



**BIODIESEL PRODUCTION AND EVALUATION OF HETEROGENEOUS
CATALYST USING SOUTH AFRICAN OIL PRODUCING TREES**

Modiba Edward Magoma

209131241

**Dissertation submitted in fulfillment of the requirements for the Magister
Technologiae: Engineering: Chemical**

Supervisor: Dr Hillary Rutto

Co-supervisor: Prof Peter Osifo

January 2014

Abstract

This study presents the use of sodium methoxide as a homogeneous catalyst and impregnated Perlite (potassium hydroxide/perlite) as heterogeneous catalyst for production of biodiesel using Baobab and Marula oil respectively. One factor at a time experimental design was used to study the effect of temperature, time, amount of catalyst and methanol to oil ratio on the transesterification of baobab oil using sodium methoxide as a catalyst. Response surface methodology was used to study the effect of temperature, time, amount of catalyst and methanol to oil ratio on the transesterification of marula oil using perlite as a catalyst. Biodiesel yield produced using sodium methoxide and baobab oil was 96% at 1 hr reaction time, 30 wt.% methanol to oil ratio, 1 gram of catalyst and 60°C reaction conditions. Biodiesel yield produced using perlite and marula oil was 91.38% at 3.55 hr reaction time, 29.86 wt.% methanol to oil ratio, 3.46 grams of catalyst and 70.41°C reaction conditions. Perlite catalyst was reusable for transesterification of marula oil while sodium methoxide was not reusable for transesterification of baobab oil. Baobab and Marula biodiesel fuel properties are comparable to American Society for Testing Materials standard (ASTM).

Publications and Presentations Derived from this Thesis

Publication

Modiba, E.M., Osifo, P.O., and Rutto, H.L., 2014. Biodiesel production from baobab (*Adansonia digitata* L.) seed kernel oil and its fuel properties. *Industrial Crops and Products*, Volume 59, 50-54.

Modiba, E.M., Osifo, P.O., and Rutto, H.L., 2014. The use of impregnated perlite as a heterogeneous catalyst for biodiesel production from marula oil. *Chemical Papers*, DOI 10.2478/s11696-014-0583-1.

Declaration

I, Modiba Edward Magoma hereby declare that the following research information is solely my own work. This research is submitted in fulfilling requirements for the Magister Technologiae in Chemical Engineering at the Vaal University of Technology, Vanderbijlpark. This work has not been submitted before to any educational institution or published by any other individual.

MODIBA EDWARD MAGOMA

Acknowledgements

I, hereby, am expressing my sincere gratitude and thanks giving to the following exceptional individuals who have contributed towards the completion and submission of this document successfully:

- God for giving me faith and gratitude towards my studies.
- My parents Modiba Mabule William and Modiba Rosinah Mmatlala for supporting, guiding and believing in me.
- My supervisor Dr Hillary Rutto for his excellent motivation, guidance, encouragement and his enthusiasm towards developing future engineering researchers.
- My co-supervisor Dr Peter Osifo for his incredible academic support.
- My friend Mr. Mashamba Doctor for being my pillar of strength, my research colleagues Ms. Mahwilere Puledi and Mr. Nkosi Gadi for their admirable willingness and help in seeing my research work completed successfully.
- Mr. Shoko Lay for his workmanship in the laboratory.

Glossary of abbreviations and definitions

ANOVA - Analysis of Variance

ASTM - American Standard Testing Methods

AV - Acid value

BaoME - Baobab methyl ester

BBD - Box Behnken Design

BET - Brauner Emmet Teller

CaO - Calcium oxide

CCD - Central Composite Design

CFPP - Cold Filter Plugging Point

CN - Cetane number

CP - Cloud Point

DF - Degree of Freedom

DoE - Design of experiment

DSC - Differential scanning calorimetry

DTA - Differential thermal analysis

EMA - Engine Manufactures Association

EN - European standard

FAAE - Fatty acid alkyl ester

FAME - Fatty Acid Methyl Esters

FFA - Free Fatty Acids

FID - Flame ionization detector

FTIR - Fourier transform infrared spectroscopy

GC - Gas Chromatography

HPLC - High Performance Liquid Chromatography

ID - Internal Diameter

IE - Immobilized enzyme

KOH - Potassium hydroxide
NaOH - Sodium hydroxide
NIR - Near infra-red
NMR - Nuclear magnetic resonance
NO - Nitrogen Oxide
OA - Orthogonal array
OS - Oxidation Stability
PPD - Plackett-Burman design
PP - Pour Point
RSM - Response Surface Methodology
SEM - Scanning Electron Microscopy
TGA - Thermogravimetric Analysis
TG - Triglycerides
TLC - Thin Layer Chromatography
XRD - X-ray diffraction

% - Percentage
wt.% - Weight percent
°C- Degree Celsius
μl - Micron
 C_o - Number of central points
g/cm³ - Density
g - Gram
hr - Hour
 k - Number of factors
m²/g - Specific surface area
mg KOH/g - Acid value
ml - Millilitre
mm²/s - Kinematic viscosity
nm - Nanomicron

$R_{A,B,C}$ - Fatty acid chain

Rpm - Revolutions per minute

Vol.% - volume percent

X_1, X_2, X_3 - Independent variables

β - Regression coefficient

δ^2 - Variance error

R^2 - Coefficient of determination

Table of contents

Abstract	i
Publications and Presentations Derived from this Thesis.....	ii
Declaration	iii
Acknowledgements	iv
Glossary of abbreviations and definitions	v
Table of contents.....	viii
List of figures	xii
List of tables	xiii
Chapter 1: Introduction.....	1
1.1. Background and Motivation	1
1.2. Problem statement.....	3
1.3. Objective of the project.....	4
1.4. Specific objectives.....	4
1.5. References.....	5
Chapter 2: Literature review	7
2.1. Biodiesel and Feedstock	7
2.2. South African oil producing trees.....	10
2.2.1. Baobab	10
2.2.2. Marula	11
2.2.3. Jatropha.....	12
2.2.4. Manketti.....	13
2.3. Biodiesel production methods.....	13
2.3.1. Microemulsion	13
2.3.2. Pyrolysis.....	14

2.3.3. Transesterification.....	15
2.4. Catalyst for biodiesel production.....	16
2.4.1. Homogeneous acid catalyst.....	16
2.4.2. Homogeneous base catalyst.....	17
2.4.3. Heterogeneous acid catalyst	20
2.4.4. Heterogeneous base catalyst.....	21
2.4.5. Lipase catalyst.....	22
2.5. Factors affecting transesterification process	23
2.5.1. Temperature	23
2.5.2. Catalyst.....	24
2.5.3. Reaction time	24
2.5.4. Alcohol type	25
2.5.5. Free fatty acid and Water	25
2.6. Fuel properties of biodiesel.....	26
2.6.1. Viscosity and density	26
2.6.2. Cloud point.....	27
2.6.3. Flash point	27
2.6.4. Pour point	28
2.6.5. Oxidation stability	28
2.6.6. Cetane Number.....	28
2.6.7. Cold filter plugging point.....	29
2.6.8. Acid value	29
2.6.9. Lubricity	30
2.6.10. Heat of combustion	30
2.7. Biodiesel characterization techniques	32
2.7.1. Chromatography	32

2.7.2. Thermal stability and Spectroscopic technique	33
2.8. Catalyst Characterization	34
2.8.1. Fourier Transform Infrared Spectroscopy	34
2.8.2. Brunauer-Emmett-Teller	34
2.8.3. X-Ray Diffraction.....	34
2.8.4. Scanning Electron Microscopy	35
2.9. Statistical analysis	35
2.9.1. Response surface methodology	35
2.9.2. Design of Experiments.....	38
2.10. Types of DOE.....	39
2.10.1. Central Composite Design (CCD)	39
2.10.2. Box-Behnken Design (BBD).....	39
2.10.3. D-optimal design.....	40
2.10.4. Plackett–Burman Design (PBD).....	41
2.10.5. Taguchi	41
2.10.6. One factor method	41
2.10.7. References	42
Chapter 3: Biodiesel Production from Baobab oil: An optimized Process.....	57
3.1. Abstract	57
3.2. Introduction	57
3.3. Materials and Methods.....	59
3.3.1. Material.....	59
3.4. Methodology.....	59
3.4.1. Determination of Baobab oil fatty acid	59
3.4.2. Transesterification procedure of Baobab oil	60
3.4.3. Gas chromatography	61

3.4.4. Characterization technique and Equipment.	63
3.4.5. Characterization of fuel properties of biodiesel from Baobab oil.....	64
3.5. Results and discussion	64
3.6. Conclusion	70
3.7. Reference	71
Chapter 4: Biodiesel production from Marula oil using Perlite as a heterogeneous catalyst	73
4.1. Abstract	73
4.2. Introduction	73
4.3. Materials and Methods.....	75
4.3.1. Catalyst preparation	75
4.3.2 . Catalyst characterization.....	76
4.3.2.1. X-ray diffraction.....	76
4.3.2.2. Brunauer-Emett-Teller	76
4.3.3. Gas chromatography	76
4.3.4. Fatty acid determination of Marula oil	77
4.3.5. Transesterification of Marula oil	78
4.3.6. Characterization of Marula biodiesel fuel properties	79
4.3.7. Design of experiment	80
4.4. Results and discussion.....	83
4.4.1. X-ray diffraction	84
4.4.2. BET surface analysis.....	85
4.4.3. Regression model development.....	86
4.5. Effect of experimental variables on transesterification.	89
4.6. Catalyst recyclability.....	99
Chapter 5: Conclusion and Recommendation	101

5.1. Conclusion and Recommendation	101
4.8. Reference	102

List of figures

Figure 2.1: World production and Distribution of palm oil. Data from USDA Foreign Agricultural Services PSD Online database (USDA, 2011).....	9
Figure 2.2: World production and Distribution of soybean oil. Data from USDA Foreign Agricultural Services PSD Online database (USDA, 2011).....	9
Figure 2.3: Transesterification process (Van Gerpen, 2005).....	15
Figure 2.4: Acid catalyzed transesterification mechanism (Christie, 1989)	17
Figure 2.5: Base catalyzed transesterification mechanism (Ejikeme et al., 2010).	19
Figure 2.6: CaO as a heterogeneous base catalyst in transesterification (Masato et al, 2008).	22
Figure 3.1: Experimental procedure followed during the research.	62
Figure 3.2: The effect of temperature on transesterification process of baobab.....	65
Figure 3.3: The effect of methanol to oil ratio on the transesterification process of baobab oil.....	66
Figure 3.4: The effect of time on transesterification process of baobab oil.	67
Figure 3.5: The effect of catalyst on the transesterification of baobab oil.....	68
Figure 4. 1: Effect of KOH to perlite ratio.....	83
Figure 4. 2: XRD of pure perlite and modified perlite catalyst.	84
Figure 4. 3: Nitrogen adsorbtion/desorption isotherms of unmodified perlite and modified perlite with KOH up to 1:6 ratio of KOH/Perlite.	85
Figure 4. 4: Experimental versus Predicted biodiesel yield values.	88

Figure 4. 5: Effect of catalyst and temperature on transesterification, (a) response surface and (b) two dimension plot with amount of catalyst held at (+) 2.75 g and (-) 4.25 g.....	89
Figure 4. 6: Effect of methanol to oil ratio and temperature on transesterification, (a) response surface and (b) two dimension plot with methanol to oil ratio held at (+) 40 wt.% and (-) 20 wt.%.....	91
Figure 4. 7: Effect of reaction time and temperature on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr	93
Figure 4. 8: Effect of reaction time and methanol to oil ratio on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr.....	94
Figure 4. 9: Effect of methanol to oil ratio and amount of catalyst on transesterification, (a) response surface and (b) two dimension plot with methanol to oil ratio held at (+) 40 wt.% and (-) 20 wt.%	95
Figure 4. 10: Effect of reaction time and amount of catalyst on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr.....	97
Figure 4. 11: Effects of individual variables affecting transesterification of marula oil to biodiesel. A-temperature, B-amount of catalyst, C-methanol to oil ratio, D-reaction time.	98
Figure 4. 12: Effect of catalyst reusability.	99

List of tables

Table 2.1: Biodiesel advantages and disadvantages (Agarwal, 2005).....	7
Table 2.2: Types of oils and feedstock sources (Demirbas, 2009).	8
Table 2.3: Oxidation stability of Marula oil compared with other oils (Burger et al., 1987).	12
Table 2.4: Optimized and typical reaction variables for biodiesel production (Zhang et al., 2003).	26

Table 2.5: Biodiesel properties requirements (Knothe, 2010; Lopez et al., 2008).....	31
Table 3.1: List of materials.	59
Table 3.2: Equipment and uses.....	63
Table 3.3: Fuel properties and ASTM used (Van Gerpen, 2002).	63
Table 3.4: Fatty acid composition (wt. %) of Baobab oil.....	64
Table 3.5: Baobab methyl esters (BaoME) fuel properties were compared with methyl esters (biodiesel) and EN and ASTM standard.	70
Table 4.1: Fatty acid composition of Marula oil compared to other vegetable oils (wt.%)	77
Table 4.2: Typical chemical compositions of pure perlite from Infigro Natural Technologies.....	79
Table 4.3: Levels of transesterification process variables employed.....	81
Table 4.4: Central composite design of the experiments and FAME results.....	82
Table 4.5: ANOVA analysis of the regression model equation without insignificant terms.	87
Table 4.6: Fuel properties of marula biodiesel compared to other biodiesel and ASTM standard.	100

Chapter 1: Introduction

1.1. Background and Motivation

Recently, there has been depletion of fossil fuels causing instability in the price of petroleum and also environmental concern due to air pollution caused by vehicles. Therefore, biodiesel is receiving increasing attention as an optional, non-hazardous, ecological, renewable source of fuel energy produced from fresh or waste vegetable oils and animal fats (Yisu-Hsu and Shaik, 2005). Studies conducted in Turkey showed the possibility of reduction in fossil fuel productions which requires urgent alternative fuel energy sources by 2038 (Edigera et al., 2006; Edigera and Akar, 2007). Sources of feed stocks that can be used in biodiesel production are generally classified into edible and non-edible oils. Edible oils such as canola, soybean, sunflower, peanut, corn and animal fats have been used as alternative sources of biodiesel production in various countries and the results showed that edible oils can really be used as biodiesel sources. However, food consumption by men versus biodiesel production should be well studied to avoid shortage of edible oils by human (Freedman et al., 1986). The non-edible oils such as *Jatropha curcas*, and waste oils such as soybean soap stock and yellow grease have been used in the production of biodiesel (Leung and Guo, 2006; Wang et al., 2007; Alcantara et al., 2000; Mittelbach, 2004).

There are several South African trees that can be used as feed stocks for biodiesel production these include: Marula (*Sclerocarybirrea*), Baobab (*Adansoniadigitata*) and Manketti/Mongongo (*Ricinodendronrautanenii*). These are deciduous trees that grow naturally in many parts of South Africa, Botswana and Namibia (Leakey, 1999). The edible oil can generally be extracted from their nuts which are nutritious and rich in proteins and minerals. The oils also contain active anti-oxidants (Vitamin E) which make them useful active ingredients in cosmetic products (Leakey, 1999). Since the oils contain anti-oxidants, these oils can be used in small amounts to improve the oxidation stability of other biodiesel produced from edible or non-edible oils. The production of

biodiesel is performed through transesterification of triglyceride using alcohol. The products of the reaction are fatty acids esters and glycerine. Homogenous and heterogeneous catalysts are main types of catalysts that can be used to produce biodiesel from feedstock. Homogeneous catalysts react in the same phase with the reactant mixture, whereas heterogeneous catalysts react in different phase with the reactant mixture. Homogenous catalysts can be classified into two main classes namely: homogenous bases and homogeneous acids. Strong alkaline catalysts are used industrially for biodiesel production processes. Potassium hydroxide, sodium hydroxide, sodium methoxide are the commonly used homogenous basic catalysts (Surbhi et al., 2011). Sulphuric acid is the most common homogenous acid catalyst that has been used to esterify excess free fatty acids (Schuchardt et al., 1998).

Homogenous catalysts have disadvantages, because they cannot be recovered, they are intolerant to high free fatty acid (FFA) oils and also require washing of biodiesel with fresh water to remove the impurities. This results in wastewater generation, water contamination and loss of biodiesel as a result of water washing and this increases cost on municipal wastewater treatment plants. Heterogeneous catalysts can be classified into two main classes: namely; heterogeneous acid and heterogeneous base catalysts. Heterogeneous acid catalyst for example, heteropolyacid impregnated on different supports (silica, zirconia, alumina, and activated carbon), $\text{SO}_4\text{-ZrO}_2$ and $\text{WO}_3\text{-ZrO}_2$ as solid acid catalysts have been used in canola oil transesterification with methanol as the alcohol (Canakci and Van Gerpen, 2001; Kulkarni et al., 2006; Laosiripojana et al., 2010). Unfortunately, these catalysts required longer reaction time to reach completion and higher temperatures which make them unfavourable. Heterogeneous solid base catalyst such as calcium oxide has some advantages over homogeneous catalyst because the catalyst can be reutilized, has a tolerance of moisture and free fatty acids, is economical, it is insoluble in methanol, it is non-corrosive and non-pollutant.

Fuel properties of biodiesel such as cold filter plugging point (CFPP), cloud point (CP), pour point (PP) and oxidation stability (OS) can be enhanced and modified by blending

biodiesel from different oils. Previous studies show that the CFPP of palm oil methyl ester was improved up to 15°C by blending with canola methyl ester, iodine value and oxidation stability index of soybean methyl ester was improved to satisfy European standard EN 14214 specifications through blending with canola and palm or sunflower methyl esters (Moser, 2008). Transesterification process is affected by many process variables such as temperature, reaction time, methanol to oil ratio and the amount of catalyst. These factors can be optimized by statistical method or by a one factor-at-a time method. The surface response methodology is a powerful statistical method, usually it includes the application of design expert software that can be used to test multiple process variables because few experimental runs are needed compared to a one factor-at-a time method (Montgomery, 2001). In addition, identification of various variables interactions is easy.

Although biodiesel has been produced from edible and non-edible oils, limited study has been conducted on the production of biodiesel from South African oil producing trees focusing mainly on Baobab and Jatropha. There are abundant and cheap minerals in South Africa that can be used to produce biodiesel. Minerals such as: lime, limestone, bentonite, perlite and kaolin have high catalytic stability. Perlite heterogenised with KOH was used in this study as a heterogeneous catalyst to produce biodiesel using Marula oil.

1.2. Problem statement

South Africa has joined other countries on the Kyoto protocol to reduce usage of fossil fuels energies as the world is experiencing a huge demand for different sources of energy and its environmental impact and the search is increasing to develop/produce low-cost alternative fuels. Among those countries, biodiesel has lot of interesting attraction as a promising alternative fuel source which can be used to replace fossil fuel such as diesel and petrol. Biodiesel has been produced for many years mainly from waste vegetable oil, edible oils (sunflower, canola etc.) and non-edible oils (jatropha, karanja, etc.), especially in European countries. The main objective of the project is to

produce biodiesel and evaluate heterogeneous catalysts using South African oil producing trees (baobab, manketti and marula). Currently no researchers or only few has produced biodiesel using baobab, marula oil and the effect of blending both biodiesel using different feedstock's to improve fuel properties such as oxidation stability, pour and cloud point. This project will focus on producing biodiesel from these oils and characterize their fuel properties. Major amount of biodiesel produced in SA use homogeneous catalysts (potassium hydroxide and sodium hydroxide) as the main catalysts and no study has been conducted for producing biodiesel from marula, baobab and manketti oils focusing on different types of heterogeneous catalysts which are less expensive, but can produce good quality biodiesel. Heterogeneous catalysts will be used to produce biodiesel from these oils. Important fuel properties such as oxidation stability, CFPP, viscosity, density, flash point, pour point and cloud point of biodiesel produced at optimum conditions will be compared to the fuel properties of biodiesel using American Society for Testing Materials standard (ASTM) and South African standard.

1.3. Objective of the project

The main aim of the project is biodiesel production and the evaluation of homogeneous and heterogeneous catalysts using South African oils producing trees (Baobab and Marula).

1.4. Specific objectives

- a. To carry out transesterification of Baobab and Marula oil using homogeneous and heterogeneous catalyst.
- b. To synthesis perlite catalyst by impregnation with homogeneous catalyst and
- c. To determine and compare the important fuel properties of Baobab and Marula biodiesel with ASTM.

- d. To determine and optimize variables (reaction time, reaction temperature, amount of catalyst and methanol to oil ratio) affecting transesterification process on the yield of fatty acid methyl ester from Marula oil using response surface methodology.
- e. To determine and evaluate Perlite as a heterogeneous catalyst.

1.5. References

Alcantara, A., Amores, J., Canoira, L., Fidalgo, E., Franco, M.J., and Navarro, A., 2000. Catalytic production of biodiesel from soybean oil used frying oil and tallow. *Biomass and Bioenergy* 18, 515-527.

Canakci, M and Van Gerpen, V.J., 2001. Biodiesel production from oils and fats with high free fatty acids. *Transaction of the American Society of Agricultural Engineers* 44, 1429-1436.

Edigera, V.S and Akar, S., 2007. ARIMA forecasting of primary energy demand by fuel in Turkey. *Energy Policy* 35, 1701-1708.

Edigera, V.S., Akar, S., and Ugurlu, B., 2006. Forecasting production of fossil fuel sources in Turkey using a comparative regression and ARIMA model. *Energy Policy* 34, 3836-3846.

Freedman, B., Butterfield, R.O., and Pryde, E.H., 1986. Transesterification kinetics of soybean oil. *Journal of the American Oil Chemists' Society* 63, 1375-1380.

Kulkarni, M.G., Gopinath, R., Meher, L.C., and Dalai, A.K., 2006. Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification. *Green Chemistry* 8, 1056-1062.

Laosiripojana, N., Kiatkittipong, W., Sutthisripok, W., and Assabumrungrat, S., 2010. Synthesis of methyl esters from relevant palm products in near-critical methanol with modified-zirconia catalysts. *Bioresource Technology* 101, 8416-8423.

Leakey, R.R.B., 1999. Potential for novel food products from agroforestry trees. *Review. Food Chemistry* 66, 1-14.

Leung, D and Guo, Y., 2006. Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process Technology* 87, 883-890.

Mittelbach, M and Remschmidt, C., 2004. Biodiesel. Boersdruck, Gesellschaft mit Beschränkter Haftung, Austria.

Montgomery, D.C., 2001. Design and analysis of experiments. John Wiley and Sons, New York, USA.

Moser, B.R., 2008. Influence of blending canola, palm, soybean, and sunflower oil methyl esters on fuel properties of biodiesel. *Energy and Fuels* 22, 4301-4306.

Schuchardt, U., Ricardo, S.R., and Vargas, R.M., 1998. Transesterification of vegetable oils: A review. *Journal of Brazilian Chemical Society* 9, 199-210.

Surbhi, S., Ajay, K.A., Rajendra, P.B., and Deepak, K.T., 2011. Biodiesel production using heterogeneous catalysts. *Bioresource Technology* 102, 2151-2161.

Wang, Z.M., Lee, J.S., Park, J.Y., Wu, C.Z., and Yuan, Z.H., 2007. Novel biodiesel production technology from soybean soap stock. *Korean Journal of Chemical Engineering* 24, 1027-1030.

Yi-Hsu Ju and Shaik, R.V., 2005. Rice bran as a potential resource for biodiesel. *Journal of Scientific and Industrial Research* 64, 866-882.

Chapter 2: Literature review

2.1. Biodiesel and Feedstock

Biodiesel is a renewable, non-poisonous biofuel produced from various natural feedstocks such as edible, non-edible oils and animal fats (Marchetti et al., 2007; Zhang et al., 2003). This process occurs by reacting feedstock with a catalyst under certain temperature at a given time using alcohol. The reaction yield glycerin as a byproduct. This process is known as transesterification process. Several advantages and disadvantages of biodiesel as source of energy are shown in Table 2.1.

Table 2.1: Biodiesel advantages and disadvantages (Agarwal, 2005).

Advantages	Disadvantages
Easily combustible and reduce greenhouse gases on the environment	Highly viscosity and hygroscopic
Reduce sulfur content in the atmosphere	Poor flow property due to its low pour point
Nontoxic and biodegradable	Increase engine heating ignition rate
Prepared from natural renewable resources	Might contribute to acid rain due to nitrogen oxide (NO _x) emitted
Easy to blend with other energy sources	The upgrading of some current engines might be expensive in order to use the fuel
Can reduce fossil fuel usage	Might be expensive due to increasing price of oils such as corn and soybean
Less susceptible to fire hazard due to its high flash point	

Natural feedstocks are used as the main source of any biodiesel production in the world. Different kinds of feedstock such as animal fats and vegetable oils are available at large in the world, however different regions has different kinds of feedstock. The choice of

using vegetable oil as biodiesel feedstock is mostly affected by the type of the soil the region possess, ecological changes such as temperature and humidity, the availability of the land required to grow the feedstock, the probability of the feedstock seed to grow in the region, the amount of time required to reap the feedstock and the usage of edible oils as source of biofuel versus source of food. Several feedstocks with the origin of their sources are given in Table 2.2.

Table 2.2: Types of oils and feedstock sources (Demirbas, 2009).

