crude oil in biodiesel production, finding the catalyst could be used for only three cycles with 86.5% yield at 65°C, 4wt% and 24:1 methanol-to-oil ratio. The loss in activity was due to the dissolution of active metal in the catalyst.

Boey *et al.* (2008) tested catalyst reusability of CaO catalyst from fresh water mussels, revealing that the catalyst could be used 11 times without losing its activity. In another study by Hu *et al.* (2011), they reported that the catalyst from freshwater mussel without any treatment could not be used more than eight times. The catalyst was active for seven reaction cycles with yield above 90%. Furthermore, Rezaei *et al.* (2013) investigated the reusability of catalyst from mussel shell. This was tested in two different ways: firstly, with catalyst calcined after each use, and secondly, with the catalyst washed with methanol. The results showed that the catalyst re-calcined after use lost its activity after three times as compared to the catalyst washed with methanol, which could be used more than five times and the yield was maintained at 99.68%. The re-calcined catalyst decreased in activity due to the reduction in surface area and amount of calcium in the catalyst caused by re-calcination.

Liu *et al.* (2008) compared the activity of CaO with K₂CO₃/γ-Al₂O₃ and KF/γ-Al₂O₃ catalysts, observing that CaO had high reusability for approximately 20 cycles as compared to

$K_2CO_3/\gamma-Al_2O_3$ and $KF/\gamma-Al_2O_3$. Jazie *et al.* (2013) tested the reusability of calcined eggshell using rapeseed oil; the catalyst could be used 14 times before gradually losing activity (97%). The catalyst was completely deactivated after being used more than 18 times. Birla *et al.* (2012) showed that CaO catalyst from snail shell can be reused up to 14 times with no apparent loss of activity, as after 14 times the cycle of transesterification yield was still 88%. Navajas *et al.* (2012) indicated that catalyst from eggshell could be repeatedly used for 18 times due to its surface area and chemical composition. Boro *et al.* (2011) studied the reusability of CaO from waste shell *Turbonilla striatula* with mustard oil and the catalyst was used more than three times, with a yield of 93.3%. Tang *et al.* (2013) investigated the deactivation of modified CaO, observing that the catalyst could be reused for 15 cycles without any modification in its catalytic activity.

Deactivation and the stability of CaO catalyst are still unresolved problems in biodiesel production (Tang *et al.*, 2013). Deactivation of catalyst may occur after several cycles, as proven by different studies, and factors affecting the catalyst reusability may vary from one production to the other such as the following:

- *Accumulation of water which may dilute the catalyst.* The catalyst deterioration could be due to the change of catalyst surface structure. The calcium oxide is transformed to calcium hydroxide $Ca(OH)_2$ gradually, due to the moisture in the reactants, which deteriorates the activity of the catalyst (Hu *et al.*, 2011; Kouzu & Hidaka, 2012; Jazie *et al.*, 2013).
- *Catalyst poisoning.* The catalyst should be kept away from air, atmospheric H_2O and CO_2 , to prevent poisoning and deterioration (Liu *et al.*, 2008; Boey *et al.*, 2011; Kouzu & Hidaka, 2012).
- *Re-calcination of catalyst:* Re-calcination leads to reduction of catalyst activity due to reduction in surface area occurring during calcination in the catalyst reusability phase (Rezaei *et al.*, 2013).
- *Leaching of CaO in methanol:* CaO is more soluble in methanol. Leaching of surface CaO into $Ca(OCH_3)_2$ due to methanol has become an issue because of its considerable influence on the recyclability of catalysts and degree of purity for biodiesel and glycerol application. This issue has become a barrier inhibiting future success (Lee *et al.*, 2009; Kouzu & Hidaka, 2012).
- *Loss of catalyst during washing and filtration* (Boro *et al.*, 2011).

The ability of CaO catalysts to be reused has a large impact on the economic aspect of biodiesel production.

2.2 Physical and chemical properties of biodiesel

Prior to the use of the biodiesel, an analysis of the chemical and physical properties is required to assess suitability for use in diesel engines. These properties are usually compared against standards like those of the American Society for Testing Materials (ASTM), European Union Standard for biodiesel fuel (EN 14214), Germany (DIN 51606), Austria (ON) and Czech Republic (CSN). The most popular international standard specifications applied are the American Standard for Testing Materials (ASTM) and European Standard (EN 14214), as shown in Table 2.12.

Biodiesel is characterised by different physical and chemical properties depending on the feedstock used in the manufacturing process: Acid number, cetane number, oxidative stability, viscosity, flash point, cloud point, pour point, density, free and total glycerol moisture content, phosphorus content, sulphated ash test and carbon residue. Since biodiesel can be made from different feedstock, some properties differ from one product to another.

2.2.1 Acid number

Acid number is an indicator of FFA content. This acid value can be elevated if the fuel is not properly manufactured or has undergone oxidative degradation. The acid level and viscosity may increase as biodiesel ages in storage, but high acid content in the oil results in lower conversion efficiency and may cause severe corrosion in fuel supply system (Meher *et al.*, 2006; Atabani *et al.*, 2012). Pure biodiesel, however, is not acidic but can be contaminated with water during storage which will lead to FFA formation. ASTM D664 and EN 14 104 approved a maximum acid value of 0.5mg KOH/g (Atabani *et al.*, 2012).

2.2.2 Cetane number

The *cetane number* of biodiesel depends on its fatty acid profile and increases with an increase of fatty acid proportions. Long chains and more saturated fatty acid lead to high a cetane number (Ong *et al.*, 2013). Biodiesel has a higher cetane number than diesel fuel and contains 10-11% oxygen by weight (Canakci *et al.*, 2001). These characteristics reduce the emissions of carbon monoxide (CO) and hydrocarbon (HC) as compared to petroleum-based diesel fuel, reducing engine noise (Canakci *et al.*, 2001). A biodiesel cetane number, according to ASTM D613 and EN ISO 5165, varies from 48-65 as compared to diesel which

varies from 40-55 (Atabani *et al.*, 2012). A high cetane number helps ensure good cold start properties and minimises the formation of white smoke. However, biodiesel from saturated fats has a higher cetane number than biodiesel from unsaturated oil.

2.2.3 Oxidation

Biodiesel has a technical problem: its susceptibility to *oxidation* — a phenomenon which can cause the fuel to become acidic — can form insoluble gums and sediments that can plug fuel filters, as well as an increased viscosity. Factors influencing the oxidation process of biodiesel are light, temperature, heat, traces of metal, fatty acid structure (presence of double bond) and presence of air (Kapilan *et al.*, 2009; Ong *et al.*, 2013). Most biodiesel contains significant amounts of oleic, linoleic or linolenic acid which influence the oxidative stability of the fuel (Knothe, 2005). Oxidation occurs due to the presence of unsaturated fatty acid chains and double bonds in the oil reacting with oxygen in the presence of air (Atabani *et al.*, 2012). Various methods have been employed to determine oxidative stability: active oxygen method, ASTM D2274, ASTM D4625, pressurised differential scanning calorimetry, and oxidation stability index (OSI) which confirms the catalysing effect of methyl on oxidation (Knothe, 2005; Waynick, 2005). Biodiesel made from feedstock high in saturated fat such as palm oil or tallow tends to oxidise slower.

2.2.4 Viscosity

Viscosity is an indicator to measure the effectiveness and completeness of biodiesel production. Viscosity is one of the specifications for compliance in the production of biodiesel. The product with less viscosity is the one with higher total FAME content (Babajide *et al.*, 2010). Fuel with high viscosity tends to form large droplets on injection pump which causes poor combustion and increased smoke and emission (Hamamre *et al.*, 2014). Viscosity of biodiesel is 10-15 times greater than that of petroleum diesel due to its large molecular mass and chemical structure (Atabani *et al.*, 2012). The maximum limit of viscosity in biodiesel, according to ASTM D445, varies between 1.9-6.0mm²/s and 3.5-5mm²/s in EN ISO 3104 (Table 2.12).

2.2.5 Flash point

Flash point is the temperature at which the fuel inflames due to the formation of a homogeneous mixture of fuel vapour and air above the fuel surface. Flash point, an

important parameter to be considered concerning fuel storage and handling, is influenced by the methanol content (Hamamre *et al.*, 2014). Biodiesel has a relatively high flash point which makes it less volatile and safer to transport than petroleum diesel (Buasri, 2009; Atabani *et al.*, 2012). ASTM specifies that biodiesel flash point must be in the range 100-170°C (Table 2.12). Hamamre *et al.* (2014) demonstrated that an increase of 0.5% in methanol content leads to a 50°C decrease of biodiesel flash point.

2.2.6 Cloud point

Cloud point is the most commonly used measurement of low temperature operability, and fuels are generally expected to operate at temperatures as low as their cloud point. Biodiesel made from waste oil or animal fats has a higher cloud point relative to that made from refined oil. Conventional diesel cloud point is typically lower than that of biodiesel, which starts to get colder as soon as the temperature drops. Cloud point depends mostly on the type and quality of impurities in the fuel, such as monoglycerides. The values range between -3 to 15°C for biodiesel and -35 to 5°C for conventional diesel, according to ASTM standard, as shown in Table 2.12 (Atabani *et al.*, 2012).

2.2.7 Pour point

Pour point is the temperature at which a fluid begins to flow under specific conditions, a characteristic directly proportional to the viscosity of the crude oil. Biodiesel made from different feedstock may have different pour points, making it suitable over conventional diesel. Biodiesel has a pour point in the range of -5 to 10°C above conventional diesel, which is -35 to -15°C (Table 2.12) (Atabani *et al.*, 2012).

2.2.8 Density

Density of biodiesel depends on the feedstock used in the production process. Biodiesel produced from saturated fats tends to have higher density than biodiesel from unsaturated ones (Ong *et al.*, 2013). Oils that are denser contain more energy (Atadashi *et al.*, 2011).

2.2.9 Free and total glycerol

Glycerol is essentially insoluble in biodiesel. Free glycerol may remain as suspended droplets or in a very small amount in biodiesel. *Free glycerol* is the amount of glycerol left in

the final biodiesel product; so the free glycerol content is dependent on the production process (Atabani *et al.*, 2012). Accumulation of glycerol may damage the fuel injection and increases mass transfer difficulty, resulting in lower biodiesel yield (Atabani *et al.*, 2012; Zhao *et al.*, 2013). High yields of glycerol in biodiesel may result from insufficient separation during the washing step of the methyl ester product. EN 14105 has a free glycerol limit of 0.02% while ASTM requires that total glycerol be less than 0.24% of the final biodiesel production (Atabani *et al.*, 2012).

Table 2.12: ASTM and EN specification for biodiesel (adapted from Atabani *et al.*, 2012)

Fuel properties	Diesel	Biodiesel	
		ASTM	EN
Density lb/gal (kg/m ³)	7.1 (850)	7.3 (880)	7.3 (880)
Carbon (wt%)	84-87	77	77
Hydrogen (wt%)	12-16	12	12
Oxygen (wt%)	0-0.31	11	11
Sulfur (wt%)	0.0-0.0024	0.0015 max	0.02max
Boiling point °C	180-340	315-350	315-350
Flash point °C	60-80	100-170	100-170
Cloud point °C	-35 to 5	-3 to 15	-3 to 12
Pour point °C	-35 to-15	-5 to10	-5 to 10
Cetane number	40-55	48-65	48-65
Viscosity at 40°C(cSt)	2.6	1.9-6.0	3.5-5.0
Acid value (Mg KOH/g)	0.062	Max 0.50	Max 0.50
Oxidation	3min	-	6min

2.3 Optimisation of biodiesel production

Biodiesel production yield optimisation can be assessed using statistical analysis design expert software (e.g. Mini Tab, Design-Expert Stat-Ease 6.0.8, Design Expert 9). There are different approaches — response surface method (RSM), factorial design, fractional factorial, crossed and mixture design — used to discuss and explain the production yield generated from the experiment (Bezerra *et al.*, 2008; Omar *et al.*, 2011; Wan *et al.*, 2011). Two are explained below:

- *Fractional factorial*: This is used to estimate main effect, interaction and screening of many factors to find significant few. This factorial can be irregular, general, D-optimal, placket Burman or Taguchi OA (Omar *et al.*, 2011).

- *Response surface methodology*: This is used to investigate the influence of the reaction parameters of the process, to predict the optimum process condition, as well as to minimise the number of experiments. These properties may be determined by using different approaches: central composition design (CCD), Box-behnken, 3-level factorial, hybrid, 1-factor, pentagonal, hexagonal, D-Optimal, distance-based, modified distance, user-defined and historical data (Bezerra *et al.*, 2008; Wan *et al.*, 2011).

In this present study, response surface methodology (RSM) was applied for data analysis with CCD technique tool to achieve optimum purity and yield of biodiesel production. This also was used to determine which variables have an impact on the response interest. The choice of the design technique was due to its ability to give multiple responses and its ability to use more than three factorial levels as compared to Box-behnken, which uses fewer than three levels of factorial.

2.3.1 Response surface method (RSM)

RSM is simple, based on a linear function, and is the most frequently used method for statistical analyses in the optimisation of biodiesel (Bezerra *et al.*, 2008). The aim of RSM is to explain the interaction effects among process variables obtained from experimental data to construct a 3-D response surface and contour plot following a regression model. This experimental design methodology offers not only an efficient way of assessing uncertainty but also provides inference with minimum number of simulations. There are two major classes of RSM: Central Composite design (CCD) and Box-behnken design. These two methods have different structures. Before applying RSM, it is important to choose an experimental design that would define which experiment should be carried out in the study area (Bezerra *et al.*, 2008).

2.3.1.1 Box-behnken design

Each numerical factor is varied over three levels and has fewer runs than three level factorials. The factors are placed at one of the three spaced value coded as -1, 0, 1 and the design must fit a quadratic model (Figure 2.6). The ball is located inside the box defined by a wire frame that is composed of the edges of the box. This method does not need many central points because the points on the outside are closer to the middle (Rezaei *et al.*

2013). The Box-behnken design has limited capability to orthogonal blocking as compared to CCD and is used for large number of variables.

