



BOTSWANA INTERNATIONAL UNIVERSITY
OF SCIENCE & TECHNOLOGY

**COMPARISON OF CaO-NPs AND CHICKEN EGG
SHELL DERIVED CaO FOR THE PRODUCTION OF
BIODIESEL FROM *Schinziophyton rautanenii*
(MONGONGO) NUT OIL**

by

KEENE C. MMUSI

Reg. No: 17100005

Department of Chemical and Forensic Sciences,

Faculty of Science,

Botswana International University of Science and Technology (BIUST)

A Dissertation Submitted to the College of Science for the Study Leading to a
Dissertation in Fulfilment of the Requirements for the Award of the Degree of Master of
Science in Chemistry of BIUST

Supervisor: Dr Sebusi Odisitse

November 2020

ABSTRACT

The ever-increasing population growth and economic developments have led to a demand for energy. Therefore, this has resulted in a depletion and ever rising prices of petroleum diesel, hence increasing environmental degradation. These complications have motivated this study for the search of an alternative eco-friendly and renewable source of energy such as biodiesel. Biodiesel has been found to be a potential alternative fuel for diesel. It has the potential to solve the energy crisis depending on the availability of feedstock and catalyst. In this study, biodiesel was produced by transesterification of the mongongo (*Schinziophyton rautanenii*) nut oil in the presence of a heterogeneous catalyst CaO. CaO is used in this study because it is highly active and is the commonly used solid catalyst for transesterification reaction. CaO was derived from eggshell ash and synthesized CaO-nanoparticles. The catalyst from eggshell ash and synthetic CaO-nanoparticles were calcined at a temperature of 800 °C and characterized through; Scanning Electron microscope- Energy Dispersive X-Ray Analyzer (SEM-EDX) where both catalysts showed agglomerated and porous particles and high elemental composition of Ca and O. Powder X-ray Diffraction (XRD) showed that CaO was present in both catalysts and the average crystalline size calculated was 42 and 50 nm for CaO-nanoparticles and eggshell ash respectively. Finally, Fourier Transmission-Infrared (FTIR) spectrometer showed the absorption bands of CaO from both catalysts which were at 875 and 713 cm^{-1} for CaO-nanoparticles and eggshell ash respectively.

Schinziophyton rautanenii (mongongo) is a multipurpose plant species in Southern Africa with an ecosystem that provides a variety of goods and services such as food security, employment and source of income to people from rural communities in Southern Africa. The *Schinziophyton rautanenii* generally contains at least 60% of oil extracted from its nut which has potential to produce biodiesel. The characterization of mongongo nut oil and mongongo methyl esters (biodiesel) was done according to the European biodiesel specification (EN 1421) and American society for testing and material (ASTM D675) which are the standards set for biodiesel. The measured physicochemical properties of the biodiesel were in the range of these international standards. The analysis of

mongongo methyl ester was through Gas chromatography-mass spectrometry (GC-MS) and the methyl esters were identified using mass spectrometric libraries. Statistically, there was no significant difference between CaO-NPs and eggshell ($P>0.05$). However, in terms of catalyst loading, the eggshell was a better catalyst as it required a low catalyst load to obtain an optimum yield of 83% at 6 wt.% compared to CaO-NPs with an optimum yield of 85% at 12 wt.%. The reactions were all performed at constant reaction conditions of 9:1 methanol to oil ratio, 3 h reaction time and 65 °C reaction temperature.

DECLARATION AND COPYRIGHT

I, **Keene C. Mmusi** declare that this dissertation/thesis is my own original work and that it has not been presented and will not be presented to any other university for a similar or any other degree award



Signature:

This dissertation/thesis is copyright material protected under the Berne Convention, the Copyright Act of 1999 and other international and national enactments, in that behalf, on intellectual property. It must not be reproduced by any means, in full or in part, except for short extracts in fair dealing; for researcher private study, critical scholarly review or discourse with an acknowledgement, without the written permission of the office of the Provost, on behalf of both the author and the BIUST.

CERTIFICATION

The undersigned certifies that they have read and hereby recommend for acceptance by the College of Sciences a dissertation/thesis titled: COMPARISON OF CaO-NPs AND CHICKEN EGG SHELL DERIVED CaO FOR THE PRODUCTION OF BIODIESEL FROM *Schinziophyton rautaneii* (mongongo) nut oil, in fulfilment of the requirements for the degree of Master of Science in Chemistry of Botswana International University of Science and Technology.

Dr Sebusi Oditse
(Supervisor-BIUST)



.....
Date: 13th November 2020

AKNOWLEDGEMENTS

The research in this thesis would have not been completed without the encouragement of many people in my life. I am delighted to acknowledge those who have supported me through this journey.

First of all, I humbly wish to express my profound gratitude to God Almighty, the creator and the ruler of the Universe, he who gives us life. I believe I would not be here without his protection and guidance. He has given me strength, patience and faith to work hard in this journey.

I would like to thank my supervisor Dr. Sebusi Odisitse for his support, insight and assistance. You mentored me to become an independent scientist which has remarkably improved my confidence and always encouraging me in difficult times.

I am particularly thankful to my mentor Dr. Florence Nareetsile for always believing and advising me. I would also like to thank you for allowing me to use your lab when I was working in University of Botswana.

I would like to appreciate my best friend and colleague James T. P Matshwele. You have always supported me in everything and I appreciate all you have done for me from the time we realized that we share a common interest which is the love for Chemistry.

I would like to appreciate Lebogang Julius for his contribution to my work. I will forever appreciate your assistance. Thank you.

I would like to extent my heartfelt gratitude to Botswana International University of science and technology (BIUST) that helped to fund my research, also the University of Botswana (UB) and Botswana Institute for technology research and innovation (BITRI).

Finally, my deep and sincere gratitude to my beloved family (my mother, sister, brother and nephews) and also my friends (Obakeng, Obonye, Thapelo, Crystal, Neo and Katso) for their continuous and unparalleled love, help and support. Also I am thankful to my colleagues for their support.

DEDICATION

Tebelelo Bibi Mmusi

I am forever indebted to you for giving me the opportunities and experiences that have made me who I am. Thank you for giving me strength to reach the stars and chase my dreams. I love you Mama.

TABLE OF CONTENTS

CHAPTER 1	1
1.0 INTRODUCTION.....	1
1.1 Background.....	1
1.2 Biodiesel Production	3
1.2.1 Transesterification	4
1.2.2 Factors Affecting the Production Biodiesel	9
1.3 Catalysts in Transesterification Process	11
1.3.1 Homogeneous Acid and Base Catalyst	12
1.3.2 Heterogeneous Acid and Base Catalyst	13
1.3.3 Enzymatic Catalyst	14
1.4 Calcium Oxide Nanoparticles (CaO-NPs) in Biodiesel Production	14
1.5 <i>Schinziophyton rautanenii</i> (Mongongo).....	15
1.6 Statement of the Problem	17
1.7 Research Questions.....	17
1.8 Aim and Objectives of the Study	18
1.9 Justification and Significance.....	18
1.10 References	20
CHAPTER 2	29
2.0 MATERIALS AND METHODS	29
2.1 Materials and Reagents	29
2.2 Instruments	30
2.3 Sample Collection	32
2.4 Extraction of Oil from Nut	32

2.5	Determination of Physical and Chemical Properties of Mongongo Nut Oil and Biodiesel.....	32
2.5.1	Saponification Value.....	32
2.5.2	Acid Value.....	33
2.5.3	Peroxide Value.....	34
2.5.4	Iodine Value.....	35
2.5.5	Density.....	35
2.5.6	Refractive Index.....	36
2.5.7	Kinematic Viscosity.....	36
2.6	Preparation of Catalyst.....	36
2.6.1	Chicken Eggshell.....	36
2.6.2	Synthesis of Calcium Oxide Nano-Particles (CaO-NPs) Catalyst.....	37
2.7	Transesterification Reaction.....	37
2.8	Gas Chromatography- Mass Spectrometer (GC-MS) Analysis.....	38
2.9	References.....	40
CHAPTER 3	41
3.0	RESULTS AND DISCUSSION.....	41
3.1	Preparation and Characterization of Calcium Oxide Nanoparticles (CaO-NPs) and Chicken Eggshell Ash.....	41
3.1.1	Powder X-Ray Diffraction (XRD) Characterization.....	41
3.1.2	Fourier Transform Infrared Spectroscopy (FTIR) Analysis.....	47
3.1.3	Scanning Electron Microscope- Elemental Dispersive X-ray (SEM-EDX) Analysis.....	50
3.2	Physicochemical Properties of Mongongo Nut Oil and its Biodiesel.....	55
3.3	Characterization of Biodiesel.....	61
3.3.1	Gas Chromatography- Mass Spectrometer (GC-MS) Analysis.....	61

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis	66
3.3.3 Effect of Amount of Catalyst.....	67
3.4 References	70
CHAPTER 4	79
4.0 CONCLUSIONS AND RECOMMENDATIONS	79
4.1 Conclusions	79
4.2 Recommendations.....	80
4.3 APPENDIX A: Powder XRD Spectra.....	81
4.4 APPENDIX B: Statistical Calculations.....	83

LIST OF ABBREVIATIONS

CaO-NPs- Calcium Oxide Nanoparticles

COD- Crystallography Open Database

FAMEs- Fatty acid methyl esters

FFA- Free fatty acid

FTIR- Fourier transform Infrared Spectrometer

GC-MS- Gas Chromatography- Mass Spectrometer

MMEs - Mongongo methyl esters

MNO- Mongongo nut oil

NIST- National Institute of Standards and Technology

NPs- Nano-Particles

PDF- Powder Diffraction File

Powder XRD- Powder X-ray Diffraction

SEM-EDX- Scanning Electron Microscope-Electron Dispersive Microscope

LIST OF FIGURES

<i>Figure 1-2: Images taken by Keene Mmusi of mongongo nutshell (A), mongongo fruit (B), mongongo tree (C) and mongongo nuts (D).....</i>	17
Figure 3-1: XRD pattern of samples; (a) eggshell (black) and (b) eggshell ash calcined at 800 °C (red).....	43
Figure 3-2 The XRD pattern of eggshell ash calcined at 800 °C	44
Figure 3-3: XRD pattern of samples; (a) Ca(OH) ₂ (b) CaO-NPs calcined at 800 °C and (c) CaO-NPs calcined at 900 °C	45
Figure 3-4: XRD pattern of CaO-NPs calcined at 800°C	47
Figure 3-5: Fourier Transform Infrared Spectroscopy of (a) eggshell (red) (b) eggshell ash calcined at 800 °C (black).....	48
Figure 3-6: Fourier Transform Infrared Spectra of (a) Ca(OH) ₂ (b) CaO-NPs calcined at 800 °C and (c) CaO-NPs at 900 °C	50
Figure 3-7: SEM images of eggshell ash catalyst calcined at 800 °C.....	52
Figure 3-8: SEM-EDX spectrum of eggshell ash calcined at 800 °C	52
Figure 3-9: SEM images of CaO-NPs calcined at 800 °C.....	54
Figure 3-10: SEM-EDX analysis of CaO-NPs calcined at 800 °C.....	54
Figure 3-11: Chromatogram of MMEs catalyzed by eggshell ash	62
Figure 3-12: Chromatogram of MMEs catalyzed by CaO-NPs.....	64
Figure 3-13: Showing the IR spectrum on MNO (green), MMEs using eggshell ash (orange) and MME using CaO-NPs (pink).....	67
Figure 3-14: The effect of the amount of catalyst on the production of biodiesel	69

LIST OF TABLES

Table 1-1: showing the major non edible and edible oil sources which have been used to produce biodiesel [20]	3
Table 1-2: The benefits and limitations of using an Acid Catalyzed and Base Catalyzed Transesterification (adapted from [26] [27] [28]).....	8
<i>Table 2-1: Chemicals and reagents</i>	<i>29</i>
<i>Table 2-2: The main Instruments which were utilized for the production of biodiesel....</i>	<i>30</i>
<i>Table 2-3: GC-MS parameters for the analysis of Biodiesel.....</i>	<i>39</i>
Table 3-1: Various planes for d-spacing of eggshell ash calcined at 800 °C	44
Table 3-2: d-spacing for various planes of CaO-NPs calcined at 800°C	46
Table 3-3: Elemental composition of eggshell ash calcined at 800 °C	53
Table 3-4: Elemental composition of CaO-NPs	55
Table 3-5: Physiochemical properties of Mongongo nut oil and its methyl esters from eggshell ash and CaO-NPs (adapted from [7] and [43]).....	60
Table 3-6: FAMEs composition of biodiesel using eggshell ash.....	62
Table 3-7: FAMEs composition of biodiesel using synthesized CaO-NPs.....	65
Table 3-8 : Major bands of FTIR spectra for MNO and MMEs	67

LIST OF SPECTRA

Spectrum 4-1: The XRD pattern of eggshell ash calcined at 800 °C	81
Spectrum 4-2: The XRD pattern of Ca(OH) ₂	81
Spectrum 4-3: XRD pattern of CaO-NPs calcined at 800 °C	82

LIST OF SCHEMES

Scheme 1-1: A typical transesterification reaction (adapted from [23])	4
Scheme 1-2: A schematic transesterification reaction (Adapted from [21])	5
Scheme 1-3: Base catalyzed transesterification reaction equation (Adapted from [23])..	6
Scheme 1-4: The mechanism of acid catalyzed transesterification reaction (adapted from [25]).....	7
Scheme 1-5: Classification of catalyst (adopted from [16])	12
<i>Scheme 2-1: The chemical reaction in the calcination process.....</i>	<i>36</i>
<i>Scheme 2-2: The chemical reactions used for the synthesis of CaO-NPs</i>	<i>37</i>
<i>Scheme 2-3: Schematic diagram of Transesterification reaction</i>	<i>38</i>

CHAPTER 1

1.0 INTRODUCTION

1.1 Background

Ever since the revolution of industrialization, energy instability has been a challenging problem [1] [2]. Globally scientists have been working hard in search of finding reliable, secure, clean, affordable and sustainable energy resources [2] [3] [4]. Energy resources can be categorized into three (3) major groups: fossil fuels, renewable and fissile [5]. Fossil fuels generate greenhouse gases and with the rapid growth of population results in the consumption rate of fossil fuels becoming high, thus, increasing the risks of global warming [6]. Fossil fuels include petroleum, coal, bitumen, natural gas, tar sands and oil shales. Fissile fuels are nuclear energy forms [7]. Fissile sources of energy include uranium and thorium. Renewable energy source include biomass, hydro, wind, solar, marine and hydrogen [8]. Fossil fuels are non-renewable source of energy and they have a negative impact to the global climate through global warming [9].

Gandure *et al.*, suggested that the production of biodiesel is prompted by the ever increasing oil and petrol prices, the possibility of job creation, economic diversity and fuel security [10]. The fossil fuels were a major share in the global primary energy consumption in the period of 1995 to 2015. According to BP's energy outlook, it has been predicted that in the period of 2014-2035 the energy consumption will increase by approximately 34% with fossil fuel being the most dominant [11]. Therefore, there is need to come up with alternatives for petro-diesel engines which emit less greenhouse gases such as carbon dioxide. There should also be a revisit to the policy so as to instill tight regulations on exhaust emissions [12]. There has been an interest in green chemistry in recent years as scientists have recognized the importance of conserving the environment. Biodiesel is one of the sources that fall under green chemistry. The production of biodiesel has been viewed as among the important substitute for petrol and diesel, the aim being to reduce the ever growing demand for fuel and also reducing pollution from auto-mobiles and industries [13].

As a way to reduce emissions from pollutants the awareness and strict compliance of environmental legislations has forced scientists to adopt ways in which the environment would not be endangered [14]. Otta reports that there are set world guidelines on the emission of exhaust which includes the Copenhagen summit which agreed that for this century the global temperature rise should be kept at 2 °C [13]. This initiative has encouraged countries to come up with detailed measures, the main goal being to reduce the level of certain emissions from internal combustions. In other reports, the European Union (EU) gave each of its members a target that transport fuel obtained from renewable sources should not be less than 20% by the year 2020 [15] [16].

Currently research on alternative fuels is becoming a topic of interest worldwide. This is observed as more scientists are trying to find ways to reduce the ever-rising demand for energy in today's highly populated world [17]. Biodiesel is one of the great alternative sources of energy because it is a renewable source of energy. Biodiesel has a high combustion efficiency, biodegradable, acts as a lubricant and it is sustainable and clean [18]. Vegetable oils are often used as a raw material for the production of biodiesel. Examples of the major non-edible and edible vegetable oils which have been used for the production of biodiesel are shown in Table 1-1. They have attracted much needed attention as an alternative source of energy because of their easier accessibility. They do not endanger the environment and are also renewable sources of energy. Even though the use of vegetable oils for biodiesel is a threat to food security, their use for biodiesel is associated with ease of reproducibility and the fact that it is green (not producing harmful products and also economic) [19].

Table 1-1: showing the major non edible and edible oil sources which have been used to produce biodiesel [20]

Type of Oil	Oil yield (wt. %)
Jatropha seed	30-40
Rubber seed	40-50
Castor	53
<i>Pongamia pinnata</i>	30-40
Sea mango	30-40
Soy bean	20
Palm	20
Rapeseed	20

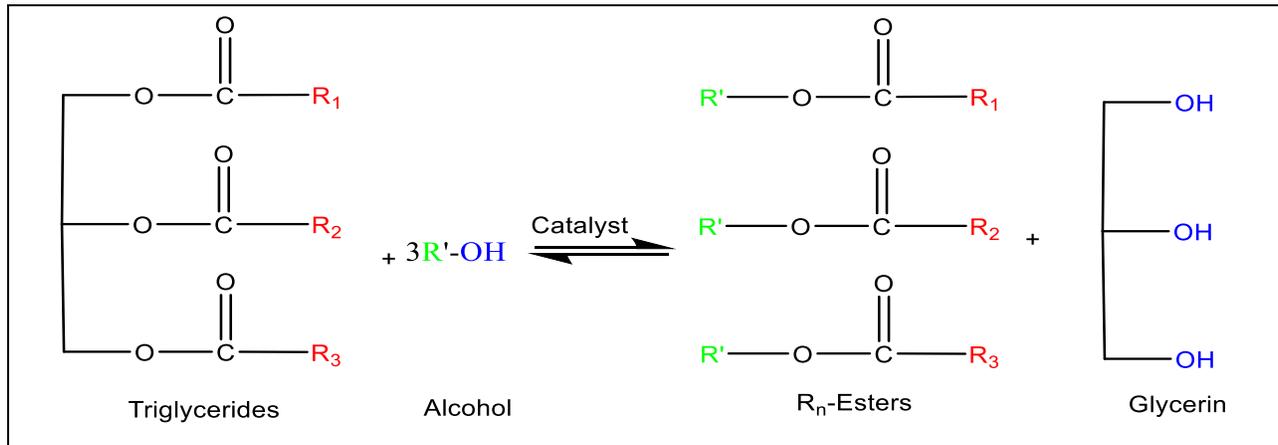
1.2 Biodiesel Production

Biodiesel is produced from triglycerides obtained from biological sources. This includes plants, vegetables, animal fats, waste oils and microalgae [7] [8]. Researchers have reported different findings in ways that biodiesel can be produced from waste vegetable oils [9]. Some were focused on; (a) the effect of a catalyst such as heterogeneous catalyst, enzymatic catalyst and homogenous catalyst; (b) effect of reaction time; (c) effect of temperature; and also (d) the effect of alcohol used (mole ratio of alcohol to oil) [10] [11] [12] [13] [14] [21].

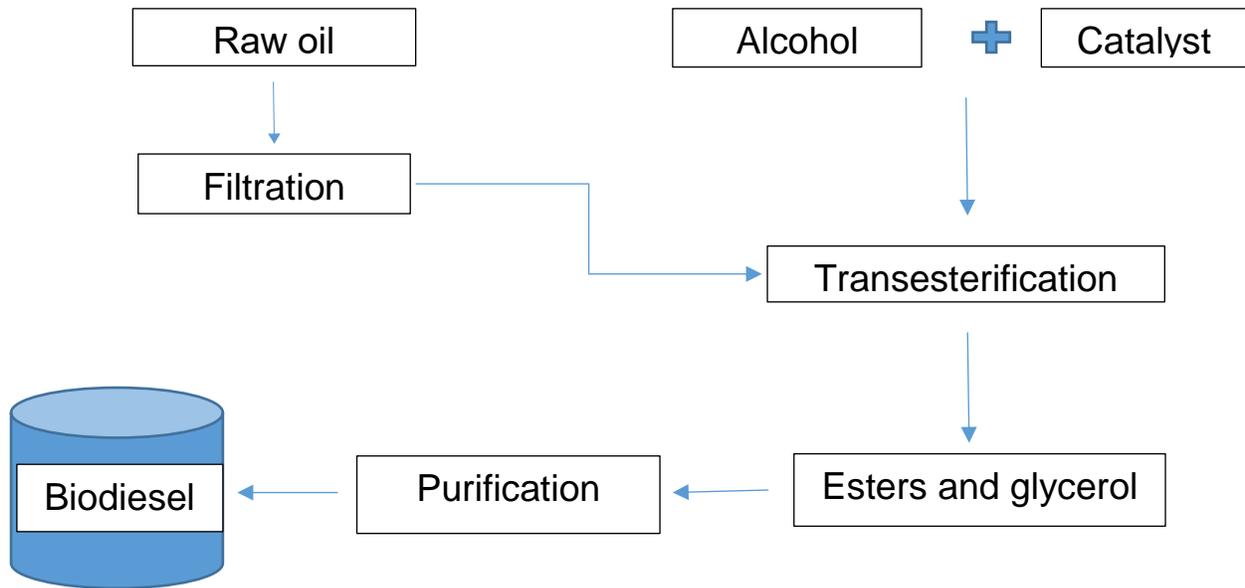
Biodiesel is popularly produced in a commercial scale by the process known as transesterification. Transesterification also called alcoholysis is the reaction of triglycerides with alcohol in the presence of a catalyst. This catalyst is most commonly sodium or potassium hydroxide and suitable alcohols such as methanol, ethanol, propanol and butanol [9]. This project is focused on the production of biodiesel from mongongo (*Schinziophyton rautanenii*) nut oil.

1.2.1 Transesterification

Transesterification is a method used to produce alkyl esters (biodiesel) from oils/fats (triglycerides) in the presence of an alcohol and catalyst, as shown in scheme 1-1 [17] [18]. The reaction involves a catalyst as shown in a flow chart scheme 1-2 which speeds up the process and improves the yield. The amount of catalyst is determined by the fatty acid present in the oil [22]. The process of transesterification involves a sequence of reversible reactions. The initial step involves the conversion of triglycerides to diglycerides, thereafter, diglycerides are converted to monoglycerides and lastly monoglycerides are converted to glycerol [19] [20]. The transesterification reaction can be represented as in scheme 1-1 and scheme 1-2.