TYPE OF OILS	SOURCE OF OIL
Edible oils	Canola, Olive, Coconut, Soybean, Peanut, Avocado, Macauba, Pecan, Safflower, Sunflower, Corn, Sesame, Baobab, Marula
Non edible oils	Rubber seed, Tall, Jatropha, Algae, Jojobe, Manketti, Mahau, Karanja, Neem, Copaiba
Animal fat	Yellow grease, Tallow, Lard

The development of biodiesel feedstock and biodiesel production processes has attracted interest in countries such as United State, India, China, etc. and these countries are using their available waste land to grow several biodiesel feedstock. Indonesian industries has made palm oil the most regular feedstock for their biodiesel production Figure 2.1, while the United States has made soybean oil the most common feedstock (Singh and Singh, 2010) for biodiesel production Figure 2.2.

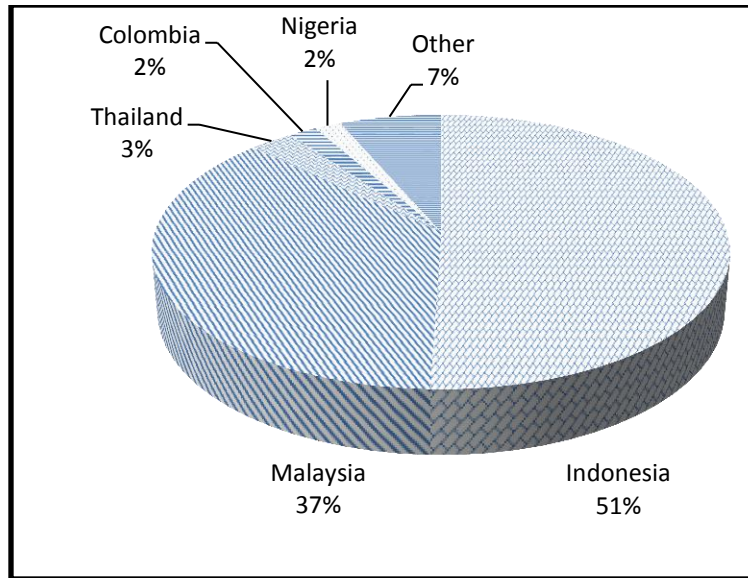


Figure 2.1: World production and Distribution of palm oil. Data from USDA Foreign Agricultural Services PSD Online database (USDA, 2011).

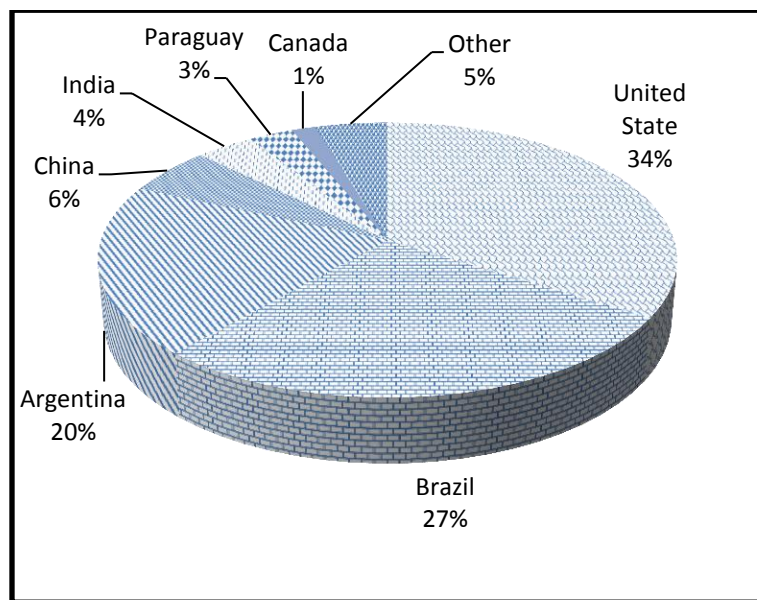


Figure 2.2: World production and Distribution of soybean oil. Data from USDA Foreign Agricultural Services PSD Online database (USDA, 2011).

Refined vegetable oils and animal fats have been used to produce biodiesel by alkali transesterification. Advantage of animal fats as biodiesel feedstock was their low usage demand and economical because this fats are by-products of agricultural animals (Ali and Hanna, 1994a; Ali and Hanna, 1994b; Freedman et al., 1984a). Dunn et al. (1996) showed that lower amounts of saturated fatty acids are contained in vegetable oils than in animal fats. These fats had relatively high melting points which increased precipitation and reduced cold flow properties of the engine. Blending of biodiesel from animal fats with petroleum fuel was successfully completed to compare and improve some flow properties. Although animal fats are naturally produced and extracted, a significant variance in their properties such as single or double bonded molecules is what makes animal feedstock unfavorable. Biodiesel with a good oxidation stability and high iodine value is usually associated with high saturated oil but possess poor flow properties at low temperature regions (WWI, 2006).

2.2. South African oil producing trees

2.2.1. Baobab

Baobab tree (*Adansoniadigitata*) is a tree which belongs to Bombacaceae family and is a very deciduous tree found in South Africa, Botswana, Malawi, Zambia and Namibia (Kurebgaseka, 2005; Leakey, 1999). Baobab tree can grow up to 15 meters height with its swollen bottle shaped like trunk. These trees produce a spherical yellowish shell fruit with internal edible small seeds cover with a pulp layer. Flowering of the trees can occur at any time on the commencing of the dry seasons and the flowers are axially paired leaf, large and hermaphrodite (Baum et al., 1998; Baum, 1995). The tree can survive many years and the tree can be successfully grafted. Grafted trees can grow fully within three years but grafted trees may produce only 30% of the fruits. The tree can live up to 500 years and it stores water in its spongy fibers (Sedibe and Williams, 2002).

2.2.2. Marula

Marula (*Sclerocaryabirrea*) is an indigenous tree with height between 15-20m and is silvery colored, mottled bark, peeling in disc-shaped flakes (Palmer and Pitman, 1972). Marula tree grows in most of the Southern and Eastern Africa and it belongs to Anacardiaceae family. Marula tree is more dominant in Phalaborwa in the Limpopo Province and Mpumalanga and each tree can produce 500kg of marula fruit yellowish in color when ripen (Department of Agriculture, Forestry and Fisheries, 2010). The fruit has a whitish edible pulp covering woody seed and the pulp is consumable by human and animals. When the woody seed or the kernel is dry, oil can be well extracted using correct methods or the kernel can be opened and the small seed inside can be eaten.

Marula leaves are spirally arranged, odd-pinnate and aligned much at the branch ends, with 3-7 pairs of opposite to sub-opposite leaflets (Palgrave, 2002). Currently, a large amount of the marula oil is used in cosmetics production. Marula oil contains high amount of unsaturated fatty acids, usually 8 percent linoleic acid and 70 percent oleic (National Research Council, 2008). These trees are capable of growing in the driest regions where the most commonly known oil seeds cannot grow and this success has stimulated curiosity in marula seed oil as a valuable renewable source of energy (Jerekias and Ketlogetswe, 2011). The oxidation stability of marula oil is greater than that of palmolein, sunflower, olive and cotton oil (Burger et al., 1987) and this has a great potential for biodiesel storage. Table 2.3 shows different types of vegetable oils and their oxidation stability using Rancimat method.

Table 2.3: Oxidation stability of Marula oil compared with other oils (Burger et al., 1987).

Type of oil	Oxidation Stability (hr)
Marula oil	34.2
Palmolein oil	8.5
Sunflower oil	1.9
Olive oil	4.6
Cottonseed oil	3.1

2.2.3. Jatropha

Jatropha curcas (*Jatropha*) is a tree that produces non-edible *jatropha* oil and the oil has a greater potential to be used as a source of biodiesel production. Countries such as India and China are developing the usage of *jatropha* biodiesel and the main advantage of *jatropha curcas* is that it can grow in a waterless regions and no extensive fertilizer is required to cultivate the tree (Rakesh et al., 2007). *Jatropha curcas* can live up to more than 30 years and it is not browsed by animals. The kernels produced by *jatropha curcas* are chemically, mechanically or enzymatically extracted to produce *jatropha* oil. *Jatropha* oil can be used in cosmetic industries, paraffin substituent, making of soap and candles (Raja et al., 2011).

India alone has more than 200 thousand metric tons of *jatropha* oil produced annually (Srivastava and Prasad, 2000). However, *jatropha* oil contains more than 14% FFA which leads to soap formation when used in transesterification process. A saponification process is more visible especially when homogeneous base catalysts are used with the oil. *Jatropha* oil can be esterified using homogeneous acid catalysts to reduce free fatty acid (FFA) content then followed by normal base transesterification process. Raja et al.

(2011) showed few properties of jatropha oil and it was found that the oil had 0.92 g/cm³ density, viscosity of 40.4 centistokes at 31°C, 101.7 iodine value, 38.2 acid value and 195 saponification value.

2.2.4. Manketti

Manketti or Mangogo (*Schinziophytonrautanenii*) is a tree that belongs to Euphorbiaceae gymnosperm family (Mohammad and Syed, 2005). The tree can grow up to 18m height with a large trunk and a large crown (Tchoundjeu and Atanganan, 2006). Manketti trees are abundantly found in Angola, Botswana, Namibia, Tanzania, Zambia, Southern Africa, Zimbabwe, Malawi and DRC (Tchoundjeu and Atanganan, 2006). The tree produces edible mangogo nuts that are rich in natural proteins and can be extracted to produce oil and often the oil is used in cosmetic products. The large masculine rounded crowns consist of greenish or reddish 5 to 7 leaflets and stalks covered with hairs (Van Wyk and Van Wyk, 1997). The nuts can grow up to 35 mm with their hard shells covering the nuts and often the tree grows in Woodland and Kalahari sands (Carruthers, 2000).

2.3. Biodiesel production methods

2.3.1. Microemulsion

Microemulsion is a colloidal equilibrium dispersion of isotropic fluid microstructures, with dimensions in the range of 1-150 nanomicon and the formation occur through two immiscible liquids with inclusion of one or more ionic or non-ionic amphophiles (Schwab et al., 1987). Tsai and Chang (1993); Isono et al. (1995) studied biodiesel production using microemulsion method to optimize high viscous biodiesel with methanol, 1-butanol and ethanol solvents. The results revealed a reduction in fuel viscosity but engine combustion activity was not efficient due to incomplete reaction of the fuel. Another biodiesel production method using microemulsion was studied by Ziejewski et al. (1984). The study was conducted using 53 volume percent (vol.%) emulsions, sunflower oil, 13

vol.% ethanol and 34 vol.%. Viscosity of 6.31 centistokes at 40°C, ash amount lower than 0.01% and cetane value of 25 were obtained. Goering et al. (1984) showed that 200 h EMA (Engine Manufacturers Association) engine performed very well with ionic and non-ionic microemulsions, but incomplete combustion were due to poor engine performance. Incomplete combustion led to high agglomeration of carbon deposits, caused injector nozzles to block and delayed engine start-up process (Ziejewski et al., 1984; Goering et al., 1984). Another study by Masjuki et al., (1994) and Sii et al. (1995) on palm oil, diesel fuel and 5-10% microemulsions revealed a similar performance with minor engine wear.

2.3.2. Pyrolysis

Pyrolysis is the conversion of one substance into another by substantially using high temperature conditions such as heating without oxygen at temperatures from 450°C to 850°C (Sonntag, 1979). Feedstocks such as vegetable oils, animal fats and wood chips have been used in pyrolysis, although research is mainly focusing on vegetable oils. Biofuel production from copra and palm oil by pyrolysis was accomplished by Pioch et al., (1993). The oils were cracked over a standard petroleum catalyst $\text{SiO}_2/\text{Al}_2\text{O}_3$ at 450°C to produce low molecular weights of gases, solids and liquids. Biogasoline and biodiesel fuel were produced by condensing and separating organic phases. Heavy hydrocarbons percentage compositions of the fuel were similar to that of fossil fuel and the process was simple and effective compared to other pyrolysis processes. The process was eco-friendly, because of its low air pollution and low waste water production. Alternatively, pyrolysis was performed using catalyst that produced cleavages of chemical bonds yielding smaller molecules (Weisz et al., 1979). Regions with low petroleum deposits had used fats as a source of pyrolysis (Srinivasa, 1983). Another pyrolysis process was achieved using rapeseed in a tubular reactor to produce methyl ester (Billaud et al., 1995). The high cost of pyrolysis equipment and the high consumption of energy are the major factors mitigating against the usage of pyrolysis in biodiesel production.

2.3.3. Transesterification

Transesterification is the process whereby vegetable oil reacts with alcohol in the presence of a catalyst (e.g., enzyme, acid or base catalyst depending on the amount of FFA present in the oil) to form a glycerin and a lighter dense liquid known as methyl ester (biodiesel). This is shown in Figure 2.3. The success of using transesterification is obtained by using homogeneous and heterogeneous catalysts. In Figure 2.3, R_A , R_B , R_C are the oil or fat fatty acid chains, commonly and naturally consisting of palmitic, stearic, oleic, or linoleic (Sendzikiene et al., 2005).

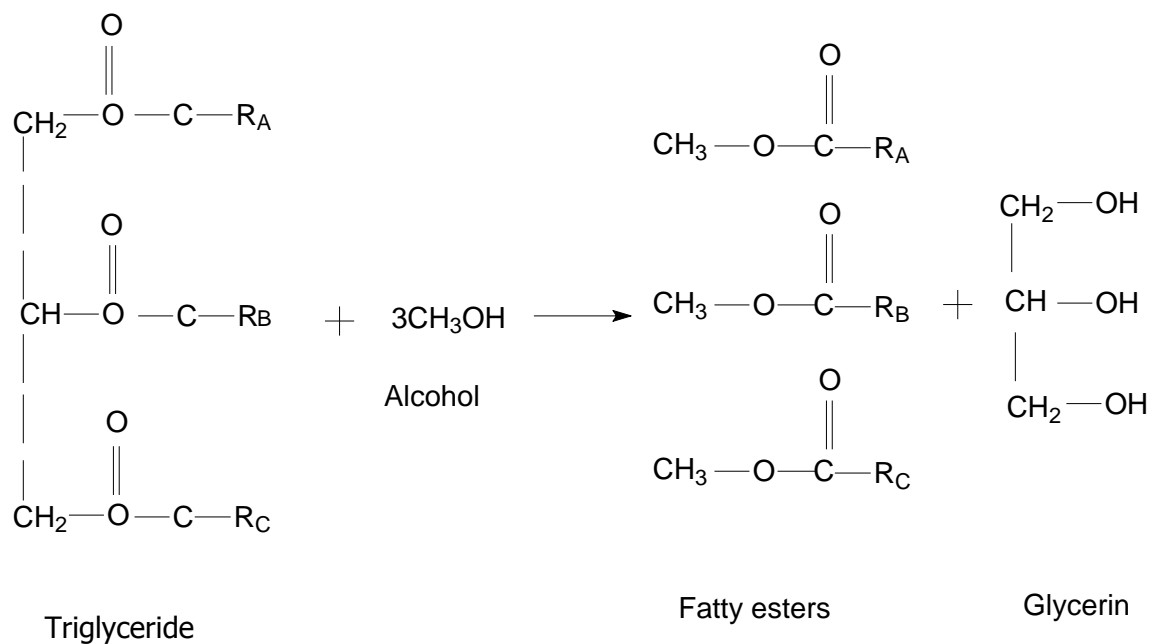


Figure 2.3: Transesterification process (Van Gerpen, 2005).

2.4. Catalyst for biodiesel production

2.4.1. Homogeneous acid catalyst

Sulfuric, phosphoric and hydrochloric acids have been used as homogeneous acid catalysts in transesterification process to produce biodiesel. They are several disadvantages of using homogeneous acid catalysts over homogeneous base catalysts. Homogeneous acid catalysts react very slowly with the reactants and they require excess reaction time to complete the reaction. Again, some homogeneous acid catalysts require high temperatures in order to complete the transesterification reaction. Therefore, low cost feedstock such as used cooking oil and high FFA Jatropha oil can simultaneously be esterified and transesterified into biodiesel, and achieve better conversion compared to homogeneous base catalysts that will require esterification first then transesterification after. Transesterification of soybean oil with methanol using 1 weight percent (wt.%) concentrated sulfuric acid was investigated to determine the effect of homogeneous acid catalyst on transesterification (Freedman et al., 1986). Temperature of 65°C and a molar ratio of 30:1 methanol to oil ratio was used. The reaction took about 69 hours to achieve 90% methyl esters conversion. Another study investigated the effect of molar ratio of alcohol to soybean oil, reaction temperature, amount of catalyst and the reaction time on ester conversion by using homogeneous acid catalyst (Canakci, 2001). Increase in ester conversions was achieved at increased molar ratios of alcohol to oil, reaction temperatures, concentrations of sulfuric acid, and reaction time.

The reaction mechanism of homogeneous base catalyst for biodiesel is shown in Figure 2.5 (Christie, 1989). The initial steps involve protonation of triglyceride by acid catalyst. Alcohol react with the proton to form intermediate which cause the RO⁻ to nucleophilically attack carbonyl group of triglyceride to form tetrahedral intermediate. Then finally the intermediate is broken down to ester while RO⁻ is regenerated to repeat the sequence.

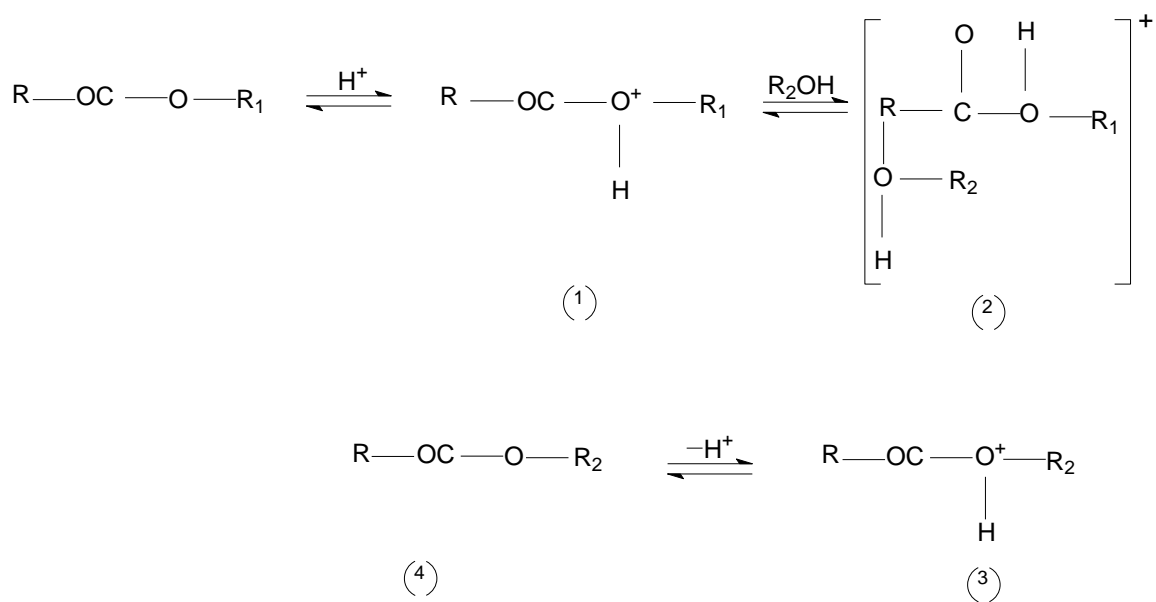


Figure 2.4: Acid catalyzed transesterification mechanism (Christie, 1989)

2.4.2. Homogeneous base catalyst

Sodium hydroxide and potassium hydroxide are the most common homogeneous base catalysts used in biodiesel production. Transesterification using homogeneous acid catalyst is 4000 times slower than homogeneous base catalyst (Srivastava and Prasad, 2000). Nevertheless, homogeneous base catalysts are sensitive to high FFA feedstock, sensitive to feedstock with high water content which results in hydrolysis of the end-product and produce soap, poor end-product separation, high cost of water during washing process, pollution of environment by by-products (Wright et al., 1944) and high cost of pre-acid treatment in high FFA feedstock (Keim, 1945). All these disadvantages necessitate modifications and optimization of this catalyst by finding alternative catalysts such as heterogeneous catalysts that have shown better alternative results on addressing these issues.

Catalysis process involves protonation process which is related to the acid catalyst and deprotonation which is related to basic catalyst. Ejikeme et al. (2010) explained base

catalyst transesterification of vegetable oils in four ways. Firstly, alcohol reacts with base catalyst to produce alkoxide and protonated catalyst. Secondly, alkoxide ion nucleophilic attack on the backbone of glycerol occurs, usually at the carbon of the carbonyl group (C=O bond), which creates a tetrahedral intermediate (Taft, 1950; Meher et al., 2006). Thirdly, formation of alkyl ester occurs, leaving glyceride anion unattached to the carbonyl group. Finally, the catalyst deprotonates, hence redeveloping the active species which react with a second molecule of alcohol, regenerate another catalytic cycle. This mechanism will repeat itself until all diglycerides and monoglycerides are converted into alkyl ester and glycerol. This is well shown in Figure 2.6.

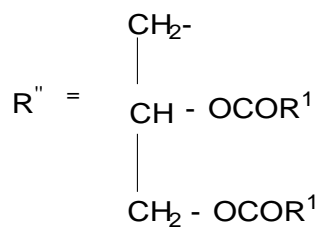
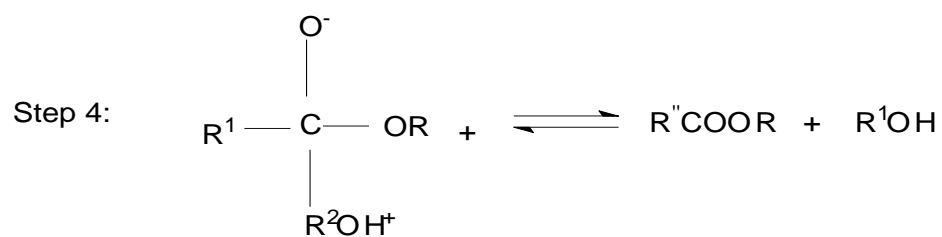
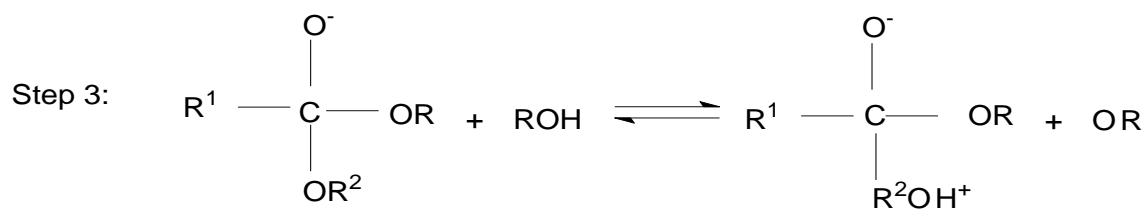
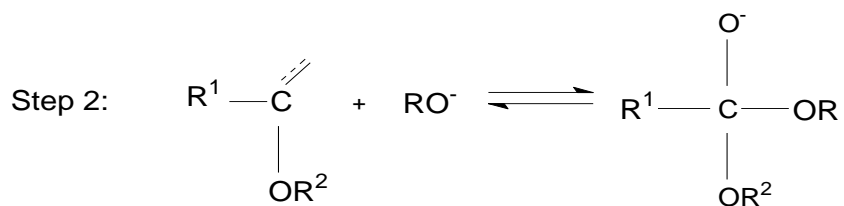


Figure 2.5: Base catalyzed transesterification mechanism (Ejikeme et al., 2010).

2.4.3. Heterogeneous acid catalyst

Heterogeneous acid catalysts have been studied marginally over homogeneous catalysts due to their excellent strength and accessibility in biodiesel production. A significant development in characterizing heterogeneous catalysts has led into researcher to investigate several properties of heterogeneous catalysts. These characterization techniques has allowed researchers to investigate the effect of heterogeneous solids catalysts by considering their reusability, surface area, structural buildup components, costs, etc. Heterogeneous catalysts are receiving accolades because they are easily separated from biodiesel mixture due to their insolubility and their capacity to resist higher temperatures compared to homogeneous catalysts (Yang et al., 2009). Pore size of the catalyst plays an important role, because if pores are compact (closed) the reaction is likely to occur on the exterior surface area and the reaction rate might be reduced. Yogesh and Singh (2011) reviewed that solid catalysts should possess large pores, good catalytic stability, be economically feasible, reusable and have excellent hydrophobic surface.

Modified Zeolite with Lanthanum (La/zeolite) as a solid acid catalyst was investigated in transesterification of soybean oil (Shu et al., 2007). The morphological structure of the zeolite showed that it contained numerous silica zeolites which were the source of catalytic activity and reusability. Catalyst was prepared by suspending zeolite in an aqueous solution of lanthanum nitrate $\text{La}(\text{NO}_3)_3$ at room temperature for 3 hours stirring constantly. The catalyst was dried at 100°C for 24 hours and calcined for 4 hours at 250°C. Methyl ester conversion of 48.9% was achieved and catalytic stability was related to the high content of Silica/Alumina (Si/Al) ratio. La/zeolite showed a better conversion compared to zeolite because the La/zeolite contained high amount of Bronsted external acid sites. Other methods such as impregnation of catalyst to increase surface area are explained well by Garcia et al. (2008) and Furuta et al. (2004).