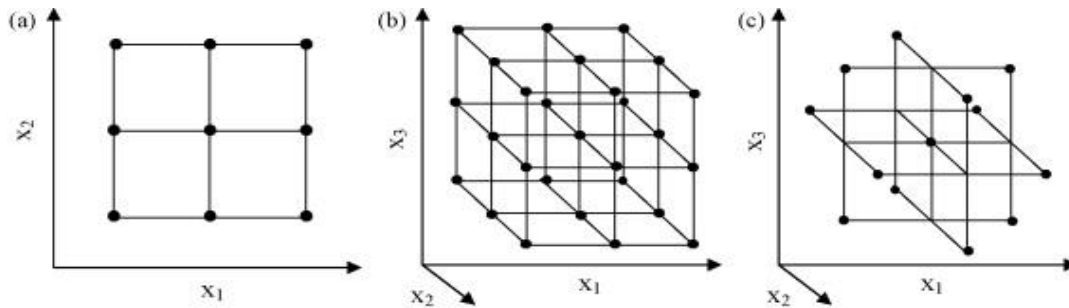


Figure 2. 6: Profile of Box-behnken design at three levels (adapted from Bezerra et al., 2008)

Nakatami *et al.* (2009) used combusted oyster shell as catalyst for transesterification of soybean. The reaction condition was optimised using factorial design. Results showed that the time (5h) and catalyst concentration (2.5wt%) were the most important factors affecting biodiesel purity (98% conversion). Rezaei *et al.* (2013), using Box-behnken design to evaluate the effects of calcination, temperature, catalyst concentration and methanol-to-oil molar ratio on the purity and yield of produced biodiesel, found that this method was effective with 100% purity and 94.5% yield at 24:1 methanol/oil ratio and 2wt% catalyst concentration. It was also observed that molar ratio and catalyst loading were the most important factors in the production of biodiesel. Su *et al.* (2013) used Box-behnken design to investigate the reaction factors affecting FFA conversion from esterification of enzyme-hydrolysed FFA and methanol. The effects of reaction time, reaction temperature, methanol to FFA ratio and hydrolysed concentration were investigated: all factors were significant with an interval of 99.9%.

2.3.1.2 Central composite design (CCD)

CCD is a standard RSM design tool used to study transesterification reaction parameters and predict the variables. CCD is suitable for sequential experiments and fit a quadratic surface, which usually works well for process optimisation (Jazie *et al.*, 2013). In CCD, all the corner points lay on the surface by using a ball, as shown in Figure 2.7. Each number of factors is varied over five levels: plus and minus alpha (axial point), plus and minus one (factorial point) and centre point. CCD design performs a more detailed design as compared to Box-behnken design (Rezaei *et al.*, 2013).

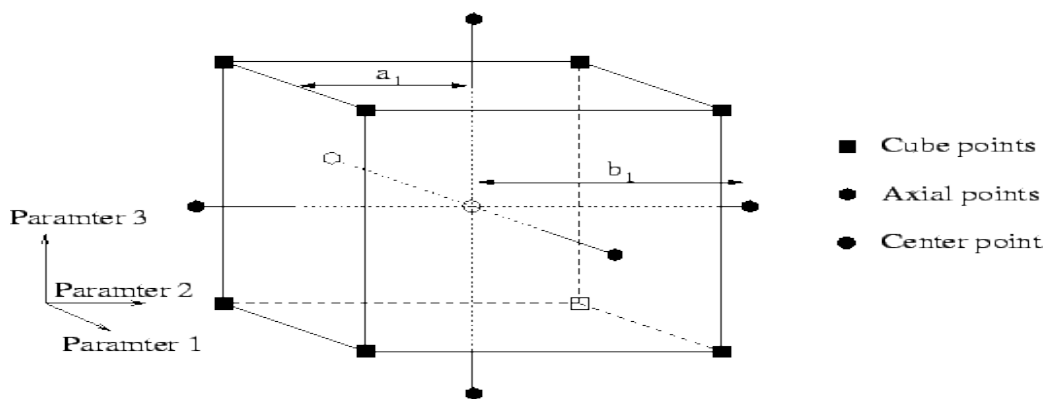


Figure 2. 7: Central composite design profile with three inputs

Omar *et al.* (2011) studied the interactions of process variables using the CCD method to predict the optimum process conditions for FAME. By applying RSM, CaO catalyst performance was investigated. The results gave a good prediction at a high confidence level of 95% CCD with full 2^4 factorial designs. Jazei *et al.* (2013) used RSM with a CCD tool resulting in a quadratic polynomial equation. Omar and Amin (2011) employed RSM to study the interaction of methanol-to-oil ratio, reaction temperature, reaction time, catalyst loading and FFA conversion using CCD by applying 2^4 full factorial design in the production of biodiesel from waste cooking palm oil with Sr/ZrO₂. Boey *et al.* (2011) applied mud crab shell as catalyst in biodiesel production and performed a statistical analysis using CCD. Based on the experimental and predicted results, the most important factors affecting biodiesel yield were catalyst concentration, reaction temperature and methanol-to-oil molar ratio, with a 93% yield. Based on the aforementioned studies, the parameters selected for optimisation in this current study are temperature, oil-to-methanol ratio and catalyst loading.

2.4 Kinetics of biodiesel production

Biodiesel production is very complex from which to derive a suitable model, and very few kinetics studies on biodiesel production have been conducted, either experimentally or by using computational models (Herbinet *et al.*, 2008; Boey *et al.*, 2011; Quing *et al.*, 2011). Due to the complexity of biodiesel and the size of its constituent molecules, direct modelling of its combustion has historically been unfeasible (Lai *et al.*, 2011; Mohamed-Ismael *et al.*, 2013). The overall reaction kinetics is dependent on the individual rate constant for the conversion of triglycerides to diglycerides, monoglycerides and the ester product (Yusuf *et al.*, 2011).

There have been several studies related to kinetics of transesterification using base catalyst (Casas *et al.*, 2011; Quing *et al.*, 2011; Yusuf *et al.*, 2011). Kinetic models should be derived based on three consecutive reversible reaction steps, and the rate constant of each reaction step is usually different (Mohamed-Ismael *et al.*, 2013). If the reaction temperature increases, the rate constant will also increase and therefore the reaction will proceed at a faster rate (Issariyakul *et al.*, 2014). As a result, the reaction temperature should be kept below boiling point of the alcohol: 65°C for methanol and 78°C for ethanol. If the reaction is operated at a temperature higher than the boiling point of the corresponding reaction alcohol, pressure must be applied to the reaction mixture in order to maintain the reaction alcohol in liquid state (Issariyakul *et al.*, 2014). The largest methyl ester that has been studied kinetically was methyl butanoate with a chain of only four carbon atoms attached to the methyl ester group. These studies have concluded that the fuel produced kinetic feature of methyl ester, but did not produce any kinetic feature with diesel fuel with larger chains of between 16-18 carbon atoms (Herbinet *et al.*, 2008; Mohamed-Ismael *et al.*, 2013).

Developing an accurate detailed kinetics model for biodiesel is challenging since the fuel is a mixture of a number of long hydrocarbon molecules (Mohamed-Ismael, 2013). Most models in biodiesel have been developed according to the Curran *et al.* model (1998) and different models have been used according to the catalyst composition used in transesterification method (Herbinet *et al.*, 2008). Therefore, there is a clear need for more studies to be conducted to more fully ascertain benefits and drawbacks for the kinetics of biodiesel fuel.

One way to alleviate this situation is by constructing a model approximate to the one in the form of the surrogate fuel model (Mohamed-Ismael *et al.*, 2013). In response to this challenge, the first detailed kinetic model for biodiesel, based on the combustion of methyl butanoate, was developed by Fisher *et al.* (2000) (Mohamed-Ismael, 2013; Lin *et al.*, 2013). To address this issue, Herbinet *et al.* (2008) developed a kinetic model for methyl decanoate ($C_{10}H_{20}O_2$) with cetane number 47 and studied the oxidation of methyl decanoate with 10 carbon atoms attached to a methyl ester group, following the rules established by Curran *et al.* (1998). This feature reacted closely to biodiesel and diesel fuel compared to methyl butanoate. Quing *et al.* (2011) used kinetics mechanism of biodiesel from waste oil using carbon based solid acid catalyst to determine the reaction order, for the reaction was found to be second order. Furthermore, Chantrasa *et al.* (2010) focused on the transesterification of tricaprillin (TCP) and methanol on solid base hydrotalcite catalyst in order to investigate the reaction kinetics in the temperature range of 60-120°C and 15:1 molar ratio. Vujicic *et al.* (2009) studied kinetics of biodiesel synthesis from sunflower oil using CaO heterogeneous catalyst; a first order reaction was established. More recently, Birla *et al.*, in 2012, studied

the kinetics of biodiesel using CaO from snail shell with waste oil, based on reaction temperature and time; a first order reaction was obtained between 5-8h.

Different assumptions have been made in studying kinetics of waste oil (Quing *et al.*, 2011):

- Catalyst concentration is constant; therefore, forward and reverse reaction rates follow the law of mass action.
- Forward and reverse reactions follow 2nd order kinetics in the liquid phase.
- Triglyceride of palmitic acid, oleic acid and linoleic acid has the same reaction rate and reaction mechanism.

2.5 Summary

With recent increases in petroleum prices and concomitant challenge to contend with the population demand, biodiesel is certainly a potential alternative fuel, renewable, biodegradable, and environmentally-friendly. In order to make biodiesel more environmentally friendly and less expensive, alternative use of waste as raw materials is important. The usability of this waste has the potential to reduce the production costs of biodiesel. A promising catalyst for the production of biodiesel is in demand. CaO as catalyst from natural sources such as chicken eggshell is a potential alternative. CaO reusability provides the opportunity to operate on a continuous process in industrial applications (Tang *et al.*, 2013). CaO is superior to many other solid bases in the catalytic performance for transesterification of oil and methanol (Lai *et al.*, 2011), and can tolerate moisture in the feedstock with higher FFA (Boey *et al.*, 2011).

CHAPTER 3

MATERIALS AND METHODS

CHAPTER 3

MATERIALS AND METHODS

3.1 Feedstock

Waste vegetable oil (WVO) was collected from the CPUT staff restaurant, in Bellville. Analyses (of TLC and GC) were conducted on the waste oil to determine the quantity and quality of free fatty acid and a pre-treatment process was undergone to remove impurity. Pre-treatment was conducted in two steps: filtration and dehydration.

- *Filtration*: this process consisted in removing the solid dirt content in the waste vegetable oil using filter paper for 24h.
- *Dehydration*: this process removed traces of water content present in oil by using a low pressure distillation process (105°C).

3.2 WVO Analyses

WVO was analysed using thin layer chromatography (TLC) and gas chromatography (GC) to determine the oil composition. The TLC method only indicated the presence of fatty acids (FA) while the GC method quantified the amount of FFA present. For TLC analysis, 750µl of oil was dissolved in 20ml of n-hexane. A line of 1cm was drawn on the TLC plate from the bottom and 10µl of the mixture was applied on the line drawn on the plate. The oil sample on the plate was in the volumetric ratio of 80:20:1.5. The forward movement was driven by capillary action and once the solvent reached the top of the plate, the plate containing the oil mixture was removed and dried. After drying, 2,5-Bis (5 -tert -butyl -benzoxazol- 2yl) thiophene was sprayed on the plate to visualise the spot formed under ultra violet light (UV).

The gas chromatography-mass spectrometric method was carried out by weighing 500mg of oil, dissolved in 25ml chloroform methanol and butylated hydroxytoluene (BHT) stock solution. 50µl of an internal standard (heptadecanoic acid; C17:0) was added to the solution and evaporated. After evaporation, 2ml of 95% methanol, 5% sulphuric acid and 0.005% BHT were added. This was incubated for two hours at 70°C, then cooled, and then followed by addition of 2ml of n-hexane and 2ml of water, and finally, this was vortexed. The phases were allowed to separate and the hexane layer was removed. Sodium carbonate was added

to the hexane layer and a concentrate to 100µl under nitrogen stream. This was injected into the GC.

In calculating the FA mass, the concentration of the internal standard was multiplied by the ratio of the peak of the FA and the peak of the internal standard.

3.1.1 FFA characterisation

FFA content was determined by mixing waste oil with potassium salts using 70% methanol themyl blue. Then FFA was collected from the oil mixture using 0.5 H₂SO₄, which was converted into methyl ester using methanol and sulphuric acid, using the transesterification process. The methyl ester produced was diluted into 5µm hexane solvent, and 1µm of the solution (methyl ester and hexane) was collected and injected into the GC. A peak count was observed on the GC. Finally, FFA composition was calculated according to the peak.

3.3 Catalyst Preparation

Eggshell is mainly composed of CaCO₃ (Boro *et al.*, 2011) which was converted into calcium oxide (CaO) by calcination at 800°C for 24hrs (Figure 3.1). The eggshell was washed using distilled water to remove impurities; this was followed by drying in an oven at 105°C. The sample was then crushed by agate mortar equipment to a fine particle of 75µm. The fine particles were then calcined in a muffle furnace at 800°C to eliminate any form of carbon and to get a complete conversion of CaCO₃ to CaO. The ash obtained was used as a heterogeneous base catalyst in the production of methyl ester.

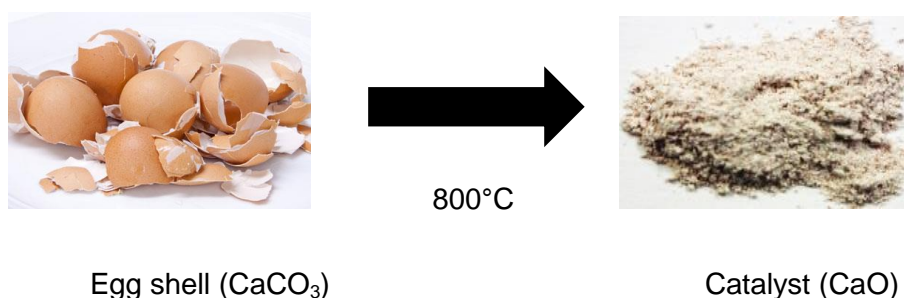


Figure 3.1: Calcination of eggshell to convert CaCO₃ to CaO

3.3.1 Catalyst characterisation

The basic strength of catalyst was determined by a Hammett indicator titration, as 25mg of catalyst was shaken with 5ml of methanol solution in a Hammett indicator and left to

equilibrate for 2h. Colour changes were observed. The Hammet indicator used was phenolphthalein (H_9.3).