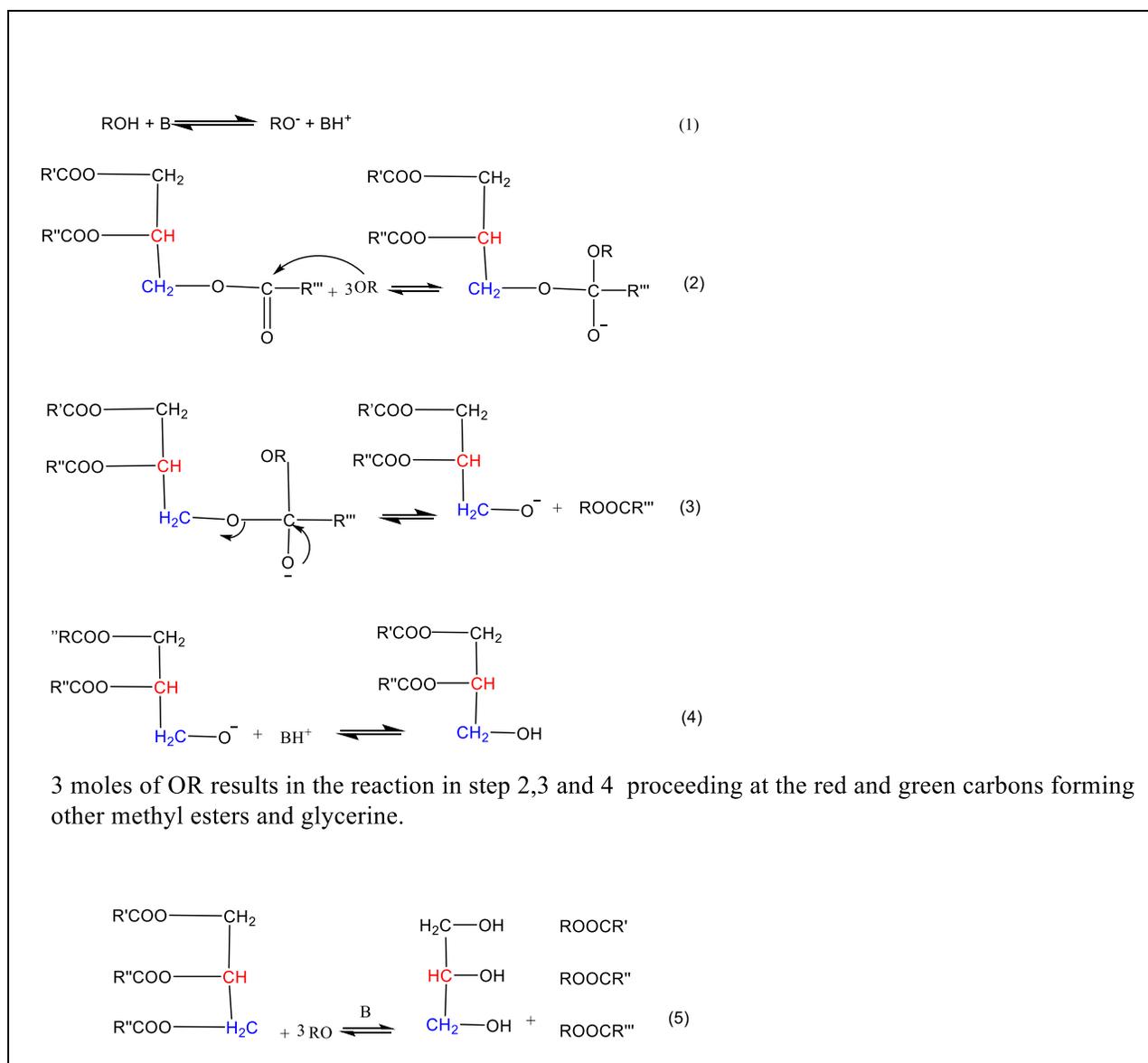


Scheme 1-1: A typical transesterification reaction (adapted from [23])



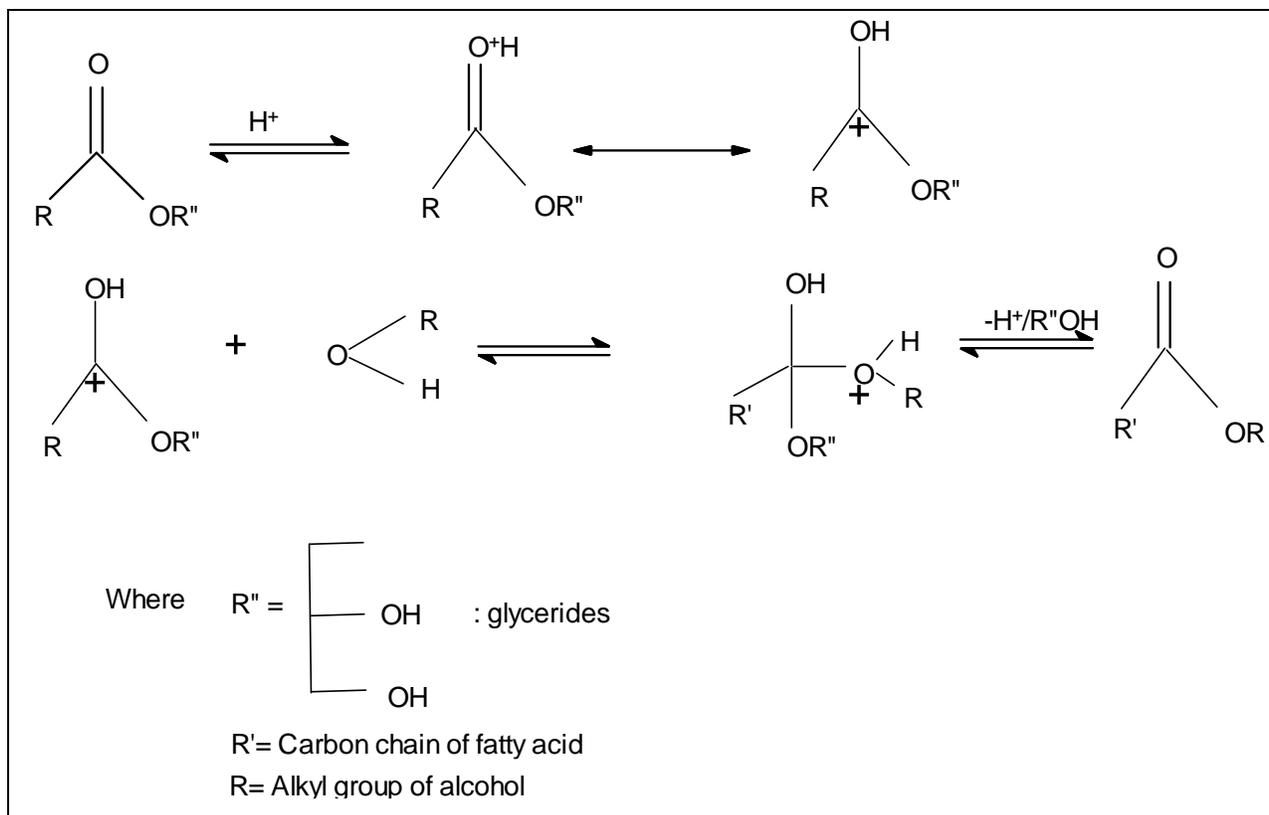
Scheme 1-2: A schematic transesterification reaction (Adapted from [21])

Different types of catalysts have been used for transesterification [24] [25] [26] [27]. The most common methods applied are base catalyzed transesterification and acid catalyzed transesterification [22]. Table 1-1 shows the benefits and limits of base catalyzed transesterification and acid catalyzed transesterification. The mechanism of a base catalyzed transesterification shown in scheme 1-3 involves the reaction of the base with alcohol, producing an alkoxide ion in reaction 1. Then a tetrahedral intermediate is produced in reaction 2 after a nucleophilic attack of the alkoxide ion onto carbonyl carbon of the triglyceride molecule, resulting in the formation of an alkyl ester and anion of the diglycerides. The final step in reaction four (4) proceeds by the deprotonation of the catalyst by the diglycerides. Resulting in the regeneration an active species which will be ready to react with a second molecule of the alcohol. The same mechanism is performed in diglycerides and monoglycerides for the production of alkyl esters and glycerol [19] [23] [28].



Scheme 1-3: Base catalyzed transesterification reaction equation (Adapted from [23])

Acid catalyzed transesterification of triglycerides uses Bronsted-Lowry acids usually sulphuric, hydrochloric and phosphoric acids which give a very high yield of alkyl esters [19]. The mechanism is shown in scheme 1-4. It involves the protonation of carbonyl which leads to the formation of a carbo-cation. A tetrahedral intermediate is formed after a nucleophilic attack of the alcohol and a new alkyl ester is generated which eliminates glycerol [23]. This method occurs in a single step by mixing the oil directly with the acidified alcohol [24].



Scheme 1-4: The mechanism of acid catalyzed transesterification reaction (adapted from [25])

Table 1-2: The benefits and limitations of using an Acid Catalyzed and Base Catalyzed Transesterification (adapted from [26] [27] [28])

Method	Advantages	Disadvantages
Base-catalyzed Transesterification	<ul style="list-style-type: none"> • The process gives high yields of triglycerides and can be converted faster. • Easily accessible and economical. • High activity and longer catalytic lifetime. The catalyst can be easily removed from the products. • Non-corrosive. 	<ul style="list-style-type: none"> • It is energy intensive. • Recovery of glycerol is complex due to the sensitivity of this process especially to water and free fatty acids. • Alkaline catalyst has to be removed from the product.
Acid-Catalyzed Transesterification	<ul style="list-style-type: none"> • Insensitive to free fatty acids compared to base catalyzed transesterification. • Acid catalysts can be used for both esterification and transesterification simultaneously. 	<ul style="list-style-type: none"> • Catalytic and molar ratio needed in high concentration. • The conversion of oil to biodiesel occurs at a slow rate thus they require high temperature and more time for the conversion to be complete.

1.2.2 Factors Affecting the Production Biodiesel

The production of biodiesel is affected by temperature, alcohol to oil ratio, catalyst, time, water content and fatty acid [29]. These factors are discussed below;

a. Effect of Temperature and Time

Temperature is an important criterion in the process of transesterification and it affects the yield of biodiesel [30]. The importance of heating a reaction during transesterification has been emphasized because it speeds up the rate of reaction depending on the type of catalyst used [31]. The maximum temperature one can use depends on the boiling point of the solvent. Canakci *et al.*, studied the effect of temperature in the production of an ester using methanol. The three temperatures which they used were 25, 45 and 60 °C. The range did not surpass 65 °C since methanol has a boiling point of 65 °C. The ester conversions were 8.3, 57.2 and 87.2% respectively [32]. Reaction time tells the efficiency of the transesterification reaction of the feedstock. Gondra reported that the only limitation that affects time in the reaction of transesterification is when there is not enough time for the reaction to be complete. Therefore, allowing the reaction enough time will avoid any implications and ensure the completion of the reaction [33]. Emeji obtained a yield of 99% FAME using Li-CaO as a catalyst [4]. This reaction took 3 h with a 6:1 methanol oil ratio and 5 wt. % of catalyst.

b. Effect of Catalyst

A catalyst is important in producing high yields of esters in transesterification reaction. In most cases the catalyst used is either alkaline or acidic materials. The catalysts can be divided into heterogeneous and homogeneous catalysts. Heterogeneous catalysts are developed for simplicity and easy separation from the reaction mixture, as compared to homogeneous catalysts as their separation from the product proved to be complex [29] [34]. A number of factors should be considered when one is selecting a catalyst; (a) type of feedstock, (b) operation condition, (c) activity of the required catalyst and (d) availability and cost [35].

The amount of the catalyst affects transesterification as it is hugely dependent on it when it comes to the rate of conversion of an ester from oil. For instance there has been reports that a heterogeneous catalyst is more advantageous as the production costs can be reduced because of the amount of alkaline waste water [36] [37]. Heterogeneous catalysts can be grouped into five (5) categories:

- i. Metallic (metal complexes, transition metal complexes)
- ii. Solid base and acids (Inorganic oxides)
- iii. Natural catalyst
- iv. Zeolites
- v. Ion exchange resins (Phosphorus oxide)

c. Effect of mole ratio of alcohol and oil

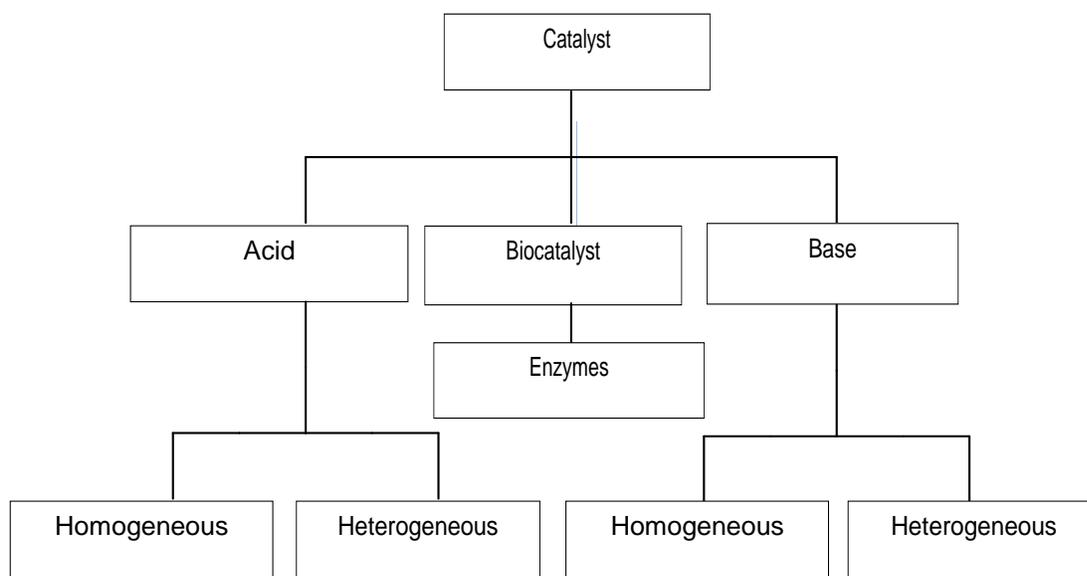
Conversion of oil to ester can also be influenced by the mole ratio of alcohol and oil [32]. Phan *et al.*, report that greater conversion results of an ester are directly proportional to the mole ratio [38]. This means that the higher the molar ratio the more chances that the oil is likely to be converted to an ester in a shorter time. Freeman *et al.*, investigated the effect of mole ratio on the yield of an ester [39]. The study was done using methanol as the alcohol and sunflower oil, the ratios were varied from 6:1 to 1:1. The conclusion was that a mole ratio of 6:1 obtained a conversion of oil to ester up to 85%. As the molar ratio decreased the percentages of the converted oil also decreased to 82% using mole ratio of 3:1. Another investigation was reported by Meher *et al.*, who were focused on the transesterification of *Cynara cardunculus* oil with ethanol at mole ratios between 3:1 and 15:1 [40]. The results obtained showed that the ester conversion increased with the increase in mole ratio up to a value of 12:1 and the best results which gave a higher ester conversion were for mole ratios between 9:1 and 12:1. As for mole ratios less than 6:1, the reaction was not complete. The ester yield decreased at a mole ratio of 15:1 because the separation of glycerin is difficult which results in some of the glycerol remaining in the biodiesel phase. It was concluded that a mole ratio of 9:1 gave the most conversion compared to other ratios.

d. Effect of water content and Fatty acid

Transesterification reaction can be affected by water content and free fatty acids (FFA) content of oils [11]. Ribeiro *et al.*, found out that the reaction of water with an alkali catalyst and also FFA results in the formation of soap (glycerol) and at ambient temperatures the saponified products tend to strengthen and form a gel which makes it difficult to recover [41]. Atadashi *et al.*, found out that excessive soap can negatively affect the process of transesterification by making it difficult to separate glycerol from biodiesel. The effectiveness of the catalyst is reduced and deteriorates the quality of biodiesel. The authors also noted that these implications result in a decrease of heat of combustion, corrosion of fuel system components and acceleration of hydrolytic reaction [42]. The sensitivity of transesterification to water is high such that even small amounts of water affect the reaction (about 0.1%), resulting in the reduction of an ester from oil [43]. Kusdiana *et al.*, state that water content has a greater negative effect compared to FFA as it consumes the catalyst and reduces its efficiency, thus, it is important that water content be kept lower than the allowed FFA content to at least 0.06% [44].

1.3 Catalysts in Transesterification Process

Catalysts play a major role in the transesterification reaction for the production of biodiesel. They are normally used in order to improve the rate of reaction, yield and quality of biodiesel produced [45] [46]. Transesterification can be performed either by using homogenous, heterogeneous or enzymatic catalyst [47] [48]. These catalysts can be classified into three (3) groups: acid catalyst, enzymatic catalyst and base catalyst as shown in scheme 1-5.



Scheme 1-5: Classification of catalyst (adopted from [16])

1.3.1 Homogeneous Acid and Base Catalyst

Homogeneous catalysts are normally used in commercial processes and these catalysts exist in the same phase as the reactants. They are divided into acid catalysts (hydrochloric acid (HCl), sulphuric acid (H₂SO₄), sulfonic acid and phosphoric acid) or basic catalysts (potassium hydroxide (KOH), potassium methoxide (KOCH₃), sodium hydroxide (NaOH) and sodium methoxide (CH₃NaO)) [49] [50]. Homogeneous alkaline catalysts are more efficient as compared to homogeneous acid catalysts which is the reason they are the most common and preferably used in the process of transesterification. The benefits of using these catalysts are that they are readily available, able to work at low temperatures and pressure [51]. Emeji reported a yield of over 95% using NaOH (0.5 -2 wt.%) at a methanol oil molar ratio of 6:1 and temperature of 60- 65 °C [4].

Most oils contain fatty acids which cannot be converted into biodiesel using a base catalyst because of the production of soap which makes it difficult to separate the ester and glycerine [49]. Acid catalyzed transesterification reaction does not produce soap or glycerol. It is also a single step reaction which enables transesterification with high FFA and water content. However, the reaction is slow hence making it less popular especially for industrial processes [29].

1.3.2 Heterogeneous Acid and Base Catalyst

Heterogeneous catalysts have gained a lot of recognition in recent years, as shown by a number of reports, focusing on the use of this catalyst on the production of biodiesel [52]. Basic solid catalysts such as metal oxides, zeolites and acidic solids are gradually becoming more popular because they are economical and environmentally friendly [53]. These catalysts are non-corrosive, highly selective, have a prolonged life and cheaper manufacturing processes [54]. The benefit of using heterogeneous base catalysts are that they are easily separated from the product by filtration and they can be recycled [55]. However, the limiting factor of using this catalyst is that the biodiesel feedstock should have a low FFA <3 wt.% and water content 1 wt.%. This is to avoid unfavorable reactions such as oil hydrolysis and saponification which tend to reduce the percentage yield of the product. Examples of heterogeneous catalysts are lanthanum oxide (La_2O_3), barium oxide (BaO), calcium oxide (CaO), calcium carbonate (CaCO_3), strontium oxide (SrO) and magnesium oxide (MgO) [56].

Acidic heterogeneous catalysts are suitable for the production of biodiesel due to their insensitivity to FFA and tolerance to the water content [53]. One of the benefits of using acid heterogeneous catalysts is that they can be easily removed from the mixture without affecting the catalytic activity. These catalysts are expensive as compared to the base heterogeneous catalysts. They operate at high temperatures, require long reaction time and high alcohol/oil mole ratio which may result in producing a low yield of biodiesel [35]. In recent studies Nafion-NR50, sulfated zirconia and tungstated zirconia have been used as acidic heterogeneous catalysts in the production of transesterification as they have acidic features such as sufficient acid site strength [52] [57].

Calcium oxide (CaO) has been the most utilized catalyst for the process of transesterification reaction because it is; easily prepared, has a high alkali pH value, insoluble in the reaction and non-toxic to the environment [58]. It is easily accessible as it can be found in chicken eggshell, ostrich eggshell, meretrix venus shell or synthesized in the lab using materials that contain calcium carbonate [35] [59] [60]. There has been reports of high yield production using CaO with over 95% recovery using soybean oil [61].

In other studies Romero *et al.*, doped CaO with Lithium and found that the modification of CaO to Li-CaO increases the yield of biodiesel [53].

1.3.3 Enzymatic Catalyst

Lipases are the most utilized enzymes when it comes to using biological catalysts which can be extracted from plants, animals and micro-organisms such as *Mucor miehei* (*Lipozym IM 60*), *Candida antarctica*, (*Novozym 435*), *Pseudomonas cepacia* (*PS 30*), *rhizopus oryzae*, *Penicillium expansum* and *Bacillus subtilis* [45]. The benefits of using biocatalyst is that they produce higher yields, better recovery of glycerol, insensitive to high free fatty acids without saponification products (by product) and also the process can be performed at low temperatures (up to 323 K) [62]. Therefore, enzyme catalyzed biodiesel production has high possibilities of becoming an eco-friendly process. However, their limitations are that they are more expensive than chemical catalysts. The glycerol in the reaction mixture can cause reduction of the catalytic activity hence resulting in a reduction of the biodiesel yield, slow reactions and enzyme deactivation [63]. Arumugan *et al.*, used an immobilized lipase enzyme on activated carbon for the process of transesterification and this was performed on waste sardine oil. The methyl ester produced was about 94.55% for a ratio of 9:1 methanol to oil and also the reusability of immobilized enzyme was found to be five (5) times [64]. In other studies, Lopressor *et al.*, performed an investigation on the production of biodiesel using an immobilized lipase from *Pseudomoms cepacia* as a catalyst in waste vegetable oil [62]. The biocatalyst showed interesting results due to its high catalytic specific surface, easy recovery, regeneration and reutilization.

1.4 Calcium Oxide Nanoparticles (CaO-NPs) in Biodiesel Production

Nano-materials are particles that can either be natural or man-made with at least one dimension of 100 nm or even less. Examples include carbon nano-tubes, nano-fibers, nano-clays, nano-composites, nano-wires and nano-particles [65] [66]. Nano-materials can be used in a wide range of applications in the industries; power generations, nuclear reactors, biomedical and biofuel. In recent years a large number of scientists have been

using nano-particles as catalysts for the production of biodiesel due to the fact that they have nano dimensional pores on the surface of the nano-particle, highly selective and high catalytic activity [67]. Several state of the art instruments have been used to characterize the nano-materials to find out their actual size, shape, surface structure, valency, chemical composition, electron band gap, bonding environment, light emission, absorption, scattering and diffraction properties. These include; nuclear magnetic resonance spectroscopy (NMR), infra-red spectroscopy (IR), ultra-violet and visible spectroscopy (UV-Vis), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), extended X-ray adsorption fine structure spectroscopy (EXAFS), X-ray absorption near-edge spectroscopy (XANES), X-ray emission spectroscopy (XES), photoluminescence spectroscopy (PL), small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) [68] [69] [70] [71].

Recently, nano catalytic technology has gained a lot of recognition with regard to the production of biodiesel [65]. Nano catalysts have a high catalytic efficiency, large surface area, high resistance to saponification and good rigidity [72]. The benefits of CaO is that it has minor toxicity, it can be reused and environmentally friendly. Tshizanga *et al.*, are among the scientists who studied this catalyst. They studied the effect of the reusability of CaO and their findings were that CaO can be reused ten (10) times with sustained catalytic activity [35]. Mansourpanah *et al.*, prepared CaO-Au nano-particles which he reported that they also exhibited a high catalytic activity and its reusability was reported to be analyzed up to ten (10) times without a significant loss of the activity [66].

1.5 *Schinziophyton rautanenii* (Mongongo)

Schinziophyton rautanenii (shown in Figure 1-2) is a multipurpose plant species found in Southern Africa with an ecosystem that provides a variety of goods and services. The fruits from these trees are highly nutritious, rich in proteins and minerals. They also contain active antioxidants used for cosmetic and skin care products which has been consumed by the bushmen in the Kalahari desert in Botswana for over 7000 years [73]

[74]. Mongongo tree belongs to *Euphorbiaceae* family and the monotypic genus *Schinziophyton*. It is a large, deciduous tree which normally grows in sandy soils found from coast to coast in Southern Africa scattered around northern Namibia, southern Angola, Zambia, Botswana, Zimbabwe, Mozambique and Malawi. It prefers to grow in semi-arid climatic conditions. Usually the nuts are harvested from February to April when it starts to fall off the trees. They bear fruits during the months of November to January depending on the climatic variations such as temperature and rainfall. It is a unique tree and easy to identify more especially in dry seasons. It is identified by its large size and symmetric shape of its crown. Normally, the trees are densely populated in the area where they are found and the seeds are readily available year round [75]. The seeds are protected by a very hard and thick shell and they make up to 70% of the fruit. Most rural communities in Southern Africa consider mongongo tree as an important source of food security and income [73]. The oil recovered from the seeds can be at most 60% which can be used for cooking, cosmetic application, fuel and medicinal purposes and the protein content from the nuts is about 30% while the leaves can be used as animal feed [76]. Even though, mongongo oil is used for cosmetic and skin care products also as a source of food, not enough work has been done on the production of biodiesel.

Most edible vegetable oils have been used to produce biodiesel and have shown great potential to replace diesel like canola, palm, rapeseed, corn and soybean [77]. They have limiting factors which affect the quality of biofuels, such as high viscosity and high molecular mass of triglycerides. These factors can result in an incomplete combustion, high carbon deposits, injection nozzle problems and high pour point of the biodiesel [53].