2.4.4. Heterogeneous base catalyst

The development of heterogeneous base catalyst is an important study which requires meticulous understanding of development methods for low-cost catalysts. Distributed pore sizes in catalyst such as the micro pores and macropores sizes plays important role in catalysis, because these sizes are the building structures of surface area (Aurelien et al., 2007). Very often reactions take place at the exposed exterior surface area before extending into interior surface area, thus mass transfer occurs. This implies that the bigger the catalyst particle size the lower the rate of reaction and vice versa. Heterogeneous base catalysts possess excellence advantages such as, low costs, insolubility, high basicity and accessibility over other catalysts (Zabeti et al., 2009). Calcium oxide (CaO) was used as a solid base catalyst for soybean transesterification (Liu et al., 2008). The Brunauer-Emmett-Teller (BET) surface area of the catalyst was $0.56\text{m}^2/\text{g}$. The reaction was carried out using methanol to oil ratio of 12:1, 8 wt.% catalyst concentration at 65°C . Methyl ester conversion of 95% was obtained after 3 hours.

Other authors also reported comparative activity of CaO with $\text{K}_2\text{CO}_3/\gamma\text{Al}_2\text{O}_3$ and $\text{KF}/\gamma\text{Al}_2\text{O}_3$ catalysts. Catalysts were prepared by impregnating aqueous solution of potassium carbonate/potassium fluoride and then calcined at 550°C for 5 hr. It was observed that CaO maintained its catalytic activity and proved to be reusable up to 20 cycles and the yield was not affected, while $\text{K}_2\text{CO}_3/\gamma\text{Al}_2\text{O}_3$ and $\text{KF}/\gamma\text{Al}_2\text{O}_3$ catalytic activity was reduced and the biodiesel yield was affected. Methanol dissolves alkali metal compounds and this can reduce biodiesel yield as the active sites of the catalyst are reduced (Liu et al., 2008). The results also showed that the presence of water (about 2.8 wt.%) acted as catalyst promoter, but if water was above 2.8 wt.% it hydrolyzed FAME and formed soap. Masato et al. (2008) studied the effect of CaO as a solid base heterogeneous catalyst for transesterification of soybean oil and the mechanism is shown in Figure 2.6. The mechanism show the protonation, deprotonation and nucleophilic attack during transesterification. FAME yield obtained after an hour of transesterification was 93% using soybean oil as a feedstock and 99% FAME was obtained after re-using the catalyst with waste vegetable oil.

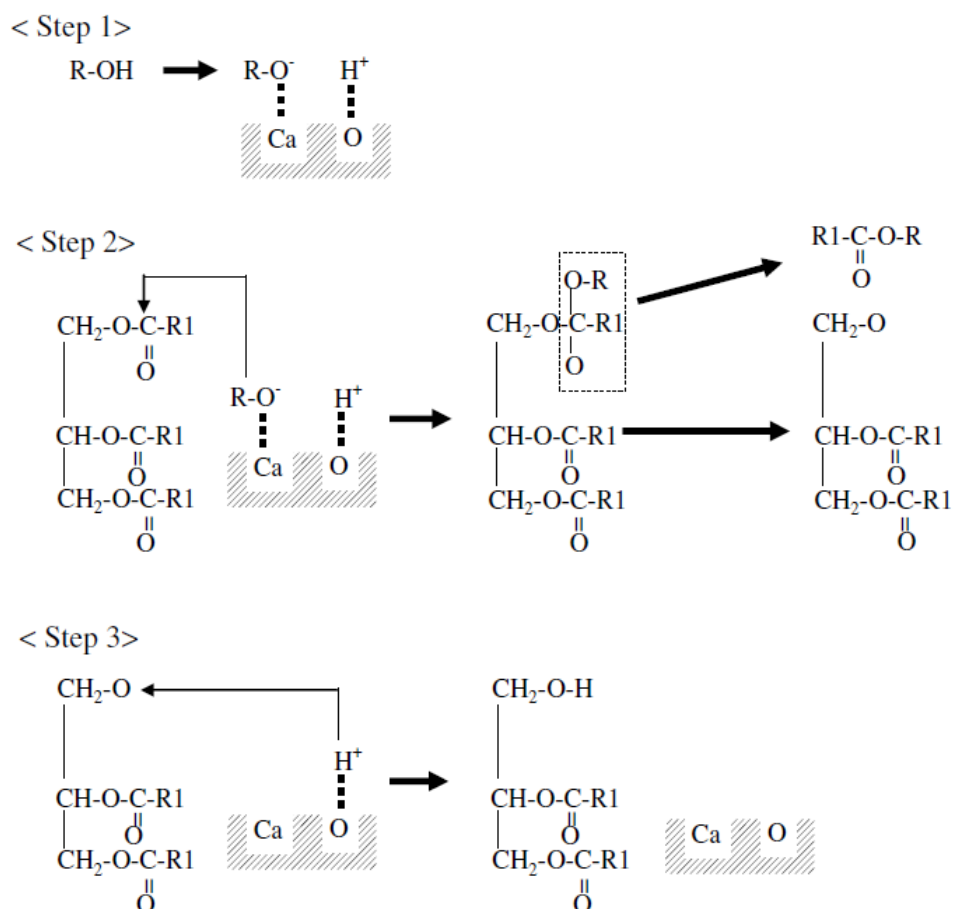


Figure 2.6: CaO as a heterogeneous base catalyst in transesterification (Masato et al, 2008).

2.4.5. Lipase catalyst

The most common enzyme used in transesterification is lipase. This catalyst is versatile, inexpensive and capable of catalyzing both hydrolysis and transesterification of triglycerides at very mild conditions (Goncalves et al., 1996; Huge-Jensen et al., 1988; Oliveira et al., 1997). Currently, the catalysts are being improved by the application of immobilized enzymes which improves stability and reusability (Cao, 2005; Salis et al.,

2008). Immobilized enzyme (IE) is an enzyme correlated to bioprocess without dissolving in the medium so that it can be maintained well, with its catalytic activity being reusable. Insolubility of (IE) provides a good product separation and purification of the product, while catalytic activity allows long life usage, storage and recycling of the catalyst. Chen et al. (2006) transesterified waste cooking oil using immobilized *R. oryzae* lipase in a reactor. Biodiesel yield above 88% was achieved at 40°C with immobilized lipase to oil weight ratio of 30%, methanol to oil ratio of 4%, reaction time of 30 hours and 1 bar pressure. Further studies on IE have been conducted by Mamoru et al., (2001) and Otavio et al., (2007).

2.5. Factors affecting transesterification process

2.5.1. Temperature

Transesterification can occur at either high or low temperature depending on the type of catalyst, the amount of alcohol to oil ratio and the reaction time. Some studies showed that a high temperature diminished residence molecular interaction time between methanol-oil-catalyst causing poor biodiesel yield and resulted in increased thermal degradation which completely reduce the yield (Wan Nor and Nor Aishah, 2011; Arumugam et al., 2009). Viscosity decrease with an increase in temperature therefore high optimum temperature will increase biodiesel flow property but reduce reaction time between reactants, methanol and catalyst. This can result in low biodiesel yield because a low mass transfer is subdominant at very high temperature. At low temperature the activation energy will not be enough to break the intermolecular chain boundaries between methanol and the oil thus causing a poor biodiesel yield, hence extended reaction time might be required to overcome the impact. Freedman et al. (1984) studied the effect of temperature on biodiesel at 32°C, 45°C and 60°C and a 94% methyl ester conversion was achieved at 60°C optimum temperature.

2.5.2. Catalyst

Optimum catalyst amount is essential in order to accelerate the rate at which transesterification occurs. The aim of using catalyst is to obtain optimum biodiesel yield without losing activity of the catalyst, especially when using heterogeneous catalyst. Some researchers have shown that solubility of some catalysts is affected by methanol ratios and this effect usually extends the forces of separation between glycerol and FAME to be inseparable. This is due to the fact that at high methanol to oil ratio a reversible reaction is favored and biodiesel yield is reduced (Lin et al., 2009). Triglyceride conversion into methyl ester is prone to insufficient amount of catalyst thus biodiesel yield decreases. High ratio of catalyst increase the amount of soap in the glycerol-FAME mixture and the process described as saponification is favoured due to the excess amount of catalyst than esterification of triglycerides (Leung and Guo, 2006).

2.5.3. Reaction time

One of the most essential variable in transesterification process is the reaction time. Realistically, it will be advantageous to produce FAME or biodiesel with greater conversion and improved biodiesel properties at a minimum optimum reaction time than obtaining greater conversion after long reaction period. A minimum energy usage and water treatment process are minimized at low reaction time, but extensive reaction time reduces biodiesel yield because of saponification process being favored, reverse transesterification which leads to the increase in soap formation and hydrolysis (Lu et al., 2010). Low reaction time beyond the optimum minimum reaction time leads to incomplete reaction and causes least molecular reaction of triglyceride with methanol to methyl ester thus reducing biodiesel yield.

2.5.4. Alcohol type

The success of biodiesel production has been possible by using different alcohols in converting triglyceride into glycerol and biodiesel. Generally, methanol alcohol is commonly used due to its structural formation consisting of short chain molecules, low cost and the biodiesel conversion is greater than when using butanol or ethanol alcohols (Zhou et al., 2003). Three moles of methanol are required to react with one mole of oil to achieve transesterification. A low methanol to oil ratio below optimum methanol to oil ratio condition leads to incomplete reaction and partial conversion of triglyceride into glycerol and biodiesel resulting in low biodiesel yield (Eevera et al., 2009). Incomplete reaction leads to poor separation between glycerol, biodiesel and some triglyceride. Excess methanol increment beyond its optimum leads to conversion of glycerol and biodiesel back to the initial reactants thus biodiesel yield is reduced and the equilibrium shifts to the left hand.

2.5.5. Free fatty acid and Water

Transesterification of high FFA (>3%) biodiesel feedstock is complex, especially when using homogeneous base catalyst and this leads to low biodiesel yield. However, the reduction in biodiesel yield will depend on the type of catalyst used. Homogeneous base alkaline catalyst such as KOH are said to react ± 4000 faster than homogeneous acid catalyst but when the feedstock contains significant amount of FFA, it becomes problematic to convert and react both feedstock or oil, methanol and FFA into glycerol and biodiesel (Furuta et al., 2004). During this process a saponification is greater which allows homogeneous base catalyst to react with FFA thereby producing soap which hinders the conversion of oil and methanol into biodiesel and separating the product is always difficult. The problem can well be solved by either esterification of the FFA with acid catalyst.

The choice of variables to study during experimental design depends on researcher and the objectives he wants to achieve. Zhang et al. (2003) has studied several biodiesel

production variables and gave the following typical reaction conditions shown in Table 2.4.

Table 2.4: Optimized and typical reaction variables for biodiesel production (Zhang et al., 2003).

Variables	NaOH base catalyst	H₂SO₄ acid catalyst
FFA (%)	<0.5	>4
Temperature (°C)	±65	±80
Catalyst (wt.%)	0.5-2	10
Methanol to oil ratio (wt.%)	6:1	50:1
Reaction time (hr)	1	4
FAME conversion (%)	+95%	+95%

2.6. Fuel properties of biodiesel

2.6.1. Viscosity and density

Viscosity is the ability of the liquids to flow under the influence of temperature. Viscosity and density plays important roles in any liquid phases, because the propensity of liquid to flow through nozzles and filters is determined by how dense and viscous the fuel is. The determination of viscosity can be correlated to the low temperature properties (pour point and cold filter plugging point), because often viscosity decreases with an increase in temperature and vice versa. Though it is possible to fuel engine with vegetable oil, transesterification produces a less viscous biodiesel than its mother oil.

High viscous fuel leads to poor fuel distribution in nozzles and the head of the distribution pump is reduced due to high viscosity. Increase in unsaturated bonds on

biodiesel provides a low viscosity compared to saturated biodiesel which is highly viscous (Knothe, 2005; Rodrigues et al., 2006). The better the optimization of pour and cloud point, the easier the flow of the fuel through the pumps and nozzles. Different feedstocks have different viscosities due to the amount of saturated and unsaturated bonds. Therefore, it is much easier to predict which fuel will have better flow ability by merely looking at the feedstock. However, it should be noted that all other biodiesel properties should be analyzed before making any conclusions.

2.6.2. Cloud point

Cloud point (CP) is the temperature at which the liquid forms a visible cloudy crystal solid as the fuel temperature decreases (Knothe, 2005). The CP is a crucial performance factor for all diesels especially during winter season in different regions. Solids and crystals form when the CP temperature is less than that required by the biodiesel standards and these formations reduce fuel distribution into the engine injectors and filters thus causing engine failure during start-up (Gog, 2007). Nevertheless, it is much difficult to predict maximum CP for any type of biodiesel. This is because different regions have different temperatures every season and climate changes for the following seasons will have impact on CP.

2.6.3. Flash point

Flash point is a measure of the temperature at which the vapours above the fuel become flammable (Gog, 2007). Engines are the core automobiles parts where the fuel is fully utilized, the engines become less efficient when the injector nozzles are blocked by small carbon particles deposited on the injectors during the starting of the engine (Orhan and Semih, 2004). The inefficiency of the engine injectors is associated with the increase in flash point (Raja et al., 2011). Depending on the biodiesel measuring standards, biodiesel has a minimum estimate flashpoint of approximately 120°C which is often above that required by other petrol diesel fuel and this flashpoint makes biodiesel to be less susceptible to fire hazards.

2.6.4. Pour point

Pour point is the capability of the fuel to flow at the lowest temperatures (Westbrook and LeCren, 2003). Most often liquid fuel will withstand only minimum temperatures in order to flow through the engine pipelines. At low temperature, solids and crystals are formed. Solids and crystals will grow and agglomerate, blocking fuel lines and filters and causing main engine operational problems (Refaat, 2009). Poor cold flow properties in biodiesel are related to feedstock that has high melting point due to long saturated fatty acids (Dunn, 2005).

2.6.5. Oxidation stability

Oxidation stability (OS) is a tendency of biodiesel to degrade when exposed to successive oxygen or light. Oxidation stability of biodiesel is related to how the fuel reacts after certain periods under different storage environment conditions. Biodiesel storage problem is aggravated by storing and exposing the biodiesel to direct air or direct light, exposing biodiesel to temperatures above ambient and the amount of unnecessary impurities and materials with catalytic effect on oxidation (Kapilan et al, 2009). Auto-oxidation of unsaturated fatty compounds increases, depending on the number and location of double bonds. The CH_2 positions allylic to double bonds in the fatty acid chains are those prone to oxidation (Knothe, 2009). The O-O bond breaks easily and forms radicals of the form HO, when hydroperoxides polymerize with other free radicals. Unwanted peroxides and hydroperoxides are formed during extended period of time which polymerize into resin at a later stage by forming aldehydes and ketones. The polymerization increases fuel density in engines and prevents a good fuel flow through injectors and filters (Knothe, 2009; Sendzikiene et al., 2005). Antioxidants are usually used to improve oxidation stability of biodiesel (Lian and Schwarzer, 1998).

2.6.6. Cetane Number

Cetane Number (CN) is a relative measure of the interval between the starting of injection and the onset of auto ignition of the fuel (Refaat, 2009). Low CN fuel often experience poor engine start-up, high carbon dioxide emission and creation of

unnecessary engine noise (Mohammed, 2009). Methyl ester with high unsaturated fatty acids chain reduces CN, which will affect engine operation (Knothe et al., 2003) and the more saturated the methyl ester chains, the higher the CN, which reduces engine delay time and combustion (Geller and Goodrum, 2004).

2.6.7. Cold filter plugging point

Cold filter plugging point (CFPP) is the lowest temperature where 20ml of fuel can be drawn through a 45 micron screen in 60 seconds with 200 mm of water (1.96 kPa) vacuum (Westbrook, 2003). The CFPP correlates a good relation of performance towards winter seasons in different regions. Reduced temperature below CFPP increase viscosity of the fuel and the fuel might not flow appropriately through the lines affecting performance of the engine (Moser, 2009). The CFPP is a reliable indicator of low temperature operability than PP or CP, because fuel with low content and adequate amount of solids renders engine operability due to filter plugging if CFPP is achieved (Dunn and Bagby, 1995; Dunn et al., 1996; Park et al., 2008).

2.6.8. Acid value

Acid value (AV) is the amount of potassium hydroxide (in mg) required to neutralize free fatty acids contained in gram of oil sample (Beare-Rogers et al., 2001). Acid value need to be specified to ensure proper fuel ageing properties especially during storage. When oxidation stability occurs, FAME start to degrade due to braking down of molecules, this increases fatty acid chains which will increase AV. Fuel with high acid content corrodes engine parts and creates deposits which block fuel injectors (Refaat, 2009).

2.6.9. Lubricity

Lubricity is the property of a lubricant that measures the reduction in friction of a lubricant (Gog, 2007). Poor lubricity of low-sulfur petrodiesel fuel requires additives or blending with another fuel of enough lubricity to regain lubricity (Knothe, 2005).

2.6.10. Heat of combustion

Heat of combustion is the thermal energy that is liberated upon combustion under standard conditions. Energy content of biodiesel is affected by oxygen and ratio of carbon to hydrogen (Moser, 2009). Other studies shows that energy content of fatty acid alkyl ester (FAAE) is directly proportional to chain length (Knothe, 2008; Moser, 2009), because longer chain FAAEs contain more carbons with similar oxygen atoms numbers. Fatty acid alkyl ester with low carbon to oxygen ratio has high energy content and increasing oxygen content of FAAE reduces energy content (Moser, 2009).

Table 2.5: Biodiesel properties requirements (Knothe, 2010; Lopez et al., 2008).

TEST PROPERTY	USA TEST METHOD	USA (ASTM 6751-08) LIMITS	RSA TEST METHOD	RSA (SANS 1935) LIMITS
Free glycerin (wt.%)	D6584	0.020	EN14105 EN1406	0.02 max
Flash point (°C)	D93	130 min	ISO 3679	120 min
Acid number (mg KOH/g)	D664	0.80 max	E14104	0.50 max
Cloud point (°C)	D2500		-	-
Water and sediment (% volume)	D2709	0.05 max	ISO12937	0.05 max
Total Sulfur (wt.%)	D5453	0.05 max	ISO20846 ISO20884	0.05 max
Copper strip corrosion	D130	No. 3 max	ISO2160	Class 1 max
Oxidation Stability			EN14112	6 min
Phosphorus (wt.%)	D4951	0.0010	EN14107	0.0010
Kinematic Viscosity @ 40 °C (mm ² /s)	D445	1.9 – 6.0	ISO3104	3.5 – 5.0
Sulfated ash (wt.%)	D874	0.020 max	ISO3987	0.020 max
Distillation temperature (°C)	D1160	360 °C max, at 90% distilled	N/A	-
Carbon residue (wt.%)	D4530	0.050 max	ASTMD1160	0.30 max
Cetane number	D613	47 min	ISO5165	51 min
Total glycerin (wt.%)	D6584	0.240	EN14105	0.25 max

2.7. Biodiesel characterization techniques

2.7.1. Chromatography

Biodiesel producers measure and analyze the final transesterification product which is methyl esters according to the applicable standards. The standards are often provided by application of different equipment used in gaining detailed understanding of the behavior of methyl esters under different conditions. Different chromatographical techniques have been developed to analyze biodiesel these include: gas chromatography (GC), thin layer chromatography/flame ionization detector (TLC/FID), and high performance liquid chromatography (HPLC) (Marcos et al., 2008). The first method for monitoring methyl and butyl esters was developed by Freedman et al. (1984b) using soybean as a transesterification source. Glycerides analysis and quantification of transesterification reaction mixture was performed using TLC/FID with latroscan. The results showed that minimum individual components were separated using butyl soyate, but classes of compounds were still able to be analyzed. The analysis time was minimal, 30 samples could be analyzed in 2 to 3 hours, however the method showed lower accuracy, sensitivity to humid material and the cost of the instrument is high (Freedman et al., 1984a; Cvengros and Cvengrosova , 1994). Gas chromatography (GC) is the most widely applied technique in biodiesel analysis studied with detection methods such as flame ionization detector (FID).

The ability of GC to quantify minor components obtained in biodiesel analysis makes it more beneficial over other methods (Knothe, 2006). Technical factors which affect GC analysis include: baseline drift, coinciding signals and ageing of standards (Knothe, 2006). TLC/FID was first developed to replace column chromatography which had long response time of results (Hamilton, 1998). Another study by Cvengros and Cvengrosova (1994) using TLC /FID was employed to correlate bound glycerol content to acyl conversion determined by GC. The results showed that the acyl conversion to methyl esters was greater than 96% and the amount of bound glycerol was greater than 0.25 wt.%. The most essential concentrations of biodiesel such as FAME, glycerol and fatty

acids are generally analyzed chromatographically either by gas chromatography (GC) or high-performance liquid chromatography (HPLC). High-performance liquid chromatography analysis is not widely applied in biodiesel characterization, but its analysis time is shorter than GC and derivatization of samples is omitted (Marcos, 2008). High-performance liquid chromatography technique is more appropriate for analyzing blended biodiesel than GC.

2.7.2. Thermal stability and Spectroscopic technique

Thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA) are becoming extremely vital technique for supplying data that can be useful in the establishment of thermal stability of biodiesel (Conceicao, 2007) and characterization of biodiesel (Dantas et al, 2007). TGA is a technique used to characterize thermal stability of compounds by measuring changes in its physicochemical properties expressed as weight change as a function of temperature (Coats and Redfern, 1963). The development of spectroscopic techniques to analyze transesterification was first introduced by Gilbard et al. (1995). Nuclear Magnetic Resonance spectroscopy (NMR), Near Infra-Red (NIR) and Fourier Transforms are the most widely used spectroscopic methods for transesterification analysis. NMR analysis on transesterification was found to be simpler and faster than the GC, but its maintenance cost was very high (Marcos, 2008). Two types of NMR have been developed to determine the yield of transesterification product, the proton nuclear magnetic resonance ^1H NMR (Morgenstern et al, 2006) and the ^{13}C NMR carbon-13 nuclear magnetic resonance (Dimmig et al., 1999). Degree of fatty acid unsaturation in methyl esters was determined using ^1H NMR in transesterification of soybean oil (Morgenstern et al., 2006).

2.8. Catalyst Characterization

2.8.1. Fourier Transform Infrared Spectroscopy

The advancement of technology today has incorporated Infrared and good background of reflection mechanism to determine structures of solids and liquids by using technique such as Fourier Transform Infrared (FTIR). Functional group, structural bonding and chemical properties of solids and liquids can be well determined and measured using the FTIR quantitative technique (Russell and Fraser, 1994). This method is suitable for monitoring structural changes because it requires small quantity of sample for analysis and it is possible to conduct in situ process for physiological conditions (Braiman and Rothschild, 1988). Furthermore, the introduction of infrared has increased the capability of FTIR to detect and analyse micron levels of the samples and identification of chemical and biological samples (Da-Wen, 2009).

2.8.2. Brunauer-Emmett-Teller

Generally, solid catalysts are porous in nature and the porosity develops often during catalyst preparation. Solids total surface area increase due to the amount of porosity available as compared to external surface area (Leofanti et al., 1997). Commonly, solid catalysts have a specific surface area between 1 and 1000 m²/g and external specific surface area in the range 0.01-10 m²/g (Leofanti et al., 1997). Brunauer-Emmett-Teller (BET) is a technique used to determine specific surface area of solid materials catalysts.

2.8.3. X-Ray Diffraction

Catalysts are made of different structures, which develop the surface area of catalysts. X-ray diffraction (XRD) is the main technique used to determine bulk structure and active sites of the catalysts. Active sites in heterogeneous catalysts are usually located on the solid surface, the bulk structure plays an important role, because most of the

catalysts characteristics depend on it (Giovanni, 1998). XRD can be well used to determine Intra-lattice crystallographic porosity parameters in microporous material, physical/morphological features (Crystallite size), identify and quantize crystalline phases of a material (Giovanni, 1998).

2.8.4. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a technique used to analyze and image microstructures of materials such as catalyst, clay, etc. (Saka, 2012). This method helps to qualitatively examine surface texture of material. The characterization resolution of the images can vary up to 10 nm and it can be possible to evaluate relative surface texture heights using a single SEM technique (Stachowiak et al., 2004). SEM has greater advantages over other microscopic techniques for topographical examination because it has a greater focus point to determine large surface areas of specimen and spatial resolution (Devaney et al., 1977). Micrographs of surface fractures using SEM can be achieved by using secondary emitted electrons which are most commonly used due to their high reliability in presenting topographical features and back-scattered electrons which are used to determine the compositional mean of the surface fractures (Hatch, 1984).