The Brunauer Emmet Teller surface area (BET), pore volume, pore diameter as well as the structure of the catalyst were each determined using micromeritics physisorption and chemisorption analysers at 77.33K, at the Central Analytical Facilities Unit of Stellenbosch University, Cape Town. 0.30g of eggshell ash (catalyst) was pre-treated by applying a combination of heat, vacuum and flowing gas to remove adsorbed contaminants acquired from atmospheric exposure. The solid was then cooled under vacuum, usually to cryogenic temperature. An adsorptive (N_2 [2ml/min], CO_2 , 10% NH_3 in helium ramped at $1^\circ C/min$ for 1h for CO_2 -TPD and NH_3 -TPD, respectively) was admitted to the solid in controlled increments. After each dose of adsorptive, the pressure was allowed to equilibrate and the quantity of gas adsorbed was calculated. The CO_2 and NH_3 were removed in the gas phase form, at room temperature, only after purging with N_2 .

Different analyses were conducted on the catalyst at the Central Analytical Facilities Unit of Stellenbosch University to determine the morphology, and the different composition and structure of the element, which were as follows:

- *X-ray diffraction* (XRD) was carried out to show the major component phase of the element. XRD analysis was performed with Mac science X-ray diffraction system (MXP3A-HF) with $CuK\alpha$ X-ray source ($\lambda=0.15nm$).
- *Scanning electron microscope* (Model: F E I Quanta FEG 200) was employed to determine the morphology structure of the element.
- *X-ray fluorescence* (XRF) (Thermo Scientific ARL OP-TIM'X 166) gave the element composition of the calcined catalyst (eggshell ash).

3.3.2 Catalyst reusability

CaO catalyst was removed from the mixture after the centrifugation process and washed with an appropriate amount of methanol; finally, it was dried at room temperature for 24hrs and reused without further post pre-treatment. The catalyst was recycled and reused 18 times.

3.4 Application of the response surface method (RSM)

Response surface method (RSM) was applied to optimise the process and to check the influence of the process parameters of the transesterification process on the yield of

biodiesel. A 2³ CCD design of experiment was used (three factors each at two levels). The factors chosen – catalyst loading (wt%), oil-to-methanol molar ratio and temperature (°C) – were selected based on the background in the literature (Table 3.1 and Table 3.3). Table 3.2 shows independent variables (temperature, oil-to-methanol molar ratio and catalyst loading) with two coded levels of combinations, namely low (-1) and high (+1), to achieve maximum response for biodiesel yield, whereas the star points were coded as (-2) and (+2), the distance of star point from the centre, allowing the design to rotate. The centre points (middle point level) were represented by zero (0) and were repeated two to three times to determine the experimental error as well as its reproducibility (Lee *et al.*, 2011).

The standard column represented the order of experiments done in the laboratory. Eight combinations were considered, plus six centre points and six star points, so a total of 20 experimental runs were conducted. Replications of the experiments were also carried out. The selection of the factors was based on the operating conditions that have a significant influence on the biodiesel process. After a set of preliminary experiments, the higher and lower level values of the variables were chosen as follows: higher value of catalyst was 5wt%, lower value 2wt%; higher temperature value was 70°C and lower value 60°C by considering the boiling point of methanol; oil-to-methanol ratio high value was 1:30 and the lower value 1:15. In accordance with a previous experiment (Pradhan *et al.*, 2012), agitation speed did not have much effect on the process and selection of the levels was based on results obtained in preliminary studies.

Table 3.1: Experimental range of independent variable (DOE)

Factors	Symbols	Lower star point (-2)	Lower level (-1)	Centre point (0)	Higher level (+1)	Higher star point (+2)
Temperature (°C)	X ₁	56.6	60.0	65.0	70.0	73.4
Oil/methanol ratio	X ₂	9.9	1:15.0	1:22.5	1:30.0	35.1
Catalyst loading (wt%)	X ₃	0.98	2.0	3.5	5.0	6.02

Table 3.2: 2³ full CCD design of experiment with coded factors

Std	Run	Block	Coded factors		
			Factor A (X ₁)	Factor B (X ₂)	Factor C (X ₃)
6	1	1	+1	-1	+1
16	2	1	0	0	0
10	3	1	+2	0	0
8	4	1	+1	+1	+1
17	5	1	0	0	0
18	6	1	0	0	0
12	7	1	0	+2	0
15	8	1	0	0	0
14	9	1	0	0	+2
20	10	1	0	0	0
5	11	1	-1	-1	+1
2	12	1	+1	-1	-1
1	13	1	-1	-1	-1
9	14	1	-2	0	0
13	15	1	0	0	-2
7	16	1	-1	+1	+1
11	17	1	0	-2	+1
19	18	1	0	0	+1
3	19	1	-1	+1	-1
4	20	1	+1	+1	-1

X₁: reaction temperature (°C); X₂: methanol-to-oil ratio; X₃: catalyst loading (%) based on the oil weight; (0): middle point level; (-1): low point; (+1): high level; (-2): lower star point; and (2): high start point

Table 3.3: 2³ full CCD design of experiment with uncoded factors

Std	Run	Block	Uncoded factors		
			Temperature (°C) (X ₁)	Oil/methanol molar ratio (X ₂)	Catalyst loading (X ₃)
6	1	1	70.0	1:15.0	5.0
16	2	1	65.0	1:22.5	3.5
10	3	1	73.4	1:22.5	3.5
8	4	1	70.0	1:30.0	5.0
17	5	1	65.0	1:22.5	3.5
18	6	1	65.0	1:22.5	3.5
12	7	1	65.0	1:35.1	3.5
15	8	1	65.0	1:22.5	3.5
14	9	1	65.0	1:22.5	6.02
20	10	1	65.0	1:22.5	3.5
5	11	1	60.0	1:15.0	5.0
2	12	1	70.0	1:15.0	2.0
1	13	1	60.0	1:15.0	2.0
9	14	1	56.6	1:22.5	3.5
13	15	1	65.0	1:22.5	0.98
7	16	1	60.0	1:30.0	5.0
1	17	1	65.0	1:9.9	5.0
19	18	1	65.0	1:22.5	5.0

Table 3.3: Cont

3	19	1	60.0	1:30.0	2.0
4	20	1	70.0	1:30.0	2.0

3.5 Transesterification process

Experiments were conducted using a reflux fitted system (Figure 3.2) in which the mixture of WVO, methanol and catalyst were added to a 500ml three-necked flask and immersed in a water bath at five different temperatures: 56.59°C, 60°C, 65°C, 70°C and 73.41°C. The catalyst loading for this project were taken as 0.98wt%, 2wt%, 3.50wt%, 5wt% and 6.02wt% with constant mass of oil of 50g, and oil/methanol molar ratios of 1:9.89; 1:15; 1:22.50; 1:30 and 1:35.11. The agitation speed of 600rpm remained constant. These values were generated by the response surface method (Table 3.3). The time taken for each experiment was 5h30min.

3.5.1 Equipment set-up

A liquid reaction mixture was placed in a 500ml three-necked flask and fitted with an overhead stirrer to achieve a homogeneous mixture at a constant mixing speed of 600rpm. This flask was connected to a Braham condenser, such that any vapours given off were cooled back to liquid, and fell back into the reaction flask (Figure 3.2). The flask was heated in the hot water bath for the 5h30m course of the reaction. Different temperatures were maintained for different runs of the experiment.

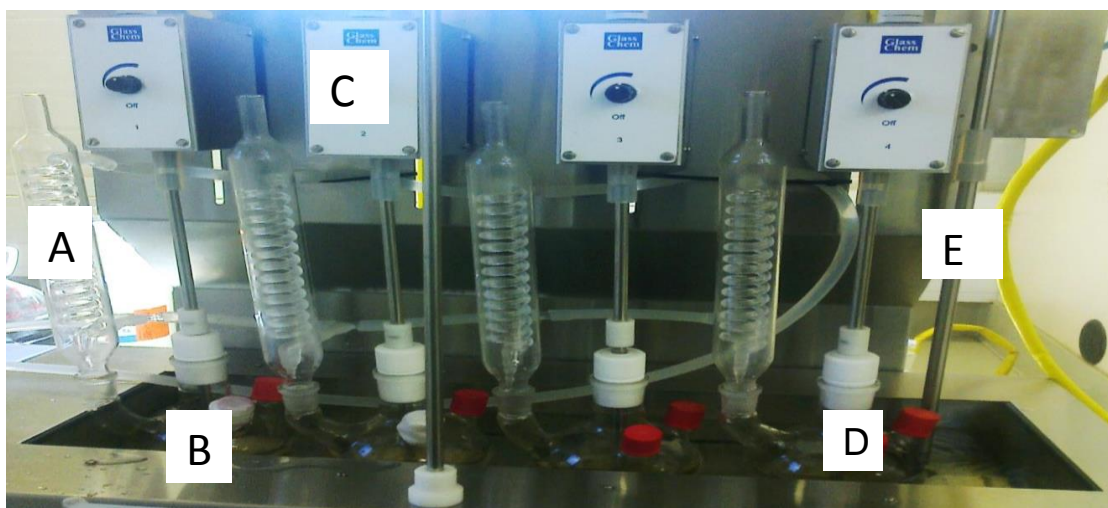


Figure 3.2: Experimental set-up (A) condenser; (B) water bath; (C) overhead stirrer; (D) three-necked flask; and (E) overhead stirrer for the water bath.

3.5.2 Experimental procedure

In order to investigate the effect of temperature, oil-to-methanol molar ratio and the catalyst loading, 20 separate experimental runs were conducted, as shown in Table 3.3.

Methyl ester was synthesised in a 500ml three-necked boiling flask. Four boiling flasks were placed in the water bath, each flask having a different molar ratio and catalyst concentration while maintaining a constant temperature and agitation speed. A reflux column was connected to the first opening of the flask and water was slowly introduced through the column, as a sudden increase in pressure would result in the tubes disengaging from the fittings. The first run was kept at 70°C flasks with 5wt% catalyst loading, and a 1:15 oil-to-methanol ratio. The flask was placed in the water bath and preheated before adding 50ml of waste vegetable oil. This was followed by adding 51ml of methanol and the appropriate amount of catalyst. The reaction time was 5h30min. The mass of CaO to be measured out was determined as a percentage of the weight of the oil to be reacted. After collection of the mixture, the sample was left to cool down for 15-20min, after which the two-phase system was carefully separated using a centrifuge apparatus. The bottom layer of the system consisted of glycerine, while the top layer was made up of a mixture of methyl esters, unreacted methanol and intermediates. All the experiments were conducted by following identical procedures at different experimental conditions.

All the samples were analysed using a GC to determine the mass of biodiesel produced. Biodiesel samples for GC analysis were prepared by diluting 1ml of each sample with 1ml of hexane separately, making a total biodiesel concentration of 10 000ppm by volume. Then the samples of 1ml were injected into the column in split ratio of 40:1, and the injection port temperature and interface line temperature were set to 320°C. To construct calibration curves, 100ml of methyl ester was dissolved in 50ml hexane to make standard solutions of 30 000ppm by volume, then diluted to 500, 750, 1000, 1250 and 2000ppm solutions.

The viscosities of all samples of biodiesel were measured using a gravitational viscometer. The u-tube in the viscometer was filled with approximately 50ml of biodiesel. Waste vegetable oil served as reference fluid.

3.5.3 Crude biodiesel purification

After obtaining the optimum point, the crude biodiesel was purified by washing it with 28% (by volume of the feedstock) of distilled water using a separation funnel. Since both glycerol

and methanol are highly soluble in water, crude biodiesel was mixed with distilled water and agitated gently to avoid formation of emulsion, then slowly percolating droplets of water through the ester (Atadashi *et al.*, 2011). The process was repeated until colourless wash water was obtained, indicating complete removal of impurities.

This purification was done to meet the international standard specification provided by American Society for Testing and Materials (ASTM). Otherwise, the contaminants such as residual methanol, glycerol, catalyst, glycerides and FFA could reduce biodiesel quality and affects engine performance (Atadashi *et al.*, 2011).

3.6 Product estimation

The yield and conversion were calculated as follows:

$$\text{Yield (\%)} = \frac{\text{Weight}_{\text{Biodiesel}}}{\text{Weight}_{\text{Oil}}} \times 100 \quad (3.1)$$

$$\text{Conversion(\%)} = \frac{\text{Weight}_{\text{Triglyceride}} - \text{Weight}_{\text{Biodiesel}}}{\text{Weight}_{\text{Triglyceride}}} \times 100 \quad (3.2)$$

Where the weight of triglyceride was taken as the initial mass of oil, which was 50g. The weight of biodiesel produced from each run was obtained from the GC result.

3.7 Determination of kinetics

The reaction was isothermal and irreversible. The product concentration was monitored for different sets of feed condition. The objective was to measure the appearance of ester and the disappearance of triglyceride. The product sample was collected after each 1h30min during the transesterification process, for a maximum period of time of 8h30min, under optimum conditions (65°C, 3.50wt% catalyst and 1:22.5 oil-to-methanol molar ratio).

3.7.1 Constants

The constants taken were catalyst concentration, weight of oil and volume of methanol. Samples taken at various time intervals were analysed.

3.7.2 Rate law

To determine the kinetics of the reaction, the effect of reaction time was measured and the reaction was found to be a second order reaction. The detail of calculations to obtain the value of rate is shown in Appendix B. The rate of reaction for the forward and reverse reaction was expressed as follows:

$$-r_A = \frac{\Delta C_A}{\Delta t} = \frac{dC_A}{dt} = K \times C_A^\alpha \times (C_{MeOH}^\beta)^3 \quad (3.3)$$

Where C_A^α is the concentration of triglyceride; C_B^β is the concentration of methanol; K is the equilibrium rate constant; and α and β are both unknown. Because the methanol is in excess its concentration remained unchanged during the reaction process and was considered as constant. Therefore $K[C_B^\beta]^3 = K'$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln K' + \alpha \ln C_A \quad (3.4)$$

It was assumed that the initial triglyceride concentration was C_{A0} at time zero and C_{Af} at final time. This produced the following equation:

$$C_A = C_{A0} - C_{Af} \quad (3.5)$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln K' + \alpha(\ln C_{A0} - \ln C_{Af})$$

$$\left[\frac{\ln\left(-\frac{dC_A}{dt}\right)}{\ln K'} \right] = \alpha(\ln C_{A0} - \ln C_{Af}) \quad (3.6)$$

By derivation $\left| \frac{\ln\left(-\frac{dC_A}{dt}\right)}{\ln K} \right| = K \times t$

$$\text{Therefore } K \times t = \alpha(\ln C_{A0} - \ln C_{Af}) \quad (3.7)$$

$$X_{Me} = 1 - \frac{(C_A)}{(C_{A0})} \quad (3.8)$$

Where X_{ME} is conversion of methyl ester yield

$$-\ln(1 - X_{ME}) = K \times t \quad (3.9)$$

K is the equilibrium rate constant, which can be calculated as follow:

$$K = \frac{-\ln(1 - X_{ME})}{t} \quad (3.10)$$

A kinetics study was conducted and reaction order was calculated according to the values obtained from above equations. The activation energy, E_a , is one of the most important factors affecting the rate of a chemical reaction. According to Freedman *et al.* (1986), the activation energy range is between $33,490 \text{ Jmol}^{-1} - 83,736 \text{ Jmol}^{-1}$. Its value was calculated using an Arrhenius equation:

$$K = Ae^{\frac{E_a}{RT}} \quad (3.11)$$

Where E_a is activation energy.