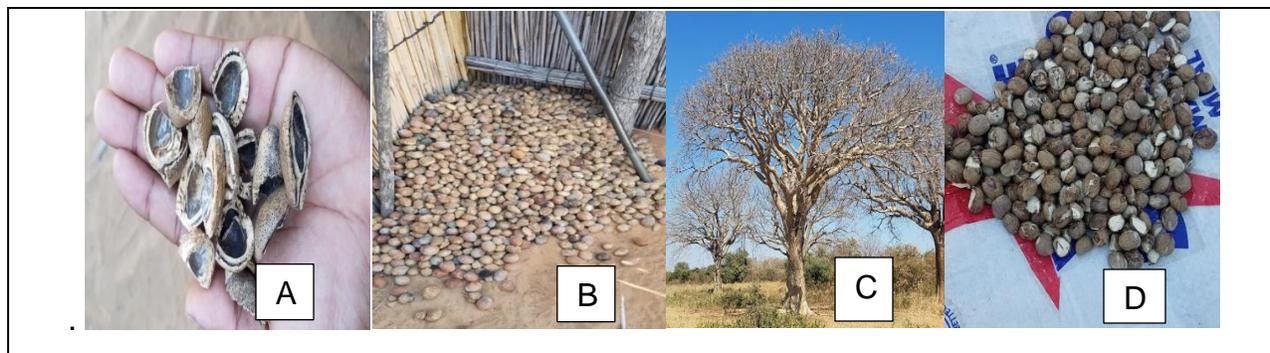


Figure 1-1: Images taken by Keene Mmusi of mongongo nutshell (A), mongongo fruit (B), mongongo tree (C) and mongongo nuts (D)

1.6 Statement of the Problem

The use of diesel has caused a lot of damage in the environment especially in industrialized countries through combustion engine emissions. This damage has contributed to global warming and climate changes. The accumulation of these greenhouse gases does not only affect the environment but also cause health problems to human beings and animals. The ever-increasing demand for diesel and oil has resulted in the increase of prices of petroleum diesel. This has led to the production of biodiesel which is biodegradable, to also reduce the demand for fuels and reduce pollution issues. Biodiesel has the potential to play an important role as an alternative source for diesel. Therefore, this study is focused in the preparation, characterization of two (2) heterogeneous catalysts and compare their catalytic activity for biodiesel from *Schinziophyton rautanenii* (mongongo) nut oil.

1.7 Research Questions

The research questions which are going to be investigated in the study are as follows;

- Which catalyst can give a better catalytic performance for the production of biodiesel from MNO between CaO nanoparticles and eggshell.
- How does the physicochemical properties on MNO affect the production of biodiesel.

- What is the optimum catalyst amount for CaO nanoparticles and eggshell required to produce high yields of biodiesel from MNO by transesterification reaction.

1.8 Aim and Objectives of the Study

The aim of this study was to prepare and characterize heterogeneous catalysts and compare their catalytic behavior towards biodiesel production from *Schinziophyton rautanenii* (mongongo) nut oil (MNO).

Objectives;

- (a) to determine the physicochemical properties of MNO;
- (b) to prepare and characterize CaO from eggshell;
- (c) to synthesize and characterize CaO-nanoparticles;
- (d) to produce biodiesel from transesterification of MNO using CaO from eggshell and CaO-nanoparticles;
- (e) to determine the physicochemical properties of biodiesel; and
- (f) to compare the performance of CaO-nanoparticles and CaO from eggshell as heterogeneous catalysts in the production of biodiesel.

1.9 Justification and Significance

Recently, there has been an increase of fuel prices around the world and with the rapid increase of the population this has also caused an increase in demand of fuel. Moreover, fossil fuels are depleting at an alarming rate, not only that the gases produced are not environmentally friendly hence the need to come up with an alternative for fuel. Therefore, biodiesel is one alternative which can efficiently replace fuel as it environmentally friendly and the costs of production are low.

After this study is successfully completed, it will give people more knowledge on green chemistry such as the production of biodiesel from mongongo nut oil seeds using heterogeneous catalysts; CaO from chicken eggshell and CaO-nanoparticles. Furthermore, mongongo tree is readily available in the northern part of Botswana and has

shown great potential for the production of biodiesel. This can help local communities where mongongo is available to sustain their income. Therefore, this research is necessary as it encourages an important part of the solution to a cleaner and more sustainable future on earth

1.10 References

- [1] J. Banerjee, R. Vijayaraghavan, A. Arora, D. R. MacFarlane, and A. F. Patti, "Lemon juice based extraction of pectin from mango peels: Waste to wealth by sustainable approaches," *ACS Sustain. Chem. Eng.*, vol. 4, no. 11, pp. 5915–5920, 2016.
- [2] Z. Taghizade, "Determination of biodiesel quality parameters for optimization of production process conditions," Ph.D dissertation, Polytechnic Institute of Bragança, Portuguese University of Applied Sciences, June, 2016.
- [3] D. A. M. San, "Biodiesel Production from Jatropha and Waste Cooking Oils in Mozambique," M.S thesis, Energy Technology, KTH School of Industrial Engineering and Management, September, 2016.
- [4] I. Emeji., "Production and Characterisation of Biofuel from Waste Cooking Oil," *2015 Int. Conf. Chem. Eng. 2015.*, August, p. 18, 2015.
- [5] J. Ongena and G. Van Oost, "Energy for future centuries prospects for fusion power as a future energy source," *Fusion Sci. Technol.*, vol. 57, no. 2, pp. 3–15, 2010.
- [6] J. Ge, S. Yoon, and N. Choi, "Using Canola Oil Biodiesel as an Alternative Fuel in Diesel Engines: A Review," *Appl. Sci.*, vol. 7, no. 9, p. 881, 2017.
- [7] N. Sukasem and S. Manopphan, "The Development of Biodiesel Production from Vegetable Oils by Using Different Proportions of Lime Catalyst and Sodium Hydroxide," *Energy Procedia*, vol. 138, pp. 991–997, 2017.
- [8] H. K. Balsora and P. Gautam, "Biofuels and Bioenergy (BICE2016)," *Springer Proc. Energy*, vol. 7, no. 3, pp. 93–106, 2017.
- [9] N. Cheikhoussef, "Profiling Studies of Five Namibian Indigenous Seed Oils Obtained Using Three Different Extraction Methods," 2018.
- [10] J. Gandure and C. Ketlogetswe, "Marula Oil and Petrodiesel: A Comparative Performance Analysis on a Variable Compression Ignition Engine," *Energy Power*

- Eng.*, vol. 3, no. 3, pp. 339–342, 2011.
- [11] Y. Gonfa Keneni and J. Mario Marchetti, “Oil extraction from plant seeds for biodiesel production,” *AIMS Energy*, vol. 5, no. 2, pp. 316–340, 2017.
- [12] P. K. Sahoo and L. M. Das, “Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils,” *Fuel*, vol. 88, no. 9, pp. 1588–1594, 2009.
- [13] W. O. Otta, P. K. Sahoo, J. M. Onyari, and F. J. Mulaa, “Effects of antioxidants on oxidation and storage stability of Croton megalocarpus biodiesel,” *Int. J. Energy Environ. Eng.*, vol. 7, no. 1, pp. 85–91, 2016.
- [14] E. M. Shahid and Y. Jamal, “Production of biodiesel: A technical review,” *Renew. Sustain. Energy Rev.*, vol. 15, no. 9, pp. 4732–4745, 2011.
- [15] European Union Committee, “The EU’s Target for Renewable Energy: 20% by 2020,” *House of Lords*, vol. I, no. October, 2008.
- [16] A. Froggatt, “A Comparison of the European Climate and Energy 2020 and 2030 Packages,” no. November 2015, pp. 1–39, 2015.
- [17] A. S. Nejad and A. R. Zahedi, “Optimization of biodiesel production as a clean fuel for thermal power plants using renewable energy source,” *Renew. Energy*, vol. 119, pp. 365–374, 2018.
- [18] I. M. Atadashi, M. K. Aroua, and A. A. Aziz, “Biodiesel separation and purification: A review,” *Renew. Energy*, vol. 36, no. 2, pp. 437–443, 2011.
- [19] M. I. Al-Widyan and A. O. Al-Shyoukh, “Experimental evaluation of the transesterification of waste palm oil into biodiesel,” *Bioresour. Technol.*, vol. 85, no. 3, pp. 253–256, 2002.
- [20] M. M. Gui, K. T. Lee, and S. Bhatia, “Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock,” *Energy*, vol. 33, no. 11, pp. 1646–1653, 2008.
- [21] C. Olgun, “The Role of the Eastern Member States in the European Union’s Energy

and Climate Policy,” 2017.

- [22] A. Rajalingam, S. P. Jani, A. S. Kumar, and M. A. Khan, “Production methods of biodiesel,” *Available online www.jocpr.com J. Chem. Pharm. Res.*, vol. 8, no. 3, pp. 170–173, 2016.
- [23] L. C. Meher, D. Vidya Sagar, and S. N. Naik, “Technical aspects of biodiesel production by transesterification - A review,” *Renew. Sustain. Energy Rev.*, vol. 10, no. 3, pp. 248–268, 2006.
- [24] Z. L. Chung, Y. H. Tan, Y. San Chan, J. Kansedo, N.M. Mubarak, M. Ghasemi and M.O. Abdullah, “Life cycle assessment of waste cooking oil for biodiesel production using waste chicken eggshell derived CaO as catalyst via transesterification,” *Biocatal. Agric. Biotechnol.*, vol. 21, pp. 101-117, 2019.
- [25] K. F. Yee, J. Kansedo, and K. T. Lee, “Biodiesel production from palm oil via heterogeneous transesterification: Optimization study,” *Chem. Eng. Commun.*, vol. 197, no. 12, pp. 1597–1611, 2010.
- [26] K. Tahvildari, Y. N. Anaraki, R. Fazaeli, S. Mirpanji, and E. Delrish, “The study of CaO and MgO heterogenic nano-catalyst coupling on transesterification reaction efficacy in the production of biodiesel from recycled cooking oil,” *J. Environ. Heal. Sci. Eng.*, vol. 13, no. 1, 2015.
- [27] S. A. Scott, M. P. Davey, J. S. Dennis, I. Horst, C. J. Howe, D. J. Lea-Smith, and A. G. Smith, “Biodiesel from algae: Challenges and prospects,” *Curr. Opin. Biotechnol.*, vol. 21, no. 3, pp. 277–286, 2010.
- [28] U. Schuchardt, R. Sercheli, and R. M. Vargas, “Transesterification of vegetable oils: A review,” *J. Braz. Chem. Soc.*, vol. 9, no. 3, pp. 199–210, 1998.
- [29] N. Tshizanga, E. F. Aransiola, and O. Oyekola, “Optimisation of biodiesel production from waste vegetable oil and eggshell ash,” *South African J. Chem. Eng.*, vol. 23, pp. 145–156, 2017.
- [30] S. T. Keera, S. M. El Sabagh, and A. R. Taman, “Castor oil biodiesel production

- and optimization,” *Egypt. J. Pet.*, 2018.
- [31] F. X. Liu, S. F. Fu, X. F. Bi, F. Chen, X. J. Liao, X. S. Hu and J.H. Wu, “Physico-chemical and antioxidant properties of four mango (*Mangifera indica* L.) cultivars in China,” *Food Chem.*, vol. 138, no. 1, pp. 396–405, 2013.
- [32] M. Canakci and J. Van Gerpen, “Biodiesel Production Via Acid Catalysis,” *Trans. ASAE (American Soc. Agric. Eng.)*, vol. 42, no. 1984, pp. 1203–1210, 1999.
- [33] Z. A. Gondra, “Study of factors influencing the quality and yield of biodiesel produced by transesterification of vegetable oils,” M.S thesis, Faculty of Engineering and Sustainable development, University of Gavle, June, 2010.
- [34] M. Nurdin, F. Fatma, M. Natsir, and D. Wibowo, “Characterization of methyl ester compound of biodiesel from industrial liquid waste of crude palm oil processing,” *Anal. Chem. Res.*, 2017.
- [35] N. Tshizanga, E. F. Aransiola, and O. Oyekola, “Optimisation of biodiesel production from waste vegetable oil and eggshell ash,” *South African J. Chem. Eng.*, vol. 23, pp. 145–156, 2017.
- [36] W. N. N. Wan Omar and N. A. Saidina Amin, “Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology,” *Biomass and Bioenergy*, vol. 35, no. 3, pp. 1329–1338, 2011.
- [37] B. L. Salvi and N. L. Panwar, “Biodiesel resources and production technologies - A review,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 6, pp. 3680–3689, 2012.
- [38] A. N. Phan and T. M. Phan, “Biodiesel production from waste cooking oils,” *Fuel*, vol. 87, no. 17–18, pp. 3490–3496, 2008.
- [39] B. Freedman, E. H. Pryde, and T. L. Mounts, “Variables affecting the yields of fatty esters from transesterified vegetable oils,” *J. Am. Oil Chem. Soc.*, vol. 61, no. 10, pp. 1638–1643, 1984.
- [40] L. C. Meher, D. Vidya Sagar and S.N. Naik, “Technical aspects of biodiesel

- production by transesterification—a review,” *Renew. and Sustain. Energy Rev.*, vol. 10, pp. 248–268, 2006.
- [41] A. Ribeiro, F. Castro, and J. Carvalho, “Influence of Free Fatty Acid Content in Biodiesel Production on Non-Edible Oils,” *WASTES Solut. Treat. Oppor.*, no. c, 2011.
- [42] I. M. Atadashi, M. K. Aroua, A. R. A. Aziz, and N. M. N. Sulaiman, “The effects of water on biodiesel production and refining technologies : A review,” *Renew. Sustain. Energy Rev.*, vol. 16, no. 5, pp. 3456–3470, 2012.
- [43] A. Demirbas, “Progress and recent trends in biodiesel fuels,” *Energy Convers. Manag.*, vol. 50, no. 1, pp. 14–34, 2009.
- [44] D. Kusdiana and S. Saka, “Effects of water on biodiesel fuel production by supercritical methanol treatment,” *Bioresour. Technol.*, vol. 91, no. 3, pp. 289–295, 2004.
- [45] M. K. Lam, K. T. Lee, and A. R. Mohamed, “Homogeneous , heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel : A review,” *Biotechnol. Adv.*, vol. 28, no. 4, pp. 500–518, 2010.
- [46] O. Ogunkunle, O. O. Oniya, and A. O. Adebayo, “Yield Response of Biodiesel Production from Heterogeneous and Homogeneous Catalysis of Milk Bush Seed (*Thevetia peruviana*) Oil Yield Response of Biodiesel Production from Heterogeneous and Homogeneous,” *Energy Policy Res.*, vol. 4, no. 1, pp. 21–28, 2017.
- [47] J. H. S. K. Jayamaha, L. Francisco, F. Luis, and C. Joaquim, "Supported Enzymes as Catalysts for Biodiesel Production." *Sri Lanka energy managers association*, vol. 12, pp. 1-64, 2015.
- [48] M. Ahmad, M. Zafar, S. Rashid, S. Sultana, H. Sadia and M. Ajab Khan, “Production of methyl ester (biodiesel) from four plant species of *Brassicaceae*: optimization of

- the transesterification process,” *International journal of green energy*, vol. 10, no. 4, pp. 362-369, 2013.
- [49] N. S. Talha and S. Sulaiman, “Overview of catalysts in biodiesel production,” *ARPJ. Eng. Appl. Sci.*, vol. 11, no. 1, pp. 439–442, 2016.
- [50] L. Meher, D. Vidyasagar, and S. Naik, “Technical aspects of biodiesel production by transesterification—a review,” *Renew. Sustain. Energy Rev.*, vol. 10, no. 3, pp. 248–268, 2006.
- [51] P. K. Sahoo, L. M. Das, M.K. G.Babu, P. Arora, V.P. Singh, N. R. Kumar, and, T.S Varyani, “Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine,” *Fuel*, vol. 88, no. 9, pp. 1698–1707, 2009.
- [52] S. Semwal, A. K. Arora, R. P. Badoni, and D. K. Tuli, “Biodiesel production using heterogeneous catalysts Bioresource Technology Biodiesel production using heterogeneous catalysts,” *Bioresour. Technol.*, vol. 102, no. 3, pp. 2151–2161, 2011.
- [53] R. Romero, S. Luz, and R. Nativi, “Biodiesel Production by Using Heterogeneous Catalysts,” *Altern. Fuel*, March, 2011.
- [54] Z. Helwani, M. R. Othman, N. Aziz, J. Kim, and W. J. N. Fernando, “Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review,” *Appl. Catal. A Gen.*, vol. 363, no. 1–2, pp. 1–10, 2009.
- [55] A. H. Al-Muhtaseb, F. Jamil, L. Al-Haj, M. T. Z. Myint, E. Mahmoud, M. N. Ahmad and S. Rafiq, “Biodiesel production over a catalyst prepared from biomass-derived waste date pits,” *Biotechnol. Reports*, vol. 20, 2018.
- [56] H. V. Lee, J. C. Juan, N. F. Binti Abdullah, R. Nizah MF, and Y. H. Taufiq-Yap, “Heterogeneous base catalysts for edible palm and non-edible Jatropha-based biodiesel production,” *Chem. Cent. J.*, vol. 8, no. 1, pp. 1–9, 2014.
- [57] T. Gebreyohans, “Production and characterization of biodiesel from Jatropha

- curcas seed by use K_2O / fly ash as a catalyst," M.S thesis, Chemical and Bio Engineering, Addis Ababa Institute of technology school of chemical and Bio engineering, June, 2018.
- [58] Z. X. Tang, D. Claveau, R. Corcuff, K. Belkacemi, and J. Arul, "Preparation of nano-CaO using thermal-decomposition method," *Mater. Lett.*, vol. 62, no. 14, pp. 2096–2098, 2008.
- [59] Y. Hua, M. Omar, C. Nolasco-hipolito, and Y. H. Taufiq-yap, "Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil : Catalyst characterization and biodiesel yield performance," *Appl. Energy*, vol. 160, pp. 58–70, 2015.
- [60] N. Tshizanga, E. F. Aransiola, and O. Oyekola, "Optimisation of biodiesel production from waste vegetable oil and eggshell ash," *South African J. Chem. Eng.*, vol. 23, pp. 145–156, 2017.
- [61] D. Y. C. Leung, X. Wu, and M. K. H. Leung, "A review on biodiesel production using catalyzed transesterification," *Appl. Energy*, vol. 87, no. 4, pp. 1083–1095, 2010.
- [62] C. G. Lopressor, S. Naccarato, L. Albo, M. G. De Paola, S. Chakraborty, S. Curcio, and V. Calabrò, "Enzymatic transesterification of waste vegetable oil to produce biodiesel," *Ecotoxicol. Environ. Saf.*, vol. 121, pp. 229–235, 2015.
- [63] S. Kumar, "Enzymatic Transesterification of Waste Animal Fats for Production of Biodiesel," M.S thesis, Biological Engineering, Dalhousie University Halifax, July, 2013.
- [64] A. Arumugam and V. Ponnusami, "Production of biodiesel by enzymatic transesterification of waste sardine oil and evaluation of its engine performance," *Heliyon*, vol. 3, no. 12, pp. 486, 2017.
- [65] C. Contado, "Nanomaterials in consumer products: A challenging analytical problem," *Front. Chem.*, vol. 3, no. AUG, pp. 1–20, 2015.

- [66] Y. Mansourpanah, R. Molaei, E. Bet-Moushoul, K. Farhadi, A. M. Nikbakht, and M. Forough, "Application of CaO-based/Au nanoparticles as heterogeneous nanocatalysts in biodiesel production," *Fuel*, vol. 164, pp. 119–127, 2015.
- [67] H. R. Harsha Hebbar, M. C. Math, and K. V. Yatish, "Optimization and kinetic study of CaO nano-particles catalyzed biodiesel production from Bombax ceiba oil," *Energy*, vol. 143, pp. 25–34, 2018.
- [68] L. Habte, N. Shiferaw, D. Mulatu, T. Thenepalli, R. Chilakala, and J. W. Ahn, "Synthesis of nano-calcium oxide from waste eggshell by sol-gel method," *Sustain.*, vol. 11, no. 11, pp. 1–10, 2019.
- [69] S. S. Madan and K. L. Wasewar, "Optimization for benzeneacetic acid removal from aqueous solution using CaO 2 nanoparticles based on Taguchi method," *Rev. Mex. Trastor. Aliment.*, 2017.
- [70] R. Sharma, D. P. Bisen, U. Shukla, and B. G. Sharma, "X-ray diffraction : a powerful method of characterizing nanomaterials," vol. 4, no. 8, pp. 77–79, 2012.
- [71] P. K. Tandon, "Catalysis : A Brief Review on Nano-Catalyst," August 2014, 2015.
- [72] S. Hashmi, S. Gohar, T. Mahmood, U. Nawaz, and H. Farooqi, "Biodiesel Production by using CaO-Al₂O₃ Nano Catalyst," *Int. J. Eng. Res. Sci.*, vol. 2, no. 3, pp. 2395–6992, 2016.
- [73] A. Maroyi, "Contribution of Schinziophyton rautanenii to Sustainable Diets , Livelihood Needs and Environmental Sustainability in Southern Africa," 2018.
- [74] L. Gwatidzo, B. M. Botha, and R. I. McCrindle, "Fatty acid profile of Manketti (Schinziophyton rautanenii) nut oil: Influence of extraction method and experimental evidence on the existence of -eleostearic acid," *J. Cereal. Oilseeds*, vol. 8, no. 5, pp. 33–44, 2017.
- [75] N. Cheikhyoussef, M. Kandawa-Schulz, R. Böck, C. de Koning, A. Cheikhyoussef, and A. A. Hussein, "Characterization of Schinziophyton rautanenii (Manketti) nut oil from Namibia rich in conjugated fatty acids and tocopherol," *J. Food Compos. Anal.*,

vol. 66, no. October, pp. 152–159, 2018.

- [76] A. E. Atabani, M. Mofijur, H. H. Masjuki, I. A. Badruddin, W. T. Chong, S. F. Cheng, S. W. Gouk, “A study of production and characterization of Manketti (*Ricinodendron rautonemii*) methyl ester and its blends as a potential biodiesel feedstock,” *Biofuel Res. J.*, vol. 1, no. 4, pp. 139–146, 2014.
- [77] H. L. Rutto and C. C. Enweremadu, “Optimization of production variables of biodiesel from manketti using response surface methodology,” *Int. J. Green Energy*, vol. 8, no. 7, pp. 768–779, 2011.

CHAPTER 2

2.0 MATERIALS AND METHODS

2.1 Materials and Reagents

All reagents were of analytical grade and were purchased from different suppliers as shown in Table 2-1.

Table 2-1: Chemicals and reagents

Chemical name	Supplier
99.5% Methanol	Skylabs
95% Ethanol	Skylabs
38% Hydrochloric acid AR	Skylabs
99% Potassium hydroxide	Rochelle Chemicals
99.5% Acetic acid	Glassworld
99% Chloroform	Sigma Aldrich
99% Sodium thiosulphate	Sigma Aldrich
99.5% Diethyl ether	Rochelle Chemicals
99% Sodium hydroxide pellets	Rochelle Chemicals
99% Calcium nitrate tetrahydrate	Rochelle Chemicals
Magnesium carbonate AR	Skylabs
n-Hexane	Skylabs
98% Phenolphthalein	Sigma Aldrich
99.8% Iodine	Sigma Aldrich
95% Petroleum ether	Sigma Aldrich
99% Potassium iodide	Sigma Aldrich

2.2 Instruments

Table 2-2 shows all the equipment which were utilized during the project.