2.9. Statistical analysis

2.9.1. Response surface methodology

Response Surface Method (RSM) is a combination of mathematical and a statistical technique used in developing, improving, and optimizing processes and is often used to assess factors affecting the process in both interacting and non-interacting experiments (Ramsay, 2001). This method was primarily developed by Box and Wilson in 1951. Using this statistical tool it is much easier to develop models from the experimental data, and computer simulation is one of the approaches used in constructing models based on

experimental observations (Priya, 2009; Jacquez, 1998). RSM has two primary features which are the experimental design and the method of analysis (Box, 1954; Davies, 1960). RSM engrosses three techniques or methods in its application (Myers and Montgomery, 2002) which are: (a) Statistics of experimental design, in which two level factorials or fractional factorial are used, (b) Regression modeling method and (c) Optimization methods. Demirkol et al. (2006) reported the success of using lipase of Lipozyme (*Rhizomucormiehei*) for the methanolysis of refined soybean oil with methanol to give methyl ester. Response Surface Method based on a three level, three-factor (variables) face-centered cube design was used for the optimization of methanolysis. The independent variables studied were enzyme to oil weight ratio, oil to methanol molar ratio, and reaction temperature. Response of methyl ester content of 76.9% was produced and critical conditions of the process were concluded to be 2.37 methanol to oil ratio, 50°C, and 0.09 enzyme to oil weight ratio.

It is helpful to use one of the common first-order or second-order designs (such as the factorial or composite designs) with response surface methods to generate good conclusion on the experimental observation.

Jae-Saeob, (2005) designed procedure of RSM as follows:

- i. Experimental design to achieve sufficient and dependable response measurement.
- ii. Second order mathematical modeling with best fits.
- iii. Minimum and maximum responses values at optimum experimental variables.
- iv. Develop 2 D or 3 D plots with all direct and interacting effects of variables.

Response Surface Method is on the idea that several process variables affect the process and the method will determine the influence of these variables on the objective function/response function.

Assume that all variables are measurable, the response (y) will be as follows (Montgomery, 2005):

$$y = f(x_1, x_2, x_3, \dots, x_k) + \varepsilon \quad (1)$$

Equation (1) represent empirical model known as response surface model. The function f represents true response function, $x_1, x_2, \text{ and } x_k$ represent controlled variables (independent factors), and ε symbolizes variability not accounted for in true response. Assume that ε is a statistical error. Since the development of suitable approximation of f can be done by estimating first, second or n-order polynomials, therefore first order model will be represented by:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_k x_k \quad (2)$$

This equation (2) is known as multiple linear regression model. β_i represents unknown parameters or regression coefficients and β_0 is the model constant.

If the independent variables (x_1, x_2) contact with each other during the process, then equation (2) will have a contact function in its original form of equation (3):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \dots \beta_k x_k + \sum_{i < j} \sum_{i=2}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 \quad (3)$$

where ($x_1 x_2$) is the contact term and $\beta_{11}, \beta_{22},$ are the quadratic coefficients. If the application of first order fails, then it will be appropriate to introduce second order model (two factors, i.e. $k = 2$) which will be represented by equation (4):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 \quad (4)$$

The shape of the surface representing the quadratic model is determined by the coefficients (β_i) and these coefficients together with the quadratic nature makes the model to be sufficient for most practical application (Ching, 2008). It has been reported that second order model is mostly preferred in RSM because it is easy to estimate the β parameters model, the least squares method is used and there is extensive experiential practicality. Again, RSM indicates that second order models can solve real response surface problems and second order model is flexible and different functional forms is obtained and is closer to a true response surface (Myers and Montgomery, 2009). Practically the following situations might occur during experiments (Ching, 2008):

- (a) Experimental data may vary.
- (b) Independent variables may fall outside optimum conditions or points.
- (c) Dependable variables may be disaffected by one or more variables used in the experimental design.

Further again in physical experiments ambiguity is due to errors of measurements, while in computer experiments ambiguity is due to poor iterative process from numerical noises, rounding-off errors and discrete presentation of physical phenomena (Giunta et al., 1996; Toropov et al., 1996). First-order orthogonal designs, central composite designs (CCD) and spherical designs are suitable for experimental response fitting in RSM.

2.9.2. Design of Experiments

Engineers often perform and conduct various experiments in order to obtain optimum conditions for their experiments by determine the effects of either single or multiple variables. Method such as one-factor-at-a-time, which varies one variable at a given time while keeping other variables constant, can be used to determine the effect of single parameter on the experiments (Frey and Wang, 2006). But this method can be time consuming because of few experimental runs at a time, recent development has proved that Design of Experiment (DoE) method is more efficient when varying several

variables simultaneously at a time. Design of experiments was discovered in 1920s by Sir Ronald A. Fisher (Antony, 2003). DoE is a systematical method that is used to estimate optimum number of experiments which can consecutively satisfy dual criteria of minimum number of experimental runs and large enough sample size to maintain statistical importance (Mason et al., 1989; Montgomery, 1984; Thompson, 1982). Determination of the relationship between independent variables and the response (output) variable can be well studied using this method.

2.10. Types of DOE

2.10.1. Central Composite Design (CCD)

One of the most important design methods of constructing a second order model with central composite is called Central Composite Design (CCD). CCD is generally utilized for systems with potential interactions effect(s) between variables (Mason, 1989; Montgomery, 1984; Thompson, 1982). CCD constitutes 2^K factorial points with n or C_0 central point and $2K$ axial points. The number of experiments (N) required for CCD development is given by $N = 2^K + 2K + C_0$. Axial points are used to estimate quadratic terms, center point is used to estimate the magnitude of the experimental error (Myers and Montgomery, 2002) and factorial points are used to estimate interaction terms (Prasanphanich, 2009). Normally the variables are coded according to the experimental design levels and these levels can be represented by -1, 0 and +1 (high, medium and low levels) respectively.

2.10.2. Box-Behnken Design (BBD)

Box-Behnken Design (BBD) was developed by Box and Behnken, it provides three levels of rotatable or nearly rotatable second order designs based on three levels incomplete factorial designs (Box and Behnken, 1960). The design has proved that the experimental number (N) developed for BBD conforms to $N = 2K(K - 1) + C_0$ (where k is number of

factors and C_0 is the number of central points) (Andre' and Siuli, 2010). Box-Behnken Designs are said to be more economical and useful when it is expensive to perform large sets of experimental runs that are time consuming and financially expensive. During experiments extreme conditions may occur which will lead to unacceptable results or biased conclusions and these can be avoided by using BBD method (Ferreira et al., 2007).

2.10.3. D-optimal design

A design is considered to be D-optimal when it minimizes the volume of the scattered ellipsoid for estimates of regression equation coefficients (Mark and Anderson, 2005). The D-optimal design technique can be used to create a model of minimum number of points at a given accuracy (Unal, 1998). In the D-optimal design procedure design point sets (simulation runs) are selected from a larger set of candidate points, based on minimization of the determinant of the matrix $(X'X)^{-1}$ or, equivalently, maximization of the determinant $(X'X)$ (Mark and Anderson, 2005). The design points based on the D-optimal design technique will lead to minimization of the variance associated with the estimates of model coefficients.

$$V(\beta) = \delta^2 (X'X)^{-1} \quad (5)$$

$V(\beta)$ is the variance related to the estimates of the coefficients β in the model, X is the D-optimal design matrix, δ^2 is the error variance, X' is the transpose and $(X'X)^{-1}$ is the information matrix. The fitting quality can be improved by minimizing the information matrix (Ramsay and Clark, 2001).

2.10.4. Plackett–Burman Design (PBD)

Plackett–Burman Design (PBD) allows determination of the effect of variables with a minimum number of experiments especially if number of controlled variable (k) is large. Unfortunately, PBD does not yield estimates of the extent or type of interaction between variables (Motola and Agharkar, 1992). This method is more economical than the first order 2^k factorial design and its number of experiments (N) is given by $N = K + 1$ (Andre' and Siuli, 2010).

2.10.5. Taguchi

Taguchi's technique is important in selecting orthogonal array (OA) which helps to determine optimum levels for each experimental variable in experiments and determine the significance of each variable on the process (Kaladhar et al., 2011). Again, OA in Taguchi can easily determine smallest number of experiments and OAs are determined by the number of factors and levels considered in the process. The main purpose of Taguchi technique is to determine control factor settings that create acceptable responses despite natural environmental and process variability (SAS, 2008). The unique aspects of Taguchi's approach are the use of noise and signal factors, inner and outer arrays, and signal-to-noise ratios. The control factors, used to tweak the process, form the inner array. The noise factors, associated with process or environmental variability, form the outer array and signal-to-noise ratios are functions of the observed responses over an outer array (SAS, 2008).

2.10.6. One factor method

One-factor-at-a-time method varies one variable at a given time while keeping others constant. This method is suitable when estimation of effect of main factors of individual experiment is required, but the method cannot determine interactions between experimental factors nor provide a guarantee of identifying the optimal factor settings (Daniel et al., 2003). Again, the method is discouraged because the analysis conclusion

is not general, it requires more runs, and the optimal settings of factors might be overlooked (Box et al., 1978; Czitrom, 1999; Logothetis and Wynn, 1994; Wu and Hamada, 2000).

2.10.7. References

Agarwal, A.K., 2005. Experimental investigations of the effect of biodiesel utilization on lubricating oil tribology in diesel engines. *Journal of Automobile Engineering* 219, 703-713.

Ali, Y and Hanna, M.A., 1994a. Alternative diesel fuels from vegetable oils. *Bioresource Technology* 50, 153-163.

Ali, Y and Hanna, M.A., 1994b. Physical properties of tallow ester and diesel fuel blends. *Bioresource Technology* 47, 131-134.

Andre', I.K and Siuli, M., 2010. Response surface methodology. *WIREs Computation Statistics* 2, 128-149.

Antony, J., 2003. *Design of Experiments for Engineers and Scientists*. Elsevier, Oxford, UK.

Arumugam, S., Kien, Y.C., Paolo, F., Francis, K., Sergey, Z., and Stanislav, M., 2009. Catalytic Applications in the Production of Biodiesel from Vegetable Oils. *Chem Sus Chem* 2, 278-300.

Aurelien, V., Alexandre, L., Zhong-Yong, Y., and Bao-Lian, S., 2007. Self-formation of hierarchical micro-meso-macroporous structures: Generation of the new concept "Hierarchical Catalysis". *Colloids and Surfaces. Physicochemical Engineering Aspects* 300, 70-78.

Baum, D.A., 1995. The comparative pollination and floral biology of baobabs (*Adansonia Bombacaceae*). *Annals of the Missouri Botanical Garden* 82, 322-348.

Baum, D.A., Small, R.L., and Wendel, J.F., 1998. Biogeography and floral evolution of baobabs (*Adansonia Bombacaceae*) as inferred from multiple datasets. *Systematic Biology* 47, 181-207.

Beare-Rogers, J., Dieffenbacher, A., and Holm, J.V., 2001. *Lexicon of Lipid Nutrition*. International Union of Pure and Applied Chemistry Joint Committee of International Union of Nutritional Sciences and Iupac Commission on Food. *Pure Applied Chemistry* 73, 685-744.

Billaud, F., Dominguez, V., Broutin, P., and Busson, C., 1995. Production of hydrocarbons by pyrolysis of methyl esters from rapeseed oil. *Journal of American Oil Chemists' Society* 72, 1149-1154.

Box, G. E. P., 1954. *Biometrics*. McGraw-Hill Book, New York, USA.

Box, G. E. P., Hunter, W. G., Hunter, J. S., 1978. *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*. John Wiley and Sons, New York, USA.

Box, G.E.P and Behnken, D.W., 1960. Some new three-level designs for the study of quantitative variables. *Technometrics* 2, 455-475.

Box, G.E.P and Wilson, K.B., 1951. On the experimental attainment of optimum conditions. *Journal of the Royal Statistical Society* 13, 1-45.

Braiman, M.S and Rothschild, K.J., 1988. Fourier transform infrared techniques for probing membrane protein structure. Review. *Biophysics Biophysical Chemistry* 17, 541-570.

Burger, A. E. C., de Villiers, J. B. M., and Du Plessis, L. M., 1987. Composition of the kernel oil and protein of the marula seed. *South African Journal of Science* 83, 733-735.

Canakci, M and Van Gerpen, V.J., 2001. Biodiesel production from oils and fats with high free fatty acids. *American Society of Agricultural Engineers* 44, 1429-1436.

Cao, L., 2005. Immobilized enzymes: science or art? *Current Opinion in Chemical Biology* 9, 217-26.

Carruthers, V., 2000. The Wildlife of South Africa: A Field Guide to the Animals and Plants of the region. Struik publication, Cape Town, SA.

Chen, G., Ying, M., and Li, W., 2006. Enzymatic conversion of waste cooking oils into alternative fuel biodiesel. *Applied Biochemistry and Biotechnology* 132, 911-21.

Ching, T.H., and Jei-Fu, S., 2008. *Biocatalysis and Bioenergy*. John Wiley and Sons, Hoboken, New Jersey.

Christie, W.W., 1989. *Gas chromatography and lipids: a practical guide*. Oily Press, Ayr, Scotland.

Coats, A. W and Redfern, J. P., 1963. Thermogravimetric Analysis. *Analyst* 88, 906-924.

Conceição, M.M., Candeia, R.A., Silva, F.C., Bezerra, A.F., Fernandes Jr, V.J., and Souza A.G., 2007. Thermochemical Characterization of Castor Oil Biodiesel. *Renewable and Sustainable Energy* 11, 964.

Cvengros, J., and Cvengrosova, Z., 1994. Quality Control of Rapeseed Oil Methyl Esters by Determination of Acyl Conversion. *Journal of the American Oil Chemists' Society* 71, 1349-1352.

Czitrom, V., 1999. One-Factor-at-a-Time versus Designed Experiments. *The American Statistician* 53, 126-131.

Daniel, D.F., Fredrik, E., and Edward, M.G., 2003. A role for "one-factor-at-a-time" experimentation in parameter design. *Research in Engineering Design* 14, 65-74.

Dantas, M.B., Almeida, A.A.F., Conceição, M.M., Fernandes Jr, V.J., Santos I.M.G., Silva F.C., Soledade, L.E.B., and Souza, A.G., 2007. Characterization and kinetic compensation effect of corn biodiesel. *Journal of Thermal Analysis and Calorimetry* 87, 847.

Davies, O.L., 1960. *Design and Analysis of Industrial Experiments*. Hafner, New York.

Da-Wen, S., 2009. *Infrared Spectroscopy for Food Quality Analysis and Control*. Elsevier, Oxford, UK.

Demirbas, A., 2009. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management* 50, 14-34.

Demirkol, S., Aksoy, H.A., Tüter, M., Ustun, G., and Sasmaz, D.A., 2006. Optimization of enzymatic methanolysis of soybean oil response surface methodology. *Journal of the American Oil Chemists' Society* 83, 929-932.

Department of Agriculture, Forestry and Fisheries, 2010. Marula production guideline. Directorate Plant Production, Pretoria.

Devaney, J.R., Leedy, K.O., and Keery, W.J., 1977. Semiconductor Technology: Notes on SEM examination of microelectronic devices. National Bureau of Standards 35, Washington DC.

Dimmig, T., Radig, W., Knoll, C., and Dittmar, T., 1999. *Chemische Technik* 51, 326.

Dunn, R.O and Bagby, M.O., 1995. Low-temperature properties of triglyceride based diesel fuel: transesterified methyl esters and petroleum middle distillate/ester blends. *Journal of American Oil Chemists' Society* 72, 895-904.

Dunn, R.O., 2005. Cold Weather Properties and Performance of Biodiesel. In: Knothe, G., Van Gerpen, J., Krahl, J. *The Biodiesel Handbook*. American Oil Chemists' Society Press, Champaign, IL, USA.

Dunn, R.O., Shockley, M.W., and Bagby, M.O., 1996. Improving the low temperature properties of alternative diesel fuel: vegetable oil derived methyl esters. *Journal of American Oil Chemists' Society* 73, 1719-1728.

Eevera, T., Rajendran, K., and Saradha, S., 2009. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renewable Energy* 34, 762-765.

Ejikeme, P.M., Anyaogu, I.D., Ejikeme, C.L., Nwafor, N.P., Egbuonu, C.A.C., Ukogu, K., and Ibemesi, J.A., 2010. Catalyst in biodiesel production by transesterification process: An Insight. Review. *Electronic Journal of Chemistry* 7, 1121-1122.

Ferreira, S.L.C., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandao, G.C., Da-Silva, E.G.P., Portugal, L.A., Dos-Reis, P.S., Souza, A.S., and Dos-Santos, W.N.L., 2007. Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta* 597, 179-186.

Freedman, B., Butterfield, R.O., and Pryde, E.H., 1986. Transesterification kinetics of soybean oil. *Journal of American Oil Chemists' Society* 63, 1375-1380.

Freedman, B., Pryde, E.H., and Mounts, T.L., 1984a. Variables affecting yield of fatty ester from transesterified vegetable oils. *Journal of the American Oil Chemists' Society* 61, 1638-1643.

Freedman, B., Pryde, E.H., and Kwolek, W.F., 1984b. Thin-Layer Chromatography Flame-Ionization Analysis of Transesterification Vegetable Oils. *Journal of the American Oil Chemists' Society* 61, 1215-1220.

Frey, D.D. and Wang, H., 2006. Adaptive One-Factor-at-a-Time Experimentation and Expected Value of Improvement. *Technometrics* 48, 418-31.

Furuta, S., Matsushashi, H., and Arata, K., 2004. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catalysis Communications* 5, 721-723.

Garcia, C.M., Teixeira, S., Marciniuk, L.L., and Schuchardt, U., 2008. Transesterification of soybean oil catalyzed by sulfated zirconia. *Bioresource Technology* 99, 6608-6613.

Geller, D.P and Goodrum, J.W., 2004. Effects of specific fatty acid methyl esters on diesel fuel lubricity. *Fuel* 83, 2351-2356.

Gilbard, G.O., Bres, R.M., Vargas, F., Vielfure., and Schuchardt, U.F., 1995. Proton NMR Determination of the Yield of Transesterification of Rapeseed with Methanol. *American Oil Chemists' Society* 72, 1239-1241.

Giovanni, P., 1998. Characterization of heterogeneous catalysts by X-ray diffraction techniques. *Catalysis Today* 41, 251-259.

Giunta, A.A., Balabanov, V., Haim, D., Grossman, B., Mason, W.H., Watson, L.T., Haftka, R.T., 1996. Wing design for a high-speed civil transport using a design of experiments methodology. AIAA paper 96-4001-CP, Proceedings of 6th AIAA/NASA/ISSMO Symposium on Multidisciplinary Analysis and Optimization, Bellevue WA, Part 1, 168-183.

Goering, C.E and Fry, B., 1984. Engine durability screening test of a diesel oil/soy oil/alcohol microemulsion fuel. Journal of the American Oil Chemists' Society 61, 1627-1632.

Gog, A, Chintoanu, M., Roman, M., Gabriela, P., Luca, E., and Irimie, F.D., 2007. Biodiesel As Alternative Fuel – General aspects. Agricultura – StiinŃăsiptică 3-4, 24-25.

Goncalves, A.P.V., Lopes, L.M., lemos, F., Ramoa, R.F., Prazeres, D.M.F., Cabral, J.M.S., and Aires-Barros, M.R., 1996. Zeolites as support for enzymatic hydrolysis reactions. Comparative study of several zeolites. Journal of Molecular Catalysis B-Enzymatic 1, 53-60.

Hamilton, R.J., 1998. Lipid Analysis in Oils and Fats. Chapman and Hall, London.

Hatch, J.E., 1984. Aluminum: Properties and Physical Metallurgy. American Society for Metals, Ohio, USA.

Huge-Jensen, B., Galluzzo, D.R., and Jensen, R.G., 1988. Studies on free and immobilized lipases from Mucormiehei. Journal of American Oil Chemists' Society 65, 905-910.

Isono, Y., Nabetani, H., and Nakajima, M., 1995. Inter esterification of triglyceride and fatty acid in a micro aqueous reaction system using lipase-surfactant complex. Bioscience, Biotechnology and Biochemistry 59, 1632-1635.

Jacquez, J., 1998. Design of experiments. Journal of the Franklin Institute 335, 259-279.

Jae-Seob, K., 2005. Application of Taguchi and response surface methodologies for geometric error in surface grinding process. International Journal of Machine Tools and Manufacture 45, 327-334.

Jerekias, G and Ketlogetswe, C., 2011. Chemical Extraction and Property Analyses of Marula Nut Oil for Biodiesel Production. *Advances in Chemical Engineering and Science* 1, 96-101.

Kaladhar, M., Subbaiah, K.V., Srinivasa, R., and Narayana, R.K., 2011. Application of Taguchi approach and Utility Concept in solving the Multi-objective Problem when turning AISI 202 Austenitic Stainless Steel. *Journal of Engineering Science and Technology* 4, 55-61.

Kapilan, N., Ashok, T.P., and Reddy, R.P., 2009. Technical Aspects of Biodiesel and its Oxidation Stability. *International Journal of Chemical Technology Research* 1, 278-282.

Keim, G.I., 1945. Treating fats and fatty oils. U.S. Patent No. 2, 383-601, Awarded 28-August-1945.

Knothe, G., 2010. Analytical Methods for Biodiesel. USDA, ARS, NCAUR, Peoria, IL, 97-136.

Knothe, G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology* 86, 1059-1070.

Knothe, G., 2006. Analyzing Biodiesel, Standards and Other Methods. Review. *Journal of American Oil Chemists Society* 83, 10-15.

Knothe, G., 2008. Designer biodiesel: Optimizing fatty ester composition to improve fuel properties. *Energy Fuel* 22, 1358-1364.

Knothe, G., 2009. Improving biodiesel fuel properties by modifying fatty ester composition. *Energy and Environmental Science* 2, 759-766.

Knothe, G., Matheaus, A. C., and Ryan, T. W., 2003. Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. *Fuel* 82, 971-975.

Kurebgaseka, N., 2005. Report and research into Africa smoothie market and The Potential for Baobab Fruit Pulp as an Ingredient in Smoothies. *Phyto Trade Africa* 1, 1-35.

Leakey, R.R.B., 1999. Potential for novel food products from agro forestry trees. Review. Food Chemistry 66, 1-14.

Leofanti, G., Tozzola, G., Padovan, M., Petrini, G., Bordiga, S., and Zecchina, A., 1997. Catalyst characterization: characterization techniques. Catalysis Today 34, 307-327.

Leung, D and Guo, Y., 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Processing Technology 87, 883-890.

Lian, C and Schwarzer, K., 1998. Comparison of Four Accelerated Stability Methods for Lard and Tallow With and Without Antioxidants. Ibid 75, 1441.

Lin, L., Ying D., Chaitep, S., and Vittayapadung, S., 2009. Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy 86, 681-688.

Liu, X., He, H., Wang, Y., Zhu, S., and Ziao, X., 2008. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel 87, 216-221.

Logothetis, N and Wynn, H. P., 1994. Quality Through Design. Clarendon Press, Oxford, U.K.

Lopez, D.E., Goodwin, J.G., Jr, Bruce, D.A., and Furuta, S., 2008. Esterification and Transesterification Using Modified-Zirconia Catalysts. Applied Catalysis A 339, 7683.

Lu, P., Yuan, Z., Li, L., Wang, Z., and Luo, W., 2010. Biodiesel from different oil using fixed-bed and plug-flow reactors. Renewable Energy 35, 283-287.

Mamoru, I., Baoxue, C., Masashi, E., Takashi, K., and Surekha, S., 2001. Production of biodiesel fuel from triglycerides and alcohol using immobilized lipase. Journal of Molecular Catalysis B- Enzymatic 16, 53-58.

Marchetti, J.M., Miguel, V.U., and Errazu, A.F., 2007. Possible methods for biodiesel production. Renewable and Sustainable Energy 11, 1300-1311.

Marcos, R.M., Alessandra, R.P.A., Lucian, M.L., and Antonio, G F., 2008. Critical review on analytical methods for biodiesel characterization. Talanta 77, 593-605.

Mark, P.J.W and Anderson, J., 2005. "RSM simplified: optimizing processes using response surface method for design of experiment". Productivity Press, New York, USA.

Masato, K., Takekazu, K., Masahiko, T., Yoshikazu, S., Shinya, Y., and Jusuke, H., 2008. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. *Fuel* 87, 2798-2806.

Masjuki, H., Abdulmain, M.Z., Sii, H.S., Chua, L.H., and Seow, K.S., 1994. Biodiesel, an Alternate Fuel. *Journal of Energy, Heat Mass Transfer* 16, 295-304.

Mason, R.L., Gunst, R.F., and Hess, J.L., 1989. Statistical design and analysis of experiments - with application to engineering and science. John Wiley and Sons, New York, USA.

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

Mohammad, A and Syed, M.N., 2005. Taxonomic perspective of plant species yielding vegetable oils used in cosmetics and skin care products. *African Journal of Biotechnology* 4, 36-44.

Mohammed, H.C and Rafiq, A., 2009. Investigating Possibility of Using Least Desirable Edible Oil of *Eruca Sativa* L in Biodiesel Production. *Journal of Botany* 41, 481-487.

Montgomery, D.C., 1984. Design and analysis of experiment. John Wiley and Sons, New York, USA.

Montgomery, D.C., 2005. Design and Analysis of experiments. John Wiley and Sons, New York, USA.

Morgenstern, M., Cline, J., Meyer, S., and Cataldo, S., 2006. Determination of the Kinetics of Biodiesel Production Using Proton Nuclear Magnetic Resonance Spectroscopy (^1H NMR). *Energy Fuel* 20, 1350-1353.