3.8 American Society for Testing and Materials (ASTM) analysis

The main properties of biodiesel were determined using standard test methods according to the American Society for Testing and Materials (ASTM). The ASTM analysis was performed at Wear Check Laboratory, in Brackenfel, Cape Town. Various laboratory tests were carried out on the biodiesel samples, including the following:

- viscosity at 40°C and 100°C with ASTM D7279 test method to indicate the resistance of the fuel to flow at 40°C and 100°C;
- density at 20°C with ASTM D4052 test method;
- flash point with ASTM D93 test method;
- appearance/colour;
- pour point and cloud point obtained using ASTM D92 test method;
- acid number with ASTM D974 test method to determine the acidity of the fuel (lubricant);
- cetane number using ASTM D4055 test method; and
- oxidation test with ASTM D2272 test method to determine the oxidative stability of the lubricant.

The obtained results were compared with the reported properties of common biodiesel.

CHAPTER 4

RESULTS AND DISCUSSION

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of WVO

The composition of waste vegetable oil was analysed using gas chromatography (GC), with results shown in Table 4.1. GC was used to determine the amount of FFA in the oil: it was found to be 9% (Table 4.1). Studies have shown that high FFA reduces catalyst effectiveness and decreases the production yield; therefore, the recommended amount of FFA in WVO should not exceed 1wt% (Fenge *et al.*, 1945; Nye & Southwell, 1984; Mittelbach *et al.*, 1992; Demirbas, 2005; Wanodya & Budiman, 2013). In contrast, Singh *et al.* (2010) stated that heterogeneous catalysts have proven to catalyse oil with high FFA content (6-15%) without any pre-treatment. Previous reports have shown high yield (90%) under similar reaction conditions (60°C, 5h, 24:1 ratio, 4% catalyst loading) using WVO (FFA 6.6-6.8%) (Boey *et al.*, 2011; Navajas *et al.*, 2012). The observation in the current study can be attributed to the high basic strength of CaO. The moisture content of WVO (0.2 wt%) was less than the amount (≥ 0.5 wt%) that has been indicated in the literature to reduce biodiesel yield (Ma *et al.*, 1999). Iodine content ($108.4 \text{ g}^{10^{-2}} \text{ g}^{-1}$) was slightly higher due to the fatty acid composition (9.0%) which affected the iodine content (Hassani *et al.*, 2013; Ong *et al.*, 2013).

Table 4.1: Waste vegetable oil characterisation obtained using GC

Properties	Value
FFA content (%)	9.0
Water content (wt%)	0.2
Phosphorus content (mg kg^{-1})	4.8
Peroxide value (meq kg^{-1})	16.4
Iodine content ($\text{g}^{10^{-2}} \text{ g}^{-1}$)	108.4

4.2 Catalyst characterisation

The physicochemical properties of the catalyst were assessed using the following procedures: 1) X-ray diffraction (XRD) to determine the major component phase of the element; 2) X-ray fluorescent (XRF) to determine the elemental composition of the eggshell

ash; 3) Brunauer Emmet Teller (BET) to define the structure, the surface area, pore volume and pore diameter of the eggshell ash; and 4) SEM to show the morphology structure of the element.

4.2.1 Catalyst composition

CaO was derived from calcined eggshell. The chemical composition of the catalyst was determined by XRF on a dry basis. The result (Table 4.2) shows that ash from eggshell mainly contained CaO (86.4%), considered a favourable base catalyst in biodiesel production with high basic strength, minor toxicity and easy reactions with water (Zhang *et al.*, 2010). The remaining 1.8% was composed of different metal oxides (MgO, SiO₂, SO₃, P₂O₅, Na₂O, Al₂O₃, K₂O, FeO₃) in trace amounts. These oxides have been reported to be active materials for transesterification (Birla *et al.*, 2012). The basic oxides (MgO, K₂O, FeO₃) will enhance the catalyst's basic strength (Boey *et al.*, 2011), while the acidic components (SiO₂, SO₃, P₂O₅) have the potential to mediate esterification of the feedstock's FFA content (Boey *et al.*, 2011).

Table 4.2: Chemical composition of catalyst on a dry basis obtained using XRF

Major oxide	(wt%)	Nature
CaO	86.4	Basic
MgO	0.6	Basic
SiO ₂	0.2	Acid
SO ₃	0.2	Acid
P ₂ O ₅	0.2	Acid
Na ₂ O	0.2	Basic
Al ₂ O ₃	0.09	Amphoteric
K ₂ O	0.04	Basic
Fe ₂ O ₃	0.02	Basic

4.2.2 Catalyst structure, surface area, pore volume and pore diameter

The catalyst prepared was characterised by large pore diameter (91.2Å) and high surface area (30.7m²/g) which allow reactants to diffuse easily into the interior of the catalyst (Table 4.3) (Wan *et al.*, 2011; Niju *et al.*, 2014). Sharma *et al.* (2011) reported that a high pore diameter is desirable for better diffusion of reactant and product molecules. The observation is in agreement with that of Carreira *et al.* (2014) with a slightly higher (114.4Å) pore diameter

of CaO catalyst. The BET total surface area of CaO (30.9 m²/g) obtained herein compared well with what Niju *et al.* (2014) observed (30.7 m²/g) for CaO catalyst obtained from eggshell under a similar condition of calcination (800°C). Birla *et al.* (2012) obtained a BET surface (24.1m²/g) comparable to what was obtained in the current study under similar conditions of catalyst preparation. In contrast, Lee *et al.* (2011) observed the BET surface area of CaO catalyst obtained under similar calcination condition (800°C) was low (9 m²/g) Jazie *et al.* (2013) also observed a low BET surface area of eggshell calcined at 800°C (3.41 m²/g). Differences in these observations might be due to the initial particle size of the starting material. Trace pore volume of 0.07cm³/g was obtained. This observation is in agreement with results from a previous study by Birla *et al.* (2012) where a pore volume of 0.06cm³/g was obtained.

The total basic strength (H_10.8) was taken to be higher than the weakest indicator (H_9.8) that underwent a colour change. The basic site distribution of CaO (135.2µmol/g) showed the presence of good basic strength. The active site of the oxide surface will form an interaction with the proton of methanol and contribute to the breaking of hydroxide bond, thereby causing the formation of methoxide ion to initiate the transesterification reaction (Lee *et al.*, 2011). These characteristics are indications of good catalytic activity of the calcined eggshell ash obtained. Catalytic activity is a function of its specific surface area, base strength and base site concentration.

Table 4.3: Physicochemical properties of eggshell ash (CaO) using micromeritics physisorption and chemisorption analysers

Properties	Eggshell ash (CaO)
BET surface area (m ² /g)	30.9
Pore volume (cm ³ /g)	0.07
Pore diameter (Å)	91.2
Basicity (µmol/g)	135.2
Acidity (µmol/g)	95.03
Basic Strength (H_)	H_10.8

4.2.3 Catalyst morphology

The scanning electron microscopic image of a CaO catalyst (Figure 4.1) showed the morphology of CaO with irregular pores, shapes and size, varying from one surface to another (2-5µm of width). The shape of calcined eggshell was formed by tiny crystals embedded on the large particles, probably due to the heterogeneous distribution in the

mechanical properties of the eggshell used which can be regarded as an attribute of high catalytic activity (Navajas *et al.*, 2012; Tang *et al.*, 2013). This characteristic heterogeneous morphology of CaO from calcined eggshell has been noted previously under similar conditions (Wan *et al.*, 2011; Navajas *et al.*, 2012; Tang *et al.*, 2013; Niju *et al.*, 2014).

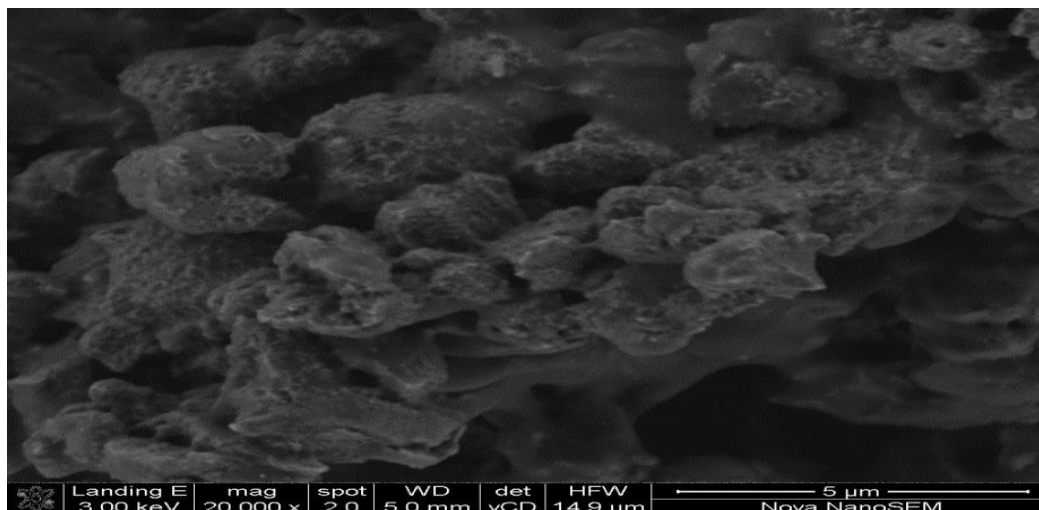


Figure 4.1: SEM Image for calcined eggshell ash

4.2.4 Catalyst major component phase

The x-ray diffraction (XRD) pattern of the CaO catalyst is shown in Figure 4.2. The XRD analysis of CaO shows a sharp peak of its separated metal oxide crystalline phases calcium and oxygen, which corroborated CaO as the dominant composition of the catalyst prepared. These peaks are similar with those reported by Sharma *et al.* (2010) and Wei *et al.* (2009) under similar conditions. It is noted that the type of eggshell (chicken eggshell, bird eggshell, reptile eggshell) does not affect the XRD patterns; therefore, the same calcination process may be used to obtain CaO catalyst regardless of type of eggshell (Navajas *et al.*, 2012).

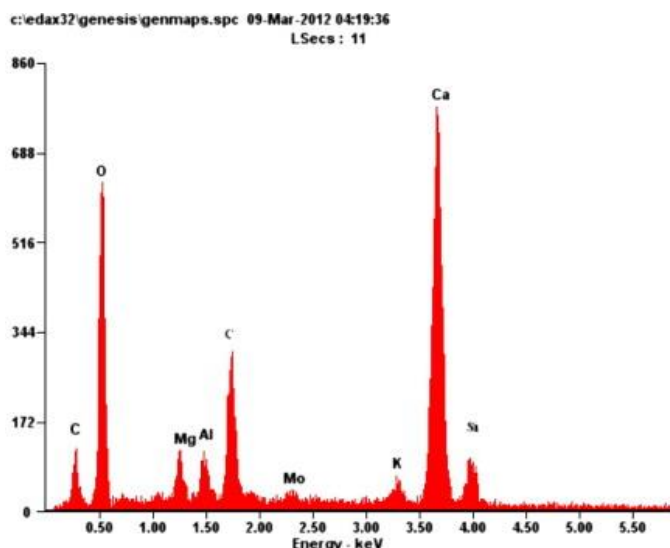


Figure 4.2: XRD for calcined catalyst

4.3 Biodiesel composition

The methyl ester produced was composed mainly of unsaturated oleic acid (48.2 wt%) and methyl linoleate ($C_{19}H_{34}O_2$, 35.7%wt) with minor saturated components such as methyl palmitate, methyl stearate, methyl linolenate and methyl arachidate (Table 4.4). The viscosity ($4.5 \text{ mm}^2/\text{s}$) obtained compared well with what was noted in the literature. In the current study, biodiesel production was optimised at a specific oil-to-methanol molar ratio of 1:22.5, a temperature of 65°C and a catalyst loading of 3.5wt% and a constant agitation speed of 600rpm.

Table 4.4: Fatty acid compositions of biodiesel using GC

Fatty acid	Structure	Composition (wt%)
Oleic	(C18:1)	48.20
Linoleic	(C18:2)	35.74
Linolenic	(C18:3)	14.20
Arachidic	(C20:0)	0.57
Stearic	(C18:0)	3.68
Palmitic	(C16:0)	7.42

Biodiesel produced was characterised as methyl oleate ($C_{19}H_{34}O_2$) using the GC analysis. Catalyst derived from eggshell was effective in the transesterification of WVO containing 9%

FFA, resulting a 91% yield. The yield of methyl ester and conversion were calculated using Equations 3.1 and 3.2.

The experimental design applied was a 2^3 CCD design (Design Expert 9). Six star points were studied and six centre points were added to determine the errors. The experiments were run at random to minimise errors between variables. The percentage of methyl ester was taken as the response of the design experiment, shown in Table 4.5 and Appendix A.

Table 4.5: Full central composite design with experimental response value

Manipulated variables			Response			
Std	Run	Blocks	Factors			
			Temperature $X_1(^{\circ}\text{C})$	oil/Met X_2	Catalyst loading $X_3(\%)$	Yield (%)
6	1	Block 1	70.00	1:15.00	5.00	50.23
16	2	Block 1	65.00	1:22.50	3.50	89.35
10	3	Block 1	73.41	1:22.50	3.50	0.79
8	4	Block 1	70.00	1:30.00	5.00	22.06
17	5	Block 1	65.00	1:22.50	3.50	90.98
18	6	Block 1	65.00	1:22.50	3.50	89.52
12	7	Block 1	65.00	1:35.11	3.50	39.50
15	8	Block 1	65.00	1:22.50	3.50	80.46
14	9	Block 1	65.00	1:22.50	6.02	74.02
20	10	Block 1	65.00	1:22.50	3.50	89.12
5	11	Block 1	60.00	1:15.00	5.00	64.29
2	12	Block 1	70.00	1:15.00	2.00	35.20
1	13	Block 1	60.00	1:15.00	2.00	69.29
9	14	Block 1	56.59	1:22.50	3.50	62.18
13	15	Block 1	65.00	1:22.50	0.98	66.52
7	16	Block 1	60.00	1:30.00	5.00	71.48
11	17	Block 1	65.00	1:9.89	3.50	42.68
19	18	Block 1	65.00	1:35.11	3.50	39.50
3	19	Block 1	60.00	1:30.00	2.00	73.39
4	20	Block 1	70.00	1:30.00	2.00	10.66

4.4 Kinetics study on biodiesel

The sample was collected after every 1h30 min for a maximum period of 8h30 min. The yield increased with increasing time, to a maximum of 91% at 5h30 min, and then decreased gradually (85.1-67%) (Table 4.6). This observation can be attributed to the increase in a reaction completion at 5h30min, beyond which there were no reactants for further conversion.