Table 2-2: The main Instruments which were utilized for the production of biodiesel

Instrument	Source	Use
Powder X-Ray Diffractometer (XRD)	Bruker D8 Advance, Bellerica, United States of America.	Powder XRD in this study was used to characterize the catalysts; eggshell ash and calcium oxide nanoparticles (CaO-NPs), by identifying the elemental composition and calculating the size of particles. It is used to acquire qualitative analysis investigating the elemental and structural materials of the eggshell ash and CaO-NPs. This instrument was used to identify crystalline phase in the samples, determine the crystalline size and shape from the diffraction peaks. This instrument comes with EVA and TOPAS software used to analyse data.
Gas Chromatography- Mass Spectroscopy (GC-MS)	Agilent 7890A, Santa Clara, United States of America.	GC-MS in this study was used to separate and identify the compounds present in mongongo methyl esters (MMEs). Prior to analysis MMEs were obtained after removal of methanol, catalyst and glycerol from the separatory funnel which also involved gentle washing of the FAMEs with warm distilled water. The separation in GC was observed in the chromatogram through retention times while MS employed the NIST (National Institute of

		Standards and Technology) software to identify peaks in the spectra.
Fourier Transmission Infrared Spectroscopy (FT-IR)	Perkin Elmer, Waltham, United States of America.	FT-IR was used to identify the functional groups present in mongongo nut oil (MNO) and MMEs. Characterization was also performed on the catalysts; eggshell ash and CaO-NPs. The functional groups were recorded from the region of 4000 to 400 cm^{-1} using a PerkinElmer System 2000 FTIR spectrometer.
Scanning Electron Microscope-Elemental Dispersion X-ray (SEM-EDX)	Jeol JSM-7100F, Tokyo, Japan	In this study the morphological and elemental analysis of the catalysts; eggshell ash and CaO-NPs were obtained using a scanning electron microscope coupled with an Elemental Dispersion X-Ray. The elemental dispersion X-ray was used to provide information on qualitative and quantitative analysis of elements present in the catalyst. This instrument captures images of samples by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, giving out various signals which have information about the sample's surface topography and composition.
Kinematic viscosity meter	Omnetic, Waddinxveen, Netherlands	A kinematic viscometer was used to measure the viscosity of MNO and MMEs. A U-Visc 210/220 hardware version 4.0 was employed for this analysis. The viscosity of a sample was obtained by measuring the time for volume of liquid through a calibrated glass capillary

		viscometer under gravity. This instrument has two water baths of different temperatures (40° and 100 °C) where viscosity was measured.
Refractometer	Atago, Tokyo, Japan	A refractometer was used to analyse the purity and concentration of MNO and MMEs.
Density meter	Anton-Paar, Gaaz, Austria	A density meter was used to measure the density of MNO and MMEs.

2.3 Sample Collection

In this study mongongo (*Schinziophyton rautanenii*) nuts used for the production of biodiesel were collected from the surroundings of a village called Ukuse, near Shakawe in the northwest region of Botswana.

2.4 Extraction of Oil from Nut

Mongongo nut oil (MNO) was extracted traditionally by crushing the nutshells with a stone to remove the nuts from inside. The nuts were then boiled in a pot with water to moisten the layer covering the nuts and make it easy to remove. Thereafter, the nuts were crushed until a sticky nut paste was produced. The paste was placed back in the pot with boiling water and heated gently. Boiling was continued for some time to allow water evaporation and decantation of the oil. The oil was allowed to cool then poured in bottles for storage.

2.5 Determination of Physical and Chemical Properties of Mongongo Nut Oil and Biodiesel

2.5.1 Saponification Value

A solution of potassium hydroxide (14.2 g, 0.5 M) was prepared in 10 mL of distilled water. The solution was made to the mark with 95% ethanol in a 500 mL volumetric flask. The solution was left for 24 h before decanting. Thereafter, 25 mL of the solution was titrated against 0.5 M hydrochloric acid using phenolphthalein indicator and the values were recorded as a blank. 2.0 g of MNO/MMEs and 25 mL of alcoholic potassium hydroxide were added into 250 mL round bottomed flask. The solution was heated and refluxed for 1 h in a steam bath with continuous stirring. Thereafter, phenolphthalein indicator was

added while the solution was still hot, and the excess potassium hydroxide was titrated with 0.5 M hydrochloric acid until a cloudy solution was formed. The method was adopted from Tesfaye *et al.*, with modifications and saponification value was calculated using Equation 4 [1].

Equation 2-1: The equation used to calculate the saponification value

$$\text{Saponification Value} = \frac{56.1 (b-a) \times N}{W}$$

Where;

b = blank titre value (mL)

a = sample titre value (mL)

N = normality of hydrochloric acid (N)

W = weight of sample (g)

2.5.2 Acid Value

2.5 g of MNO/MMEs and 50 mL of 95% ethanol were added into a 250 mL conical flask. Four (4) drops of phenolphthalein indicator were added to the mixture. The solution was titrated against 0.5 M potassium hydroxide until the first pink colour appeared and visible for 30 sec. According to American society for testing and materials (ASTM D974), acid value and free fatty acid value are calculated using equation 2-2 and 2-3, respectively [2].

Equation 2-2: The equation used to calculate acid value

$$\text{Acid Value} = \frac{56.1 \times V \times N}{W}$$

Where;

V = Volume of standard potassium hydroxide (mL)

N = Normality of the potassium hydroxide solution or Sodium hydroxide solution (N); and

W = Weight of the sample (g); hence the free fatty acid is calculated with the equation 2-3 below;

Equation 2-3: The equation used to calculate free fatty acids

$$\text{Free fatty Acid (FFA)} = \frac{\text{Acid Value}}{2}$$

2.5.3 Peroxide Value

In a 250 mL conical flask, 5.0 g of MNO/MMEs and 30 mL of mixture of acetic acid and chloroform solvents (3:2) were added and gently swirled. 1 mL of potassium iodide solution was added to the solution and kept for 1 min in the dark room with occasional shaking and then 30 mL of distilled water was added. Then liberated iodine was slowly titrated against sodium thiosulphate solution with vigorous shaking until a yellow colour was not visible. 1 mL of starch solution indicator was added to the conical flask and then continued titrating with vigorous shaking (in order to realise all I₂ from CH₃Cl layer) until all the blue colour disappeared. The method used was adapted from Tesfaye *et al.*, and peroxide value was calculated using equation 2-4 [1].

Equation 2-4: The equation used to calculate peroxide value

$$\text{Peroxide Value (PV)} = \frac{V \times N \times 100}{W}$$

Where;

V = volume of sodium thiosulphate (mL)

N = normality of hydrochloric acid (N); and

W = weight of sample (g)

2.5.4 Iodine Value

In a 250 mL conical flask, 200 mL of mixed solvents of cyclohexane and acetic acid (1:1 ratio) was prepared. 0.13 - 0.15 g of MNO/MMEs, 20 mL of the prepared solvent mixture of cyclohexane and acetic acid, and 25 mL of Wij's reagent were added into 250 mL conical flask. The flask was placed in a dark room for 1 h. The iodine value was determined according to the European standard (EN 1411) by titration using sodium thiosulphate [3] [4]. Equation 2-5 was used to calculate the iodine value.

Equation 2-5: The equation used to calculate Iodine value

$$\text{Iodine Value (IV)} = \frac{(b - a) \times N \times 1.269 \times 100}{W}$$

Where;

b = blank titre value (mL)

a = sample titre value (mL)

N = normality of thiosulphate (N); and

W = weight of sample (g)

2.5.5 Density

The densities of MNO and MMEs were determined using density meter. The MNO and MMEs were injected into the density meter using a syringe and densities recorded at temperatures of 40 and 100 °C [5] [6].

2.5.6 Refractive Index

A refractometer was used to determine the refractive index of MNO and MMEs. About 1 mL (1 drop) of MNO/MMEs was placed in the instrument at room temperature and the value was recorded.

2.5.7 Kinematic Viscosity

A U-Visc 210/220 automatic viscometer was used to determine the kinematic viscosity of MNO and MMEs. About 10 mL of the sample was drawn into viscometer tubes and placed onto the auto sampler. The viscometer tubes were placed at different oil baths at temperatures of 40 and 100 °C. The method was performed according to American society for testing and materials (ASTM D445:19) [2].

2.6 Preparation of Catalyst

2.6.1 Chicken Eggshell

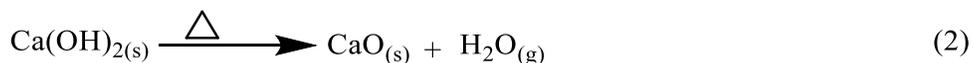
Eggshells were collected from the university cafeteria at Botswana International University of Science & Technology (BIUST) in Palapye. They were washed three (3) times with distilled water to remove dirt and contaminants. The shells were oven dried for 24 h at a temperature of 100 °C and then crushed using a mechanical pulveriser into fine particles of 100 µm. The fine powdered eggshells were then calcined at a temperature of 800 °C for 3 h using a Carbolite AAF 1100 to convert CaCO_3 into CaO . The ash was used as a heterogeneous catalyst for the conversion of mongongo nut oil into mongongo methyl esters (biodiesel) by transesterification reaction. The method used was adapted from Tshizanga *et al.*, [7]. The chemical reaction of the process is shown in scheme 2-1.



Scheme 2-1: The chemical reaction in the calcination process

2.6.2 Synthesis of Calcium Oxide Nano-Particles (CaO-NPs) Catalyst

10.0 g of calcium nitrate tetrahydrate was accurately weighed and dissolved in 100 mL of distilled water. A solution of sodium hydroxide was made by dissolving 3.3 g of the pellets in distilled water. This solution was added to calcium tetrahydrate solution dropwise while vigorously stirring the solution at room temperature. A white precipitate which is calcium hydroxide was filtered, washed with warm distilled water and oven dried for 24 h at a temperature of 80 °C. The dried calcium hydroxide was converted into calcium oxide nanoparticles (heterogeneous catalyst) by calcination at a temperature of 800 °C using a Carbolite AAF 1100 furnace for 3 h. The chemical reactions of this process are shown in scheme 2-2.



Scheme 2-2: The chemical reactions used for the synthesis of CaO-NPs

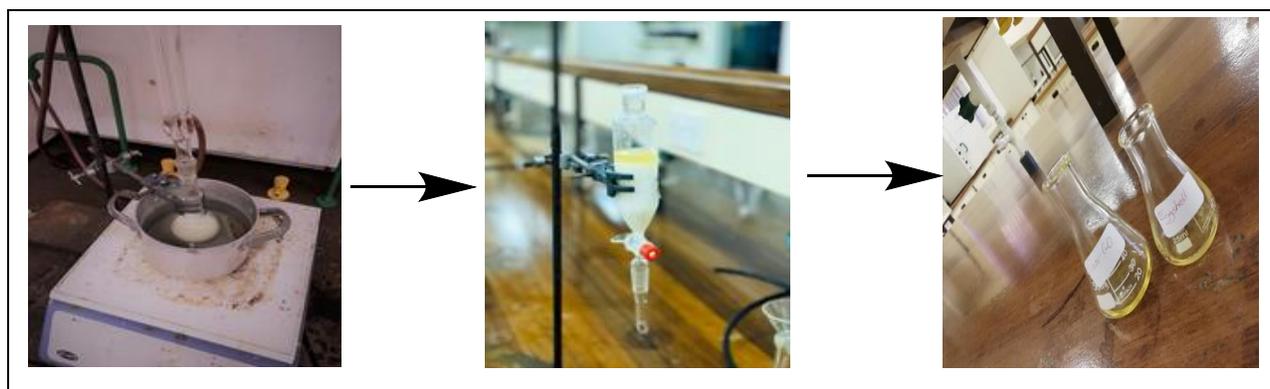
2.7 Transesterification Reaction

Transesterification method was employed for the production of biodiesel using a mole ratio of 9:1 methanol to oil for the reaction. 10.0 g of MNO was added in a 250 mL round bottomed flask. The contents were then heated under reflux to a temperature between 65-70 °C in a water bath until the oil and water bath temperature reached equilibrium. A mixture of methanol and the catalyst was made in a beaker and stirred until homogeneity was reached. Once the oil had reached a temperature between 65-70 °C a mixture of methanol and the catalyst was added to the round bottomed flask. The mixture was continuously stirred keeping the temperature kept at 65 °C for 3 h. After 3 h the reaction was stopped and the mixture was transferred into a separatory funnel and allowed to stand for phase separation. After phase separation glycerol (lower layer) was removed and only the ester mixture (top layer) was left in the separating funnel. The ester mixture was washed with warm distilled water to remove traces of the catalyst and alcohol until the water layer was clear. Then anhydrous magnesium carbonate (drying agent) was

added to get rid of any water left in the methyl ester. The method was adopted from Uprety *et al.*, with modifications [8]. The percentage yield of the methyl esters obtained was calculated using equation 2-6. Scheme 2-4 shows the schematic diagram of the reaction.

Equation 2-6: The equation used for the calculation of the % yield

$$\% \text{ yield FAMES} = \frac{\text{Weight of FAMES produced (g)}}{\text{Weight of MNO for reaction (g)}} \times 100$$



Scheme 2-3: Schematic diagram of Transesterification reaction

2.8 Gas Chromatography- Mass Spectrometer (GC-MS) Analysis

The methyl esters from biodiesel were analysed using Gas chromatography Mass spectrometer which was equipped with a NIST library for identification of peaks. The analysis was carried out by an Agilent 7890A Gas Chromatograph (Agilent Technologies, Santa Clara, United States of America) with an Agilent 5975C Mass Spectrometry Detector (Agilent Technologies) and an Agilent 7693 auto sampler (Agilent Technologies). The separation was achieved on a HP-5MS 5% phenyl methyl silox column (30 m × 250 μm × 25 μm. Approximately 1 mL of sample solution was diluted with 1 mL of hexane then placed in the auto sampler sample rack for injection in split ratio of 80:1. The parameter settings for the GC-MS are displayed in Table 2-3.

Table 2-3: GC-MS parameters for the analysis of Biodiesel

Parameter	Setting
Column Temperature program	325 °C by 1 mL/min.
Run time	35.5 mins
Injector Temperature	290 °C
Total flow	84 mL/min
Injection volume	1 µL
Split flow	80 mL/min
EM Volt	1082 V

2.9 References

- [1] B. Tesfaye and A. Abebaw, "Physico-Chemical Characteristics and Level of Some Selected Metal in Edible Oils," *Adv. Chem.*, vol. 2016, pp. 1–7, 2016.
- [2] N. Tshizanga, "A study of biodiesel production from waste vegetable oil using eggshell ash as a heterogeneous catalyst" M.S thesis, Chemical Engineering in the Faculty of Engineering, Cape Peninsula University of Technology, October, 2015.
- [3] K. O. Omeje, O. K. Iroha, A. A. Edeke, H. C. Omeje, and V. O. Apeh, "Characterization and fatty acid profile analysis of oil extracted from unexploited seed of African star apple (Udara)," *OCL - Oilseeds fats, Crop. Lipids*, vol. 26, 2019.
- [4] Z. Taghizade, "Determination of biodiesel quality parameters for optimization of production process conditions," Ph.D dissertation, Polytechnic Institute of Bragança, Portuguese University of Applied Sciences, June, 2016.
- [5] T. Gebreyohans, "Production and characterization of biodiesel from *Jatropha curcas* seed by use K_2O / fly ash as a catalyst," M.S thesis, Chemical and Bio Engineering, Addis Ababa Institute of technology school of chemical and Bio engineering, June, 2018.
- [6] I. A. Ateeq, "Biodiesel Viscosity and Flash Point Determination," M.S thesis, Faculty of Physics, Najah National University, April, 2015.
- [7] N. Tshizanga, E. F. Aransiola, and O. Oyekola, "Optimisation of biodiesel production from waste vegetable oil and eggshell ash," *South African J. Chem. Eng.*, vol. 23, pp. 145–156, 2017.
- [8] B. K. Uprety, W. Chaiwong, C. Ewelike, and S. K. Rakshit, "Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity," *Energy Convers. Manag.*, vol. 115, pp. 191–199, 2016.

CHAPTER 3

3.0 RESULTS AND DISCUSSION

3.1 Preparation and Characterization of Calcium Oxide Nanoparticles (CaO-NPs) and Chicken Eggshell Ash

3.1.1 Powder X-Ray Diffraction (XRD) Characterization

Powder X-Ray Diffraction (XRD) is an analytical technique used to investigate various solid materials, to assess the crystallinity and to estimate the composition of the material of interest. The X-ray source (usually Cu) and moveable detectors are used to measure the powdered sample and scan the intensity of the diffracted radiation as a function of 2θ where theta is the angle between the incoming incident x-ray and diffracted beams. Not only can this instrument be used to identify the crystallographic phases present in the material but it can also be used to determine the crystalline size and the spacing between parallel planes of atoms which results in diffraction of peaks [1]. In this study, Powder XRD was used to investigate freshly prepared samples to assess the purity of the expected phases and the degree of crystallization. The Debye-Scherrer's equation (equation 3-1) was used to calculate the average crystalline size of the eggshell ash and CaO-NPs.

Equation 3-1: The Debye-Scherrer's equation

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where;

D = Mean crystalline size (nm)

λ = X-Ray wave length (0.154 nm)

β = Full width at half maximum

Θ = Bragg's Angle and k = Shape factor (with $k=1$)

3.1.1.1 Chicken Eggshell Powder-XRD Characterization

The powder X-ray Diffraction (XRD) was used to analyse chicken eggshell samples. The measurements were performed at 2Θ from 0° to 90° of the eggshell ash and eggshell. The powder XRD pattern of the eggshell ash and eggshell shown in Figure 3-1 were identified as CaO and CaCO₃ respectively matched with the powder diffraction file (PDF) search CaO was successfully formed after calcination with no traces of CaCO₃ proving that the eggshell ash produced pure CaO. The results could also imply that the eggshell ash obtained was completely crystallized because of the removal of CO₂ during the thermal treatment process. The successful transformation of CaCO₃ to CaO was seen in the power XRD pattern in Figure 3-1 of the eggshell ash calcined at 800 °C and eggshell, the results were similar to those reported by Hua *et al.*, [2]. The estimated average particle size of the eggshell was calculated to be 50 nm (with $k=1$).

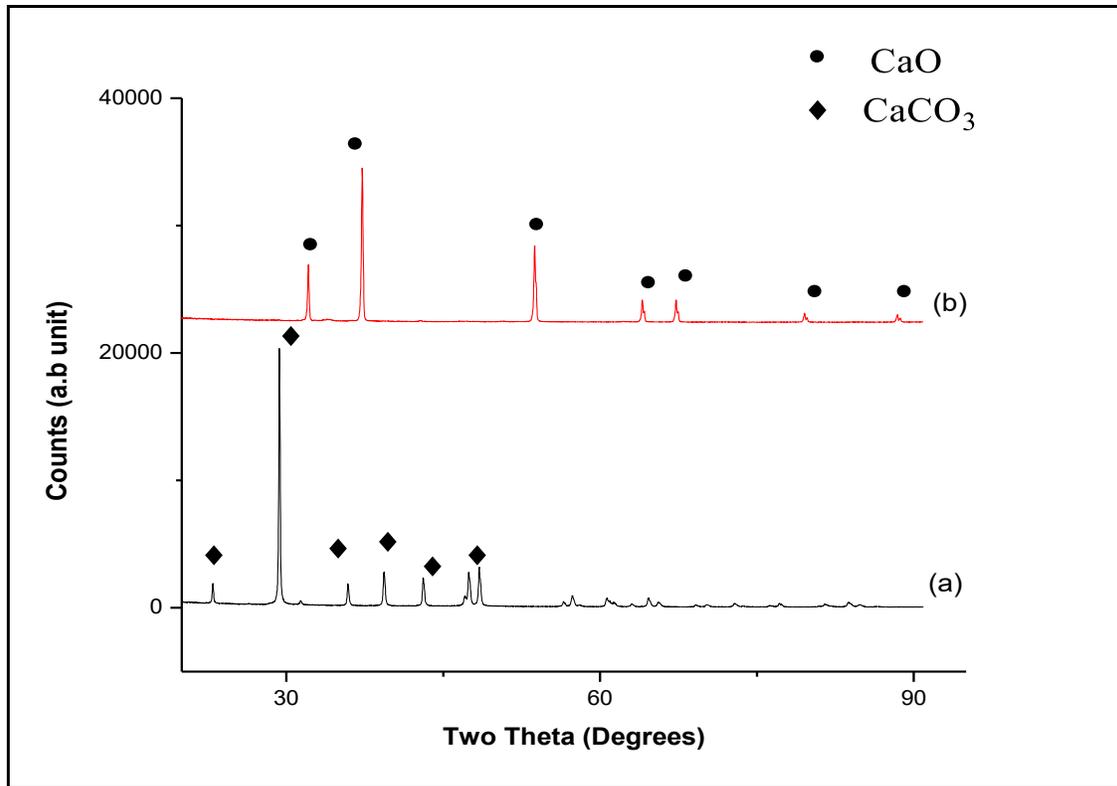


Figure 3-1: XRD pattern of samples; (a) eggshell (black) and (b) eggshell ash calcined at 800 °C (red)

Sharp and narrow peaks shown in Figure 3-2 of the metal oxide were identified as CaO matched with PDF 04-007-9734 (refer to Appendix A: Spectrum 4-1) and these were similar to those found in literature [3] [4]. The powder XRD pattern corresponding to CaO crystalline phase showed distinct peaks at $2\theta = 32.2^\circ$, 37.3° , 53.8° , 64.0° , 67.3° , 79.5° and 88.3° which respectively corresponded to (111), (200), (220), (311), (222), (400) and (321) orientation planes known as miller indices as shown in Table 3-1. Table 3-1 also shows the distance between planes of atoms (hkl) of diffracted peaks which is known as d-spacing. Peaks observed in Figure 3-2 with a high x-ray count (intensity) indicate a high content of CaO [5].

Table 3-1: Various planes for d-spacing of eggshell ash calcined at 800 °C

2 θ Angle	Diffraction peaks for CaO	d-spacing (Å)
32.2	111	2.78225
37.3	200	2.40950
53.8	220	1.70377
64.0	311	1.45298
67.3	222	1.39113
79.5	400	1.20475
88.3	321	1.10555

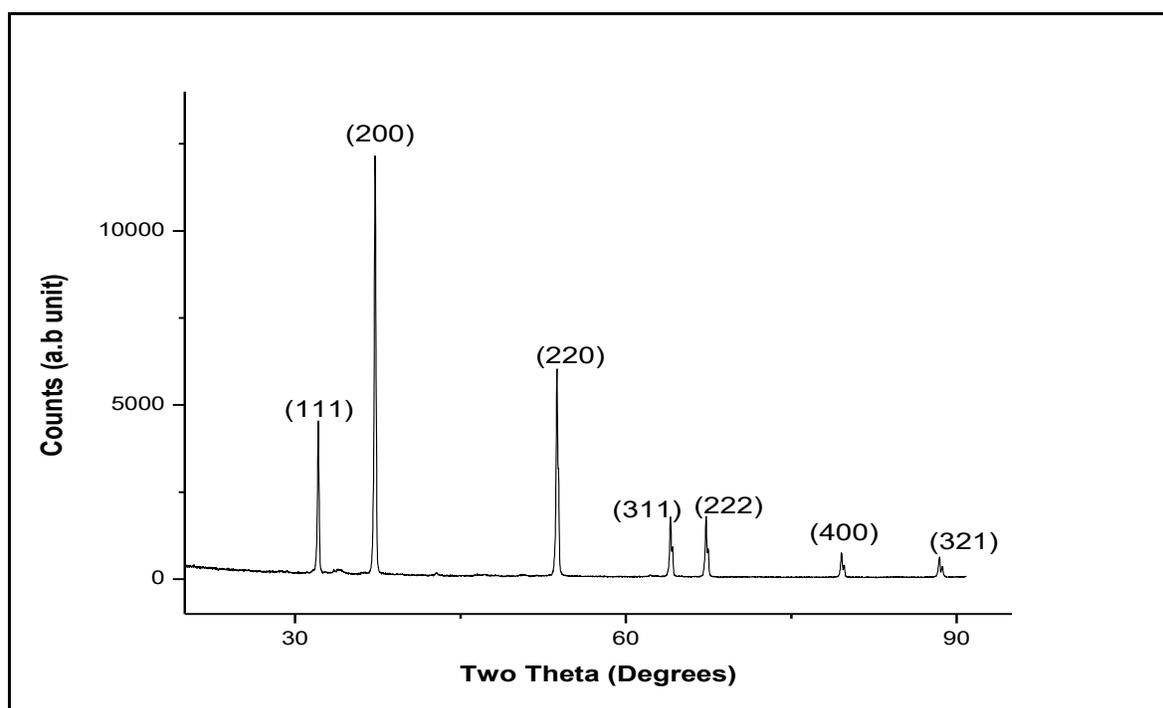


Figure 3-2 The XRD pattern of eggshell ash calcined at 800 °C

3.1.1.2 Calcium Oxide Nanoparticles (CaO-NPs) Powder-XRD Characterization

Figure 3-3 shows the powder XRD pattern of calcined CaO-NPs at 800 and 900 °C. The powder XRD pattern of CaO-NPs showed sharp and separated peaks indicating that CaO was produced from Ca(OH)₂. Mirghiasi *et al.*, also observed similar patterns [6]. The spectrum of CaO-NPs calcined at 800 °C showed higher peaks than that of CaO-NPs calcined at 900 °C, which was an indication that it had a high degree of crystallinity [3]. CaO-NPs calcined at 800 °C were chosen to be used in the production of biodiesel from mongongo nut oil because they had more of CaO and it was expected that they would give a better yield than those calcined at 900 °C.