Moser, B.R., 2009. Biodiesel production, properties, and feedstocks. *In Vitro Cellular and Development Biology-Plant* 45, 229-266.

Motola, S and Agharkar, S. N., 1992. Preformulation research of parenteral medications. New York, USA.

Myers, R.H., Montgomery, D.C., and Anderson-Cook, C.M., 2009. Response Surface Methodology: Process and Product Optimization Using Designed Experiments. John Wiley and Sons, New York, USA.

Myers, R.H and Montgomery, D.C, 2002. Response Surface Methodology: Process and Product Optimization Using Designed Experiments. John Wiley and Sons, New York, USA.

National Research Council., 2008. Lost Crops of Africa. The National Academies Press, Washington, D.C.

Oliveira, A.C., Rosa, M.F., Cabral, J.M.S., and Aires-Barros, M.R., 1997. Immobilization of *saccharomyces cerevisiae* cells and *Rhizomucormiehei* lipase for the production and extractive bio catalysis of ethanol. *Bioprocessing Engineering* 16, 349-353.

Orhan, A., and Semih, E., 2004. Carbon Deposit Formation from Thermal Stressing of Petroleum Fuels. *American Chemical Society Division of Fuel Chemistry* 49, 764.

Otavio, L.B., Juliana, V.B., Márcia, C.M.R.L., Denise, M.G.F., and Marta, A.P.L., 2007. Biodiesel Fuel Production by the Transesterification Reaction of Soybean Oil Using Immobilized Lipase. *Applied Biochemistry and Biotechnology* 136, 105-114.

Palgrave, C.K., 2002. Trees of Southern Africa. Struik publication, Cape Town, SA.

Palmer, E and Pitman, N.,1972. Trees of southern Africa. Briza publication, Balkema Cape Town.

Park, J.Y., Kim, D.K., Lee, J.P., Park, S.C., Kim, Y.J., and Lee, J.S., 2008. Blending effects of biodiesels on oxidation stability and low temperature flow properties. *Bioresource Technology* 99, 1196-1203.

Pioch, D., Lozano, P., Rasoanantoandro, M.C., Graille, J., Geneste, P., and Guida, A., 1993. Biofuel from catalytic cracking of tropical vegetable oils. *Oleagineux* 48, 289-291.

Prasanphanich, P., 2009. Gas Reserves Estimation by Monte Carlo Simulation and Chemical Flooding Optimization using Experimental Design and Response Surface Methodology. Thesis. 7.

Priya, D.J.I.S., 2009. The Energy Harvesting Technologies Book. Springer Science, New York, USA.

Raja, S.A., Robinson smart, D.S., and Lee, C.L.R., 2011. Biodiesel production from jatropha oil and its characterization. Research Journal of Chemical Sciences 1, 81-87.

Rakesh, S., Meet, S., Sinhala, S., and Amphora, R.K., 2007. Jatropha–Palm biodiesel blends: An optimum mix for Asia. Fuel 86, 1365-1371.

Ramsay, M., and Clark, W., 2001. Piezoelectric energy harvesting for bio-MEMS applications. Proceedings of SPIE 4332, 429.

Refaat, A.A., 2009. Correlation between the chemical structure of biodiesel and its physical properties. Review. International Journal of Environmental Science and Technology 6, 677-694.

Rodrigues, J.A., Cardoso, F.P., Lachter, E.R., Estevao, L.R.M., Lima, E., and Nascimento, R.S.V., 2006. Correlating chemical structure and physical properties of vegetable oil esters. Journal of the American Oil Chemists' Society 83, 353-357.

Russell, J.D and Fraser, A.R., 1994. Clay Mineralogy: Spectroscopic and Chemical Determinative Methods. Chapman and Hall, London, UK.

Saka, C., 2012. BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl_2 . Journal of Analytical and Applied Pyrolysis 95, 21-24.

Salis, A., Pinna, M., Monduzzi, M., and Solinas, V., 2008. Comparison among immobilised lipases on macroporous polypropylene toward biodiesel synthesis. Journal of Molecular Catalysis B-Enzymatic 54, 19-26.

SAS Institute Inc. 2008. JMP 8 Design of Experiments Guide. SAS Institute, Cary, North Carolina.

Schwab, A.W., Bagby, M.O., and Freedman, B., 1987. Preparation and properties of diesel fuels from vegetables oils. Fuel 66, 1372-1378.

Sedibe, M and Williams, J.T., 2002. Baobab. *Adansoniadigitata*. International Centre for Underutilized Crops. Crown publication, Southampton, UK.

Sendzikiene, E., Makareviciene, V., and Janulis, P., 2005. Oxidation Stability of Biodiesel Fuel Produced from Fatty Wastes. Polish Journal of Environmental Studies 14, 335-339.

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

Sii, H.S., Masjuki, H., and Zaki, A.M., 1995. Dynamometer Evaluation and Engine Wear Characteristics of Palm Oil Diesel Emulsions. Journal of American Oil Chemists' Society 72, 905-909.

Singh, A.K and Singh, D., 2010. Biodiesel production through the use of different sources and characterization of oils and their esters as substitute of diesel. Review. Renewable and Sustainable Energy 14, 200-216.

Sonntag, N.O.V., 1979. Reactions of fats and fatty acids. Bailey's industrial oil and fat products. Wiley and Sons, New York, USA.

Srinivasa, R.P and Gopalakrishnan, K.V., 1983. Esterified Oils as Fuel in Diesel Engines. Paper presented at 11th National Conference on I. C. Engines, I.I.T. Madras, India Proceedings, 78-84.

Srivastava, A and Prasad R., 2000. Triglycerides-based diesel fuels. Review. Renewable and Sustainable Energy 4, 111-133.

Stachowiak, G.W., Batchelor, A.W., and Stachowiak, G.B., 2004. Experimental Methods in Tribology. Elsevier, Oxford, UK.

Taft, R.W., Jr, Newman, M.S., and Verhoek, F.H., 1950. The Kinetics of the Base-catalyzed Methanolysis of Ortho, Meta and Para Substituted I-Menthyl Benzoates^{1,2}. Journal of American Oil Chemists' Society 72, 4511.

Tchoundjeu, Z., and Atangnan, A.R., 2006. Fruits for the Future 7: Ndjanssang Ricinodendronheudelotii. Southampton Centre for Underutilized Crops, Southampton, UK.

Thompson, D., 1982. Response surface experimentation. Journal of Food Processing Prevsery 6, 155-188.

Toropov, V.V., Van Keulen, F., Markine, V.L., De Boer, H., 1996. Refinements in the multi-point approximation method to reduce the effects of noisy responses, 6thAIAA/USAF/NASA/ISSMO Symposium on Multidisciplinary Analysis and Optimization, Bellevue WA, Part 2, 941-951.

Tsai, S.W., and Chang, C.S., 1993. Kinetics of lipase-catalyzed hydrolysis of lipids in biphasic organic-aqueous systems. Journal of Chemical Technology and Biotechnology 57, 147-154.

Unal, R., Lepsch, R., and McMillin, M., 1998. "Response surface model building and multidisciplinary optimization Using D-optimal designs", Proceedings of the 7th AIAA/USAF/NASA/ISSMO Symposium on Multidisciplinary Analysis and Optimization, 405-411.

USDA Foreign agricultural Service, 2011. Production, supply and distribution online. www.fas.usda.gov, accessed in May 2011.

Van Gerpen, J., 2005. Biodiesel processing and production. Fuel Processing Technology 86, 1097-1107.

Van Gerpen, J., Shanks, B., and Pruszko, R., 2004. Biodiesel Production Technology. Renewable Energy Laboratory Subcontractor Report. NREL/SR 510-36244, 1-110.

Van Wyk, B and Van Wyk, P., 1997. Field guide to trees of Southern Africa. Struik publication, Cape Town, SA.

Wan Nor, N.W.O., and Nor Aishah, S.A., 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and Bio energy 35, 1329-1338.

Weisz, P.B., Haag, W.O., and Rodeweld, P.G., 1979. Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysis. *Science* 206, 57-58.

Westbrook, S. R and LeCren, R., 2003. Automotive diesel and non-aviation gas turbine fuel, In: *Fuel and Lubricants Handbook: Technology, Properties, Performance and Testing*, Totten, G. E.

Westbrook, S.R., 2003. Fuel for land and marine diesel engines and for non-aviation gas turbines. *Significance of Tests for Petroleum Products*. ASTM International, West Conshohocken, PA.

World Watch Institute (WWI), 2006. Biofuels for Transportation, Global Potential and Implications for Sustainable Agriculture and Energy in the 21st Century. Report prepared for BMELV in cooperation with GTZ and FNR.

Wright, H.J., Segur, J.B., Clark, H.V., Coburn, S.K., Langdon, E.E., and Du-Puis, R.N., 1944. A report on ester interchange. *Oil and Soap* 21, 145-148.

Wu, C.F.J and Hamada, M., 2000. *Experiments: Planning, Analysis, and Parameter Design Optimization*. John Wiley and Sons, New York, USA.

Yang, L., Zhang, A., and Zheng, X., 2009. Shrimp Shell Catalyst for Biodiesel Production. *Energy and Fuels* 23, 3859-3865.

Yogesh, C.S and Singh, B., 2011. Advancements in solid acid catalysts for eco-friendly and economically viable synthesis of biodiesel. *Biofuels, Bioproducts and Biorefining* 5, 69-92.

Zabeti, M., Wan Daun, W.M.A., and Aroua, M.K., 2009. Optimization of the activity of CaO/Al₂O₃ catalyst for biodiesel production using response surface methodology. *General. Journal of Applied Catalysis* 366, 154-159.

Zhang, Y., Dube, M.A., McLean, D.D., and Kates, M., 2003. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology* 90, 229-240.

Zhou, W.Y., Konar, S.K., and Boocock, D.G.B., 2003. Ethyl esters from the single-phase base-catalyzed ethanolysis of vegetable oils. *Journal of the American Oil Chemists' Society* 80, 367-371.

Ziejewski, M., Kaufman, K.R., Schwab, A.W., and Pryde, E.H., 1984. Diesel engine evaluation of a nonionic sunflower oil-aqueous ethanol microemulsion. *Journal of American Oil Chemists' Society* 61, 1620-1626.

Chapter 3: Biodiesel Production from Baobab oil: An optimized Process

3.1. Abstract

This paper presents the study of the transesterification of baobab oil using sodium methoxide as a homogeneous catalyst. One factor at a time experimental design was used to study the effect of temperature, time, amount of catalyst and methanol to oil ratio on the transesterification of baobab oil. It was found out that Baobab oil contained less than 2% free fatty acids therefore a one-step transesterification was necessary. Optimum biodiesel production conditions were obtained at amount of catalyst (1 wt.%), reaction time (1 hr), methanol to oil ratio (30 wt.%), and reaction temperature (60°C). A 96wt.% of biodiesel yield was obtained. Important fuel properties such kinematic viscosity, density, flash point, pour point, cloud point and oxidation stability were measured and compared to the biodiesel properties in the European and American biodiesel standards (EN and ASTM standard). Results show that important fuel properties of biodiesel from baobab oil met both EN and ASTM standard.

Keywords: Biodiesel, Transesterification, Baobab oil, Homogeneous catalyst, Fuel properties

3.2. Introduction

In the recent decade the world is moving towards green technology by encouraging the usage of cleaner, safer and renewable energy. Among these energy sources, biodiesel is as a promising alternative fuel which can be used to replace fossil fuel such as diesel. Recently, there has been depletion of fossil fuels causing instability in the price of petroleum and also environmental concern due to air pollution caused by vehicles, therefore biodiesel is receiving increasing attention as an alternative, non-toxic, biodegradable, renewable diesel fuel produced from fresh or waste vegetable oils and animal fats (Yi-Hu and Shaik, 2005). Study conducted in Turkey showed that the fossil

fuel production peak has already been reached and indicated that fossil fuel production for Turkey will diminish in 2038 (Edigera et al., 2006; Edigera and Ajar 2007).

Biodiesel has been produced for many years mainly from waste vegetable oil, edible oils (sunflower, canola etc.) and non-edible oils (jatropha, karanja etc.) especially in European countries (Savita et al., 2007). Baobab (*Adansoniadigitata*) is a deciduous tree that grows naturally in many parts of South Africa, Botswana and Namibia (Leakey, 1999). Baobab tree can grow up to 15 meters height with its swollen bottle shaped like trunk. The tree produces a spherical yellowish shell fruit with internal edible small seeds covered with a pulp layer. Baobab can take up to 8 years to grow from a seed or can be easily grafted to reduce its growth years to 3 years. The extracted oil from baobab seeds can be used as an important feedstock for biodiesel production. Baobab products particularly derivatives of the fruit such as baobab seed oil and baobab fruit pulp are being exported overseas particularly to Europe, Canada and USA (Venter and Witkowski, 2010). The oil also contains active anti-oxidants (Vitamin E) which makes them useful active ingredients in cosmetic products (Peters, 1987). Since the oils contain anti-oxidants, these oils can be used in small amounts to improve the oxidation stability of other biodiesel such waste vegetable oil.

Although biodiesel has been produced using oil trees such as Manketti (Rutto and Enweremadu, 2011), there are no studies on the production of biodiesel from baobab oil. Thus, the main objective of this work is to produce biodiesel (FAME) from baobab oil using sodium methoxide as a homogenous catalyst. This study is aided with a statistical design using one factor at-a-time approach to determine the effect of temperature, amount of catalyst, time and methanol to oil ratio on the yield of biodiesel from baobab oil. Fuel properties of baobab methyl esters were compared with methyl esters from corn, shea butter and rubber oils and EN and ASTM standard.

3.3. Materials and Methods

3.3.1. Material

Table 3.1: List of materials.

MATERIALS	Potential supplier	
Baobab oil	Marula Pty (SA)	
CHEMICALS	Grade	Supplier
Potassium hydroxide	Analytical	Merck
Phenolphthalein	Analytical	Merck
Sodium methoxide	Analytical	Merck
Methanol	Analytical	Merck
Ethanol	Analytical	Merck
FAME standard	Analytical	Merck

3.4. Methodology

3.4.1. Determination of Baobab oil fatty acid

Determination of FFA% was performed procedurally. The oil was heated up to 100°C to remove the excess moisture in the oil. As water is immiscible in oil an increase in temperature caused the water bubbles to form above the oil level and evaporation occurred and finally the oil was cooled at room temperature. A gram of potassium hydroxide was dissolved in 1 liter distilled water using volumetric flask. A milliliter (1 ml) of oil was measured using a syringe in a 200 ml beaker and 10 ml of isopropanol was added. Few drops of phenolphthalein indicator were added into the mixture.

Approximately 50 ml burette filled with potassium hydroxide solution was used for titration, few drops of potassium hydroxide were added into the mixture while swirling the mixture until the color of the mixture became milky pink for at least 30 second. Amount of KOH ml used were recorded in order to calculate percentage FFA according to the equation given by Van Gerpen et al, (2004):

$$\% FFA = 0.546 \times KOH \text{ ml used in titration} \quad (6)$$

Baobab oil had less than 2% FFA and no esterification was required before transesterification.

3.4.2. Transesterification procedure of Baobab oil

In this study 70 g of baobab oil was measured in a round bottom flask and heated to the required temperature by using a hot plate fitted with magnetic stirrer and reflux condenser. Required amount of sodium methoxide was dissolve into methanol. The mixture was poured into the oil at a desired temperature while stirring at 400 rpm for a given reaction time. After the reaction conditions were reached, the mixture was transferred into 500 ml decanter funnel (separator funnel) and because glycerol (glycerin) has a higher density than biodiesel (methyl ester), it settled at the bottom of the funnel. The mixture was allowed to settle overnight to allow for complete separation. After draining off the glycerol, the methyl ester was washed gently with warm water to remove impurities and heated at 110°C to remove the remaining amount of water and methanol. One factor at a time experimental design was used to determine the effect of temperature, catalyst, and time and methanol ratio on biodiesel production. Figure 3.1 shows the experimental procedure followed during biodiesel production process.

3.4.3. Gas chromatography

The analysis of biodiesel products was done by a Varian gas chromatography (model number CP3400) equipped with an auto sampler (model no CP3800). A poly-siloxane coated column of length (30 m), i.d. (0.3 mm) and film thickness (0.53 μm) was used. The oven temperature was kept 160°C for 1 minute, increased at 4°C /minute up to 220°C and held for 17 minutes. The injector temperature was started at 250°C while the detector temperature was maintained at 280°C throughout the reaction. Nitrogen was used as a carrier gas. The samples were prepared using hexane as solvent and 1 μl were injected into the GC. Calibration standards were prepared from a known concentration methyl esters solution, and then the standards were used to plot a calibration curve which was used in the determination of the methyl esters. Fatty acid methyl ester (FAME) obtained from the gas chromatographic was used to calculate biodiesel yield. Biodiesel yield was calculated using the following equation:

$$\text{Biodiesel yield (wt.\%)} = \frac{\text{Amount of FAME (g)}}{\text{Amount of oil used (g)}} \times 100\% \quad (7)$$

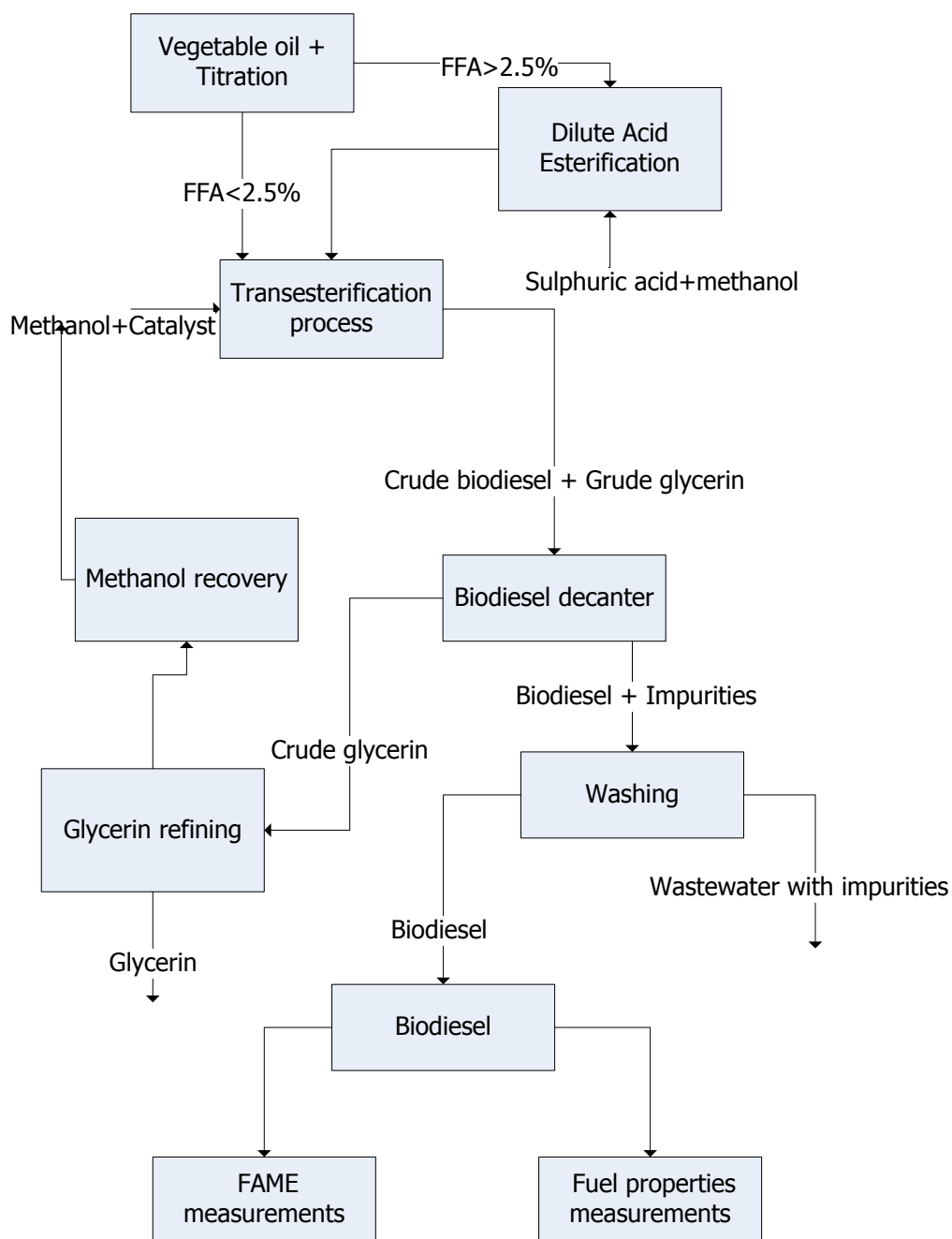


Figure 3.1: Experimental procedure followed during the research.

3.4.4. Characterization technique and Equipment.

Table 3.2: Equipment and uses.

Equipment	Use
Gas chromatography	To analyze fatty acids methyl ester
XRF and TGA	To determine the amount of active species on the prepared catalysts and used to determine the bulk composition of a catalyst
FTIR	To determine functional groups
SEM	To determine surface morphology
BET	To determine the surface areas of the catalyst

Table 3.3: Fuel properties and ASTM used (Van Gerpen, 2002).

Fuel properties	Biodiesel standards
Total and Free glycerol	ASTM D6584
Kinetic viscosity	ASTM D445
Oxidation stability	ASTM D7545
Cetane number	ASTM D613
Water and Sediment	ASTM D2709
Flash point	ASTM D93
Cloud point	ASTM 2500
Pour point	ASTM 2500
Acid value	ASTM D664

3.4.5. Characterization of fuel properties of biodiesel from Baobab oil

The biodiesel produced at optimal conditions was characterized according to the ASTM biodiesel standard. The Kinetic viscosity, density, flash point, pour point, cloud point and oxidation stability using D 445, D 4052, D 93, D 5985, D 2500 and D7462 ASTM standard respectively (ASTM, 2003).

3.5. Results and discussion

Table 3.4: Fatty acid composition (wt. %) of Baobab oil.

Fatty acid	Marula
Saturated	
Palmitic (C16:0)	20.96
Stearic C18:0	20.29
Eicosanoic C20:0	0.290
Monounsaturated	
Palmitoleic C16:1	-
Oleic C18:1	22.14
Polyunsaturated	
Linoleic C18:2	27.47
Alpha Linolenic C18:3	8.84

Fatty acids compositions of baobab oil used in this study are shown in Table 3.4. Baobab oil contains about 41.54% of saturated fatty acids and 58.46 % unsaturated fatty acids with few fatty acids not detected.

The effect of temperature on the biodiesel yield was studied at 30-70°C range as shown in Figure 3.2. The other process variables, amount of catalyst, methanol to oil ratio and reaction time were held constant at 1 wt.%, 30 wt.% and 1 hr respectively. The maximum biodiesel yield was obtained at a temperature of approximately 60°C and the biodiesel yield was 91 wt.%. The lowest biodiesel yield was obtained at 30°C; this is because the activation energy was not enough for triglyceride and methanol to react completely. Similar results were obtained by Kafuku and Mbarawa, (2010) and Prafulla and Shuguang, (2009). A decrease in the FAME yield was observed when the reaction temperature was above 65°C, this could be due to that methanol vaporizes at temperatures above 64.7°C. Temperature above 65°C resulted in poor interaction between triglyceride and methanol during transesterification which caused the yield to reduce.

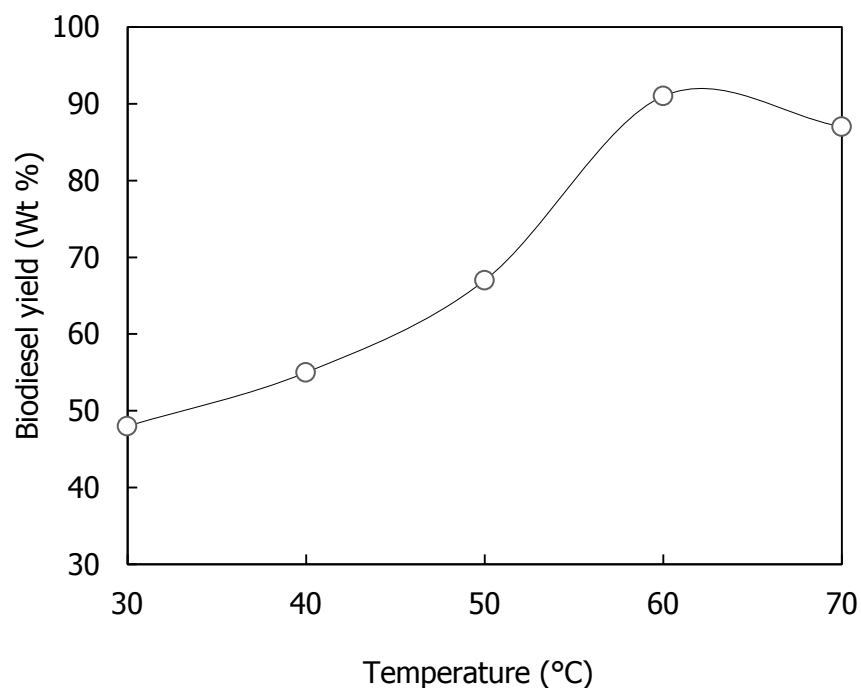


Figure 3.2: The effect of temperature on transesterification process of baobab.