The reaction constants ($K = 9.197 \times 10^{-3} \text{ min}^{-1}$, $\alpha = 0.61$ and $\beta = 1.97$) were calculated according to Equation 3.11, and a second order model was obtained using the integrated rate law (Equation 3.1).

Table 4.6: Biodiesel yield at different time

Run	Meth/oil	Temp(°C)	Catalyst loading (%)	Time(h)	Yield (%)
1	1:22.50	65	3.50	1h30	30.8
2	1:22.50	65	3.50	2h30	64.6
3	1:22.50	65	3.50	3h30	76.2
4	1:22.50	65	3.50	4h30	89.4
5	1:22.50	65	3.50	5h30	91.0
6	1:22.50	65	3.50	6h30	85.1
7	1:22.50	65	3.50	7h30	71.5
8	1:22.50	65	3.50	8h30	67.0

4.5 Effect of catalyst loading

As shown in Figure 4.3, low yield (66.5-69.3%) was obtained with low catalyst loading (1-3wt%), which was insufficient to catalyse the reaction to completion in the formation of methyl ester. This observation corroborates what Lee *et al.* (2009) reported, that heterogeneous catalyst in biodiesel production should range from 3-10wt% for higher yield. Higher biodiesel yield (91%) was observed at an optimum point of 3.5wt% catalyst loading. Beyond this range (4-5wt%), a decrease in biodiesel yield was observed. This observation can be attributed to the availability of active sites on the catalyst for transesterification reaction (Birla *et al.*, 2012). Reaction rates increased as reactants occupied more catalytic sites until saturation was reached. The impact of mass transfer limitation became more significant at higher catalyst loading, thus limiting reactants' accessibility to active sites (Tang *et al.*, 2013; Talebian-kiakalaieh *et al.*, 2013). The transesterification reaction is strongly dependent on the weight of catalyst which consequently affects the yield. An adequate increase in catalyst concentration results in an increase in the number of its active sites, thereby increasing the yield of methyl ester (Omar & Amin, 2011). Excessive catalyst loading leads to high slurry viscosity and consequent poor reaction mixtures (Taufiq-yap *et al.*, 2014).

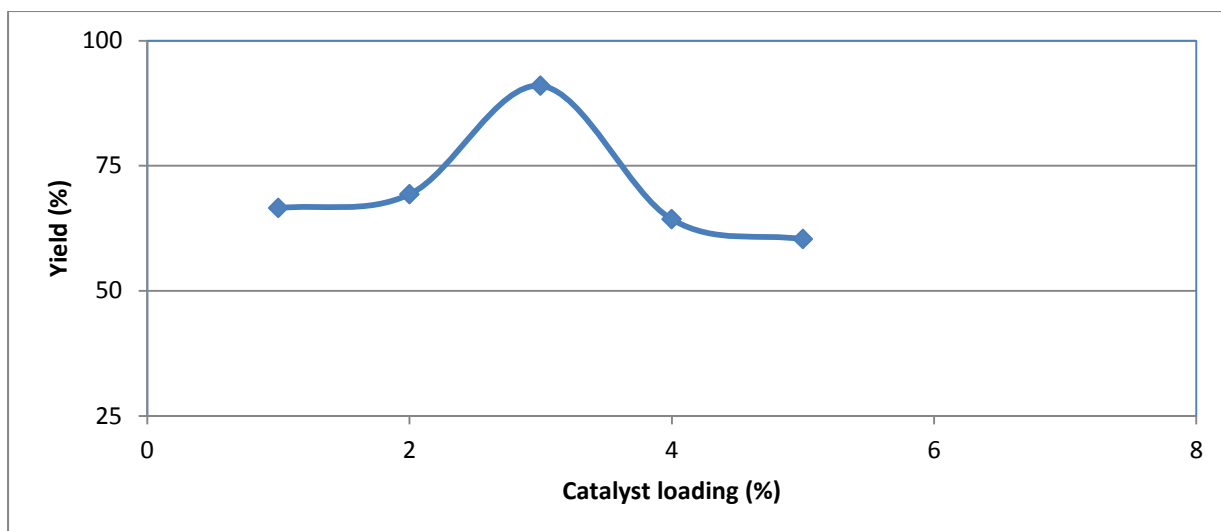


Figure 4.3: Effect of catalyst loading

4.6 Effect of temperature

Temperature has an impact on the mass transfer of the reaction: the optimum temperature was found to be 65°C with a yield of 91% under optimal conditions (catalyst loading 3.5wt%, oil-to-methanol ratio 1:22.5) (Figure 4.4). In this current research, when the reaction temperature increased to 65°C, there was also an increase in the reaction rate due to higher energy input and reduced mass transfer resistance (Birla *et al.*, 2012). Increasing the temperature beyond 65°C resulted in a decrease in the production due to the fact that any reaction occurring beyond the methanol boiling point (65°C) resulted in its continuous vaporisation. Hence it remained in the gas phase in the reflux, causing a reduction of methanol in the reaction media (Birla *et al.*, 2012; Tariq *et al.*, 2012).

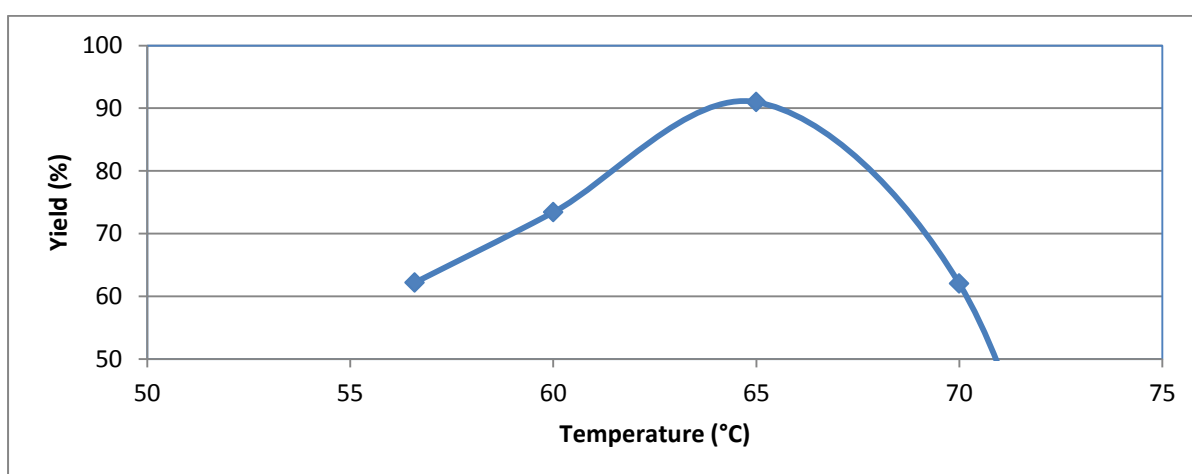


Figure 4.4: Effect of temperature on the yield

4.7 Effect of oil-to-methanol molar ratio

The optimum biodiesel yield was observed at an oil-to-methanol molar ratio of 1:22.5. It can be observed from Figure 4.5 that an increase in molar ratio beyond the optimum point (1:22.5) had a negative impact on the biodiesel yield. The yield decreased drastically to 73.4%, at an oil-to-methanol ratio of 1:30. This is due to the dilution effect of excess methanol and the interference between the high molar ratio of methanol/oil and the catalyst. There was a subsequent increase in solubility and a decrease in the separation of glycerin and methyl ester (Meher *et al.*, 2006; Tang *et al.*, 2013). Khemthong *et al.* (2012) showed that the most suitable molar ratio was found to be within the range of 1:15 and 1:25, in the production of biodiesel using eggshell ash (CaO) as heterogeneous catalyst. The overloading of methanol would inactivate the catalyst and consequently favour the backward reaction of transesterification process (Omar & Amin, 2011).

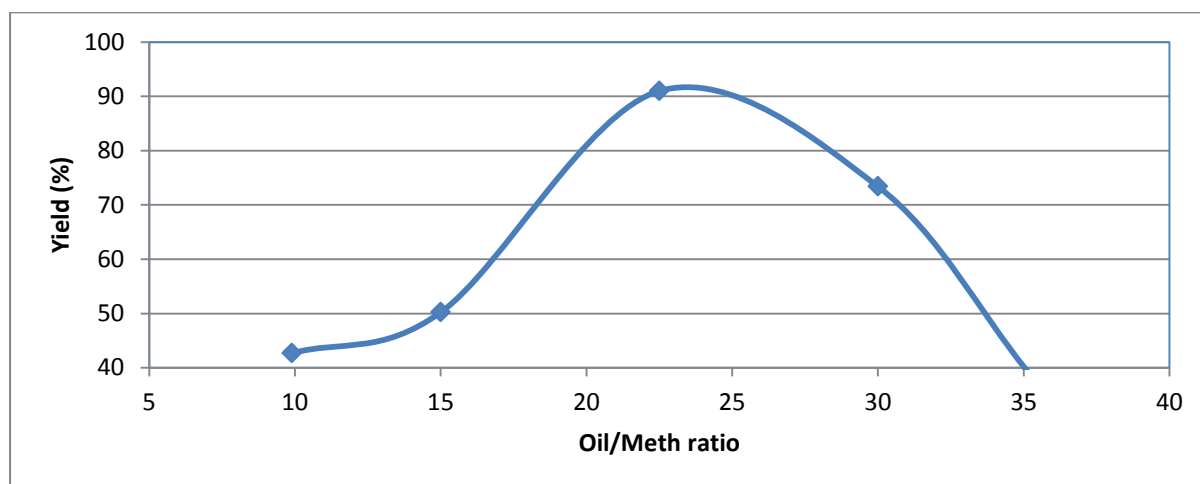


Figure 4.5: Effect of oil/methanol molar ratio on the yield

4.8 Catalyst reusability

Figure 4.6 shows that the catalyst obtained can be reused up to 10 times with no apparent loss of activity. CaO showed sustained activity after being repeatedly used for 10 times (Figure 4.6). In fact, the biodiesel yield was relatively constant at 91% during these repeated uses. Beyond this, however, the yield was reduced. This observation is similar to the results presented by Birla *et al.* (2012) who demonstrated that the catalyst from eggshell could be reused 14 times without losing its activity. In their study, Birla *et al.* (2012) found that during the 14 times of reuse of catalyst, 98% biodiesel yield was maintained. The loss in activity can be attributed to structure changing from the reaction between H₂O (generated from oil and methanol) and CaO (Birla *et al.*, 2012). Other possible causes are the leaching of CaO

in methanol (Lee *et al.*, 2009; Kouzu & Hidaka, 2012) or washing and filtration (Boro *et al.*, 2011). Taufiq-yap *et al.* (2014) used solid mixed oxide CaO-La₂O₃ catalyst with *Jatropha curcas* crude oil in biodiesel production. The catalyst was active for only three cycles with an 86.5% yield (65°C, 4wt% and 24:1 methanol-to-oil ratio). The loss in activity was attributed to the dissolution of active sites in the catalyst such as a result of catalyst poisoning, leaching of catalyst in methanol, change in catalyst surface structure or loss of catalyst during washing.

Furthermore, Navajas *et al.* (2012) indicated that CaO catalyst from eggshell could be repeatedly used for 18 times due to its surface area and chemical composition. Kouzou and Hidaka (2012) confirmed that many heterogeneous catalysts can be reused several times (three-20 cycles) depending on their chemical properties. Liu *et al.* (2008) compared the activity of CaO with K₂CO₃/γ-Al₂O₃ and KF/γ-Al₂O₃ catalysts, observing that CaO had high reusability for approximately 20 cycles as compared to K₂CO₃/γ-Al₂O₃ and KF/γ-Al₂O₃.

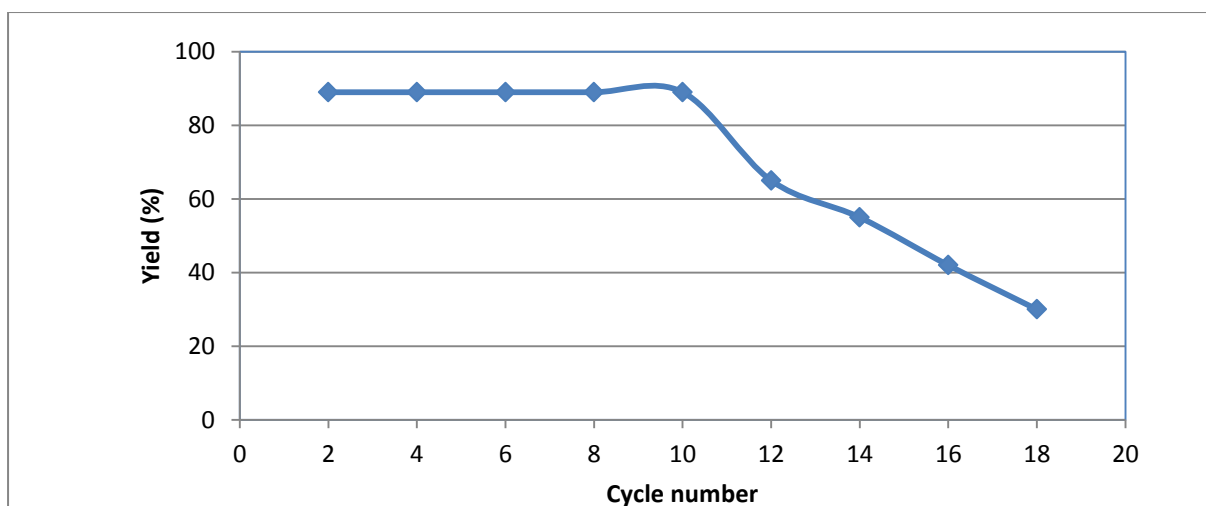


Figure 4.6: Effect of reusability of catalyst

4.9 Statistical analysis from RSM

For the current study, temperature, methanol-to-oil molar ratio and catalyst concentration were chosen as independent variables, and methyl ester yield as a dependent variable (Table 3). It has been shown that the variables mentioned above are the parameters that significantly affect the efficiency of biodiesel production (Demirbas, 2005; Lee *et al.*, 2011; Silva *et al.*, 2011; Velickovic *et al.*, 2012). A set of 20 experiments with eight combinations, six star points and six centre points were conducted, and a curvature line was observed from the results. This indicated that a second order quadratic model was the best fit for the 20

experiments (Table 4.5). The model can be considered statistically significant with 95% confidence with all three independent variables having an effect on the yield, and the fit of the model was checked with the coefficient of determination ($R^2=0.9908$) (Table 4.7). This value indicates that the variation of 99.08% for the methyl ester response is attributed to the independent variables. The distance of the star point from the centre point was given by $\alpha = 2^{n/4} = 2$ with n as number of factors. All three independent variables studied had a statistically significant effect on the methyl ester yield.