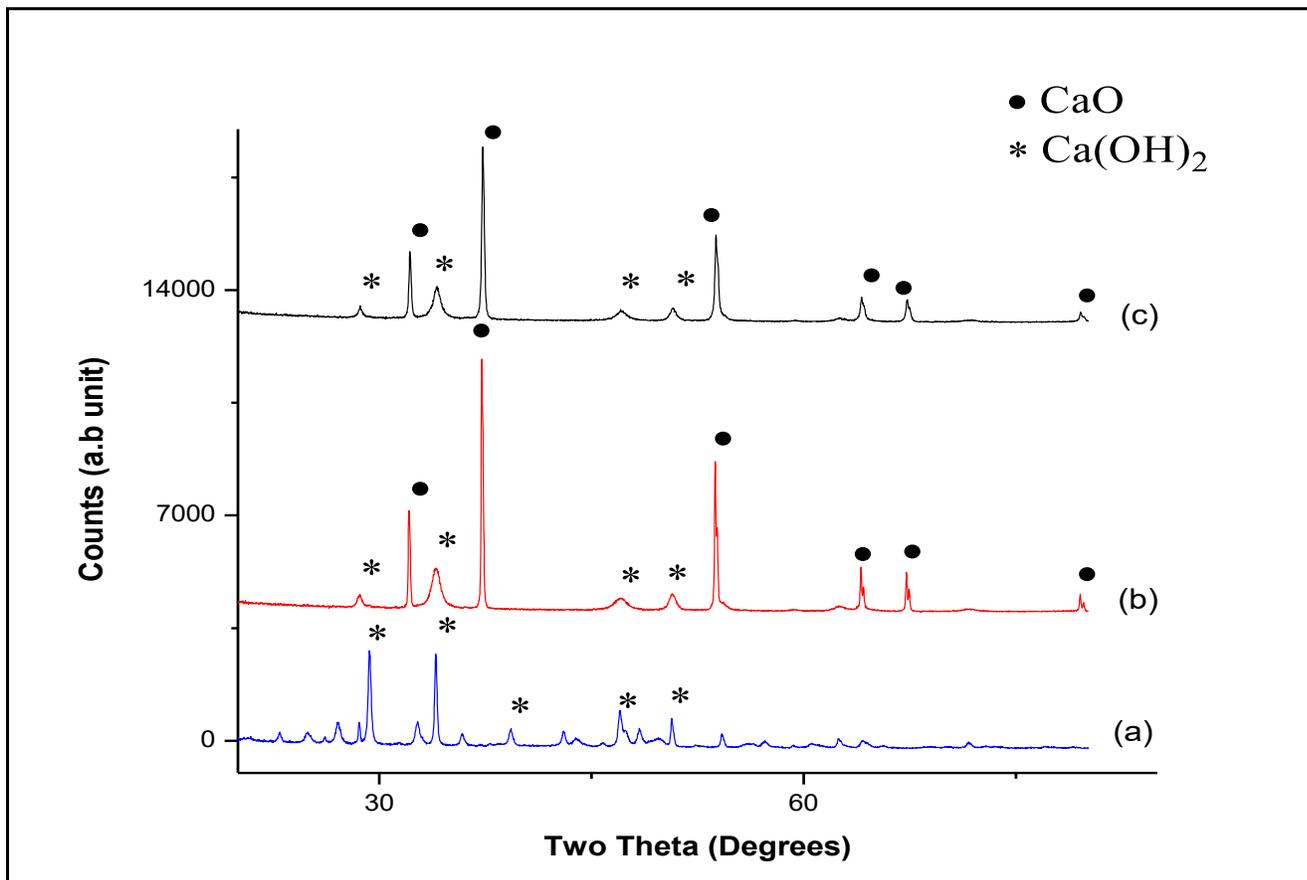


Figure 3-3: XRD pattern of samples; (a) Ca(OH)₂ (b) CaO-NPs calcined at 800 °C and (c) CaO-NPs calcined at 900 °C

Figure 3-4 showed intense peaks observed at 32.2 °, 37.4 °, 53.9 °, 64.2 °, 67.4 ° and 79.7 ° corresponding to (110), (200), (220), (311), (222) and (400) orientation planes respectively shown in Table 3-2. The distance between the diffracted peaks of CaO-NPs is also shown in Table 3-2 as d-spacing. The powder XRD pattern in Figure 3-4 showed that the CaO was successfully produced matched with COD 9006694 (refer to Appendix A: Spectrum 4-3). CaO was produced in large amounts as per the high intensity peaks. However, there were some diffraction peaks observed in low intensity which were identified as Ca(OH)₂ matched with COD 1001768 (refer to Appendix A: Spectrum 4-2). These could have been a result of CaO interacting with the water vapor found in the atmosphere or some of the reactants remained after calcination [6]. The estimated average particle size of CaO-NPs were calculated to be 42 nm (where $k=1$) not so far off from that of the eggshell ash derived CaO which was 50 nm. Nonetheless, nanoparticles are characterized by their condensed size, which results in a large surface area. Therefore, the particle size for CaO-NPs was expected to be low. It was concluded that nanoparticles were indeed produced.

Table 3-2: d-spacing for various planes of CaO-NPs calcined at 800°C

2θ Angle	Diffraction peaks for CaO	d-spacing (Å)
32.2	110	2.77700
37.4	200	2.40500
53.9	220	1.70080
64.2	311	1.45040
67.4	222	1.38870
79.7	400	1.20260

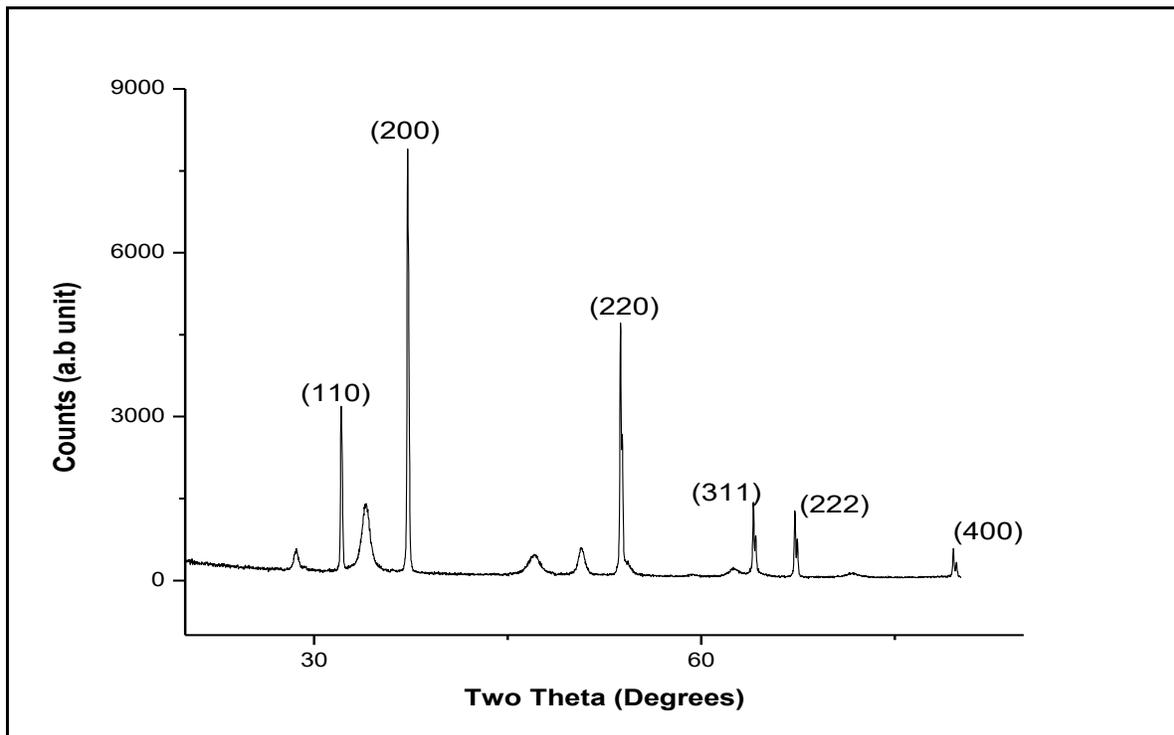


Figure 3-4: XRD pattern of CaO-NPs calcined at 800°C

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transform Infrared (FTIR) spectroscopy is a technique used to identify functional groups present in organic, polymeric, and in some cases, inorganic materials normally within wavenumber range of 400-4000 cm^{-1} . The instrument uses light which is in the infrared region of electromagnetic radiation to scan the materials and analyze the vibrational modes given in the form of stretching frequencies characteristic of the material.

3.1.2.1 Chicken Eggshell FTIR Characterization

FTIR spectrophotometer was used to determine characteristic bands of the eggshell ash and eggshell. Figure 3-5 shows the FTIR spectra for both eggshell ash and eggshell was recorded in the range of 4000-400 cm^{-1} . Figure 3-5 (a) which is a spectrum of the eggshell showed a sharp peak at 3614.37 cm^{-1} which was due to the presence of hydroxyl ($-\text{OH}$).

Witoon reported similar results of the broad (-OH) stretch vibration [7]. The presence of the stretch vibration was assumed to be due to the adsorption of atmospheric water [8]. The band observed at 1083.86 cm^{-1} was due to the CaCO_3 [3]. Figure 3-5 (b) showed eggshell ash calcined at $800\text{ }^\circ\text{C}$ with two bands at 1405.93 and 873.64 cm^{-1} which indicated the presence of (C-O) bond. Lesbani *et al.*, and Mirghiasi *et al.*, reported similar results showing that this could be due the occurrence carbonation of CaO , since CaO was in contact with air and without high temperatures for calcination [3] [6]. When the eggshell was heated at high temperatures ($800\text{ }^\circ\text{C}$) during calcination resulted in the loss of CaCO_3 hence reducing the mass of the functional groups bonded to the CO_3^{2-} ions, this is why the intensity of CaCO_3 peaks decreases [2]. The strong band observed at 713.46 cm^{-1} are due to the (Ca-O) bond which was observed and it is consistent with literature values [9] [10]. The presence of these characteristic bands proved that CaO powder had been produced.

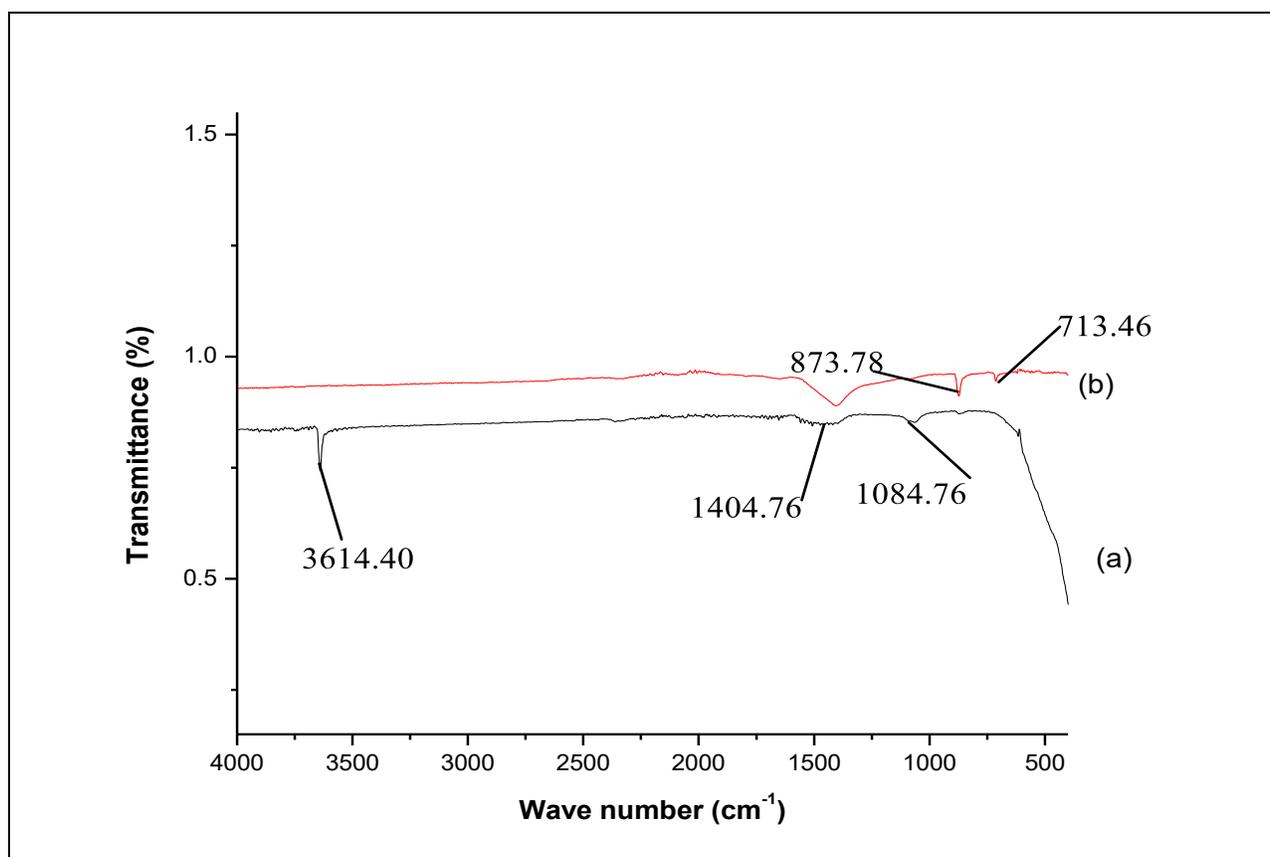


Figure 3-5: Fourier Transform Infrared Spectroscopy of (a) eggshell (red) (b) eggshell ash calcined at $800\text{ }^\circ\text{C}$ (black)

3.1.2.2 Calcium Oxide Nanoparticles (CaO-NPs) FTIR Characterization

The FTIR spectra of the CaO-NPs and Ca(OH)₂ are shown in Figure 3-6. Ca(OH)₂ shown in Figure 3-6 (a) was thermally decomposed at two different temperatures as shown in the FTIR spectra in Figure 3-6 (b) and (c). These are CaO-NPs calcined at 800 and 900 °C respectively. Figure 3-6 (c) clearly showed a sharp absorption peak 3641.15 cm⁻¹ associated with the hydroxyl (–OH) stretching group [6]. Another peak was observed at 1404 cm⁻¹ which was linked to the (C–O) bond. A low intensity peak assigned as (–OH) stretching group was also observed in Figure 3-6 (b) at 3641.15 cm⁻¹. Figure 3-6 (b) also showed peaks at 1458 and 873 cm⁻¹, these were also associated with the (C–O) bond. Figure 3-6 (b) and (c) of CaO-NPs calcined at 900 and 800 °C respectively both had an (–OH) stretch vibration which was assumed to be due to adsorption of water to CaO from the atmosphere during sample handling [11]. According to a reports by Elmastaş *et al.*, and Harsh-Hebbbar *et al.*, if CaO is exposed to open air for a long period of time it can be hydrolyzed to Ca(OH)₂ [12] [13]. The other reason was that it could be that some of the Ca(OH)₂ from Figure 3-6 (a) may have not been completely transformed to CaO, thus, some of the hydroxide ions (–OH) remaining [14]. The peaks observed at 1458, 1470 and 1404 cm⁻¹ are associated with the (C–O) bond which was related to the carbonation of CaO-NPs [15]. The band at 875.57 and 873.64 cm⁻¹ were due to the (Ca–O–Ca) bonds, Anantharaman *et al.*, reported similar results [16] [17].

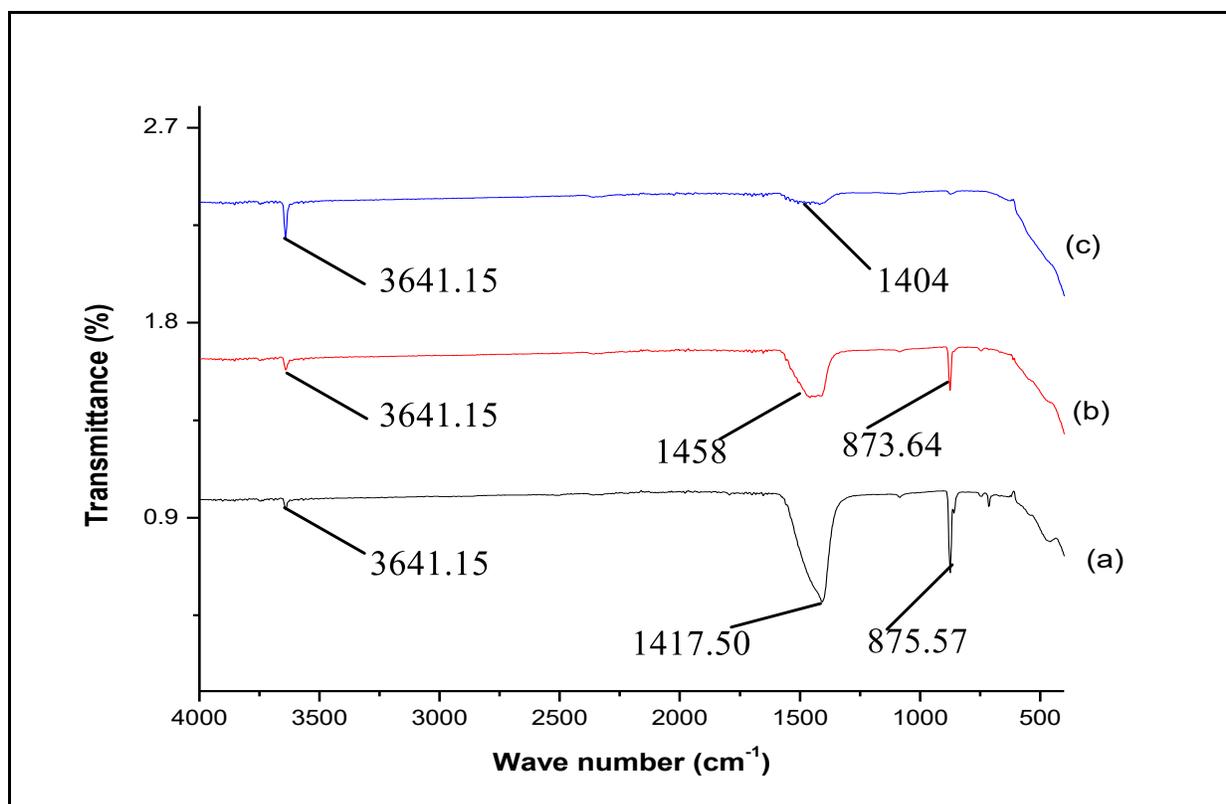


Figure 3-6: Fourier Transform Infrared Spectra of (a) Ca(OH)_2 (b) CaO-NPs calcined at $800\text{ }^\circ\text{C}$ and (c) CaO-NPs at $900\text{ }^\circ\text{C}$

3.1.3 Scanning Electron Microscope- Elemental Dispersive X-ray (SEM-EDX) Analysis

A Scanning Electron Microscope (SEM) is one of the most popularly used instruments for characterization of materials. The micrograms produced by the electron beam are easy to interpret and the information produced is diverse. SEM does not only generate qualitative information but it can also generate quantitative results about the microstructure, crystallography and electronic properties of the material being analyzed [18]. In this study the SEM used was equipped with an Elemental Dispersive X-ray (EDX) analyzer which was used to investigate the chemical composition of the samples.

3.1.3.1 Chicken Eggshell SEM-EDX Characterization

Figure 3-7 shows the SEM image of CaO from eggshell ash calcined at 800 °C. Figure 3-7 (a) showed images that indicated a granular surface which is in an unsymmetrical form, this was observed with agglomerated particles, forming a microporous structure reported to be of CaO similar to those reported by Fayyazi *et al.*, [19]. The particles also appeared to be clustered which could be due to the exposure to high temperatures during calcination [20]. Figure 3-7 (a) showed images with small particles because large amounts CO₂ gas escaped when the eggshell was exposed to high temperature during calcination (800 °C) [21]. CaCO₃ was transformed to CO₂ and CaO. Supriyanto *et al.*, also reported similar results [5]. Furthermore, they pointed out due to exposure to high temperatures the images of calcined eggshells have more porosity than before calcination due to the release of CO₂. Figure 3-7 (b) showed the SEM image with interconnected structure like irregular shapes and sizes which varied from one shape to another with tiny crystals embedded in the particles [22]. Tshizanga pointed out that it could be caused by the heterogeneous arrangement in the mechanical properties of the sample used which plays a significant role in the activity of the catalyst [23]. Figure 3-8 showed the spectrum of eggshell ash which indicated that CaO was indeed high in concentration which was satisfactory and expected results. These results were similar to those reported by Syazwani *et al.*, and Chung *et al.*, [24] [25]. The atomic compositions shown in Table 3-3 for calcium (Ca), oxygen (O), Carbon (C) and Magnesium (Mg) were 28.15, 64.40, 16.24 and 0.02% respectively. These results were satisfactory as they proved that CaO is present in the eggshell ash. Furthermore, the presence of C, Ca and O as the main elements proves the significance of carbonate phases in the sample [26].