The effect of methanol to oil ratio on the transesterification of baobab biodiesel from baobab oil was studied by varying the ratio 10-50 wt.% as shown in Figure 3.3. The other process variables, amount of catalyst, temperature and reaction time was held

constant at 1 wt.%, 60°C and 1 hr, respectively. The maximum biodiesel yield was obtained when methanol to oil ratio was 30 wt.% and yield was 91 wt.%. A significant decrease in biodiesel yield was obtained when methanol to oil ratio was increased above 30 wt.%, this is because more glycerides reacted but causing poor separation. High methanol ratios increase solubility and alter separation of glycerol, this causes the reverse reaction and thus this reduces the biodiesel yield (Lin et al., 2009).

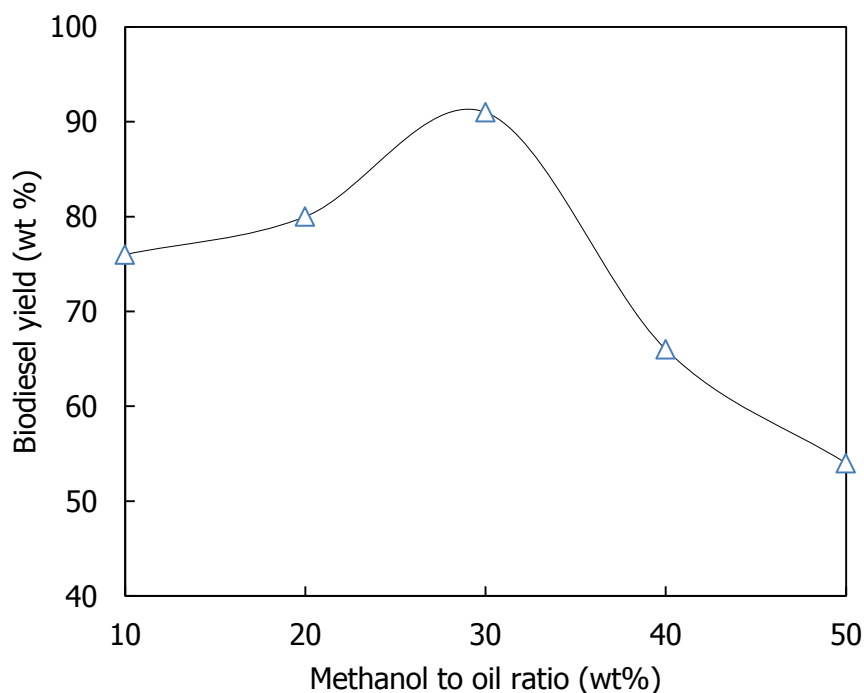


Figure 3.3: The effect of methanol to oil ratio on the transesterification process of baobab oil.

Transesterification of baobab oil was carried out at different reaction time between 0.5-2.5 hours, while keeping catalyst, temperature, and methanol ratio oil constant at levels of 1 wt.%, 60°C, and 30 wt.%. The maximum biodiesel conversion was 91 wt.% at 1 hr. The lowest conversion was about 60 wt.% obtained at 0.5 hr, this is because of inadequate time for transesterification reaction to take place. As the time increased

above 1 hr, a significant decrease in yield was observed. This is because reversible reaction occurs causing the formation of soap (Yun et al., 2011).

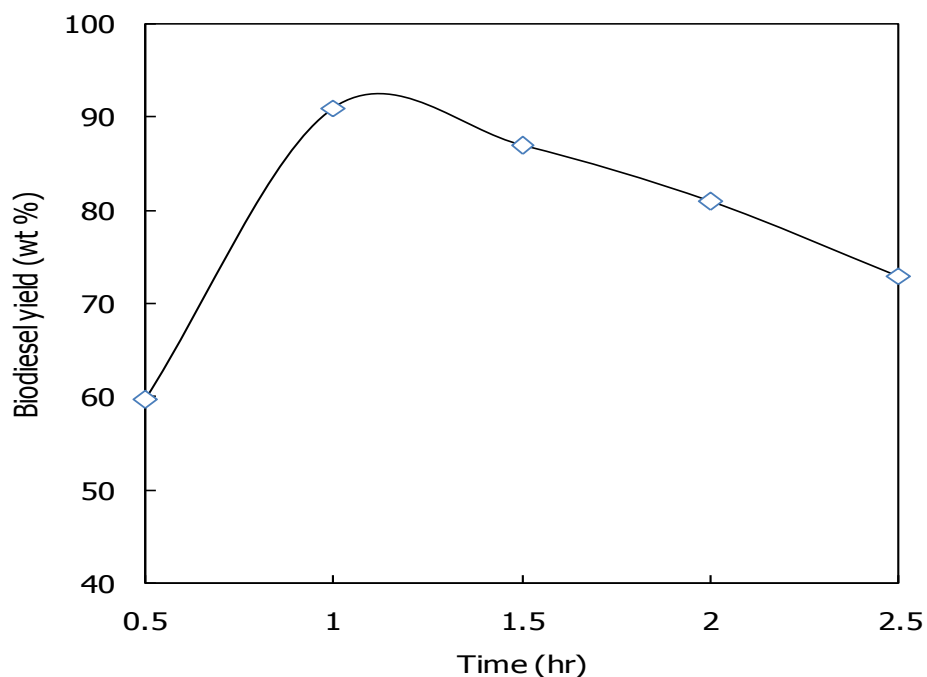


Figure 3.4: The effect of time on transesterification process of baobab oil.

The effect of sodium methoxide catalyst on biodiesel production was studied at various amounts of 0.5, 1, 1.5, 2, 2.5 wt.% catalyst as shown in Figure 3.5. The methanol to oil ratio, temperature and reaction time was held constant at 30 wt.%, 60°C and 1 hr respectively. The highest biodiesel yield was obtained at 1 wt.% catalyst, the conversion of 91 wt.%. As the catalyst is increased above 1 wt.% the biodiesel yield decreased and low biodiesel yield was obtained at 0.5 wt.% catalyst with 63 wt.% conversion. High catalyst amount increases glycerin viscosity which forms a gelled mixture which causes the formation of soap (Enciner et al., 2002).

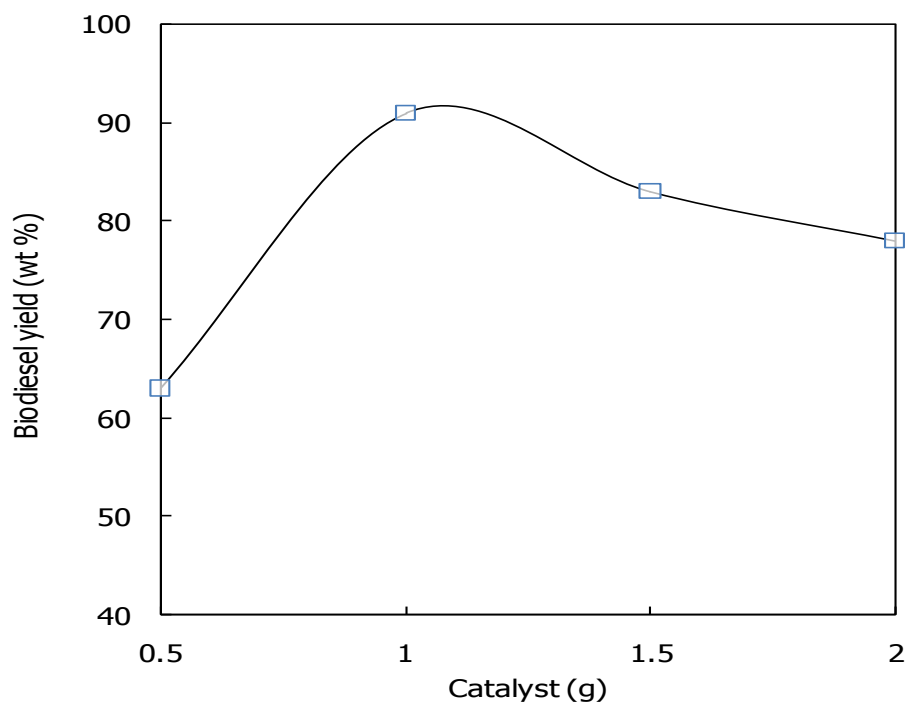


Figure 3.5: The effect of catalyst on the transesterification of baobab oil.

Baobab methyl esters (BaoME) fuel properties were compared with methyl esters (biodiesel) produced from shea butter (Enweremadu and Alamu, 2010), corn (Boulifl et al., 2010) and rubber (Ramadhas et al., 2005).

Kinematic viscosity of BaoME was found to be $4.46 \text{ mm}^2/\text{s}$, this viscosity is higher than that of shear butter ($4.42 \text{ mm}^2/\text{s}$), corn ($4.14 \text{ mm}^2/\text{s}$) and macadamia ($4.41 \text{ mm}^2/\text{s}$) methyl esters. However, all the methyl esters have met the values given in both ASTM D6751 and EN 14214 standards with maximum values given as $6 \text{ mm}^2/\text{s}$ and $5 \text{ mm}^2/\text{s}$, respectively. This is depicted in Table 3.5.

BaoME density ($882 \text{ Kg}/\text{m}^3$) is greater than that of shea butter ($877 \text{ kg}/\text{m}^3$), corn ($865 \text{ kg}/\text{m}^3$) and rubber ($874 \text{ Kg}/\text{m}^3$) methyl esters but all densities are within specified values provided in ASTM D6751 and EN 14214 standards of $860\text{-}900 \text{ kg}/\text{m}^3$.

Cloud point (CP) is related to the lowest temperature at which the liquid forms a visible cloudy crystal solid as the fuel temperature decrease (Knothe, 2005). Corn methyl ester (-5°C) has the lowest CP compared to baobab, shea butter and rubber methyl esters.

The cloud point of corn and macadamia methyl esters are less than those of BaoME (2°C), BaoME has a better CP than shea butter (6°C) and rubber (4°C) methyl esters.

BaoME has flash point of 192°C, it can be seen that flash point of BaoME is higher than that of Shea butter (171°C), corn (168°C) and rubber (130°C). All the flash points of given methyl esters are within and above minimum values given in both ASTM D6751 and EN 14214 standards which are 130°C and 120°C, respectively.

Pour point (PP) is related to the temperature below which the fuel will no longer flow (Dunn and Bagby, 1995). PP of BaoME is less than that of corn and rubber methyl esters. BaoME possess a good PP compared to shea and macadamia methyl esters, because BaoME fuel will no longer flow when the temperature is below -1°C, while shea butter will no longer flow when the temperature went below 3°C and 1°C, respectively.

The oxidation stability (OS) of BaoME was found to be 3.09 hours which correspond to the 3 hours minimum OS given in EN 14214 standards, but the OS is less than the 6 hours minimum provided in ASTM D6751 standards.

Table 3.5: Baobab methyl esters (BaoME) fuel properties were compared with methyl esters (biodiesel) and EN and ASTM standard.

Parameter	Shea Butter	Corn	Rubber	Baobab	ASTM D6751-02	EN 14214
Kinematic viscosity 40 °C (mm ² s ⁻¹)	4.42	4.14	5.81	4.46	1.9-6.00	3.5-5.0
Density at 25 °C (kg m ⁻³)	877	865	874	882	860-900	860-900
Flash point (°C)	171	168	130	192	>130	>120
Pour point (°C)	3	-6	-8	-1	-15-10	-
Cloud point (°C)	6	-5	4	2	-3-12	-
Oxidation stability (hr)	-	-	-	3.09	> 6	> 3

3.6. Conclusion

Based on the experimental results obtained, it can be concluded that production of biodiesel from baobab oil is possible via a one-step transesterification process using sodium methoxide as a homogenous catalyst. The optimum conditions required for the production of biodiesel from baobab oil are: reaction temperature of about 60 °C, amount of catalyst at 1.0 wt%, reaction time at 60 min and amount of methanol in the oil at 30 wt%. The optimum conversion of biodiesel from baobab oil was at 96 wt%. Results show that important fuel properties of biodiesel from baobab oil met both EN and ASTM standard.

3.7. Reference

Boulifl, N.E., Bouaid, A.M., Martinez M., and Aracil, J., 2010. Process optimization for biodiesel production from corn and oxidative stability. *International Journal of Chemical Engineering* 2010, 1-9.

Dunn, R.O and Bagby, M.O., 1995. Low-temperature properties of triglyceride based diesel fuel: transesterified methyl esters and petroleum middle distillate/ester blends. *Journal of American Oil Chemists' Society* 72, 895-904.

Edigera, V.S. and Akar, S., 2007. ARIMA forecasting of primary energy demand by fuel in Turkey. *Energy Policy* 35, 1701-1708.

Edigera, V.S., Akar, S., and Ugurlu, B., 2006. Forecasting production of fossil fuel sources in Turkey using a comparative regression and ARIMA model. *Energy Policy* 34, 3836-3846.

Enciner, J.M., Gonzalez J.F., Rodriguez, J.J., and Tajedor, A., 2002. Biodiesels fuel from vegetable oils: transesterification of *Cynaracardunculus* L. oils with ethanol. *Energy Fuels* 16, 443-450.

Enweremadu, C.C. and Alamu, O.J., 2010. Development and characterization of biodiesel from shea nut butter. *International Agrophysics* 24, 29-34.

Kafuku, G. and Mbarawa, M., 2010. Biodiesel production from *Croton megalocarpus* oil and its process optimization. *Fuel* 89, 2556-2560.

Knothe G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology* 86, 1059-1070.

Leakey, R.R.B., 1999. Potential for novel food products from agro forestry trees. *Food Chemistry* 66, 1-14.

Lin L., Ying D., Chaitep, S., and Vittayapadung, S., 2009. Biodiesel production from crude rice bran oil and properties as fuel. *Applied Energy* 86, 681-688.

Peters, C.R., 1987. *Ricinodendronrautaneii* (Euphorbiaceae): Zambezian wild food plant for all seasons. *Economical Botany* 41, 494-502.

Prafulla, D and Patil, S.D., 2009. Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel* 88, 1302-1306.

Ramadhas, A.S., Jayaraj, S., and Muraleedharan, C., 2005. Biodiesel production from high FFA rubber seed oil. *Fuel* 84, 335-340.

Rutto, H.L., Enweremadu, C. C., 2011. Optimization of Production Variables of Biodiesel from Manketti Using Response Surface Methodology. *International Journal of Green Energy* 8, 768-779.

Savita K., Saxena R.C., Ajay, K., Negi, M.S., Bhatnagar, A.K., Goyal, H.B., and Gupta, A.K., 2007. Corrosion behavior of biodiesel from seed oils of Indian origin on diesel engine parts. *Fuel Processing Technology* 88, 303-307.

Van Gerpen, J., Shanks, B., and Pruszko, R., 2004. Biodiesel Production Technology. Renewable Energy Laboratory Subcontractor Report. NREL/SR 510-36244, 1-110.

Venter, S.M and Witkowski, E.T.F., 2010. Baobab (*Adansoniadigitata* L.) density, size-class distribution and population trends between four land-use types in northern Venda, South Africa. *Forest Ecology and Management* 259, 294-300.

Yi-Hsu, J and Shaik, R.V., 2005. Rice bran as a potential resource for biodiesel. *Journal of Scientific and Industrial Research* 64, 866-882.

Yun, T.S., Lee, J.S., Lee, S.C., Kim, Y.J., and Yoon, H.K., 2011. Geotechnical issues related to renewable energy. *Journal of Civil Engineering* 4, 635-642.

Chapter 4: Biodiesel production from Marula oil using Perlite as a heterogeneous catalyst

4.1. Abstract

In this study biodiesel was produced from marula oil using modified perlite as a heterogeneous catalyst. The effect of experimental variables such as temperature, reaction time (hr), methanol to oil ratio (wt %), and amount of catalyst (g) on transesterification of marula oil to biodiesel were investigated. Using a central composite design (CCD) mathematical model was developed to correlate the experimental variables to the percentage of biodiesel yield. The catalyst was characterized using X-ray diffraction (XRD) and Brunauer-Emmett-Teller. The model shows optimum conditions for biodiesel production were found as follows: amount of catalyst of 3.46 grams, temperature 70.41 °C, methanol to oil ratio 29.86 wt.% and reaction time of 3.55 hr. A yield of 91.38% biodiesel was obtained. It was also possible to recycle the modified perlite up to three times. The XRD and BET surface area showed that there was a modification in the perlite structure. The results show that the important fuel properties of Marula biodiesel met the biodiesel ASTM standard properties.

Keywords: Biodiesel, Marula oil, Perlite catalyst, Transesterification, Response surface methodology, Fuel properties

4.2. Introduction

Biodiesel have been used in Asia, Europe and South Africa as a suitable fuel energy source to compete with fossil fuel. Biodiesel can be produced from non-edible oils and edible oils. Edible oils such as canola, soybean and corn have been used to produce biodiesel (Freedman et al., 1989). Moreover, non-edible oils such as *Jatropha curcas*, waste oils, Manketti and animal fats, have been used in the production of biodiesel (Leung and Guo, 2006; Wang et al., 2007; Alcantara et al., 2000). In Africa there are promising oil producing nut tress such as Marula, *Scelerocarya birrea*, and Manketti

which are deciduous in nature and are found in Southern Africa. Biodiesel have been produced from oil from Manketti nuts and found to be good as a diesel substitute (Leung and Guo, 2006).

In South Africa there are several oil producing trees such as Marula and Baobab that can be used as biodiesel sources but the exploration of these oils in biodiesel production is minimal.

Heterogeneous catalysts have shown to possess several potential advantages over homogeneous catalyst in transesterification process. Heterogeneous solid base catalyst such as calcium oxide has some advantages over homogeneous catalyst because the catalyst can be reutilized, has a tolerance of moisture and free fatty acids, is economically cheap, its insoluble in methanol, is non-corrosive and non-pollutant (Zabeti et al., 2009).

In the work of Soetaredjo et al. (2011), they developed a heterogeneous catalyst from calcined KOH/Bentonite blend, they found out that with 25% KOH loading produced biodiesel with the highest yield. The operating conditions were reaction time 3hr, amount of catalyst 3g, methanol to oil molar ration 6:1 and reaction temperature at 60 °C.

Perlites are widely used as filter media in food products, chemical and municipal systems the usage of this siliceous rock as catalyst support for transesterification process is minimal and extensive research is required to explore this usage. Perlite can be modified with other alkaline catalysts (potassium or sodium oxide) to generate catalytic support active sides of the solids that can be used as heterogeneous solid catalyst in transesterification process. Calcined perlite also contains traces of sodium oxide and potassium oxide that can act as catalyst.

Variables such as temperature, catalyst, reaction time and methanol to oil ratio on the biodiesel yield can be studied and optimized using statistical tool (design expert software) and the response surface methodology. Several optimization studies have been carried out in the production of biodiesel. Meher et al, (2006) found that the yield

of methyl ester from karanja oil under the optimal condition is 97–98%. Optimization of biodiesel production has been produced using response surface methodology with manketti oil, rapeseed oil, soybean oil and palm oil (Rutto and Enweremadu, 2011; Ghadge and Raheman, 2006; Uosukainen et al., 1999; Kansedo et al., 2009).

The objective of this study is to synthesise a perlite based catalyst by heterogenising with potassium hydroxide as homogeneous catalyst to produce biodiesel from marula oil.

4.3. Materials and Methods

Marula oil and Perlite were obtained from Marula Pty (Ltd) and Infigro Natural Technologies South Africa, respectively. Analytical grade methanol and potassium hydroxide were obtained from Rochelle Chemical Suppliers, South Africa. Fatty Acid Methyl Ester F.A.M.E Mix standard (C8-C24) catalogue number (18918.1 AMP) was obtained from the Sigma Chemical Co. Ltd.

4.3.1. Catalyst preparation

A calcined perlite was used as a heterogeneous catalyst. The impregnation of perlite with KOH solution was done by mixing necessary amount of perlite with KOH solution in a 250 ml round bottom flask equipped with a reflux condenser to reduce and retain any loss of methanol through evaporation. The KOH/perlite mixture was heated at 60°C using electrical hot plate equipped with a mechanical stirrer at speed of 600 rpm overnight. After the impregnation the catalyst was removed from the stirrer and heated at $\pm 400^\circ\text{C}$.

4.3.2 . Catalyst characterization

4.3.2.1. X-ray diffraction

The material was prepared for XRD analysis using a back loading preparation method. Two samples were scanned after addition of 20% Si for quantitative determination of amorphous content and micronizing in a McCrone micronizing mill. It was analyzed with a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert High score plus software. The relative phase amounts (weight %) was estimated using the Rietveld method.

4.3.2.2. Brunauer-Emett-Teller

Structural pores of perlite and modified KOH/perlite were obtained by measuring nitrogen adsorption/desorption isotherms using porosity and surface area analyzer. The samples were degassed under vacuum condition.

4.3.3. Gas chromatography

The analysis of biodiesel products was done using a Varian gas chromatography (model number CP3400) equipped with an auto sampler (model no CP3800). A poly-siloxane coated column of length (30 m), i.d. (0.3 mm) and film thickness (0.53 μ m) was used. Temperature of the oven was kept at 160°C for 1 minute, increased by 4°C /min until 220°C and was held for 17 minutes. The injector temperature was started at 250°C while the detector temperature was maintained at 280°C throughout the reaction. Nitrogen was used as a carrier gas. The samples were prepared using hexane as solvent and 1 μ l were injected into the GC. Calibration standards were prepared from a known concentration methyl esters solution, and then the standards were used to plot a calibration curve which was used in the determination of the methyl esters. Table 4.1

shows the composition of marula oil as compared to other vegetable oils. The biodiesel was calculated using the following equation:

$$\text{Biodiesel yield (wt.\%)} = \frac{\text{Amount of FAME (g)}}{\text{Amount of oil used (g)}} \times 100\% \quad (8)$$

Table 4.1: Fatty acid composition of Marula oil compared to other vegetable oils (wt.%)

Fatty acid	Marula	Palm	Jatropha	Soybean
Saturated				
Palmitic C16:0	10.2	36.7	14.2	11.3
Stearic C18:0	6.3	6.6	6.8	3.6
Eicosanoic C20:0	1.6	0.4	-	0.3
Monounsaturated				
Palmitoleic C16:1	1.1	0.1	1.1	0.1
Oleic C18:1	74.1	46.1	43.1	24.9
Polyunsaturated				
Linoleic C18:2	2.4	8.6	34.3	53.0
Alpha Linolenic C18:3	1.2	0.3	0.5	6.1

4.3.4. Fatty acid determination of Marula oil

The oil was heated up to 100°C to remove the excess moisture in the oil. As water is immiscible with oil, an increase in temperature caused the water bubbles to pop above oil level and evaporation occurred and finally the oil was cooled at room temperature. A gram of potassium hydroxide was dissolved in 1 liter distilled water using volumetric flask. A milliliter (1 ml) of oil was measured using a syringe in a 200 ml beaker and 10 ml of isopropanol was added. Few drops of phenolphthalein indicator were added into

the mixture. Approximately 50 ml burette filled with potassium hydroxide solution was used for titration, few drops of potassium hydroxide were added into the mixture while swirling the mixture until the color of the mixture became milky pink for at least 30 second. Amount of KOH ml used was recorded in order to calculate percentage FFA according to the equation given by Van Gerpen et al, (2004). Marula oil had about 7% FFA which is above recommended FFA amount (below 3%) and esterification process was required before transesterification. A 100 g and multiplied by 7% FFA of Marula oil and amount of methanol to be used was calculated according to:

$$\text{Amount of methanol} = 7 \times 2.25$$

Sulphuric acid was used to esterify the mixture and the amount of sulphuric acid required was calculated according to:

$$\text{Amount of sulphuric acid} = 7 \times 0.05$$

The mixture was heated at 60°C for an hour, and the mixture was poured into separating funnel and cool at room temperature. Two phases were found in the mixture, methanol was on top while the esterified oil was at the bottom of the funnel. Esterified oil was tapped out of the funnel and FFA determination was performed according similar procedure of marula oil above. Around 4% FFA was calculated and the method of esterification was repeated and finally around 2% FFA was present in the Marula oil and this allowed continuing with a normal transesterification process.

4.3.5. Transesterification of Marula oil

A known amount of Marula oil was measured in a 250 ml round bottom flask and heated at required temperature using electric magnetic stirrer. The stirring speed was kept constant for all the experiments at 350 rpm while temperature, methanol to oil ration, amount of catalyst and reaction time were varied according to the experimental design matrix generated using Design expert software. A known amount of KOH/perlite catalyst was added to a known amount of methanol, while heating the oil to a required temperature. The methanol-catalyst mixture was added to the oil and heated at required

reaction time. After the transesterification, the solution was removed and cooled at a room temperature. A vacuum pump was used to filter the catalyst from the biodiesel mixture and a 100 ml decanter was used to separate glycerol from biodiesel. Biodiesel was washed using distilled water to remove any excess glycerol and impurities in the biodiesel and finally heated at 110°C to remove excess water. Finally the biodiesel was collected for FAME analysis.

4.3.6. Characterization of Marula biodiesel fuel properties

Marula biodiesel was characterized and compared to ASTM biodiesel standard. Several biodiesel properties were measured using different methods/techniques and these include: density, by density meter at 25°C, flash point, according to D93 ASTM, kinematic viscosity by Red Wood Viscometer at a 40°C, cloud point and pour point by cloud and pour point apparatus according D2500 and D93 ASTM standards respectively and Gas chromatography for FAME analysis (ASTM, 2003).