Table 4.7: Model summary statistics

Source	Std Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	Press
Linear	24.1	0.4	0.2	0.07	1.4×10^4
2 FI	25.8	0.4	0.1	-0.3	1.9×10^4
Quadratic	3.7	0.99	0.98	0.9	1.0×10^2
Cubic	220.9	0.98	0.07	0.07	Aliased
Std Error	5.02	-	-	-	-

Table 4.8: Sequential model sum of squares

Source	Sum of squares	Degree of freedom	Mean square	F values	Prob > F
Mean	629.9	1	629.9	-	-
Linear	32.6	3	8.1	1.5	0.2
2FI	1.1	3	0.2	0.03	1
Quadratic	111.7	3	27.9	8.8	< 0.0010
Cubic	7.01	4	1	2.5	0.1
Residual	2.4	6	0.4	-	-
Total	784.7	20	28.03	-	-

Based on the CCD design and results of experiments (Table 4.4), regression analysis generated the following quadratic regression model data (based on the coded factors):

$$Y = 45.3 + 10.6 X_1 + 2.51 X_2 + 9.6 X_3 - 11.5 X_1^2 - 23 X_2^2 - 7.4 X_3^2 + 3.2 X_1 X_2 + 3.4 X_1 X_3 - 1.05 X_2 X_3 \quad (4.1)$$

Where Y is the yield of biodiesel (%); X_1 temperature ($^{\circ}\text{C}$); X_2 oil-to-methanol ratio; and X_3 catalyst concentration (w%). The statistical significance of the model equation (Equation 4.1) was evaluated by the F-test for analysis of variance (ANOVA). This equation was used to analyse the response by multiple regression through the least square method. To evaluate whether the central composite design was accurately sufficient for methyl ester production with waste oil, the statistical significance of the curvature was also studied and evaluated

using analysis of variance (ANOVA), and a second order model was required due to the curvature observed (Table 4.8). The contour plot was the most useful approach for the visualisation of the process reaction between variables (Omar *et al.*, 2011). The model F-value of 8.84 for biodiesel production indicated that the model was statistically significant, with only a 0.01% chance that a “Model F-Value” this large could occur due to noise. The value of Prob>F should always fall below 0.05 and the value obtained in the current study was found to be less than 0.001, implying that the model terms were also significant to the process (Table 4.8). Values greater than 0.1 indicate the model terms are not significant. The quadratic model showed a 5.02 error (Table 4.7), but the error was considered to be neglected as the values ranged within the 5% of significance. Using the above results, different effects of the independent variables on the response were studied by plotting a three-dimensional response surface based on the model equation. All three variables have a positive effect on biodiesel production. The statistical analysis of the experimental range studied identified initial temperature as the most important factor in biodiesel production, followed by catalyst concentration, with a slight difference as compared to temperature, and then finally, methanol-to-oil molar ratio (Equation 4.1).

4.9.1 Interaction of catalyst and temperature

The RSM indicated that the predicted optimum methyl ester yield from WVO was 91% at an oil-to-methanol molar ratio of 1:22.5, catalyst loading of 3.5% and temperature of 65°C. The interaction of catalyst and temperature are exhibited in Figure 4.7. The circular nature contour plot revealed there are significant interaction effects between catalyst loading and temperature on methyl ester yield. At lower ranges of catalyst concentration and reaction temperature, an increase of biodiesel yield was observed; however, it showed a negative effect at higher reaction temperatures (>65°C) and catalyst loading (>3.5 wt%). Decreased biodiesel yield based on this negative interaction could be due to the increase in viscosity of the reaction mixture at high catalyst loading. In a previous study, Lee *et al.* (2011) reported that at lower amounts of catalyst (3.7-4wt% of CaO-MgO), the increase of reaction temperature (115.87°C) improved the biodiesel yield (93.55%) because high temperatures enhanced the dispersion of catalyst particle in liquid medium with better mass transfer between the reactants.

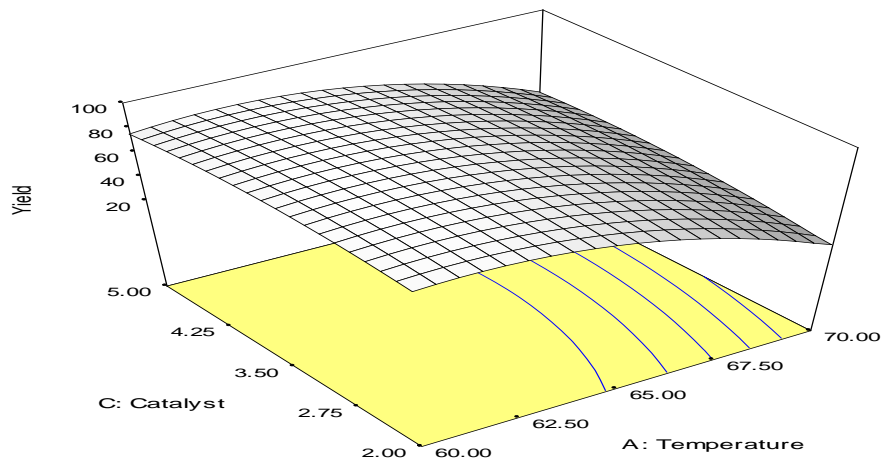


Figure 4.7: Response surface plot of combine catalyst loading and temperature

4.9.2 Interaction of oil/methanol ratio and temperature

Figure 4.8 shows the elliptical nature of the contour plot for the interaction between oil-to-methanol molar ratio and temperature. The contour indicates that the two variables are significant to methyl ester yield and that there is an interaction between them. Yield increased with an increase in oil-to-methanol ratio; however, excessive methanol decreased the yield. The predicted value from ANOVA was observed to be 89.6% as compared to the experimental value of 91%. Under such condition, an oil-to-methanol ratio gave a best yield of methyl ester at 1:22.5. This observation agrees with that of Velickovic *et al.* (2012) that yield increased with the increase of both reaction temperature and methanol-to-oil molar ratio, but the impact of reaction temperature depended on the methanol-to-oil molar ratio. At a molar ratio lower than 9.9:1, however, the reaction temperature did not influence the yield (Velickovic *et al.*, 2012). Furthermore, Pradhan *et al.* (2012) reported that both temperature and methanol-to-oil molar ratio had a significant interaction with each other but the temperature above boiling point of methanol (65°C) should be avoided because of the evaporation of methanol in the solution, decreasing biodiesel yield.

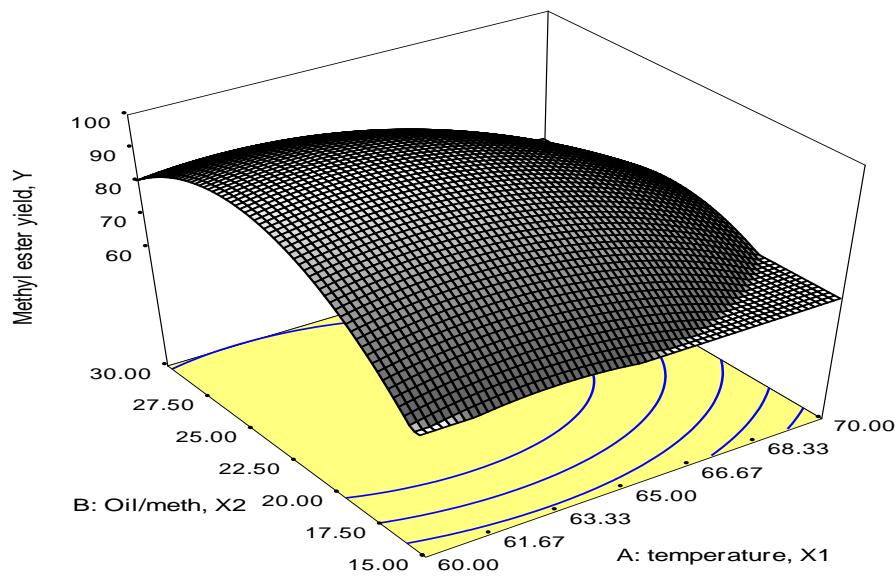


Figure 4.8: Response surface plot of combine oil/methanol ratio and temperature

4.9.3 Interaction of catalyst loading and oil-to-methanol ratio

It has been reported that good methyl ester yield increased with low catalyst concentration and methanol-to-oil ratio (Silva *et al.*, 2011). The RSM plot in Figure 4.9 illustrates that at low catalyst concentration (3.5wt%), high methyl ester yield (91%) was obtained with increased methanol-to-oil molar ratio (22.5:1). At high catalyst loading (6.02wt%) and methanol-to-oil molar ratio (30.0:1), a gradual decrease in biodiesel yield (74.02%) was observed. According to these results, an addition beyond a certain value of excess methanol-to-oil ratio and catalyst amounts resulted in poor mixing of the reaction mixture, hence aggregation and dilution of catalysts. Jazie *et al.* (2013) obtained a similar result (96%) using calcined eggshell (methanol-to-oil 9:1 with catalyst loading of 3wt%) but beyond these values the yield decreased dramatically (69%).

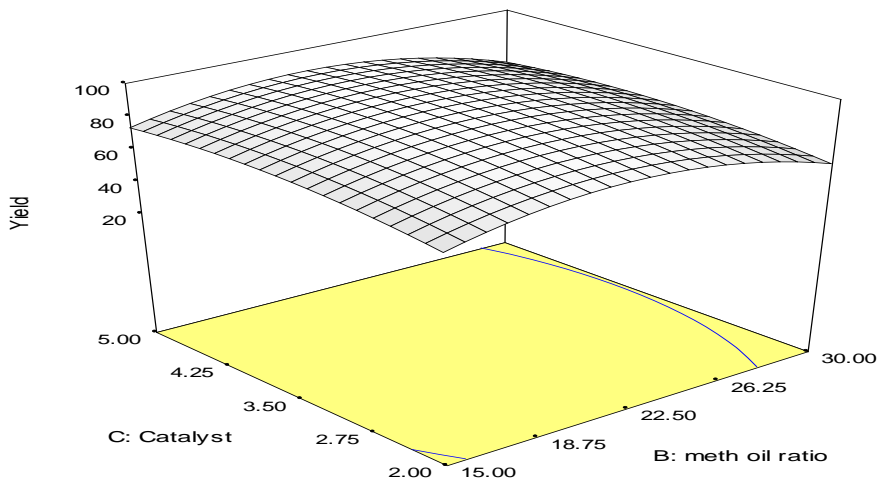


Figure 4.9: Response surface plot of combined catalyst loading and oil/methanol ratio

4.9.4 Prediction of values from RSM

To test the fitness of the model and to confirm the efficacy of the predicted model, the experimental values were compared to the predicted values using a parity plot (Figure 4.10). The model fits the data reasonably.

DESIGN-EXPERT Plot
Methyl ester yield (%)

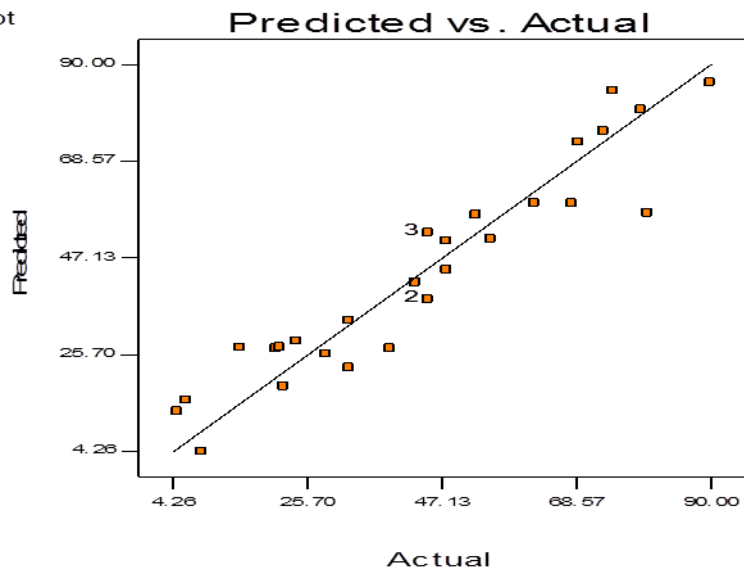


Figure 4.10: Parity chart for the model employed: plot of predicted vs. actual value

The results indicated that RSM can be used to find relationships among process variables and response in an efficient manner using a minimum number of experiments. Moreover, the recommended optimum condition of biodiesel production can also be determined via RSM.

4.10 Properties of biodiesel using ASTM standard

In order to evaluate the quality of biodiesel properties of the product after purification by distilled water, some properties were determined using the American Society for Testing and Materials standard (ASTM). ASTM identifies the parameters that pure biodiesel (B100) should fulfil before being used as a pure fuel or blended with diesel fuel (Silitong *et al.*, 2013). The summarised results (Table 4.9) show that all of the measured values were in the range of test limit.

Table 4.9: ASTM values obtained from analysis

Biodiesel properties	Test method	ASTM values obtained from current study	Standard ASTM values
Viscosity at 40°C (mm ² /s)	D 7279	4.5	1.9-6.0
Viscosity at 100°C (mm ² /s)	D 7279	3.6	1.9-6.0
Density at 20°C (kg/m ³)	D 4052	865	880
Flash point (°C)	D 93	438	100-170
Pour point (°C)	D 92	10	- 5 to 10
Acid number (mg KOH/g)	D 974	0.2	Max 0.50
Cetane number (min)	D 4055	48	48-65
Oxidation (min)	D 2272	4	-

4.11 Result summary

This research work revealed that the performance of WVO with 9% FFA in the presence of a calcined catalyst could produce high biodiesel yield (91%) under optimum conditions of reaction temperature (65°C), catalyst loading (3.5wt%) and methanol-to-oil molar ratio (22.5:1). CaO is a catalyst with high commercial value which can be reused up to 10 cycles without any loss in activity.