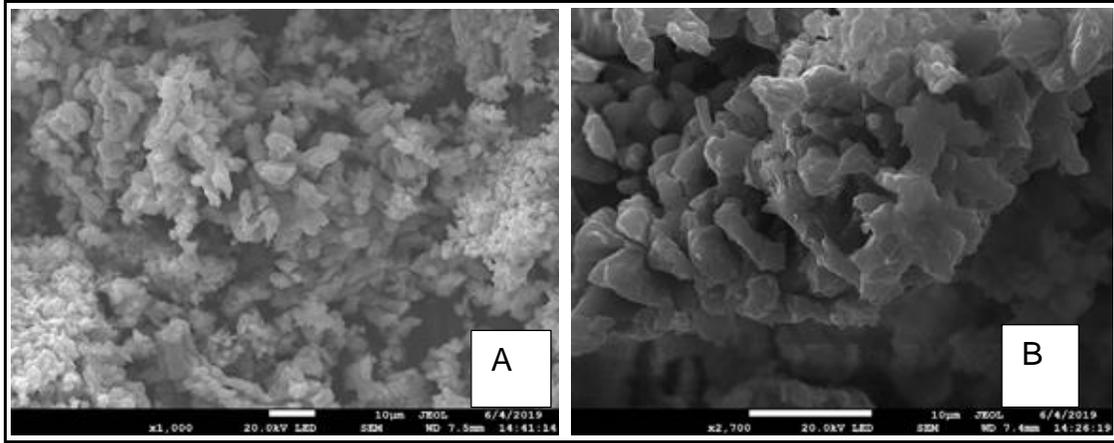


Figure 3-7: SEM images of eggshell ash catalyst calcined at 800 °C

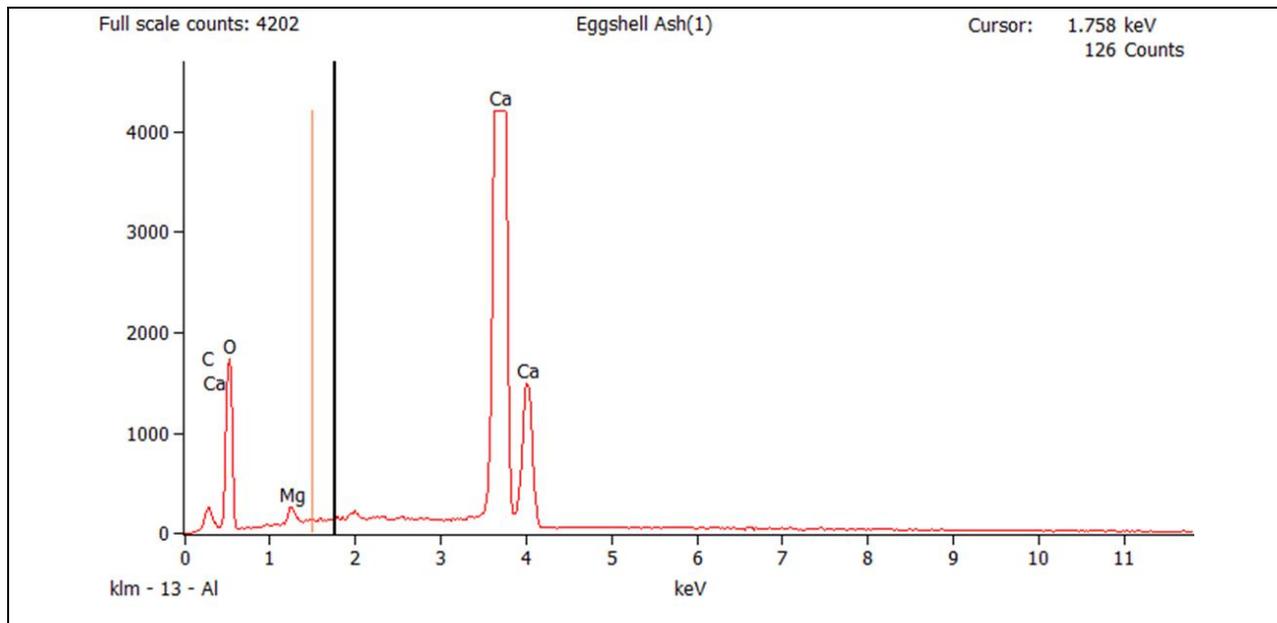


Figure 3-8: SEM-EDX spectrum of eggshell ash calcined at 800 °C

Table 3-3: Elemental composition of eggshell ash calcined at 800 °C

Formula	Atom (%)
C	6.05 (18.22)
O	64.40 (61.31)
Mg	0.01
Ca	28.15 (19.47)

NB: Literature values for elemental analysis of CaO in parenthesis [26].

3.1.3.2 Calcium Oxide Nanoparticles (CaO-NPs) SEM-EDX Characterization

The SEM images of CaO-NPs calcined at 800 °C are shown in Figure 3-9. Figure 3-9 (a) showed particles which were agglomerated to each other. According to Srivastava *et al.*, the agglomeration of particles suggest that the particles are porous in nature [27]. Figure 3-9 (b) showed particles arranged in a grain like structure with a spherical morphology. The individual particles were nano sized crystal similar to that found in literature [9] [28]. The micro pores observed in Figure 3-9 (b) were due to the release of H₂O and CO₂ during calcination and Srivastava *et al.*, pointed out that the presence of pores improve the catalytic efficiency for the production of biodiesel by transesterification reaction [27]. The EDX spectrum shown in Figure 3-10 showed the elements present in the CaO-NPs and the expected CaO was in high concentration. Their atomic compositions are shown in Table 3-4 for calcium (Ca), oxygen (O), carbon (C) and magnesium (Mg) were 38.18, 45.56, 6.05 and 0.01% respectively. The results indicate that CaO has been produced.

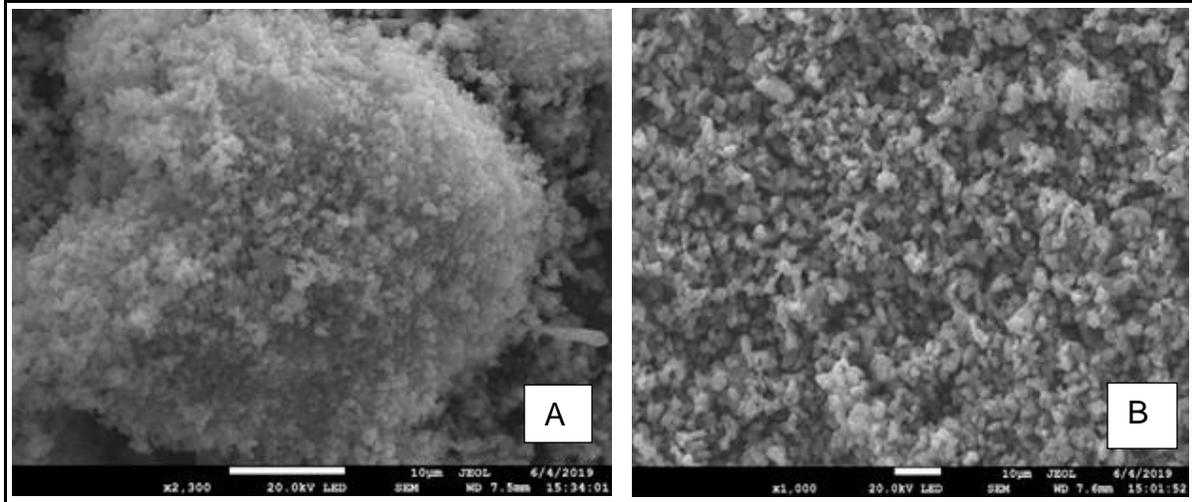


Figure 3-9: SEM images of CaO-NPs calcined at 800 °C

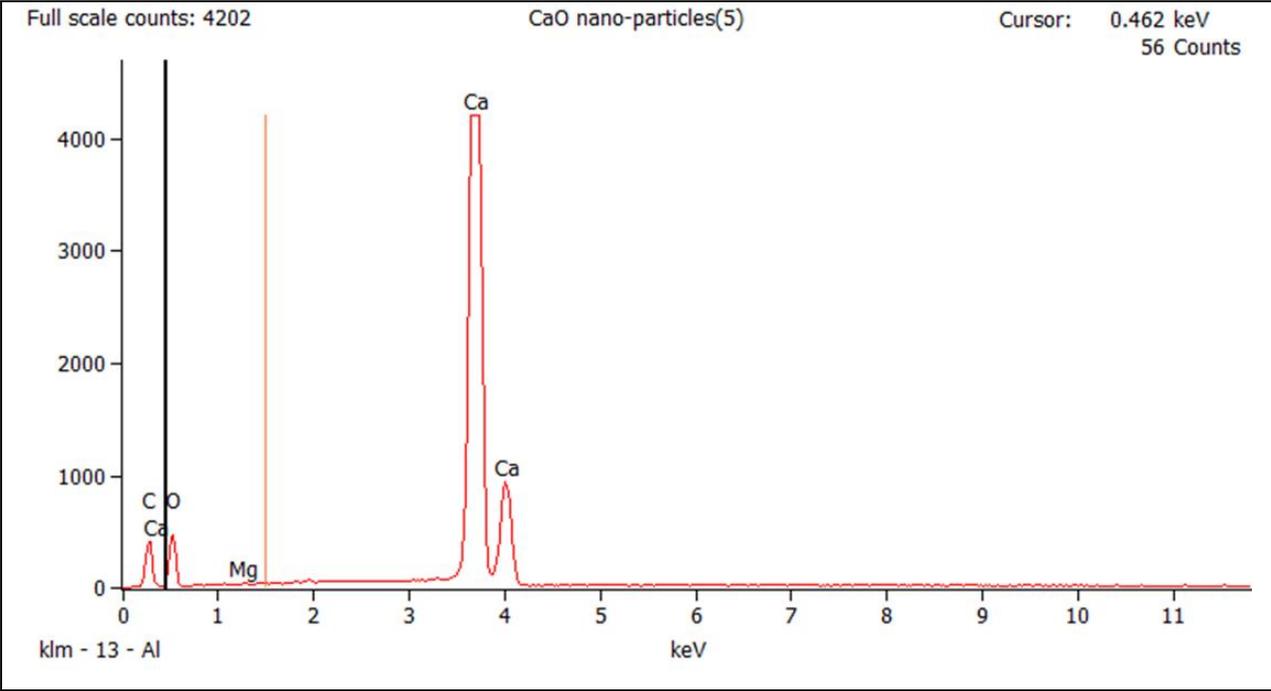


Figure 3-10: SEM-EDX analysis of CaO-NPs calcined at 800 °C

Table 3-4: Elemental composition of CaO-NPs

Formula	Atom (%)
C	16.24 (18.22)
O	45.56 (61.31)
Mg	0.02
Ca	38.18 (19.47)

NB: Literature values for elemental analysis of CaO in parenthesis [26].

3.2 Physicochemical Properties of Mongongo Nut Oil and its Biodiesel

All oils have unique physical, chemical and compositional parameters. This work describes some important properties of mongongo nut oil (MNO) and its resultant biodiesel. The properties studied are; kinematic viscosity, density, acid value, iodine value, peroxide value, saponification value, free fatty acid and refractive index. Table 3-5 shows the physicochemical properties of MNO and MMEs from the eggshell and CaO-NPs in comparison to the European biodiesel specification (EN 1421) and American society for testing and material (ASTM D675) which are the standards set for biodiesel. Having considered the information presented in Table 3-5 for MNO and MMEs (eggshell ash and CaO-NPs), it is observed that MNO had a kinematic viscosity of 88.14 and 9.676 mm²/s at temperatures of 40 and 100 °C respectively. Kinematic viscosity was measured at different temperatures which are normally found in a diesel engine during operation. The kinematic viscosity for MMEs were 6.38 and 5.94 mm²/s for eggshell ash and CaO-NPs 40 °C respectively. Furthermore, the kinematic viscosity recorded for MMEs were 2.36 and 1.32 mm²/s for eggshell ash and CaO-NPs catalyst at and 100 °C respectively. The kinematic viscosity recorded for the eggshell ash catalyst was slightly above the recommended set limit by ASTM D6751-09. The kinematic viscosity could have been high due to the fact that the oil was not taken for pretreatment method before transesterification reaction which Woo *et al.*, reported that it lowers the kinematic viscosity of the biodiesel

[29]. Even though, pretreatment method has been reported to be beneficial, Aksoy *et al.*, reported that pretreatment method is normally necessary only if the oil has a high FFA which was not the case with MNO as it had a low FFA [26]. It is very important to have a low kinematic viscosity for biodiesel because high kinematic viscosity can cause problems in the diesel engine such as poor atomization during spray. High viscosity also requires more energy from the fuel atomization and also increases the carbon deposits [30]. However, extremely low viscosities may have implications because required lubrication may not be delivered at the pumps and injector plungers. They can also form abnormalities and cause leakages in the injector and injector pumps which may result in accumulation of small or no fuel in the engine to produce power [31]. The values of the kinematic viscosity recorded are within range or close to those of the set biodiesel standards and similar to those found in literature [32]. Density is a very important parameter. It plays a significant role in the properties and characteristics of fuel quality in determining the energy of the biodiesel [33]. The density of MNO was successfully reduced from 928 to 892 kg/m³ for MMEs with eggshell ash and 889 kg/m³ for MMEs with CaO-NPs at 15 °C. The MMEs values recorded were within the standard set limit of EN 14214 for biodiesel. Furthermore, density was investigated at 40 °C and density of MNO was reduced from 911 to 877 and 864 kg/m³ for MMEs with eggshell ash and MMEs with CaO-NPs respectively. Canesin *et al.*, performed a similar work on methyl esters from different oils and the densities observed ranged between 871- 880 kg/m³ [34]. The kinematic viscosity and density measured are within the set biodiesel standards and indicate that biodiesel produced from MNO may find use as biofuel.

The acid value is used to reflect on the acidity of the sample of interest and it indicates the purity of MNO and MMEs with regard to the FFA content and it also indicates the degree of dilapidation that may transpire during storage [35]. MNO gave an acid value of 1.12 mgKOH/g which was lower than the value reported by Cheikhyoussef *et al.*, (2.44 mgKOH/g). This variation may be due to fact that the oils were collected from different regions. The environment and climatic conditions could also play a role in the composition of the oil [36]. MMEs were also investigated for acid value from the use of both eggshell ash and CaO-NPs as catalysts and the acid values obtained were 0.46 and 0.43

mgKOH/g respectively. This remarkable reduction of acid value from MNO indicates that the MMEs may have a potential to give outstanding atomization in the diesel engine [37]. The values obtained were satisfactory as they were below the limit of 0.5 and 0.8 mgKOH/g according to EN14214 and ASTM D6751 standards respectively. FFA were determined for MNO giving a value of 0.6%. FFA values of MMEs obtained were 0.23 and 0.21% using eggshell ash and CaO-NPs respectively. Kombe *et al.*, noted that the biodiesel tends to form soap for FFA >1% when using alkali transesterification. They further stated that this parameter is important as it gives information on the oil and makes it easier to select a suitable transesterification reaction [38]. Moreover, oil with high FFA has been reported to produce excessive amount of soap which interferes with the separation and washing process of biodiesel after the reaction by forming emulsions which may result in loss of yield [39]. FFA values obtained for MNO and MMEs were all below 1% hence the results were satisfactory and thus selecting alkali transesterification method for the production of biodiesel.

Sarpal *et al.*, states that iodine value is a very important parameter which gives the degree of unsaturation on oil and biodiesel. It is used to determine the stability of oxygen [40]. The stability of the fatty acid is affected by air, heat, traces of metal, peroxides and structure of compound [41]. This implies that iodine value is an indication of a high degree of unsaturation which affects the oxidation stability of the compound [42]. The determination of iodine value was performed on MNO and MMEs and the iodine value obtained for MNO was 30.47 I₂/100g while for MMEs were 24.35 and 17.01 I₂/100g using the eggshell ash and CaO-NPs catalyst respectively. The results obtained for MMEs were satisfactory as they are lower than the set standard limit for biodiesel by EN 14214. Rao *et al.*, stated that the lower the iodine value the better the fuel quality and a high value is an indication for a high potential for the degradation of biodiesel [43]. It is important that the peroxide value also be studied because just like acid value and kinematic viscosity. It is an important parameter when investigating the quality of biodiesel as they are all associated with oxidation behavior of the biodiesel. Peroxide value was determined through iodometric titration, a commonly used method which is fast and affordable. This parameter is used to determine the availability of primary and secondary oxidation

products in biodiesel [35]. Usually, the oxidation moieties in biodiesel are in the form of hydrogen peroxides which come from oxygen in the atmosphere. The reaction on hydrogen peroxides with biodiesel results in polymerization forming an insoluble material which can clog engine fuel lines and filters hence deteriorating the operation of the engine [44]. MNO gave a peroxide value of 0.73 mEq/kg which is significantly lower than that obtained by Cheikhoussef *et al.*, which was 3.98 mEq/kg [36]. The value obtained for MME using eggshell ash catalyst was 0.61 mEq/kg while for CaO-NPs catalyst was 0.59 mEq/kg. These values are within the set limit of 2.0 mEq/kg [45]. Saponification value was among the physicochemical properties which were investigated for MNO and biodiesel. It is defined as the number of milligram of KOH required to neutralize the fatty acids as result of complex hydrolysis of 1 g of oil or fat [33] [34]. It is mainly used to investigate adulterations in fuel. The value obtained for MNO was 184.56 mgKOH/g. It was similar to the saponification value of MNO (185 mgKOH/g) reported by Anguebes-Franceschi *et al.*, and Mitei *et al.*, obtained values ranging between 184-189 mgKOH/g [35] [48]. High saponification value in oil is an indication of high presence of fatty acids which may lead to soap formation during transesterification. This could result in low yield and it may become complex to separate the biodiesel from glycerol [49]. The MMEs results found were 231.41 and 253.53 mgKOH/g for eggshell ash and CaO-NPs catalysts respectively. This implies that 231 and 253 mgKOH/g are needed to saponify 1 g potassium hydroxide. The increase in saponification value of MMEs was expected because of the increase in number of the ester bonds in the FAMES [50]. Akbar *et al.*, reported a saponification value in different biodiesel produced from frying waste oil ranging between 191.03–194.10 mgKOH/g [49]. Jesikha also investigated the saponification value of biodiesel produced from a vegetable oil and the value recorded was 252 mgKOH/g [51]. Furthermore, Anyasor *et al.*, performed an assessment on the fuel quality of biodiesel from ground oil and they reported the saponification value of 244 mgKOH/g [52]. The refractive index was also measured for MNO and MMEs at room temperature. MNO gave a refractive index of 1.4890 which is similar to the refractive index of 1.48 reported by Cheikhoussef *et al.*, and there was a successful reduction to 1.4826 and 1.4821 in MMEs for eggshell ash and for CaO-NPs catalysts respectively [53]. Refractive index is a useful fluid characteristic magnitude used to investigate the purity of

the fuels [54]. In most cases refractive index is known to increase with the increase in the degree of unsaturation. Just as explained in iodine value the reduction in the degree of unsaturation improves the quality of the biodiesel. Therefore, in the case of the results observed in refractive index where there was a remarkable reduction of MNO to MMEs this may suggest that the biodiesel produced could be of good quality [55].

Table 3-5: Physiochemical properties of Mongongo nut oil and its methyl esters from eggshell ash and CaO-NPs (adapted from [7] and [43]).

Properties	MNO	MMEs (Eggshell Ash)	MMEs (CaO- NPs)	Diesel ^(c)	Standards for Biodiesel	Units
Viscosity (40 °C)	88.14	6.38	5.94	3.23	1.9-6.0 ^(a) 3.5-5.0 ^(b)	mm ² /s
Viscosity (100 °C)	9.676	2.36	1.32	1.24	N/A	mm ² /s
Density (15 °C)	928	892	889	845	860-900 ^(b)	kg/m ³
Density (40 °C)	911	877	864	824	N/A	kg/m ³
Acid Value	1.12	0.46	0.43	N/A	0.5 (max) ^(b) 0.8 (max) ^(a)	mg KOH/g
Iodine Value	30.47	24.35	17.01	N/A	120 (max) ^(b)	I ₂ /100g
Peroxide Value	0.73	0.61	0.59	N/A	2.0 (max) ^(b)	mEq/kg
Saponification Value	184.56	231.41	253.53	N/A	N/A	mg KOH/g
Free fatty Acid	0.6	0.23	0.21	N/A	1 ^(b)	%
Refractive Index (25 °C)	1.4890	1.4826	1.4821	N/A	N/A	N/A

^(a) Chaurasia *et al.*, 2018 [56]

^(b) Kivevele and Huan., 2015 [57]

^(c) Atabani *et al.*, 2014 [58]

3.3 Characterization of Biodiesel

3.3.1 Gas Chromatography- Mass Spectrometer (GC-MS) Analysis

The production of FAMEs was performed using transesterification reaction method by reacting tryglycerides of mongongo nut oil with methanol in the presence of a heterogeneous catalyst. The catalysts used were eggshell ash and CaO-NPs. The effects of the amount of catalyst; eggshell ash and CaO-NPs were evaluated with varied catalyst concentration from 3 – 12 wt.%. This reaction occurred under conditions of 9:1 methanol to oil ratio, 3 h reaction time and 65 °C reaction temperature. GC-MS was employed for analysis of FAMEs using a NIST library to identify the compounds.

3.3.1.1 Chicken Eggshell

The chromatogram shown in Figure 3-11 illustrated the peaks identified of the methyl esters with their retention times. According to the results the GC-MS method employed gave a total of seven (7) major peaks which corresponded to the different Fatty acid methyl esters (FAMEs). The FAMEs identified in order of their retention times were palmitic acid methyl esters (15.93 min), linoleic acid methyl esters (18.23 min), linoleic acid methyl esters (18.29 min), steric acid methyl esters (18.61 min), linolelaidic acid methyl esters(20.25 min), linolelaidic acid methyl esters (20.85 min) and linolein acid methyl esters (23.59 min). Further details on this FAMEs are shown in Table 3-6 below.

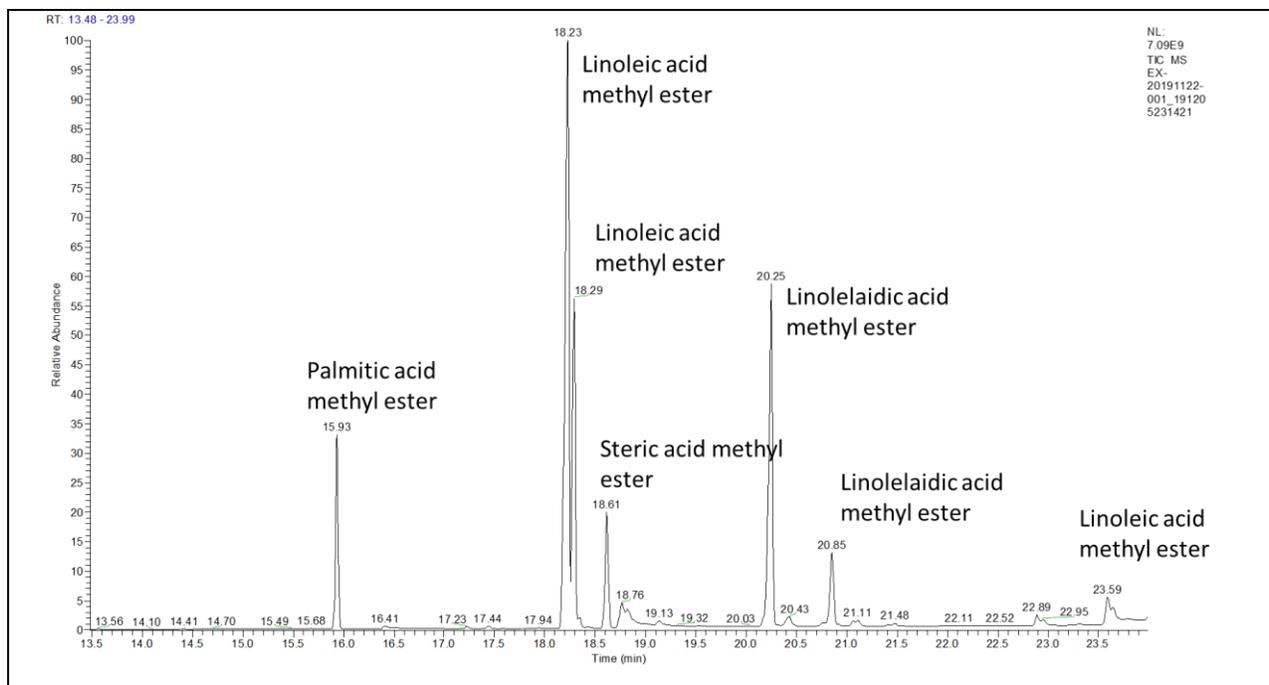


Figure 3-11: Chromatogram of MMEs catalyzed by eggshell ash

Table 3-6: FAMES composition of biodiesel using eggshell ash

Fatty acid compositions	Systematic name	Chemical formula	Molecular weight	Retention time (min)
Palmitic acid methyl ester	Hexadecanoic acid, methyl esters	$C_{17}H_{34}O_2$	270	15.93
Linoleic acid methyl ester	9-12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$	294	18.23
Linoleic acid methyl ester	9-12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$	294	18.29
Steric acid methyl esters	Methyl stearate	$C_{19}H_{38}O_2$	298	18.61

Linolelaidic acid methyl esters	Methyl (9 cis,11 trans, 13 trans)-Octadecatrienoate	C ₁₉ H ₃₂ O ₂	292	20.25
Linolelaidic acid methyl esters	Methyl (9 cis,11 trans, 13 trans)-Octadecatrienoate	C ₁₉ H ₃₂ O ₂	292	20.85
Linoleic acid methyl esters	9, 12-Octadecadienoic acid (Z,Z)-,2-hydroxyl-1-(hydroxymethyl) ethyl ester	C ₂₁ H ₃₈ O ₄	354	23.59

The results of the FAMEs found are similar to those reported by Gebreyohans and Tshizanga *et al.*, for the production of biodiesel [59] [60]. The FAMEs results show that the methyl esters can be produced from MNO using eggshell ash as a catalyst. However, the compounds found in this biodiesel are a mixture of ethers and esters. These classes of saturated fatty acids improve fuel properties such as kinematic viscosity, density, acid value and also peroxide value of the produced biodiesel as reported in the literature [61] [62]. This is so because these classes of compounds have generally low kinematic viscosity and density as a result of transesterification reaction and also being stable with regard to oxygen susceptibility [63] [64] [65]. These are some of the physicochemical parameters that improve the quality of the biodiesel and are also the most monitored parameters among the properties of biodiesel by the National Petroleum, Natural Gas and Biofuel Agency (ANP) resolutions [66].