Table 4.2: Typical chemical compositions of pure perlite from Infigro Natural Technologies.

CHEMICAL ANALYSIS	MASS PERCENTAGE (%)
Silicon dioxide	76.2
Aluminium oxide	12.1
Potassium oxide	4.8
Sodium oxide	3.4
Iron oxide	0.7
Calcium oxide	0.6
Magnesium oxide	0.1
Manganese oxide	0.1
Titanium oxide	0.1
Loss on ignition	1.9

4.3.7. Design of experiment

A Central Composite Design (CCD) was chosen for the experimental design to investigate the linear, quadratic, cubic and cross-product effects of the four experimental variables (temperature, amount of catalyst, reaction time and methanol to oil ratio) on the yield of fatty acid methyl ester (FAME). Design-Expert 6.0.6 statistical software was used to investigate and study the effect of process variable interactions and determine the optimum process conditions of producing biodiesel from Marula oil by using Response Surface Methodology. RSM was used to investigate the catalytic effect of KOH/Perlite on biodiesel yield. Response surface plots were analyzed using multiple regressions analysis obtained from the software. Four variables shown in Table 4.3 were studied and the range of the coded levels were obtained for temperature (x1), catalyst amount (x2), methanol to oil ratio (x3) and reaction time (x4). Each variable consisted of five different coded levels from very low (-2), low (-1), medium (0), high (1), very high (2). A full 2^3 factorial CCD design with two central points and eight star or axial points was employed. A full experimental design matrix is given in Table 4.4 with the number of experiments performed in triplicates to determine the replicable of the experiments. The response of the design experiments was taken as the FAME yield or biodiesel yield given as y. A quadratic model of biodiesel yield was obtained using least square mathematical method.

$$Y = \beta_0 + \sum_{j=1}^4 \beta_j X_j + \sum_{i,j=1}^4 \beta_{ij} X_i X_j + \sum_{j=1}^4 \beta_{jj} X_j^2 + \sum_{k,i,j=1}^4 \beta_{kij} X_k X_i X_j + \sum_{j=1}^4 \beta_{jjj} X_j^3 \quad (9)$$

Table 4.3: Levels of transesterification process variables employed

Variable	Coding	Units	levels				
			-2	-1	0	1	2
Temperature	x_1	°C	40	55	70	85	100
Amount of catalyst	x_2	g	2	2.75	3.5	4.25	5
Methanol to oil ratio	x_3	wt. %	10	20	30	40	50
Time	x_4	hr	2	2.75	3.5	4.25	5

Table 4.4: Central composite design of the experiments and FAME results

Experimental Variable					
Experiment no	Reaction Temperature (hr)	Amount of Catalyst (g)	Methanol to oil ratio (wt %)	Reaction Time (hr)	FAME (%)
	x_1	x_2	x_3	x_4	
E1	55	2.75	20	2.75	69.60
E2	85	2.75	20	2.75	65.28
E3	55	4.25	20	2.75	71.85
E4	85	4.25	20	2.75	75.21
E5	55	2.75	40	2.75	66.89
E6	85	2.75	40	2.75	74.62
E7	55	4.25	40	2.75	72.36
E8	85	4.25	40	2.75	74.26
E9	55	2.75	20	4.25	73.34
E10	85	2.75	20	4.25	76.15
E11	55	4.25	20	4.25	75.61
E12	85	4.25	20	4.25	69.25
E13	55	2.75	40	4.25	78.25
E14	85	2.75	40	4.25	74.30
E15	55	4.25	40	4.25	65.71
E16	85	4.25	40	4.25	68.31
E17	40	3.5	30	3.5	62.76
E18	100	3.5	30	3.5	65.43
E19	70	2	30	3.5	68.9
E20	70	5	30	3.5	66.41
E21	70	3.5	10	3.5	66.9
E22	70	3.5	50	3.5	65.21
E23	70	3.5	30	2	68.56
E24	70	3.5	30	5	68.47
E25	70	3.5	30	3.5	91.41
E26	70	3.5	30	3.5	91.79
E27	70	3.5	30	3.5	91.76
E28	70	3.5	30	3.5	91.04
E29	70	3.5	30	3.5	90.63
E30	70	3.5	30	3.5	91.47

4.4. Results and discussion

Figure 4.1 present the impregnation of KOH/perlite which was prepared according to the following ratios: 1:3, 1:4 and 1:6. Temperature, reaction time and KOH were kept constant at 60°C, 3 hr and 3 g, respectively. At 1:3 KOH/perlite ratio, biodiesel yield was very low (76%), this was due to high dominance of KOH catalyst over perlite which could have resulted in high formation of soap and reversible reaction which reduced the biodiesel yield. Biodiesel yield increased with increase in KOH/perlite ratio, the highest biodiesel yield (89%) was obtained at 1:6 ratio. Therefore experimental design was created based on this ratio of 1:6 KOH/perlite.

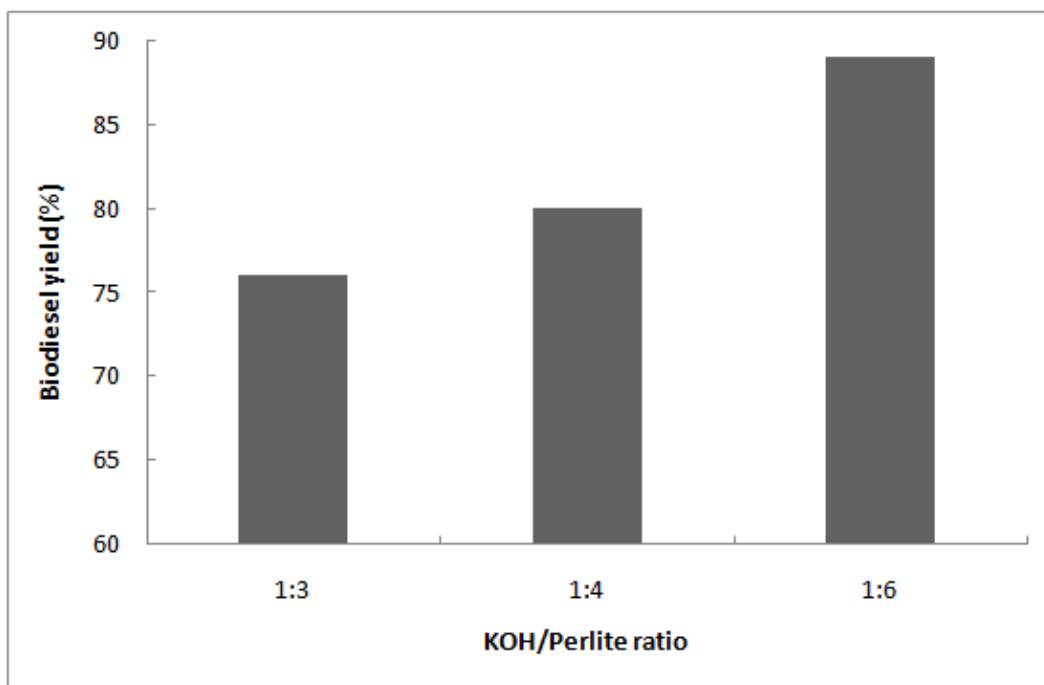


Figure 4. 1: Effect of KOH to perlite ratio.

4.4.1. X-ray diffraction

Figure 4.2 shows the XRD of unmodified perlite and modified perlite catalyst with KOH/perlite up to 1:6 ratio. It was observed that unmodified perlite diffraction peaks at 2θ were obtained at 25.39° , 33.00° , 35.99° and 41.97° . The XRD shows that the intensity patterns decreased when the amount of perlite was increased. The main dominant peaks were Cristobalite (SiO_2) at 21.93° , 36.12° , 31.46° and 41° and this is confirmed by the chemical composition of perlite shown in Table 4.2. Other compounds found were Akermanite ($\text{Ca}_2\text{MgO}_7\text{Si}_2$), Kalicinite $\text{K}(\text{CHO}_3)$ and Microcline (AlKO_8Si_3). The result shows that unmodified perlite and modified KOH/perlite at 1:3 ratio had similar XRD patterns and this can be due to good dispersion of KOH on perlite and the crystalline structure was maintained. But when the KOH/Perlite ratio was increased beyond 1:4, a new structure containing potassium and aluminum was formed which can be due to the loss of crystalline structure by poor dispersion of KOH on perlite and the structure become amorphous. Soetaredjo et al. (2011) has detailed and explained the effects of KOH/bentonite catalysts on transesterification of palm oil to biodiesel.

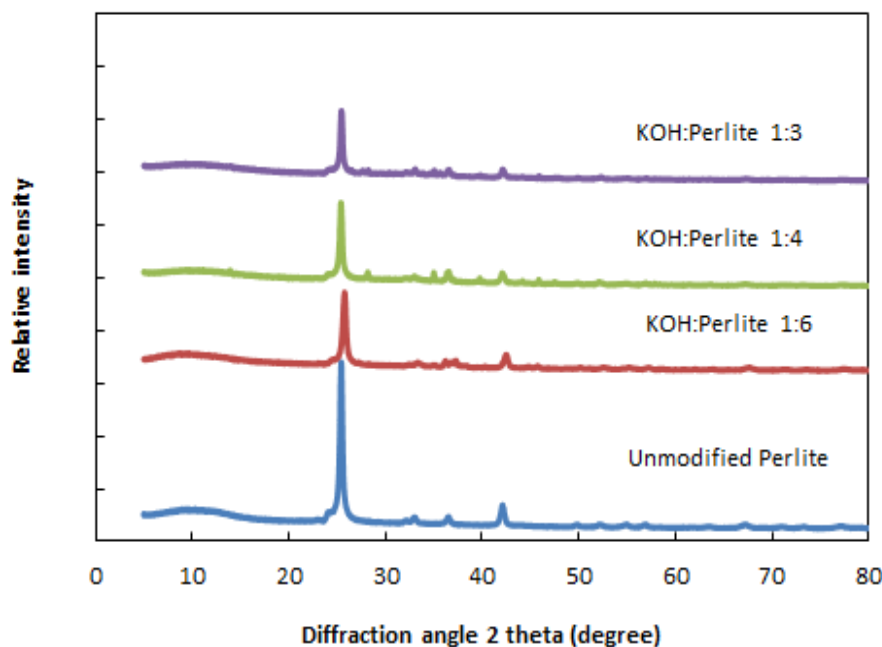


Figure 4. 2: XRD of pure perlite and modified perlite catalyst.

4.4.2. BET surface analysis

The isotherm adsorption/desorption shows that the pattern belongs to type 2 gas sorption isotherms which implies that perlite and modified perlite exhibit macroporous or nonporous solids greater than 50nm and no microporous solids exist in the structures which belongs to type 1 or Langmuir gas sorption isotherms. Similar Nitrogen sorption isotherms patterns had been presented by Tsai et al. (2011).

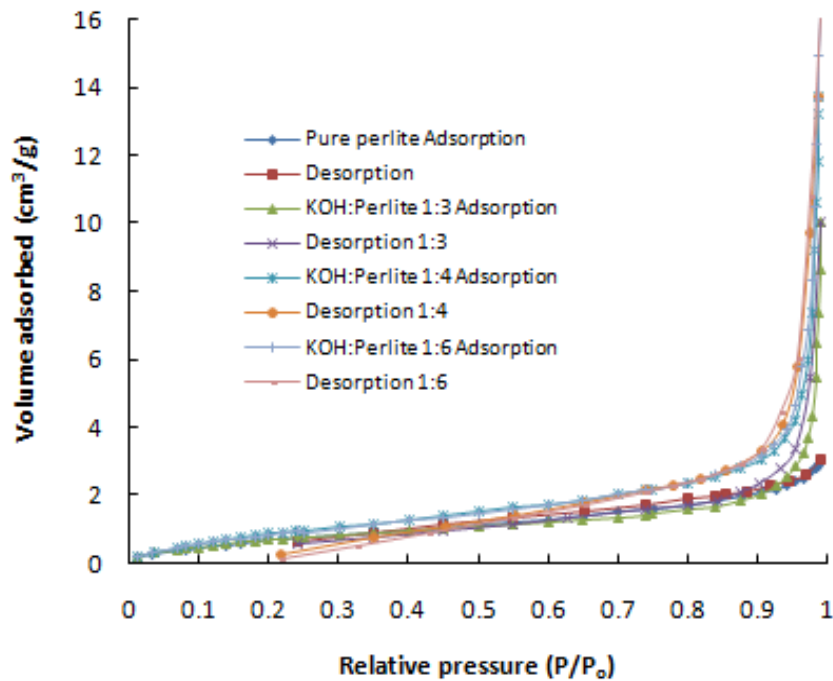


Figure 4. 3: Nitrogen adsorption/desorption isotherms of unmodified perlite and modified perlite with KOH up to 1:6 ratio of KOH/Perlite.

4.4.3. Regression model development

A final regression model using actual variables excluding the insignificant terms was developed and obtained using Fisher's Test as shown below:

$$Y = -395.99 + 3.83x_1 + 83.28x_2 + 3.88x_3 + 85.02x_4 - 0.026x_1^2 - 8.94x_2^2 - 0.054x_3^2 - 8.56x_4^2 - 4.28 \times 10^{-3}x_1x_2 + 5.33 \times 10^{-3}x_1x_3 - 0.075x_1x_4 - 0.174x_2x_3 - 4.49x_2x_4 - 0.12x_3x_4 \quad (10)$$

A negative sign on the terms indicates antagonistic effect, while a positive sign indicates a synergistic effect. Coefficient correlations were used to check the significant and quality of the model. The R^2 obtained from the experimental correlations was 0.9144 and this implies that only 0.0856 of the overall experimental variations cannot be explained by the model.

Analysis of variance (ANOVA) at 95% confidence level was used to confirm the sufficiency of the model as shown in Table 3. The quadratic model was tested to be significant as the theoretical $F_{0.05(14,15)}$ is much lower than the computed F value (2.46) (Montgomery, 2001). This indicates that the model can be used to predict Marula biodiesel yield. The quadratic term (x_1) had vast effect on Marula oil biodiesel yield than x_2 , x_3 and x_4 terms, while the interaction terms had little effect according to Table 4.5.

Table 4.5: ANOVA analysis of the regression model equation without insignificant terms.

Source	Sum of Squares	Degrees of freedom	Mean squares	of F-Test
Model	2357.61	14	168.4	11.44
x_1	3.46	1	3.46	0.23
x_2	4.91	1	4.91	0.33
x_3	1.03	1	1.03	0.07
x_4	4.74	1	4.74	0.32
x_1^2	961.58	1	961.58	65.32
x_2^2	694.23	1	694.23	47.16
x_3^2	809.01	1	809.01	54.95
x_4^2	636.16	1	636.16	43.21
x_1x_2	0.037	1	0.037	2.52E-03
x_1x_3	10.22	1	10.22	0.69
x_1x_4	11.51	1	11.51	0.78
x_2x_3	27.48	1	27.48	1.87
x_2x_4	102.26	1	102.26	6.95
x_3x_4	12.2	1	12.2	0.83
Residual	220.83	15	14.72	

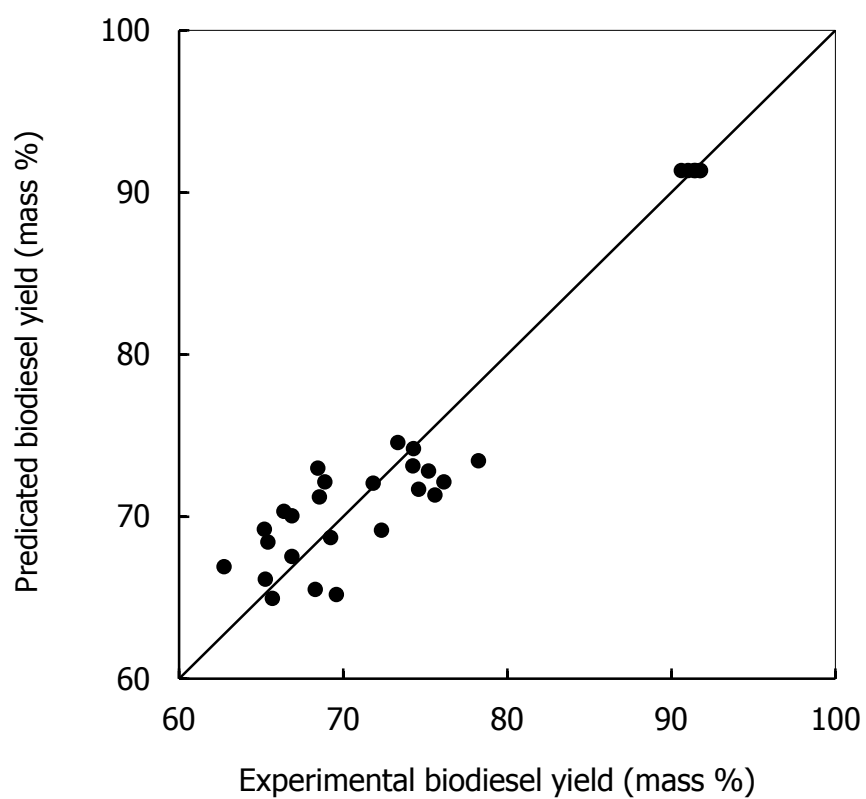
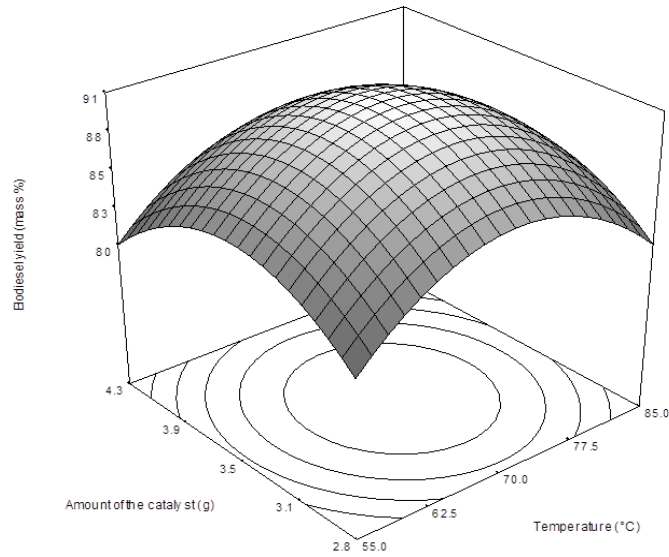


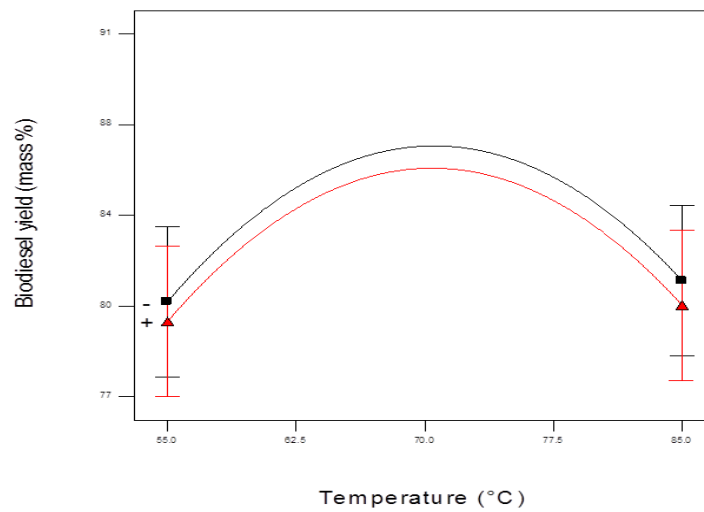
Figure 4. 4: Experimental versus Predicted biodiesel yield values.

Figure 4.4 shows the experimental versus predicted values by the regression model on biodiesel yield and the experimental data shows that it accurately fits the model. Therefore, the model accurately shows the description of the experimental results.

4.5. Effect of experimental variables on transesterification.



(a)

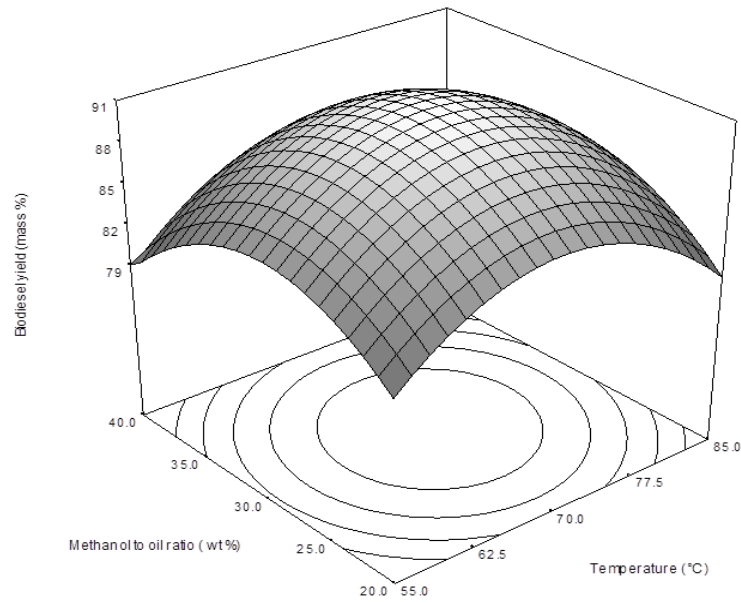


(b)

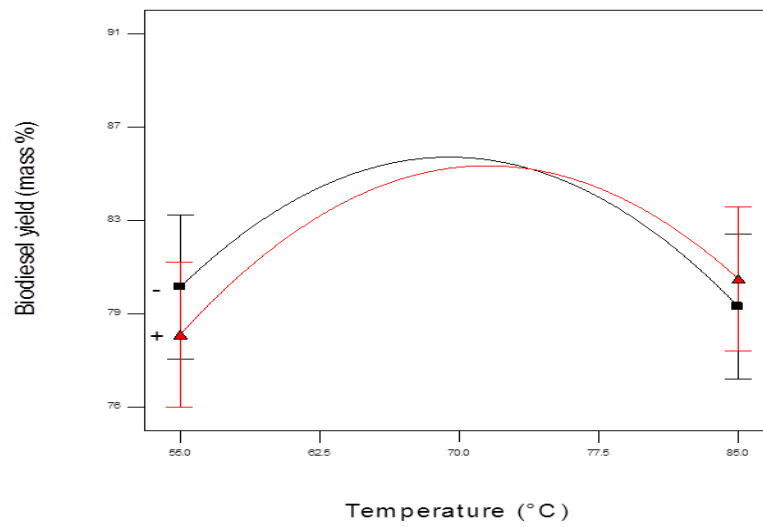
Figure 4. 5: Effect of catalyst and temperature on transesterification, (a) response surface and (b) two dimension plot with amount of catalyst held at (+) 2.75 g and (-) 4.25 g.

Figure 4.5 shows the effect of catalyst and temperature on transesterification of Marula oil, while reaction period and methanol to oil ratio were held at constant levels of 3.5 hr and 30 wt.% respectively. At high catalyst level the fatty acid methyl ester yield was low compared to the one obtained at a low catalyst level. High catalyst ratio increases the formation of more soap in the glycerol-FAME mixture and thus reducing the methyl ester yield (Leung and Gou, 2006). As shown in Figure 4.5, as the temperature increases the biodiesel yield increases to an optimum yield but decreases as the temperature increases beyond optimum, high temperature diminishes the residence molecular interaction time between the methanol-oil-catalyst causing thermal degradation and reduction of the biodiesel yield.

Figure 4.6 shows the effect of methanol to oil ratio and temperature on transesterification of Marula oil while reaction period and amount of catalyst levels were held constant at 3.5 hr and 3.5 g respectively. At low temperatures the biodiesel yield was low for both levels of methanol to oil ratio, but biodiesel yield increased as the temperature increased, however, at temperature above 73°C biodiesel yield decreased. High amount of methanol to oil ratio resulted in biodiesel yield reduction due to the occurrence of glycolysis reaction when glycerol and methyl esters are converted back to the initial reactants. However, it was observed that above 76°C the yield of methyl ester obtained at high methanol to oil ratio was greater than that obtained at low ratio, which is opposite to the previous statement that higher methanol to oil ratio reduces the biodiesel yield.



(a)



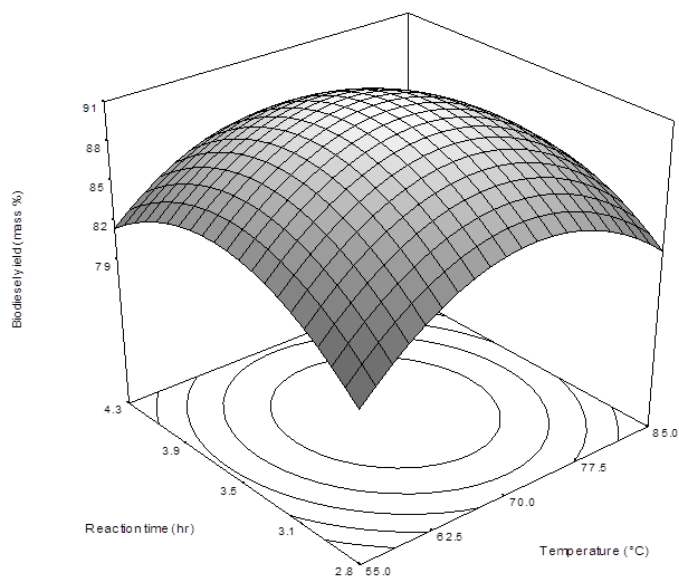
(b)

Figure 4. 6: Effect of methanol to oil ratio and temperature on transesterification, (a) response surface and (b) two dimension plot with methanol to oil ratio held at (+) 40 wt.% and (-) 20 wt.%.