Based on the experimental and empirical results obtained, it can be concluded that RSM predicted values are comparable with the experimental values (Figure 4.10). These observations make clear that RSM can be used to find the relationship among process variables and response. It also confirmed the efficacy of the predicted model. In this current study, the independent variables (temperature, catalyst loading and methanol-to-oil molar

ratio) had significant effects on the biodiesel yield. Demirbas (2005) reported that reaction temperature, oil-to-methanol molar ratio and catalyst concentration are the major factors affecting the conversion efficiency and rate of transesterification process. All interactions among variables were statistically evaluated. Furthermore, a second order polynomial equation was developed to relate the biodiesel yield and the process variables.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The aim of this project was to assess biodiesel production from waste vegetable oil in the presence of a heterogeneous catalyst prepared from chicken eggshell. Three factors were investigated – oil-to-methanol ratio, catalyst loading and temperature – in order to optimise the process. Optimal reaction conditions obtained were methanol-to-oil molar ratio (22.5:1), catalyst loading (3.5w%) and temperature (65°C). It was assumed that the catalyst was used in sufficient amount with respect to oil in order to shift the reaction toward the formation of methyl ester.

It was observed that the catalyst derived from chicken eggshell had excellent activity in mediating the transesterification of waste oil containing 9% FFA to biodiesel production. The catalyst derived through calcination was characterised with high surface area (30.9m²/g) and large pore size (91.2Å) necessary for enhanced catalytic activity. The egg shell calcined (800°C) were considered less porous due to the trace pore volume observed (0.07cm³/g). The reusability of the catalyst preparation over 10 cycles of transesterification reaction has the potential to reduce cost of biodiesel production. Eggshell ash is a potential alternative to conventional catalysts in view of tolerance to high FFA in low quality feedstock.

Centre composite design (CCD) was applied to optimise the synthesis process of methyl ester from waste oil and a heterogeneous catalyst from eggshell. A full 2³ CCD design, with a total of 20 experiments, was carried out with six centre points and six star points. A second order quadratic model was obtained and employed to fit the system. Results indicated 95% confidence that the model was statistically significant. The results also indicated that RSM can be used to determine the effectiveness and relationship among process variables and the response by reducing the number of experiments. Employing RSM, all three variables had significant effects on the heterogeneously catalysed transesterification of WVO to biodiesel. Interaction between methanol-to-oil molar ratio and catalyst loading gave the most dominant impact on methyl ester yield. Temperature was effective at 65°C due to the collision between particles in the mixture.

The empirical value of yield obtained from RSM (89.6%) was comparable to that obtained experimentally (91%). The relationship between the predicted and experimental yield

indicated that the values were in reasonable agreement and the data fit well with the model by giving a good estimate of response for the system in the range studied.

Results indicated that a second order quadratic model was the best fit for the experiments conducted. The model can be considered statistically significant at 95% confidence, with all three independent variables having an effect on the yield. The fit of the model was checked with the coefficient of determination ($R^2=0.9908$). Then a second order model was observed with constants $\alpha=0.61$ with $K = 9.197 \times 10^3 \text{ min}^{-1}$.

Pure biodiesel was determined by ASTM standards to ensure that the following important factors in the fuel production process by transesterification are satisfied: complete transesterification reaction, complete esterification of FFA, removal of glycerol, removal of catalyst and removal of alcohol. Lower viscosity value of the final product is an indication of completion of reaction and removal of heavy glycerol. The product characterisation was set to meet the requirements determined by the American Standard (ASTM) for biodiesel fuel.

5.2 Recommendations

This study reported on the primary objectives, focusing on the production of biodiesel using waste vegetable oil as feedstock in the presence of eggshell ash as catalyst. In order to minimise the cost of catalyst preparation and consequently biodiesel production cost, the following areas need to be investigated further:

- Future work should explore the economic feasibility for a better understanding and potential for implementation.
- Future work should consider studies on the particle size of the catalyst as well as its exposure to atmosphere to avoid contamination.
- Future work should investigate impregnating or modifying catalyst of CaO with potassium for improved yield and more sustained catalytic activity.
- Further studies should be conducted to reduce the huge amount of methanol recorded during the transesterification process.

REFERENCES

REFERENCES

- al-Hamamre, Z. & Yamin, J. 2014. Parametric study of the alkali catalysed transesterification of waste frying oil for biodiesel production. *Fuel*, 79: 246-254.
- Jazie A., Pramanik, H. & Sinha, S.S.K. 2013. Eggshell as Eco-Friendly Catalyst for Transesterification of Rapeseed Oil: Optimization for Biodiesel Production. *International Journal of Sustainable Development and Green Economics* 2: 2315-4721.
- Slama A., Taufiq-Yap Y.H., Chua C., Chanc E., Ravindraa P. 2013. Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, 91 (1): 131-144.
- Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I., Masjuki, H.H. & Mekhilef, S. 2012. A comprehensive review on biodiesel as alternative energy source and its characteristics. *Renewable and Sustainable Energy Reviews*, 16: 2070-2093.
- Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R. & Sulaiman, N.M.N. 2011. Refining technologies for purification of crude biodiesel. *Applied Energy*, 88: 4239-4251.
- Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R. & Sulaiman, N.M.N. 2012. Production of biodiesel using high free fatty acid feedstocks. *Renewable and Sustainable Energy Reviews*, 16: 3275-3285.
- Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R. & Sulaiman, N.M.N. 2013. The effects of catalysts in biodiesel production: a review. *Journal of Industrial and Engineering Chemistry*, 19: 14-26.
- Babajide, O., Petrik, L., Musyoka, N., Amigun, B. & Ameer, F. 2010. Use of coal fly ash as a catalyst in the production of biodiesel. *Petroleum & Coal*, 52(4): 261-272.
- Yang B.J., Zheng L., Han X.T., Zheng M.G. 2013. Development of TLC-FID technique for rapid screening of the chemical composition of microalgae diesel and biodiesel blends. *Fuel*, 111: 344-349.
- Banerjee, A. & Chakraborty, R. 2009. Parametric sensitivity in transesterification of waste cooking oil for biodiesel production. Resources. *Conservation and Recycling*, 53: 490-497.
- Birla, A., Singh, B., Upadhyay, S.N. & Sharma, Y.C. 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using heterogeneous catalyst derived from snail shell. *Bioresource Technology*, 106:95-100.
- Boey, P., Maniam, G., Hamid, S. & Ali D.M.H. 2009. Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrate*) shell as heterogeneous catalyst. *Bioresource Technology*, 100: 6362-6368.
- Boey, P., Maniam, G., Hamid, S. & Ali, D.M.H. 2011. Crab and cockle shells as catalyst for the preparation of methyl esters from low free fatty acid chicken fat. *Chemical Engineering Journal*, 88: 283-288.
- Boey, P., Maniam, G. & Hamid, S. 2011. Performance of calcium oxide as a heterogeneous catalyst in biodiesel production. *Chemical Engineering Journal*, 168: 15-22.

Bonkonic-Ilic, I.B., Stamenkovic, O.S. & Veljkovic, V.B. 2012. Biodiesel production from non-edible plant oils. *Renewable and Sustainable Energy Reviews*, 16: 3621-3647.

Borges, M.E. & Diaz, L. 2012. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reaction. *Renewable and Sustainable Energy Reviews*, 16: 2839-2849.

Boro, J., Thakur, A.J. & Deka, D. 2011. Solid oxide derived from waste shells of turbonilla striatula as a renewable catalyst for biodiesel production. *Fuel Processing Technology*, 92: 2061-2067.

Brito, A., Borges, M.E. & Otero N. 2007. Zeolite Y as a heterogeneous catalyst in biodiesel fuel production from used vegetable oil. *Energy and Fuel*, 21: 3280-3283.

Canakci, M. & Van Gerpen, J. 2001. Biodiesel production from oils and fats with high free fatty acids. *Transactions of the ASAE*, 44 (6): 1429-1436.

Casas, A., Jesus Ramos, M., & Perez, A. 2011. Kinetics of Chemical Interesterification of Sunflower Oil and Triacetim Production. *Chemical Engineering Journal*, 171:1324-1332.

Chakraborty.R., Bepari, S. & Banerjee, A. 2010. Transesterification of soybean oil catalysed by fly ash and eggshell derived solid catalyst. *Chemical Engineering Journal*, 165:798-805.

Chantrasa, A., Phlernjai, N. & Goodwin Jr., G.J. 2011. Kinetics of hydrotalcitencatalyzed transesterification of tricaprilyn and methanol for biodiesel synthesis. *Chemical Engineering Journal*, 168: 333-340.

Chia-Hung, S. 2013. Recoverable and reusability hydrochloric acid used as homogeneous catalyst for biodiesel production. *Applied Energy*, 104: 503-509.

Christopher, L.P., Kumar, H. & Zambare, V.P. 2014. Enzymatic biodiesel: challenges and opportunities. *Applied Energy*, 119: 497-520.

Clark, W.N., Medeiros, N.J., Boyd, D.J. & Snell, J.R. 2013. Biodiesel transesterification kinetics monitored by pH measurement. *Bioresource Technology*, 136: 771-774.

Correia, L.M., Saboya, R.M.A., de Sousa Campelo, N., Cecilia, J.A., Rodriguez-Castellon, Cavalcante Jr., C.L. & Vieira, R.S. 2014. Characterization of calcium oxide catalysts from naturel sources and their application in transesterification of sunflower oil. *Bioresource Technology*, 151: 207-213.

Corro, G., Tellez, N., Ayala, E. & Marinez-Ayala, A. 2010. Two-step biodiesel production from jatropha curcas crude oil using SiO₂. HF solid catalyst for FFA esterification step, *Fuel*, 2: 2315-2721.

Chung, K.H., Chang, D.R., & Park, B.G. 2008. Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. *Bioresource Technology*, 99: 7438-7443.

Demirba, A. 2005. Biodiesel production from vegetable oils via catalytic and catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31: 466-487.

Deshmane, V.G. & Adewuyi, Y.G. 2013. Synthesis and kinetics of biodiesel formation via calcium methoxide base catalysed transesterification reaction in the absence and presence of ultrasound. *Fuel*, 107: 474-482.

- Di Serio, M., Ledda, M., Cozzolino, M., Minutilo, G., Tesser, R. & Santacesaria, E. 2005. Transesterification of soybean oil to biodiesel by using heterogeneous basic catalyst: a review. *Journal of Industrial and Engineering Chemistry*, 45: 3009-3014.
- Ejikeme, P.M., Anyaogu, I.D., Ejikeme, C.L., Nwafor, N.P., Edbuonu, C.A.C., Ukogu, K. & Ibemesi, J.A. 2010. Catalysis in biodiesel production by transesterification process: an insight. *E-journal of Chemistry*, 7 (4): 1120-1132.
- Encinar, J.M., Gonzalez, J.F. & Rodriguez-Reinares, A. 2007. Ethanolysis of used frying oil, biodiesel preparation and characterization. *Fuel Processing and Technology*, 513-522.
- Endalew, A.K., Kiros, Y. & Zanzi, R. 2011. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass and Bioenergy*, 35: 3787-3809.
- Freedman, B., Butterfield, R.O. & Pryde, E.H. 1986. Kinetics of soybean oil. *Journal of American Chemist Society*, 63: 1375-1380.
- Fukuda, H. Kondo, A. & Noda, H. 2001. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, 92 (5): 405-416.
- Glisic, S.B. & Orlovic, A.M. 2014. Review of biodiesel synthesis from waste oil under elevated pressure and temperature: phase equilibrium, reaction kinetics, process design and techno-economic study. *Renewable and Sustainable Energy Reviews*, 31:708-725.
- Grana, R., Frassoldati, A., Cuoci, A., Faravelli, T. & Ranzi, E. 2012. A wide range kinetic modelling study of pyrolysis and oxidation of methyl butanoate and methyl decanoate. Note I: Lumped kinetic of methyl butanoate and small methyl esters. *Fuel*, 43: 124-139.
- Hawash, S., Diwani, G.E. I. & Kader, A.E. 2011. Optimization of biodiesel from jatropha oil by heterogeneous base catalysed transesterification. *International Journal of Engineering Science and Technology*, 3 (6): 5242-5251.
- Hassani, M., Amini, G., Najafpour, G.D. & Rabieeee, M. 2013. A two-step catalytic production of biodiesel from waste cooking oil. *International Journal of Engineering*, 26: 563-570.
- Herbinet, O., Pitz, W.J. & Westbrook, C.K. 2008. Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate. *Combustion and Flame*, 154: 507-528.
- Ismail, H.M., Ng, H.K., Gan, S., Lucchini, T. & Onorati, A. 2013. Development of a reduced biodiesel combustion kinetics mechanism for CFD modelling of a light-duty diesel engine. *Fuel*, 106: 388-400.
- Issariyakul, T, &. Dalai. A.K. 2014. Biodiesel from vegetable oils. *Renewable and Sustainable Energy Reviews*, 31: 446-447.
- Jansri, S., Ratanawilai, S.B., Allen, M.L. & Prateepchaikul, G. 2011. Kinetics of methyl ester production from mixed crude palm oil by using acid-alkali catalyst. *Fuel Processing Technology*, 92: 1543-1548.
- Kawentar, W.A. & Budiman, A. 2013. Synthesis of biodiesel from second used cooking oil. *Energy Procedia*, 32: 190-199.
- Kay, K.H., & Yasir, S.M. 2012. Biodiesel production from low quality crude jatropha oil using heterogeneous catalyst. *APCBEE Procedia*, 3: 23-27.