3.3.1.2 Calcium Oxide Nanoparticles (CaO-NPs)

CaO-NPs were used as a catalyst to produce MMEs using transesterification method. The chromatogram in Figure 3-12 illustrated the major peaks identified. The GC-MS method employed gave a total of six (6) methyl esters from MNO. Figure 3-12 showed the major peaks and their retention times. The six (7) FAMEs identified in order of their

retention times are palmitic acid methyl esters (15.94 min), linoleic acid methyl esters (18.23 min), linoleic acid methyl ester (18.26 min), Steric acid methyl esters (18.62 min), linolelaidic acid methyl esters (20.25 min), linolelaidic acid methyl esters (20.85 min), linoleic acid methyl esters (23.59 min). Further details on these compounds are shown in Table 3-7.

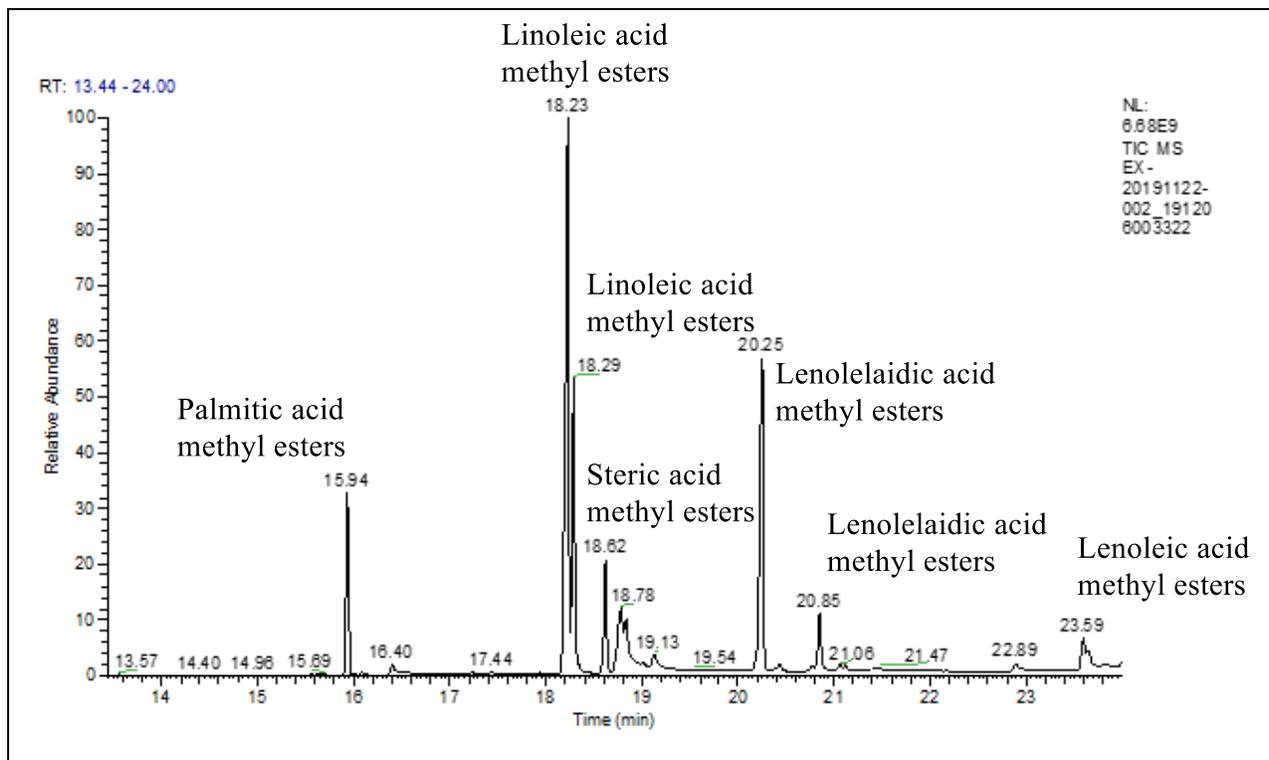


Figure 3-12: Chromatogram of MMEs catalyzed by CaO-NPs

Table 3-7: FAMES composition of biodiesel using synthesized CaO-NPs

Common names (FAMES)	Compound name	Chemical formula	Molecular weight	Retention time (min)
Palmitic acid methyl esters	hexadecanoic acid, methyl ester,	C ₁₇ H ₃₄ O ₂	270	15.94
Linoleic acid methyl esters	9, 12-Octadecadienoic acid (Z,Z) , methyl ester	C ₁₉ H ₃₄ O ₂	294	18.23
Linoleic acid methyl esters	9, 12-Octadecadienoic acid (Z,Z) , methyl ester	C ₁₉ H ₃₄ O ₂	294	18.29
Steric acid methyl esters	Methyl stearate	C ₁₉ H ₃₈ O ₂	298	18.62
Linolelaidic acid methyl esters	Methyl- (9-cis, 11 trans.t, 13)-trans-octadecatrienoate	C ₁₉ H ₃₂ O ₂	292	20.25
Linolelaidic acid methyl esters	Methyl-9-cis, 11 trans.t, 13 trans-octadecatrienoate	C ₁₉ H ₃₂ O ₂	292	20.85
Linoleic acid methyl esters	9, 12-Ocatadecadienoic acid (Z,Z)- 2-Hydroxyl-1-(hydroxymethyl)	C ₁₉ H ₃₂ O ₂	354	23.59

The results obtained for FAMEs are similar to those reported by Taghizade [67]. The FAMEs results obtained from CaO-NPs are similar to those for eggshell ash. However, it was observed that the eggshell ash catalyst was more effective than CaO-NPs. The FAMEs obtained from CaO-NPs and eggshell ash catalyst gave a total of seven (7) compounds. These results are satisfactory because they confirm the suitability of eggshells ash used as a green catalyst, as it is comparable to the CaO-NPs synthesized in the lab.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR was used to determine important functional groups present in biodiesel [68]. Figure 3-13 illustrated IR spectrum of MNO and MMEs from the use of CaO derived from eggshell ash and synthesized CaO-NPs. The appearance of broad absorption bands at 3011, 2924.4 and 2857 cm^{-1} indicate the presence of C–H stretching vibrational bands. The shoulder by 1438 cm^{-1} represents the O-CH₃ stretching which is similar to the work reported by Mumtaz *et al.*, the IR band be seen the MMEs spectra which shows a transformation of MNO into biodiesel, more so that the IR band was absent in MNO [69]. The strong absorption bands at 1741 and 1740 cm^{-1} indicate absorption due to C=O and C–O. The C–H rocking absorption bands found in fatty acids are represented by absorption bands of 998-720 cm^{-1} . The O–H band was not observed in the spectrum and this was expected as the peroxide value was low and therefore, the stability of MMEs were not affected by oxidation [44]. Table 3-8 gives details of the absorption bands observed.

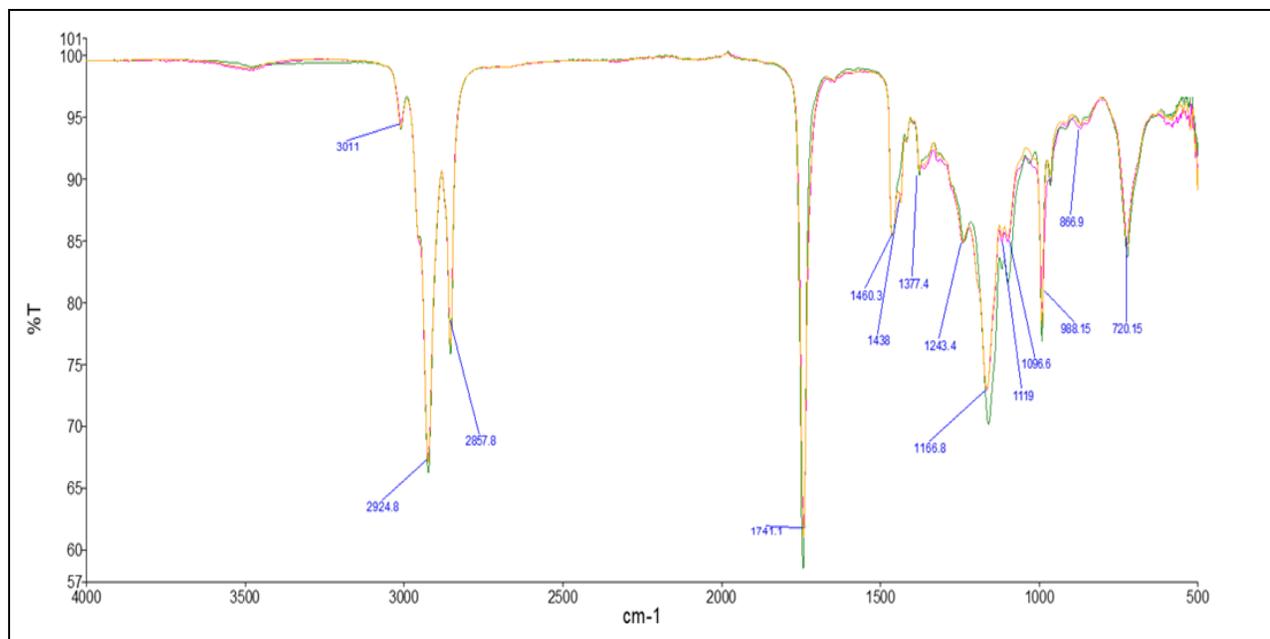


Figure 3-13: Showing the IR spectrum on MNO (green), MMEs using eggshell ash (orange) and MME using CaO-NPs (pink)

Table 3-8 : Major bands of FTIR spectra for MNO and MMEs

Frequency range (cm ⁻¹)	Bond Type
3011, 2924.8 and 2857	C–H stretch
1741 and 1740	C=O group
1438	O–CH ₃ stretch (MMEs)
1166.8	C–CH ₂ –O vibration
998-720	=C–H stretch

3.3.3 Effect of Amount of Catalyst

Biodiesel is a mixture of long chained FAMES composed of many carbons lying in the long chain [70]. In this study biodiesel was produced using different catalysts during the transesterification reaction; eggshell ash and CaO-NPs. The concentration of a catalyst is a very important parameter in the production of biodiesel [71]. Reports indicate that the amount of catalyst used in the reaction affects the amount of conversion of oil to biodiesel

hence this experiment was performed [39]. The conversion of biodiesel was relatively high because the biodiesel produced was above 60% from the two catalysts from the catalyst loading of 3 to 12 wt.%. The results for eggshell ash obtained was 73% and CaO-NPs was 53% at catalyst loading of 3 wt.%. Biodiesel yield increased with an increase of catalyst loading from 3 to 6 wt.% giving a yield of 66% for CaO-NPs. Eggshell gave a yield of 83%. The yield obtained was similar to that of Fayyazi *et al.*, who reported a percentage yield of 81% utilizing a solid base catalyst (CaO) which was derived from eggshell ash [19]. However, there was a massive drop in the yield of the eggshell ash beyond a catalyst loading of 6 wt.%, as the yield obtained was 64% for a catalyst loading of 9 wt.%. Wei *et al.*, got similar results using chicken eggshell ash as a catalyst for the production of biodiesel. They realized that increasing the catalyst loading to more than 10 wt.% resulted with the mixture becoming slurry or too viscous. This made it difficult for the reactants to mix and therefore, demanding more stirring power hence an optimum catalyst for eggshell ash was determined to be 6 wt.%. This same phenomena was experienced with MNO [71]. Boro *et al.*, also evaluated the eggshell ash catalyst incorporated with lithium to produce biodiesel in the range of 1-8 wt.% [72]. They discovered that beyond a catalyst loading of 5 wt.% the conversion became constant and later dropped.

The findings regarding the eggshell ash catalyst in this study are similar to those reported by Wilson *et al.*, and Sai *et al.*, [73] [74]. As for CaO-NPs, the yield had increased to 71% at catalyst loading of 9 wt.%. The catalyst loading was further increased to 12 wt.% and the yield for CaO-NPs increased to 85% which was highest yield recovered from CaO-NPs. Baskar *et al.*, produced biodiesel using nano-catalysts and they discovered that beyond a catalyst loading of 14 wt.%, the mixture became slurry and viscous which resulted in yield being reduced [75]. The optimum catalyst weight percentage for CaO-NPs was 12 wt.% whilst the eggshell ash catalyst did not have any significant change, it went a bit lower to 60%. CaO-NPs gave the highest yield of 85%. This yield was obtained from a reaction time of 3 h, temperature of 65 °C, the oil to methanol ratio of 9:1 and a catalyst loading of 12 wt.%. The results were expected to be this way for CaO-NPs to yield the highest biodiesel since it had an estimated average crystalline size of 42 nm as compared to eggshell ash which had an estimated average crystalline size of 50 nm.

Nonetheless, the results for eggshell ash are satisfactory more so that the average crystalline sizes are not so far off and emphasis is on the development of environmentally friendly and suitable economical catalysts. Furthermore, the use of eggshell as a catalyst can reduce the processing cost of biodiesel, making it possible for the biodiesel to compete with diesel and fuel. Therefore, based on these results statistically there was no significant difference ($P>0.05$) between CaO-NPs and eggshell (refer to Appendix B: Table 4-1). However, in terms of catalyst loading, eggshell was a better catalyst as it required a low catalyst load of 6 wt.% to obtain an optimum yield of 83% compared to CaO-NPs which obtained an optimum yield of 85% at a catalyst load of 12 wt.%. The results are shown in Figure 3-14.

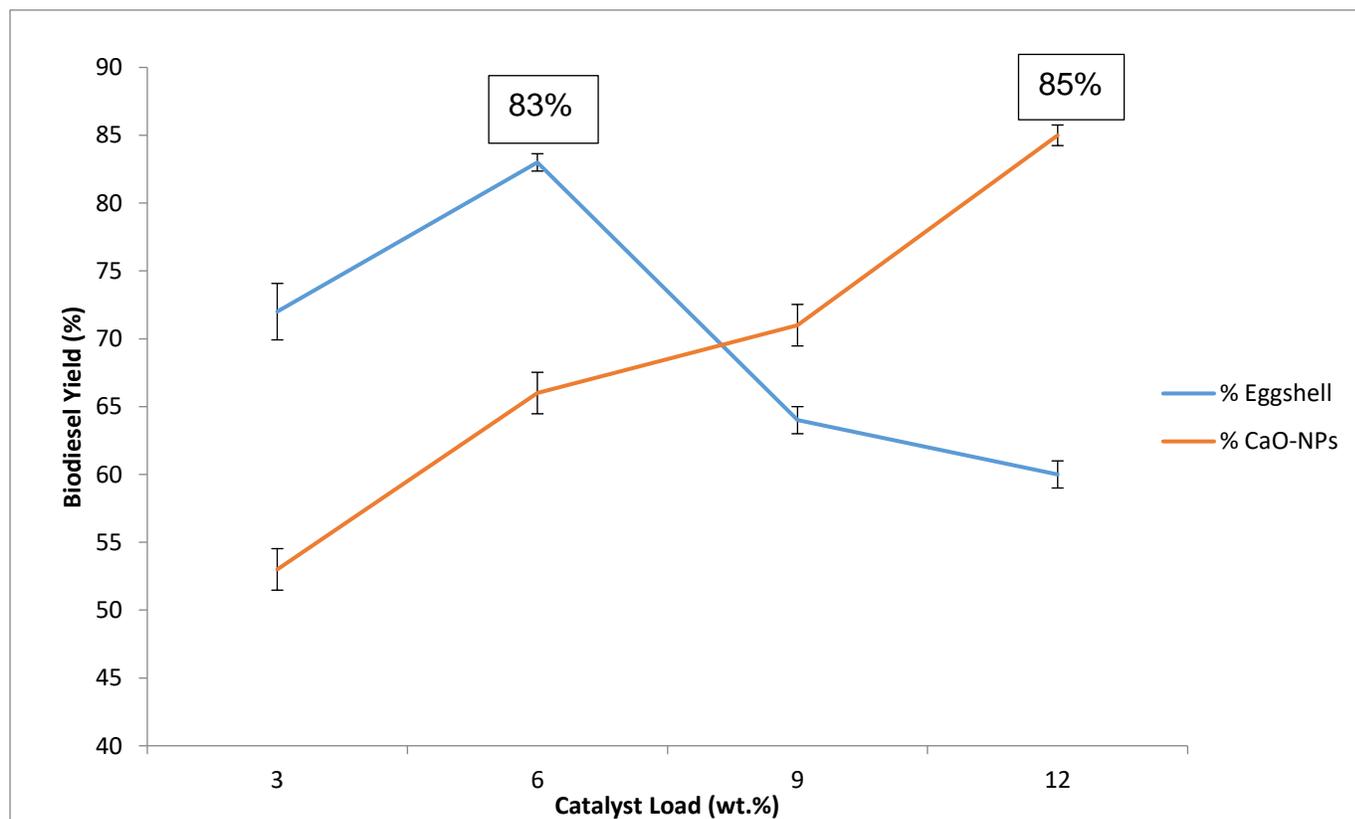


Figure 3-14: The effect of the amount of catalyst on the production of biodiesel

3.4 References

- [1] S. N. Gebremariam and J. M. Marchetti, *Biodiesel production technologies: Review*, vol. 5, no. 3. 2017.
- [2] Y. Hua, M. Omar, C. Nolasco-hipolito, and Y. H. Taufiq-yap, "Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil : Catalyst characterization and biodiesel yield performance," *Appl. Energy*, vol. 160, pp. 58–70, 2015.
- [3] A. Lesbani, S. O. Ceria Sitompul, R. Mohadi, and N. Hidayati, "Characterization and Utilization of Calcium Oxide (CaO) Thermally Decomposed from Fish Bones as a Catalyst in the Production of Biodiesel from Waste Cooking Oil," *Makara J. Technol.*, vol. 20, no. 3, p. 121, 2016.
- [4] Y. Mansourpanah, R. Molaei, E. Bet-Moushoul, K. Farhadi, A. M. Nikbakht, and M. Forough, "Application of CaO-based/Au nanoparticles as heterogeneous nanocatalysts in biodiesel production," *Fuel*, vol. 164, pp. 119–127, 2015.
- [5] N. S. W. Supriyanto, Sukarni, P. Puspitasari, and A. A. Permanasari, "Synthesis and characterization of CaO/CaCO₃ from quail eggshell waste by solid state reaction process," *AIP Conf. Proc.*, vol. 2120, July, 2019.
- [6] Z. Mirghiasi, F. Bakhtiari, E. Darezereshki, and E. Esmailzadeh, "Preparation and characterization of CaO nanoparticles from Ca(OH)₂ by direct thermal decomposition method," *J. Ind. Eng. Chem.*, vol. 20, no. 1, pp. 113–117, 2014.
- [7] T. Witoon, "Characterization of calcium oxide derived from waste eggshell and its application as CO₂ sorbent," *Ceram. Int.*, vol. 37, no. 8, pp. 3291–3298, 2011.
- [8] A. M. Khan, A. H. Safi, M. N. Ahmed, A. R. Siddiqui, M. A. Usmani, S. Khan and K. Yasmeen., "Biodiesel synthesis from waste cooking oil using a variety of waste marble as heterogeneous catalysts," *Brazilian J. Chem. Eng.*, vol. 36, no. 4, pp. 1487–1500, 2019.
- [9] A. S. Balaganesh, R. Sengodan, R. Ranjithkumar, and B. Chandarshekar,

- "Synthesis and Characterization of Porous Calcium Oxide Nanoparticles (CaO NPS)," *Int. J. Innov. Technol. Explor. Eng.*, no. 2, pp. 2278–3075, 2018.
- [10] D. Demir, S. Ceylan, F. Öfkeli, D. Şen, and N. B. Karagülle, "Eggshell Derived Nanohydroxyapatite Reinforced Chitosan Cryogel Biocomposites for Tissue Engineering Applications," *J. Turkish Chem. Soc.*, vol. 1, no. October, pp. 77–88, 2017.
- [11] J. Safaei-Ghomi, M. A. Ghasemzadeh, and M. Mehrabi, "Calcium oxide nanoparticles catalyzed one-step multicomponent synthesis of highly substituted pyridines in aqueous ethanol media," *Sci. Iran.*, vol. 20, no. 3, pp. 549–554, 2013.
- [12] M. Elmastaş, A. Demir, N. Genç, Ü. Dölek, and M. Güneş, "Changes in flavonoid and phenolic acid contents in some Rosa species during ripening," *Food Chem.*, vol. 235, pp. 154–159, 2017.
- [13] H. R. Harsha Hebbar, M. C. Math, and K. V. Yatish, "Optimization and kinetic study of CaO nano-particles catalyzed biodiesel production from Bombax ceiba oil," *Energy*, vol. 143, pp. 25–34, 2018.
- [14] T. Liu, Y. Zhu, X. Zhang, T. Zhang, T. Zhang, and X. Li, "Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method," *Mater. Lett.*, vol. 64, no. 23, pp. 2575–2577, 2010.
- [15] L. Habte, N. Shiferaw, D. Mulatu, T. Thenepalli, R. Chilakala, and J. W. Ahn, "Synthesis of nano-calcium oxide from waste eggshell by sol-gel method," *Sustain.*, vol. 11, no. 11, pp. 1–10, 2019.
- [16] A. Anantharaman and M. George, "Green Synthesis of Calcium Oxide Nanoparticles and Its Applications," *J. Eng. Res. Appl. www.ijera.com*, vol. 6, no. 10, pp. 27–31, 2016.
- [17] A. Roy and J. Bhattacharya, "Microwave assisted synthesis of CaO nanoparticles and use in waste water treatment Batch experiment with nano CaO," *NSTI-Nanotech 2011*, vol. 3, no. 1, pp. 565–568, 2011.

- [18] M. Mukenga, "Biodiesel production over supported Zinc Oxide nano- particles," pp. 4–12, 2012.
- [19] E. Fayyazi, B. Ghobadian, H. H. Van de Bovenkamp, G. Najafi, B. Hosseinzadehsamani, H. J. Heeres, and J. Yue, "Optimization of Biodiesel Production over Chicken Eggshell-Derived CaO Catalyst in a Continuous Centrifugal Contactor Separator," *Ind. Eng. Chem. Res.*, vol. 57, no. 38, pp. 12742–12755, 2018.
- [20] T. Zaman, M. S. Mostari, M. A. Al Mahmood, and M. S. Rahman, "Evolution and characterization of eggshell as a potential candidate of raw material TT - Evolução e caracterização da casca de ovo como potencial candidata de matéria-prima," *Cerâmica*, vol. 64, no. 370, pp. 236–241, 2018.
- [21] N. Tangboriboon, R. Kunanurksapong, A. Sirivat, R. Kunanurksapong, and A. Sirivat, "Preparation and properties of calcium oxide from eggshells via calcination," *Mater. Sci. Pol.*, vol. 30, no. 4, pp. 313–322, 2012.
- [22] S. Hu, Y. Wang, and H. Han, "Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production," *Biomass and Bioenergy*, vol. 35, no. 8, pp. 3627–3635, 2011.
- [23] N. Tshizanga, "A study of biodiesel production from waste vegetable oil using eggshell ash as a heterogeneous catalyst," M.S thesis, Chemical Engineering in the Faculty of Engineering, Cape Peninsula University of Technology, October, 2015.
- [24] O. N. Syazwani, S. H. Teo, A. Islam, and Y. H. Taufiq-Yap, *Transesterification activity and characterization of natural CaO derived from waste venus clam (Tapes belcheri S.) material for enhancement of biodiesel production*, vol. 105. 2017.
- [25] Z. L. Chung, Y. H. Tan, Y. San Chan, J. Kandedo, N.M. Mubarak, M. Ghasemi and M.O. Abdullah, "Life cycle assessment of waste cooking oil for biodiesel production using waste chicken eggshell derived CaO as catalyst via transesterification," *Biocatal. Agric. Biotechnol.*, vol. 21, no. June, pp. 101-117, 2019.