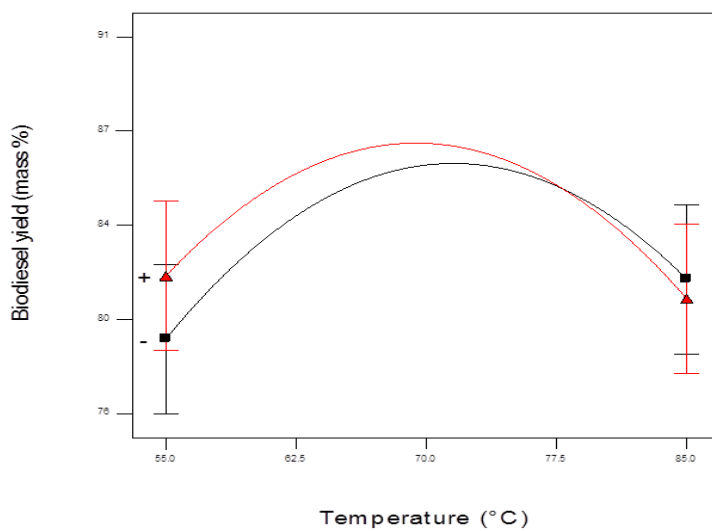
Figure 4.7 shows the effect of reaction time and temperature on transesterification of Marula oil while catalyst and methanol to oil ratio levels were held constant at 3.5 wt.% and 30 wt.%, respectively. At low temperature biodiesel yield was low for both levels of reaction time, as the temperature increased the biodiesel yield increased but decreased at about 73°C. Figure 4.7 shows that longer reaction period yielded more methyl esters, low reaction time leads to incomplete reaction and causes least molecular interaction of triglyceride with methanol reducing biodiesel yield. However, at temperature above 78°C longer reaction time reduces biodiesel yield, which contracts to the above mentioned conclusion, the reason could be excess reaction time increases the formation of more soap as the reaction is reversed.

Figure 4.8 shows the effect of reaction time and methanol to oil ratio on transesterification of Marula oil while temperature and amount of catalyst were held constant at 70°C and 3.5 g, respectively. At low levels of reaction time and methanol to oil ratio, biodiesel yield was low compared to biodiesel yield at high level of reaction time with low methanol ratio. As the methanol to oil ratio increases at both levels of reaction time biodiesel yield increased until optimum conditions of 30 wt.% methanol and 3.5 hr reaction time. A reduction in biodiesel was observed as the amount of methanol increased beyond optimum at both levels of reaction time.

Figure 4.9 shows the effect of methanol to oil ratio and amount of the catalyst on transesterification of Marula oil while temperature and reaction period levels were kept constant at 70°C and 3.5 hr, respectively. Generally, for both levels of methanol to oil ratio the biodiesel yield is lower at low amount of catalyst. As the catalyst increase the biodiesel yield decreased at approximately 3.4 g at high and low methanol to oil ratio respectively. The reduction in biodiesel is due to formation of more soap in the glycerol-FAME mixture. As seen in figure 4.9, higher amount of methanol to oil ratio reduced biodiesel yield significantly as the catalyst increases which is contrary at levels below 3.4 g as mentioned.

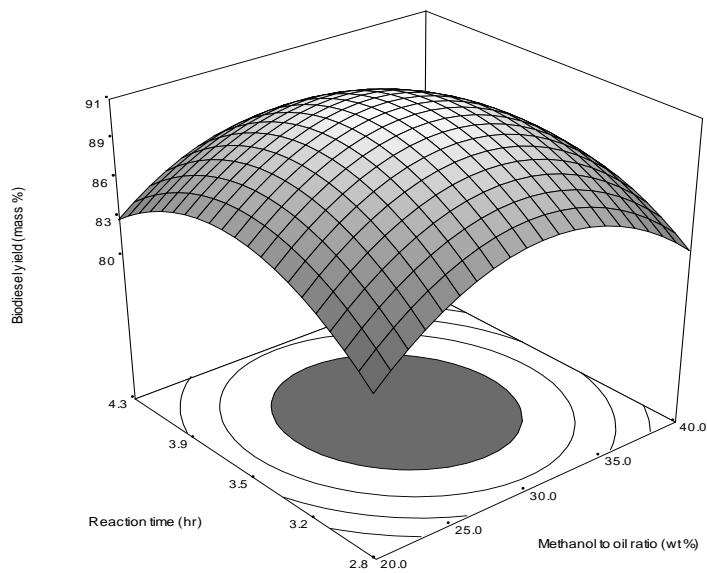


(a)

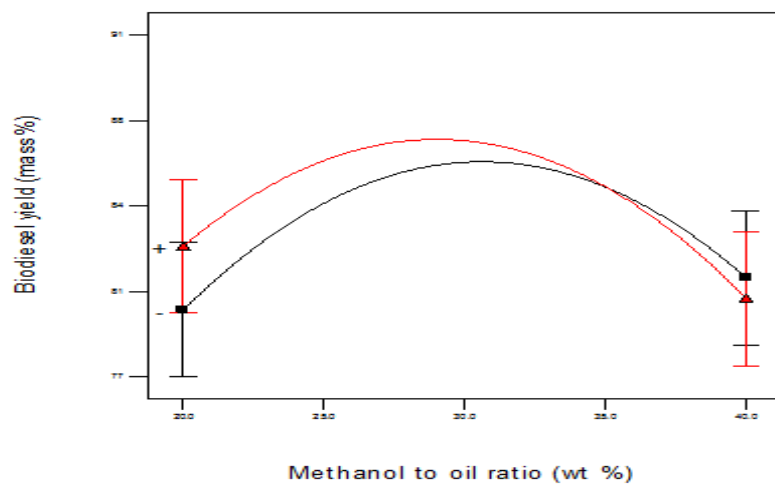


(b)

Figure 4. 7: Effect of reaction time and temperature on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr

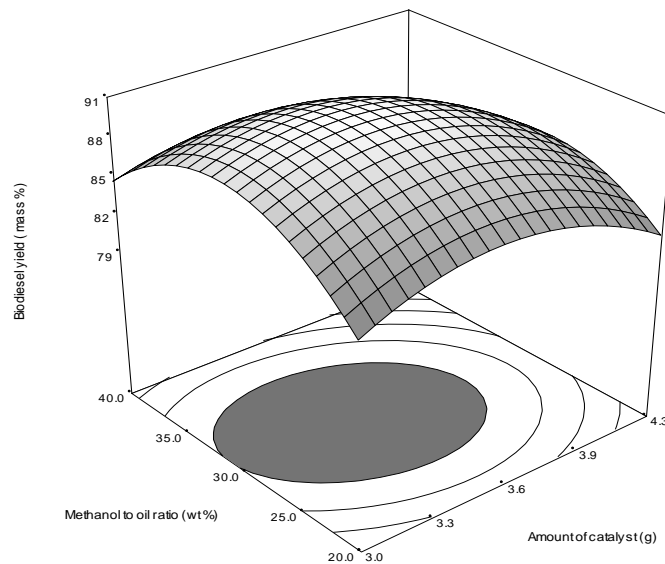


(a)

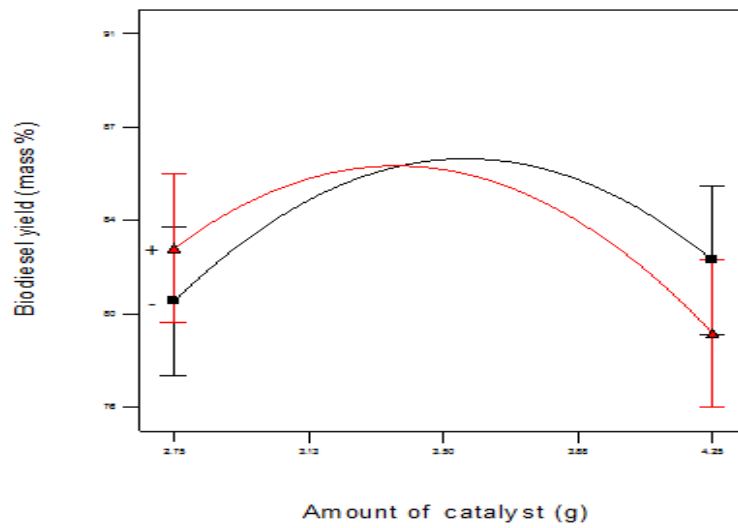


(b)

Figure 4. 8: Effect of reaction time and methanol to oil ratio on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr.



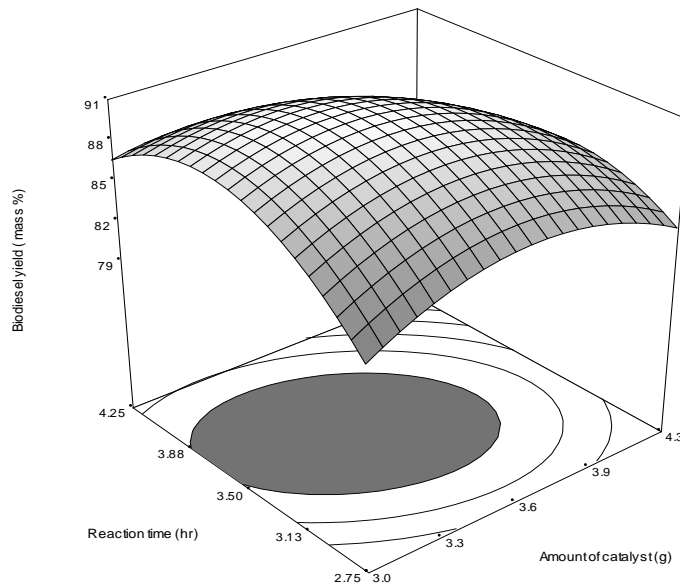
(a)



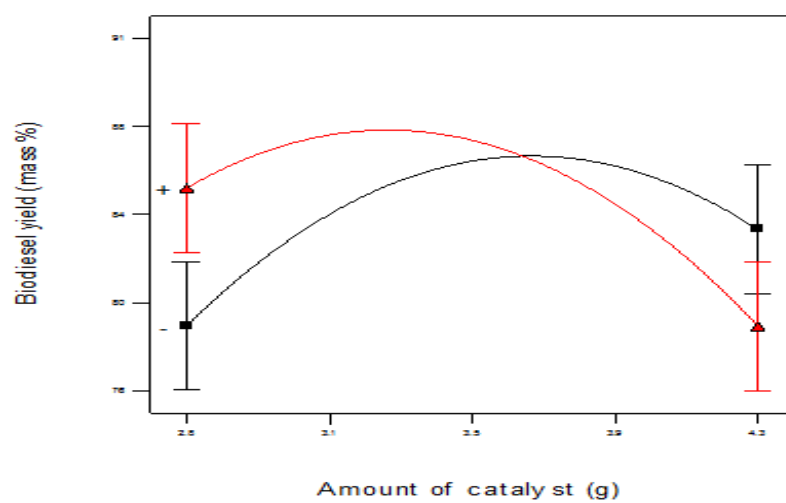
(b)

Figure 4. 9: Effect of methanol to oil ratio and amount of catalyst on transesterification, (a) response surface and (b) two dimension plot with methanol to oil ratio held at (+) 40 wt.% and (-) 20 wt.% .

Figure 4.10 shows the effect of reaction time and amount of catalyst on transesterification of Marula oil while temperature and methanol to oil ratio were held constant at 70°C and 3.5 wt.%, respectively. At high reaction time and low amount of catalyst levels, biodiesel yield was high while at low reaction time and low catalyst amount levels the biodiesel yield was low. As the amount of catalyst increased, the biodiesel yield increased at low level of reaction time until optimum amount of catalyst was reached, but further increase in catalyst beyond optimum resulted in biodiesel yield reduction at low levels of reaction time. Furthermore, as the amount of catalyst increased at high levels of reaction time the biodiesel yield increased until the optimum catalyst amount and optimum reaction time, but an increase in catalyst amount the beyond optimum reaction time at high level of reaction time resulted in reduction of biodiesel yield. High reaction time and high amount of catalyst resulted in saponification of the mixture and reversible reaction of the glycerol-FAME products to reactants.



(a)



(b)

Figure 4. 10: Effect of reaction time and amount of catalyst on transesterification, (a) response surface and (b) two dimension plot with reaction time held at (+) 2.75 hr and (-) 4.25 hr.

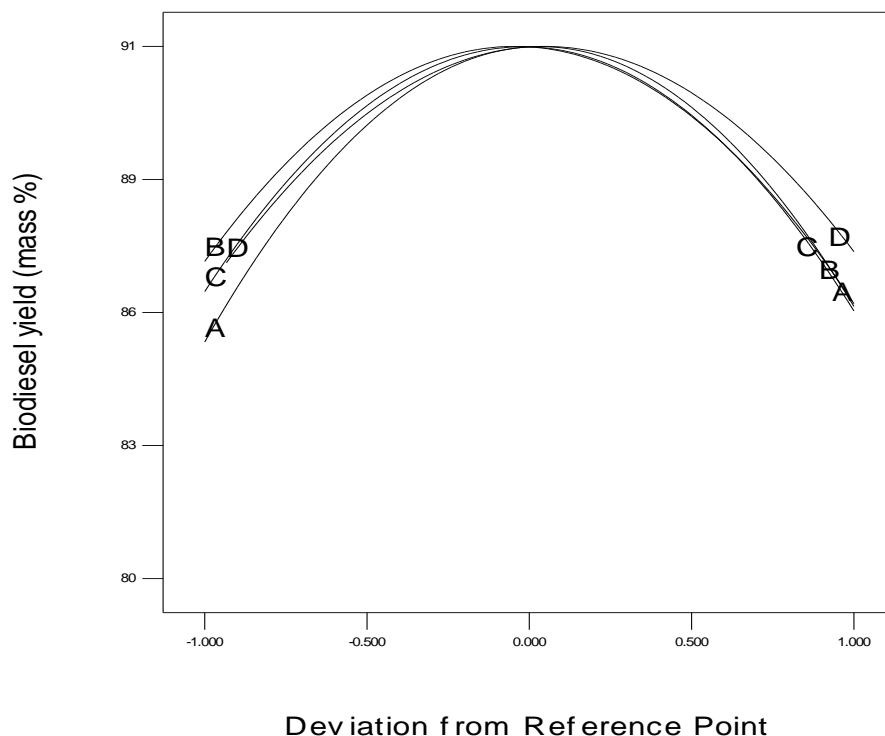


Figure 4. 11: Effects of individual variables affecting transesterification of marula oil to biodiesel. A-temperature, B-amount of catalyst, C-methanol to oil ratio, D-reaction time.

The perturbation plot shows the effect of all variables on transesterification of Marula oil. Reaction times possess greater effect on biodiesel yield compared to other variables. Reaction time was then followed by temperature, but methanol to oil ratio and catalyst amount showed the least effect the on the overall biodiesel yield. Generally, the reaction variables show a minimax behavior and therefore optimum values can be well derived.

Numerical optimization using design expert statistical software was used to obtain optimum conditions for Marula oil transesterification. The optimum conditions for the production of biodiesel were as follows: temperature (70.41°C), amount of catalyst (3.46 grams), methanol to oil ratio (29.86 wt.%) and reaction time (3.55 hr). The optimum biodiesel yield from Marula oil that can be obtained at these conditions using surface response method was 91.38%.

4.6. Catalyst recyclability

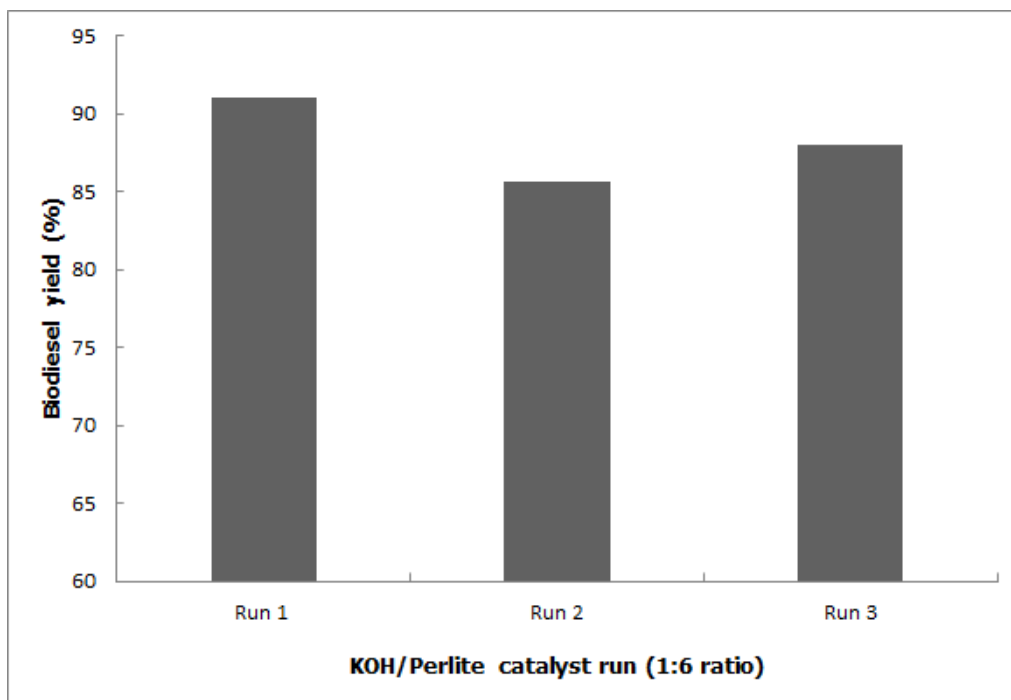


Figure 4. 12: Effect of catalyst reusability.

The catalyst was re-used to produce biodiesel in order to determine its catalyst activity on the biodiesel after the first run. It was observed that after re-using the catalyst three times, biodiesel yield obtained was 91%, 85.6% and 88% at the optimum reaction conditions. This implies that it is possible to re-use and recycle heterogeneous catalyst.

Table 4.6: Fuel properties of marula biodiesel compared to other biodiesel and ASTM standard.

Parameter	Marula	Soybean	Jatropha	Palm	ASTM D6751-02
Cloud point (°C)	6	4	-	16	-3-12
Density at 25°C (kg/m ³)	877	885	880	864.4	860-900
Flash point (°C)	171	160	163	176	>130
Kinematic viscosity 40°C (mm ² /s)	4.12	4.2	4.4	4.5	1.9-6.00
Pour point (°C)	3	-7	0	15	-15-10

Measured Marula FAME properties were compared with soybean, jatropha and palm FAMES as shown in Table 4.6. Profile of fatty acid of marula, soybean, jatropha and palm oil biodiesel and they are classified according to their monounsaturated and polyunsaturated fatty acid. Marula biodiesel properties show that they are within biodiesel ASTM standard. Marula FAME density (877 kg/m³) was greater than that of palm FAME density (864.4 kg/m³) but lower than that of soybean (885 kg/m³) and jatropha (880 kg/m³), but generally the densities are within required ASTM densities of 860-900 kg/m³. Marula FAME flash point was greater than that of soybean (160°C) and lower than that of jatropha (176°C) but all the flash points are greater than 130°C ASTM required.

Although Kinematic viscosity of marula (4.12 mm²/s) FAME was lower than that of palm (4.5 mm²/s), jatropha (4.4 mm²/s) and soybean (4.2 mm²/s) FAMES they are all within ASTM viscosity requirement. Cloud point of marula, soybean and palm biodiesel were as follows: 6°C, 4°C and 16°C, respectively while pour point were 3°C, -7°C, 0°C and 15°C respectively. Cloud point describes the temperature at which FAME cloudiness become visible while pour point describes the lowest temperature at which the fuel can still flow. PP and CP are well explained by the amount of saturated and unsaturated bonds within the FAMES (Knothe and Matheaus, 2003). Saturated FAME have higher melting point than unsaturated FAME, therefore palm oils has high CP and PP due to high saturated bonds than that of marula, jatropha and soybean (Sarin et al., 2009).

Chapter 5: Conclusion and Recommendation

5.1. Conclusion and Recommendation

Sodium methoxide was successfully used as a homogeneous catalyst for baobab oil transesterification via single step due to low fatty acid content. The optimum conditions for the production of biodiesel using baobab oil and sodium methoxide were obtained as follows: 60°C reaction temperature, 1 wt.% catalyst amount, 60 minutes reaction time and 30 wt.% methanol to oil ratio. The optimum baobab biodiesel yield was 96 wt.%. Important fuel properties (kinematic viscosity, density, flash point, pour point, cloud point and oxidation stability) of biodiesel from baobab oil met both European and American biodiesel standards (EN and ASTM standards).

Transesterification of Marula oil using impregnated perlite as a heterogeneous catalyst was successfully performed. Marula oil contained about 7% FFA which required esterification using sulphuric acid before transesterification process in order to reduce FFA content. The optimum conditions of biodiesel production using marula oil and perlite catalyst were obtained as follows: 70.41°C reaction temperature, 3.46 grams catalyst amount, 3.55 hours reaction time and 29.86 wt.% methanol to oil ratio. The optimum marula biodiesel yield was 91.38. The results showed that RSM was well utilized to predict the interactions and relationships between variables affecting biodiesel yield. Nevertheless, the interaction results obtained from the perturbation plot showed that reaction time and amount of catalyst gave the highest interaction effect on the biodiesel yield though reaction time effect was larger than the amount of catalyst. Marula biodiesel properties conform to the biodiesel ASTM standard.

Perlite catalyst was successfully re-used three times to determine the catalyst activity. Biodiesel yield obtained after reusing the catalyst were as follows: 91%, 85.6% and 88% at the optimum reaction conditions. Therefore, heterogeneous catalyst has high catalyst activity as compared to homogeneous catalyst.

4.8. Reference

Alcantara, A., Amore, J.S, Canoira, L., Fidalgo, E., Franco, M.J., and Navarro A., 2000. Catalytic production of biodiesel from soybean oil used frying oil and tallow. *Biomass and Bioenergy* 18, 515-527.

American standards for testing of materials, D 93, D 974, D 2500, D 6751 (2003).

Freedman, B., Butterfield, R., and Pryde, E.H., 1986. Transesterification kinetics of soybean oil. *Journal of the American Oil Chemists' Society* 63, 1375-1380.

Ghadge, S.V and Raheman, H., 2006. Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology. *Bioresource Technology* 97, 379-384.

Kansedo, J., Lee, K.T., and Bhatia, S., 2009. Biodiesel production from palm oil via heterogeneous transesterification. *Biomass and Bioenergy* 33, 271-276.

Knothe, G., Matheus, A.C., and Ryan III, T.W., 2003. Cetane number of branched and straight chain fatty esters determined in an ignition quality tester. *Fuel* 82, 971-975.

Leung, D and Guo, Y., 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Processing Technology* 87, 883-890

Meher, L, Dharmagadda, V., and Naik, S., 2006. Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel. *Bioresource Technology* 97, 1392-1397.

Montgomery, D.C., 2001. Design and analysis of experiments. John Wiley and Sons, New York, USA.

Rutto, H.L., Enweremadu, C. C., 2011. Optimization of Production Variables of Biodiesel from Manketti Using Response Surface Methodology. *International Journal of Green Energy* 8, 768-779.

Sarin, A., Arora, A.R., Singh, N.P., Sarin, R., Malhotra, R.K., and Kundu, K., 2009. Effect of blends of Palm-Jatropha-Pongamia on cloud point and pour point. *Energy* 34, 2016-2021.

Soetaredjo, F.E., Ayucitra, A., Ismadji, S., and Maukar, A.L., 2011. KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Applied Clay Science* 53, 341-346.

Tsai, W.T., Lai, C.W., and Hsien, K.J., 2006. Characterization and adsorption properties of diatomaceous earth modified by hydrofluoric acid etching. *Journal of Colloid and Interface Science* 297, 749-754.

Uosukainen, E., Lamsa, M., Linko, Y.Y., Linko, P., and Leisola, M., 1999. Optimization of enzymatic transesterification of rape seed oil ester using response surface and principal component methodology. *Enzyme and Microbial Technology* 25, 236-243.

Van Gerpen, J.V., Shanks, B., and Pruszko, R. Biodiesel Production Technology. Subcontract report August 2002–January 2004, Iowa State University, 23.

Wang, Z.M., Lee, J.S., Park, J.Y., Wu, C.Z., and Yuan, Z.H., 2007. Novel biodiesel production technology from soybean soapstock. *Korean Journal of Chemical Engineering* 24, 1027-1030.

Zabeti, M., Wan Daun, W.M.A., and Aroua, M.K., 2009. Optimization of the activity of CaO/AlO₃ catalyst for biodiesel production using response surface methodology. *Journal of Applied Catalysis* 366, 154-159.