- Khemthong, P., Luadthong, C., Nualpaeng, W., Changsuwan, P. & Tongprem, P. 2012. Industrial eggshell wastes as heterogeneous catalysts for microwave-assisted biodiesel production. *Catalysis Today*, 10: 1016-1024.
- Kim, H.J., Kang, B.S., Kim, M.J., Park, Y.M., Kim, D.K., Lee, J.S. & Lee, K.Y. 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catalysis Today*, 93-95, 315-320.
- Kotwal, M.S., Niphadkar, P.S., Deshpande, S.S., Bokade, V.V. & Joshi, P.N. 2009. Transesterification of sunflower oil catalyzed by flash-based solid catalysts. *Fuel*, 88: 1773-1778.
- Krithiga, G. & Sastry, T.P. 2011. Preparation and characterization of a novel bone graft composite containing bone ash and egg shell powder. *Bulletin of materials science*, 34: 177-181.
- Lai, J.Y.W., Lin, K.C. & Voli, A. 2011. Biodiesel combustion: Advances in chemical kinetic modelling. *Progress in Energy and Combustion Science*, 37: 1-14.
- Lechtanski, V.L. 2000. Inquiry-Based Experiments in Chemistry. *Journal of Chemical Education*, 78 (5):593.
- Lee, D.W., Park, Y.M. & Lee, K.Y. 2009. Heterogeneous based catalysts for transesterification in biodiesel synthesis. *Springer Science and Business Media*, 13: 63-77.
- Lee, H.V., Yunus, R., Juan, J.C. & Taufiq-yap Y.H. 2011. Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Processing*, 92: 2420-2428.
- Lim, S. & Teong, L.K. 2010. Recent trends, opportunities and challenges of biodiesel in Malaysia: an overview. *Renewable and Sustainable Energy Reviews*, 14: 938-954.
- Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S. & Mingdong, D. 2011. Opportunities and challenges for biodiesel fuel. *Applied Energy*, 88 (4): 1020-1031.
- Lin, R. Zhu, Y. & Tavlarides, L. 2013. Mechanism and kinetics of thermal decomposition of biodiesel. *Fuel*, 106: 593-604.
- Liu, X., He, H., Wang, Y., Zhu, S. & Ziao X. 2009. Transesterification of soybean oil to biodiesel using CaO as solid base catalyst. *Fuel*, 87: 216-221.
- Ma, F. & Hanna, M.A. 1999. Biodiesel production. *Bioresource Technology*, 70: 1-15.
- Lam M.K., Lee K.T., Mohamed A.R. 2010. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel. *Biotechnology Advances*, 28 (4): 500-518.
- Marchetti, J.M. 2012. A summary of the available technologies for biodiesel production based on a comparison of different feedstock's properties. *Process Safety and Environmental Protection*, 90: 157-163.
- Kouzu M., Hldaba J.S. 2012. Transesterification of vegetable oil into biodiesel catalysed by CaO: a review. *Fuel*, 93:1-12.

Meher, L.C., Vidya Sugar, D. & Naik, S.N. 2006. Technical aspects of biodiesel production by transesterification. *Renewable and Sustainable Energy Review*, 10: 248-268.

Minami, E. & Saka, S. 2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. *Fuel*, 85: 2479-2483.

Nakatani, N., Takamori, H., Takeda, K. & Sakugowa, H. 2009. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresource Technology*, 100: 1510-1513.

Niju, S., Meera, K.M., Begum, S. & Anantharaman N. 2014. Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society*, 18 (5): 702-706.

Olutoye, M.A., Lee, S.C. & Hameed, B.H. 2011. Synthesis of fatty acid methyl ester from palm oil (*Elaeis guineensis*) with $K_y(M_gCa)_{2x}O_3$ as heterogeneous catalyst. *Bioresource Technology*, 102: 10777-10783.

Ong, H.C., Silitong, A.S., Masjuki, H.H., Mahlia, T.M.I., Chong, W.T. & Boosroh, M.H. 2013. Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha curcas*, *sterculia foetida* and *ceiba pentandra*. *Energy Conversion and Management*, 73: 245-255.

Pathak, S. 2015. Acid catalysed transesterification. *Journal of Chemical and Pharmaceutical Research*, 7 (3): 1780-1786.

Shu Q, Yang B., Yvan H., Qing S., Zhu G. 2007. Synthesis of biodiesel from soybean oil and methanol catalysed by zeolite beta modified with La^{3+} . *Catalysis Communications*, 8: 2159-2165.

Shu Q., Gao J., Nawaz Z., Liao Y, Wang D., Wang J. 2010. Synthesis of biodiesel from waste vegetable oil with large amount of free fatty acids using a carbon based solid acid catalyst. *Applied Energy*, 87: 2589-2596.

Ramos, M.J., Fernandez, C.M., Casas, A Rodriguez, L. & Perez, A. 200. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology*, 100: 261-268

Rezaei, R., Mohadesi, M. & Moradi, G.R. 2013. Optimisation of biodiesel production using waste mussel shell catalyst. *Fuel*, 109: 534-541.

Semwal, S., Arora, A.K., Badoni, R.P. & Tuli, D.K. 2011. Biodiesel production using heterogeneous catalyst. *Bioresource Technology*, 102: 2151-2161.

Sharma, Y.C., Singh, B. & Upadhyay, S.N. 2008. Advancement in development and characterisation of biodiesel: a review. *Fuel*, 87: 2355-2373.

Sharma, Y.C., Singh, B. & Korstad, J. 2011. Latest developments on application of heterogeneous basis catalysts for an efficient and eco-friendly synthesis of biodiesel. *Fuel*, 90: 1309-1324.

Hu S., wang Y., Han H. 2011. Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production. *Biomass and Bioenergy*, 35: 3627-3635.

- Shu Q., Gao J., Liao Y., Wang J. 2011. Reaction kinetics of biodiesel synthesis from waste oil using a carbon-based solid acid catalyst. *Chinese Journal of Chemical Engineering*, 19 (1): 163-168.
- Silitonga, A.S., Masjuki, H.H., Mahlia, T.M.I., Ong, H.C., Chong, W.T. & Boosroh, M.H. 2013. Review properties of biodiesel diesel blends from edible and non-edible feedstock. *Renewable and Sustainable Energy Reviews*, 22: 346-360.
- Silva, G.F., Camargo, F.L., Andrea, L.O. & Ferreira. 2011. Application of response surface methodology for optimization of biodiesel production by transesterification of soybean oil with ethanol. *Fuel Process Technology*, 92: 407-413.
- Singh Chouhan A.P. & Sarma, A.K. 2011. Modern heterogeneous catalyst for biodiesel production. *Renewable and Sustainable Energy Reviews*, 15: 4378-4399.
- Pradhan S., Madankar C.S., Mohanty P., Naik S.N. 2012. Optimization of reactive extraction of castor seed to produce biodiesel using response surface methodology. *Fuel*, 97: 848-855.
- Al-zuhain S., Jayaraman K.V., Krishnan S., Wai-Hoog C. 2006. The effect of fatty acid concentration and water content on the production of biodiesel by lipase. *Biochemical Engineering Journal*, 30: 212-217.
- Al-Zuhair S., Ling F.W., Lim S.J. 2007. Proposed kinetic mechanism of production of biodiesel from palm oil using lipase. *Process Biochemistry*, 42: 951-960.
- Suppes, G.J., Dassari, M.A., Doskosal, E.J., Mankidy, P.J. & Goff, M.J. 2001. Transesterification of soybean oil with zeolite and metal catalysts: a review. *Applied Catalysts*, 257: 213-223.
- Talebian-Kiakalaieh, A., Aishah-Saidina-Amin, N. & Mazaheri, H. 2013. A review on novel process of biodiesel production from waste cooking oil. *Applied Energy*, 104: 683-710.
- Tariq, M., Ali, S. & Khalid, N. 2012. Activity of homogeneous and heterogeneous catalysts spectroscopic and chromatographic characterization of biodiesel: a review. *Renewable and Sustainable Energy Reviews*, 16: 6303-6316.
- Thompson, L.H. & Doraiswamy, L.K. 1999. Sonochemistry: science and engineering. *Industrial and Engineering Chemistry Research*, 38: 1215-1249.
- Vincente, G., Martinez, M. & Aracil, J. 2007. Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. *Bioresource Technology*, 98: 1724-1733.
- Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N. & Fawngnawakij, K. 2010. Waste shells of mollusc and egg as biodiesel production catalyst. *Bioresource Technology*, 101: 3765-3767.
- Wan, L., Liu, H. & Skala, D. 2014. Biodiesel production from soybean oil in subcritical methanol using MnCO₃/ZnO as catalyst. *Applied Catalysis B: Environmental*, 152-153, 352-359.
- Wan-Omar W.N.N, Amin N.A.S. 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. *Biomass and Bioenergy*, 35:1329-1338.

- Wang, R., Hanna, M.A., Zhou, W.W., Bhadury, P.S., Chen, Q., Song, B.A. & Yang S. 2011. Production and selected fuel properties of biodiesel from promising non-edible oils: *Euphorbia lathyris* L., *Sapium sebiferum* L. and *Jatropha curcas* L. *Energy Conversion and Management*, 48: 184-188.
- Wang, Y., Ou, S., Liu, P. & Zhang, Z. 2008. Preparation of biodiesel from waste cooking oil via two-step catalysed process. *Energy Conversion and Management*, 48:184-188.
- Wei, Z., Xu, C. & Li, B. 2009. Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresource Technology*, 100: 2883-2885.
- Westbrook, C.K., Naik, C.V., Orbinet, O., Pitz, W.J., Mehl, M. & Sarathyl, S.M. 2011. Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuel. *Combustion and Flame*, 158: 742-755.
- Suryaputra W., Winata I., Indraswati N., Ismadji S. 2013. Waste capiz (*amuseum, cristatum*) shell as a new heterogeneous catalyst for biodiesel production. *Fuel*, 50: 795-799.
- Zhao X., Fan M., Zeng J., Du U., Liu C., Liu D. 2013. Kinetics of lipase recovery from the aqueous phase of biodiesel production by microporous resin adsorption and reused of adsorbed lipase for biodiesel preparation. *Enzyme and Microbial Technology*, 52: 226-233.
- Yaakob, Z., Mahammad, M., Alherbawi, M. & Alam, Z. 2013. Overview of the production of biodiesel from waste cooking oil. *Renewable and Sustainable Energy Review*, 18: 184-193.
- Yagiz, F., Kazan, D. & Nilgun Akin. A. 2007 Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. *Chemical Engineering Journal*, 134: 262-267.
- Tang Y., Xu J., Zhag J., Lu Y. 2013. Biodiesel production from vegetable oil by using modified CaO as solid basic catalyst. *Journal of Clear Production*, 42: 198-203.
- Vyas, A.P., Verma, J.L. & Subrahmanyam, N. 2010. A review on FAME production processes. *Fuel*, 89: 1-9.
- Taufiq-yap Y.H., Teo S.H., Rashid U., Islam A., Hussein M.Z., Lee K.T. 2014, Transesterification of *jatropha curcas* crude oil to biodiesel on calcium lanthanum mixed oxide catalyst: effect of stoichiometric composition. *Energy Conversion and Management*. Article in press.
- Yusuf, N.N.A.N., Kamarudin, S.K. & Yaakub, Z. 2011. Overview on the current trends in biodiesel production. *Energy Conversion and Management*, 52: 2741-2751.
- Zhang, J., Chen, S., Yang, R & Yan, Y. 2010. Biodiesel production from vegetable oil using heterogeneous acid and alkali catalyst. *Fuel*, 89: 2939-2944.
- Zhang, Y., Dube, M.A, McLean, D.D. & Kates, M. 2003. Biodiesel production from waste cooking oil: 1. process design and technological assessment. *Bioresource Technology*, 89:1-16.
- Ziolkowska, J.R. 2014. Prospective technologies, feedstocks and market innovations for ethanol and biodiesel production in the US. *Biotechnology Reports*, 4: 94-98.

APPENDICES

APPENDICES

Appendix A: Experimental results obtained from calculation

Runs	Tem	Volume of methanol and ratio	Mass of catalyst	Mass of oil	Mass of biodiesel	Yield
1	60	1:15=35ml	5%=2.50	50.00	32.15	64.3
2	60	1:15=35ml	2.0%=1g	50.35	34.80	69.1
3	60	1:30=69.1ml	5%=2.5g	50.09	35.80	71.5
4	60	1:30=69.1ml	2%=1g	50.11	36.78	73.4
5	70	1:15=35ml	5%=2.50	50.03	25.13	50.2
6	70	1:30=69.1	5%=2.50	50.12	11.06	22.06
7	70	1:15=35ml	2%=1g	50.20	17.67	35.2
8	70	1:30=69.01ml	2%=1g	50.36	5.37	10.6
Centre point 1	65	1:22.50=52ml	3.50%=1.75	50.11	44.68	89.4
Centre point 2	65	1:22.50=52ml	3.50%=1.75	50.05	45.03	91
Centre point 3	65	1:22.50=52ml	3.50%=1.75	50.26	45.35	89.5
Centre point 4	65	1:22.50=52ml	3.50%=1.75	50.66	45.32	89.5
Centre point 5	65	1:22.50=52ml	3.50%=1.75	50.04	44.60	89.1
Centre point 6	65	1:22.50=52ml	3.50%=1.75	50.01	44.71	89.4
High star point	73.41	1:22.50=52ml	3.50%=1.75	50.41	0.40	0.8
Lower star point	56.59	1:22.50=51.8ml	3.55%=1.75g	50.02	31.10	62.2
Star point 1	65	1:35.11=80.8ml	3.50%=1.75	50.22	19.84	39.5
Star point 2	65	1:22.50=51.8ml	6.02%=3.01g	50.36	37.27	74.02
Star point 3	65	1:22.50=51.8ml	0.98%=0.49g	50.71	33.73	66.5
Star point 4	65	1:9.89=22.6ml	3.50%=1.75g	50.06	21.36	42.9

Appendix B: Kinetics calculation

1. 2.Methanol

Molecular weight: 32.04g/mol

Density: 0.792g/ml

$$Mole_{MeOH} = Mole_{initialoil} \times Stoichiometry$$

$$Mole = 5.7 \times 10^{-2} \text{ mol} \times 3 = 1.7 \times 10^{-1} \text{ mol}$$

2. Oil and rate law

Molecular weight: 879.5g/mol

Initial mass: 50g

$$mole_{oil} = \frac{50g}{879.5 \frac{g}{mol}} = 5.7 \times 10^{-2} \text{ mol}$$

$$C_{Ao} = \frac{5.7 \times 10^{-2} \text{ mol}}{250ml} = 2.3 \times 10^{-4} \text{ mol/ml} = 2.3 \times 10^{-1} \text{ mol/L}$$

$$C_{Af} = \frac{8 \times 10^{-1} \text{ mol}}{250ml} = 3.2 \times 10^{-3} \text{ mol/ml} = 3.2 \text{ mol/L} = 3.2M$$

$$Rate = \frac{3.2 - 2.3 \times 10^{-1} \text{ mol/L}}{19800s} = 1.5 \times 10^{-4} \text{ mol.s/L} = 1.5 \times 10^{-4} \text{ M/s}$$