- [26] L. Aksoy and F. E. Aysal, "Transesterification And Pretreatment Process Optimization Of Methyl Ester Production From Fish Oil Having High Free Fat Acid," *Electron. J. Mach. Technol.*, vol. 12, no. 1, pp. 39–47, 2015.
- [27] D. K. Srivastava, A. K. Agarwal, A. Datta, and R. K. Maurya, "Advances in Internal Combustion Engine Research," no. February, pp. 9–36, 2018.
- [28] C. Bhavya, K. Yogendra, K. M. Mahadevan, and N. Madhusudhana, "Synthesis of Calcium Oxide Nanoparticles and Its Mortality Study on Fresh Water Fish *Cyprinus Carpio*," *IOSR J. Environ. Sci. Toxicol. Food Technol.*, vol. 10, no. 12, pp. 55–60, 2016.
- [29] D. G. Woo and T. H. Kim, "Pretreatment methods to improve the kinematic viscosity of biodiesel for use in power tiller engines," *J. Mech. Sci. Technol.*, vol. 33, no. 8, pp. 3655–3664, 2019.
- [30] B. Tesfa, R. Mishra, F. Gu, and N. Powles, "Prediction models for density and viscosity of biodiesel and their effects on fuel supply system in CI engines," *Renew. Energy*, vol. 35, no. 12, pp. 2752–2760, 2010.
- [31] S. Singh, "Study of various methods of biodiesel production and properties of biodiesel prepared from waste cotton seed oil and waste mustard oil" Ph.D dissertation, Thapar Institute of Engineering and Technology, Thapar University, June, 2012.
- [32] A. E. Atabani, A. S. Silitonga, H. C. Ong, T. M. I. Mahlia, H.H. Masjuki, I. A. Badruddin and H. Fayaz, "Non-edible vegetable oils : A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production," *Renew. Sustain. Energy Rev.*, vol. 18, 2016, pp. 211–245, 2013.
- [33] C. Tsanaktsidis, K. Spinthiropoulos, G. Tzilantonis, and C. Katsaros, "Variation of density of diesel and biodiesel mixtures in three different temperature ranges," *Pet. Sci. Technol.*, vol. 34, no. 13, pp. 1121–1128, 2016.

- [34] E. A. Canesin, C. C. de Oliveira, M. Matsushita, L. Felicidade Dias, M. Reghiany Pedrão, and N. E. de Souza, "Characterization of residual oils for biodiesel production," *Electron. J. Biotechnol.*, vol. 17, no. 1, pp. 39–45, 2014.
- [35] F. Anguebes-Franseschi, A. Bassam, M. Abatal, O. M. Tzuc, C. Aguilar-Ucán, A. T. Wakida-Kusunoki, S. E. Diaz-Mendez and L. C. San Pedro "Physical and Chemical Properties of Biodiesel Obtained from Amazon Sailfin Catfish (*Pterygoplichthys pardalis*) Biomass Oil," *J. Chem.*, vol. 2019, 2019.
- [36] N. Cheikhyoussef, M. Kandawa-Schulz, R. Böck, C. de Koning, A. Cheikhyoussef, and A. A. Hussein, "Characterization of Schinziophyton rautanenii (Manketti) nut oil from Namibia rich in conjugated fatty acids and tocopherol," *J. Food Compos. Anal.*, vol. 66, no. October, pp. 152–159, 2018.
- [37] P. M. Ejikeme, C. A. C. Egbounu, I. D. Anyaogu, and V. C Eze, "Fatty Acid Methyl Esters of Melon Seed Oil: Characterization for Potential Diesel Fuel Application," *Leonardo J. Sci.*, vol. 75–84, no. 18, pp. 75–84, 2011.
- [38] G. G. Kombe, A. Temu, H. Rajabu, and G. D. Mrema, "High Free Fatty Acid (FFA) Feedstock Pre-Treatment Method for Biodiesel Productio," *Second Int. Conf. Adv. Eng. Technol.*, pp. 176–182, 2015.
- [39] B. Thangaraj, P. R. Solomon, B. Muniyandi, S. Ranganathan, and L. Lin, "Catalysis in biodiesel production - A review," *Clean Energy*, vol. 3, no. 1, pp. 2–23, 2019.
- [40] M. Sokoto, L. Hassan, S. Dangoggo, H. Ahmad, and A. Uba, "Influence of Fatty Acid Methyl Esters on Fuel properties of Biodiesel Produced from the Seeds Oil of *Curcubita pepo*," *Niger. J. Basic Appl. Sci.*, vol. 19, no. 1, pp. 81–86, 2011.
- [41] A. S. Sarpal, S. R. Silva, P.R. Silva, T. V. Monteiro, J. Itacolomy, V. S. Cunha, and R. J. Daroda, "Direct Method for the Determination of the Iodine Value of Biodiesel by Quantitative Nuclear Magnetic Resonance (q1H NMR) Spectroscopy," *Energy and Fuels*, vol. 29, no. 12, pp. 7956–7968, 2015.

- [42] N. Kumar, "Oxidative stability of biodiesel: Causes, effects and prevention," *Fuel*, vol. 190, pp. 328–350, 2017.
- [43] P. V. Rao, S. Clarke, and R. Brown, "Influence of iodine value on combustion and NO_x emission characteristics of a DI diesel engine." In *Chemeca 2010: The 40th Australasian Chemical Engineering Conference*. Engineers Australia, 2010, September.
- [44] J. Pullen and K. Saeed, "An overview of biodiesel oxidation stability," *Renew. Sustain. Energy Rev.*, vol. 16, no. 8, pp. 5924–5950, 2012.
- [45] B. K. Uprety, W. Chaiwong, C. Ewelike, and S. K. Rakshit, "Biodiesel production using heterogeneous catalysts including wood ash and the importance of enhancing byproduct glycerol purity," *Energy Convers. Manag.*, vol. 115, pp. 191–199, 2016.
- [46] B. Tesfaye and A. Abebaw, "Physico-Chemical Characteristics and Level of Some Selected Metal in Edible Oils," *Adv. Chem.*, vol. 2016, pp. 1–7, 2016.
- [47] K. O. Omeje, O. K. Iroha, A. A. Edeke, H. C. Omeje, and V. O. Apeh, "Characterization and fatty acid profile analysis of oil extracted from unexploited seed of African star apple (Udara)," *OCL - Oilseeds fats, Crop. Lipids*, vol. 26, 2019.
- [48] Y. C. Mitei, J. C. Ngila, S. O. Yeboah, L. Wessjohann, and J. Schmidt, "NMR, GC-MS and ESI-FTICR-MS profiling of fatty acids and triacylglycerols in some botswana seed oils," *JAOCs, J. Am. Oil Chem. Soc.*, vol. 85, no. 11, pp. 1021–1032, 2008.
- [49] E. Akbar, Z. Yaakob, S. K. Kamarudin, M. Ismail, and J. Salimon, "Characteristic and composition of *Jatropha curcas* oil seed from Malaysia and its potential as biodiesel feedstock," *Eur. J. Sci. Res.*, vol. 29, no. 3, pp. 396–403, 2009.
- [50] G. N. Anyasor, K. O. Ogunwenmo, O. A. Oyelana, D. Ajayi, and J. Dangana, "Chemical Analyses of Groundnut (*Arachis hypogaea*) Oil," *Pakistan J. Nutr.*, vol. 8, no. 3, pp. 269–272, 2009.

- [51] M. Jesikha, "Fatty Acid Methyl Esters Characteristic and Esterification of Some Vegetable Oils for Production of Biodiesel," *Int. J. Eng. Sci.*, vol. 1, no. 12, pp. 50–53, 2012.
- [52] G. N. Anyasor, K. O. Ogunwenmo, O. A. Oyelana, D. Ajayi, and J. Dangana, "Chemical Analyses of Groundnut (*Arachis hypogaea*) Oil," *Pakistan J. Nutr.*, vol. 8, no. 3, pp. 269–272, 2009.
- [53] N. Cheikhyoussef, "Profiling Studies of Five Namibian Indigenous Seed Oils Obtained Using Three Different Extraction Methods," 2018.
- [54] E. I. Bello and M. Agge, "Biodiesel Production from Ground Nut Oil," *J. Emerg. Trends Eng. Appl. Sci.*, vol. 3, no. 2, pp. 276–280, 2012.
- [55] L. Rafael, V. Conceição, C. E. F. Costa, N. Geraldo, R. Filho, and J. R. Zamian, "Obtaining and characterization of biodiesel from jupati (*Raphia taedigera* Mart.) oil," vol. 90, pp. 2945–2949, 2011.
- [56] S. P. Chaurasia, A. K. Dalai, J. Gupta, and M. Agarwal, "Preparation and characterisation of Cao nanoparticle for biodiesel production from mixture of edible and non-edible oils," *Int. J. Renew. Energy Technol.*, vol. 9, no. 1/2, p. 50, 2018.
- [57] T. T. Kivevele and Z. Huan, "An analysis of fuel properties of fatty acid methyl ester from Manketti seeds oil," *Int. J. Green Energy*, vol. 12, no. 4, pp. 291–296, 2015.
- [58] A. E. Atabani, M. Mofijur, H. H. Masjuki, I. A. Badruddin, W. T. Chong, S.F. Cheng, S. W. Gouk, "A study of production and characterization of Manketti (*Ricinodendron rautonemii*) methyl ester and its blends as a potential biodiesel feedstock," *Biofuel Res. J.*, vol. 1, no. 4, pp. 139–146, 2014.
- [59] T. Gebreyohans, "Production and characterization of biodiesel from *Jatropha curcas* seed by use K_2O / fly ash as a catalyst," M.S thesis, Faculty of Chemical and Bio Engineering, Addis Ababa Institute of technology school of chemical and Bio engineering, June, 2018.

- [60] N. Tshizanga, E. F. Aransiola, and O. Oyekola, "Optimisation of biodiesel production from waste vegetable oil and eggshell ash," *South African J. Chem. Eng.*, vol. 23, pp. 145–156, 2017.
- [61] G. Kafui, A. Sunnu, and J. Parbey, "Effect of biodiesel production parameters on viscosity and yield of methyl esters : *Jatropha curcas* , *Elaeis guineensis* and *Cocos nucifera*," *Alexandria Eng. J.*, vol. 54, no. 4, pp. 1285–1290, 2015.
- [62] T. X. Nguyenthi, J. P. Bazile, and D. Bessières, "Density measurements of waste cooking oil biodiesel and diesel blends over extended pressure and temperature ranges," *Energies*, vol. 11, no. 5, 2018.
- [63] Ş. Altun, F. Ya, and C. Öner, "The fuel properties of methyl esters produced from canola oil- animal tallow blends by basecatalyzed transesterification," *Uluslararası Mühendislik Araştırma ve Geliştirme Derg.*, vol. 2, no. 2, pp. 2–5, 2010.
- [64] Y. C. Juho, S. T. Wu, T. L. Cha, G. H. Sun, D. S. Yu, and C. C. Kao, "Single session of high-intensity focused ultrasound therapy for the management of organ-confined prostate cancer: A single-institute experience," *Urol. Sci.*, vol. 27, no. 4, pp. 226–229, 2016.
- [65] A. Demirbas, "Relationships derived from physical properties of vegetable oil and biodiesel fuels," *Fuel*, vol. 87, no. 8–9, pp. 1743–1748, 2008.
- [66] R. Gabriel, W. T. Vieira, J. I. Soletti, L. M. O. Ribeiro, and S. H. V. Carvalho, "Journal of King Saud University – Science Empirical modeling of different viscosity and density behavior of biodiesel from chichá (*Sterculia striata*) with diesel versus temperature variation," *J. King Saud Univ. - Sci.*, vol. 32, no. 1, pp. 628–635, 2020.
- [67] Z. Taghizade, "Determination of biodiesel quality parameters for optimization of production process conditions," p. 23, 2016.
- [68] A. Matwijczuk, G. Zajac, R. Kowalski, M. Kachel-Jakubowska, and M. Gagoś, "Spectroscopic studies of the quality of fatty acid methyl esters derived from waste cooking oil," *Polish J. Environ. Stud.*, vol. 26, no. 6, pp. 2643–2650, 2017.

- [69] M. W. Mumtaz, A. Adnan, F. Anwar, H. Mukhtar, M. A. Raza, F. Ahmad and U. Rashid "Response surface methodology: An emphatic tool for optimized biodiesel production using rice bran and sunflower oils," *Energies*, vol. 5, no. 9, pp. 3307–3328, 2012.
- [70] M. Nurdin, F. Fatma, M. Natsir, and D. Wibowo, "Characterization of methyl ester compound of biodiesel from industrial liquid waste of crude palm oil processing," *Anal. Chem. Res.*, 2017.
- [71] Z. Wei, C. Xu, and B. Li, "Bioresource Technology Application of waste eggshell as low-cost solid catalyst for biodiesel production," *Bioresour. Technol.*, vol. 100, no. 11, pp. 2883–2885, 2009.
- [72] J. Boro, L. J. Konwar, and D. Deka, "Transesterification of non edible feedstock with lithium incorporated egg shell derived CaO for biodiesel production," *Fuel Process. Technol.*, vol. 122, pp. 72–78, 2014.
- [73] I. Wilson, N. Sajith, P. Santhosh and S. Ashraf, "Enhanced Biodiesel Production Using Eggshell as the Catalyst," *Inter. Res. J. of Eng. and Technol. (IRJET)*., vol. 6, no.9, pp.1929–1933, 2019.
- [74] B. A. Sai, N. Subramaniapillai, M. S. B. K. Mohamed and A. Narayanan, "Optimization of Continuous Biodiesel Production from Rubber Seed Oil (RSO) using Calcined Eggshells as Heterogeneous Catalyst," *J. of Env. Chem. Eng.*, vol. 8, no. 1, pp. 103603, 2019.
- [75] G. Baskar, A.E. Selvakumari, R. Aiswarya, "Biodiesel production from castor oil using heterogeneous Ni doped ZnO nanocatalyst," *Biores. Techno.*, vol 250, pp. 793–798, 2018.

CHAPTER 4

4.0 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

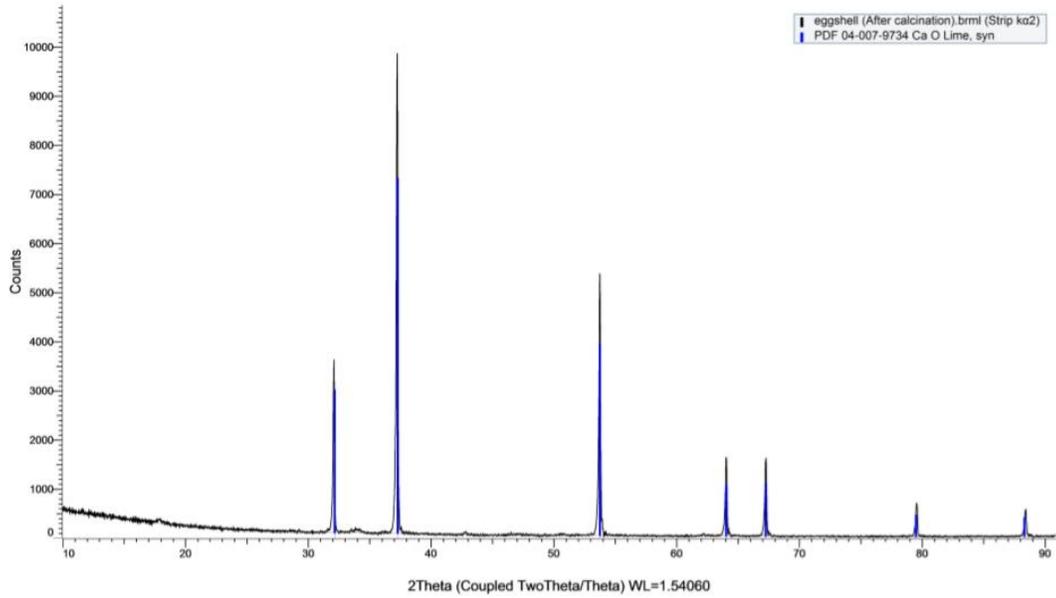
In this study, CaO catalyst was prepared from chicken eggshell and synthesis of CaO-NPs through a process of calcination at a temperature of 800 °C. These catalysts were successfully produced. Different techniques were performed on the eggshell ash and CaO-nanoparticles such as a Powder X-Ray diffraction (XRD), scanning electron microscope coupled with an elemental dispersive X-ray (SEM-EDX) and Fourier Infra-red transmission spectroscopy (FTIR). All these instruments confirmed the successful transformation of CaCO₃ (eggshell) to CaO (eggshell ash) with an estimated average crystalline size of 50 nm. They also indicated a successful synthesis of CaO-nanoparticles and the estimated average crystalline size was 42 nm.

The catalysts were used in the production of biodiesel from mongongo (*Schinziophyton rautanenii*) nut oil by transesterification method under constant optimum reaction conditions. The optimum conditions were 9:1 methanol to oil ratio, 3 h reaction time and 65 °C reaction temperature. The results show that biodiesel production using CaO-NPs gave a higher yield than eggshell at catalyst loading of 12 wt.% with an optimum mongongo methyl esters (MMEs) yield of 85%. However, the eggshell gave satisfying results with an optimum MMEs yield of 83%, at a catalyst loading of 6 wt.%. GC-MS was employed for analysis of FAMES. As a result, statistically there was no significant difference between CaO-NPs and eggshell. Consequently, in terms of catalyst loading, eggshell was a better catalyst as it required a low catalyst load to obtain an optimum yield compared to CaO-NPs. The desired physicochemical properties were within the set standards for biodiesel by European biodiesel specification (EN 1421) and American society for testing and material (ASTM D675). Therefore, it can be concluded that CaO-NPs gives a better catalytic performance than eggshell ash for the production of biodiesel from mongongo nut oil through transesterification reaction.

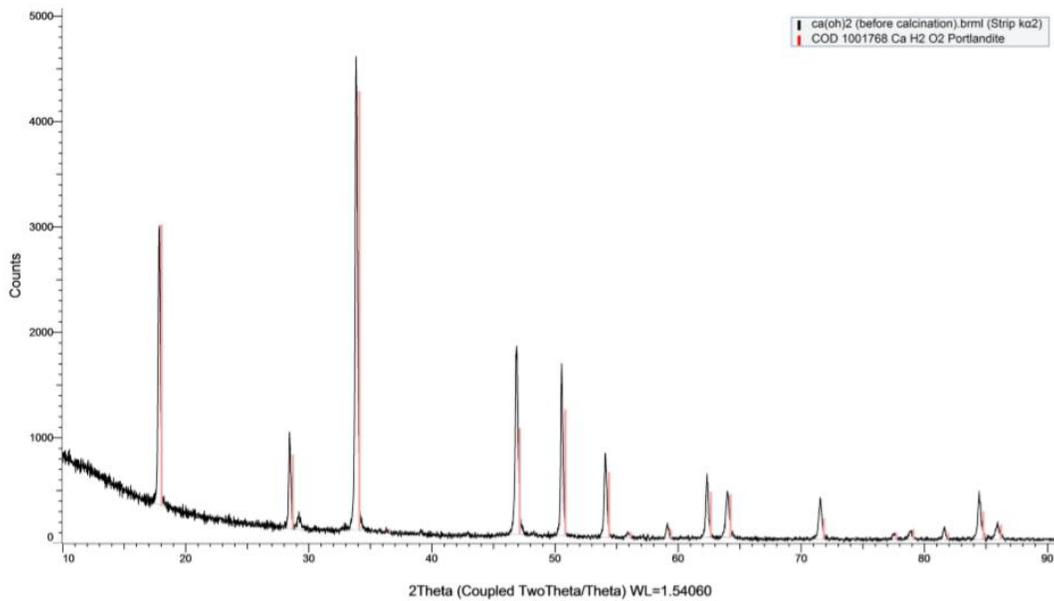
4.2 Recommendations

Further characterization should be done on the catalysts including TEM, X-ray fluorescence, TGA and BET to get more information on the morphology, elemental composition, thermal stability and particle size respectively. More studies should be done on the eggshell catalyst in order to increase its yield since it has shown a remarkable potential to produce biodiesel. Hopefully in the near future could be used in a large-scale industrial process because the process is cheap and environmentally kind. More investigation should also be done on both the eggshell and CaO-NPs with regards to contamination due to exposure to the atmosphere (oxidative stability). Lack of some technical equipment limited the study. Therefore, it is recommended that further characterization be done on the biodiesel including cetane number, flash point, cloud point, pour point and ignition delay. More studies should also be done on the low temperature biodiesel properties so as to improve its low temperature flow and make it more competitive to petrol and diesel.

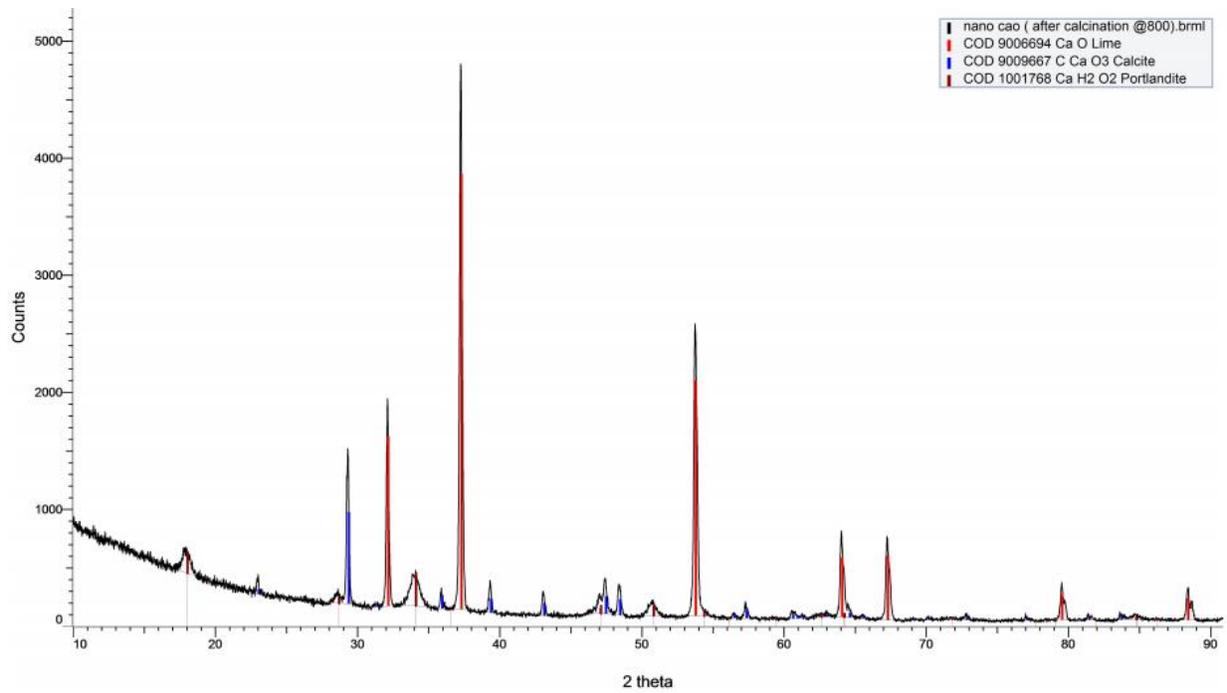
4.3 APPENDIX A: Powder XRD Spectra



Spectrum 4-1: The XRD pattern of eggshell ash calcined at 800 °C



Spectrum 4-2: The XRD pattern of $\text{Ca}(\text{OH})_2$



Spectrum 4-3: XRD pattern of CaO-NPs calcined at 800 °C

4.4 APPENDIX B: Statistical Calculations

t-Test: Paired Two Sample for Means		
	<i>Variable</i>	<i>Variable</i>
	<i>1</i>	<i>2</i>
Mean	82.73333	84.73333
Variance	0.413333	0.413333
Observations	3	3
Pearson Correlation	-0.74194	
Hypothesized Mean Difference	0	
df	2	
t Stat	-2.88675	
$P(T \leq t)$ one-tail	0.050987	
t Critical one-tail	2.919986	
$P(T \leq t)$ two-tail	0.101973	
t Critical two-tail	4.302653	