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Production of biodiesel from neem seed oil using calcinated banana ash/li-ca_o/fe₂(so₄)₃ blends as a catalyst

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**PRODUCTION OF BIODIESEL FROM NEEM SEED OIL USING
CALCINATED BANANA ASH/ Li-CaO/Fe₂(SO₄)₃ BLENDS AS A
CATALYST**

Ismail J. Madai

**A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of
Master in Materials Science and Engineering of the Nelson Mandela African
Institution of Science and Technology**

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ABSTRACT

Biodiesel is a possible remedy to the present toxic, finite sources and ever-diminishing crude fuels. Non-edible and locally available (*Azadirachta indica*) Neem Seed Oil (NSO) as a second-generation feedstock was transformed into biodiesel using Calcined Banana Ash (CBA) derived from banana peels mixed with lithium calcium oxide iron (III) sulphate $\text{Li-CaO/Fe}_2(\text{SO}_4)_3$ catalyzed transesterification. Transesterification process was employed to minimize the Free Fatty Acid (FFA) content of (NSO) to afford 99.8% yield under the condition of the reaction oil/ methanol ratio 8:1, followed by addition of 1.7 %wt calcinated banana ash and 1.3 %wt $\text{Li-CaO / Fe}_2(\text{SO}_4)_3$ catalysts in 53 minutes a notable time. It is important to note that the physicochemical properties of biodiesel in this study such as initial boiling points, flash point, pour point, cloud point, density, kinematic viscosity, final boiling points and cetane index met ASTM D- 6751 and EN 14214 standards. Decomposition profile was displayed by Thermal Gravimetric Analysis (TGA) whereas In-depth analysis by both Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), X-ray Fluorescence (X-RF), and Fourier-Transform Infrared Spectroscopy (FT-IR) revealed that the high efficiency displayed by a catalyst from banana ash calcined at 650 °C was due to the presence of Potassium, Calcium and Magnesium contents that accounted for the high basicity of up to 11.09 pH. Additionally, the nitrogen adsorption/desorption studies revealed that CBA interestingly exhibits a high BET surface area of 411 m²/g and promising mesopores (3 nm). The catalyst also displayed better recyclability evidenced by the fact that it was able to be reused after five successive runs with better recyclability of 75%. Basing on the aforementioned properties, this study come up with developing heterogeneous catalyst from available banana peel ash.

DECLARATION

I, Ismail Madai, hereby declare to the Senate of the Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor concurrently submitted for a degree or similar award in any other institution.

Ismail Madai (Candidate Name)

Date

The above declaration is confirmed

Dr. Yusufu Abeid Chande Jande
(Main supervisor)

Date

Dr. Thomas Kivevele
(Co supervisor)

Date

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CERTIFICATION

The undersigned certify that they have read and hereby recommend for acceptance the dissertation entitled “*Production of Biodiesel from Neem Seed Oil using Banana ash/ Li-CaO / Fe₂(SO₄)₃ Blends as a Catalyst*” for examination in partial fulfillment of the requirements for the degree of Masters in Materials Science and Engineering of the Nelson Mandela African Institution of Science and Technology.

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DEDICATION

I entirely dedicate this work to my wife, families and mentors who make my journey to be successful.

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LIST OF ABBREVIATIONS AND SYMBOLS

NSO	Neem Seed Oil
BET	Brunner Emmet Teller
FT-IR	Fourier Transform Infrared Spectroscopy
CBA	Calcined Banana Ash
BA	Banana Ash
GC-MS	Gas Chromatography-Mass Spectrometry
XRF	X-Ray Fluorescence
TGA	Thermogravimetric Analysis
FFA	Free Fatty Acid
ASTM	American Society for Testing and Materials

CHAPTER ONE

INTRODUCTION

1.1 Background of the Problem

Energy is among the key factors for human developments in ancient times and nowadays. In fact, also focus on various sources of energy such as fossil fuel, biofuel and gas. About 82% of the population consumption on nonrenewable fuel such as gas and oil. However the fossil fuel is highly depleting at a fast rate for numerous years and the precautions about the decline of the oil reservoir were provided (Alekkett *et al.*, 2003). The use of fossil fuel has been associated with a major environmental problem such as emission of harmful gases such as CO₂, NO₂ and SO₂ which leads to change in climatic conditions such as excessive drought, excessive rainfall, acidic rainfall and global warming (Ajugwo, 2013). Due to unsustainability of fuel, there is a need to substitute fuel that is being depleted at a rapid rate (Vasudevan *et al.*, 2008). Biodiesel may be thought as an alternative.

Biodiesel refers to a plants oil or fats oil from animals when they undergo the transesterification process. They consist of long-chain hydrocarbons attached with alkyl (methyl, ethyl, or propyl) esters (Koh *et al.*, 2011). Biodiesel is one of the preferred alternative energy sources which are renewable, environmentally friendly and biodegradable. It lowers the importation of crude oil abroad and it provides favourable energy balance and reduces greenhouse emission, as agreed in the Kyoto Protocol agreement and its locally available (Bozbas, 2008).

Literature has pointed out that vegetable oil from edible seeds such as such as, oil from rapeseed (Ramos *et al.*, 2009), soybean (Gui *et al.*, 2008), sunflower (Antolin *et al.*, 2002) and palm (Crabbe *et al.*, 2001) have gained attention in biodiesel production but unfortunately they pose a threat competition to food security. Therefore, the current studies focused on non-edible oil as a second generation of biodiesel feedstock (Barnwal *et al.*, 2005). Various non-edible seeds including neem seed, jatropha, croton and castor beans have been studied and show good performance in biodiesel production (Atabani *et al.*, 2013).

Neem tree (*Azadirachta indica*) has gained fame not only of its long life span estimated as 150-200 years (Schmutterer, 1990) but it has ability to bear fruits within 3-5 years which appear to attains maximum productivity after 10 years with an oil content that varies from 30-35% and 35-40% for kernels and seeds respectively (Kaura *et al.*, 1998). These properties make it a suitable feedstock for biodiesel production. It has been proven that 7-8 kg of neem seed has a possibility to produce one litre of oil. 'It is also worth mentioning that planting of neem trees (*Azadirachta indica*) will not only address energy challenges but also environmental challenges (Kumar *et al.*, 2013).

Production of biodiesel usually uses base catalysts that are chemically aggressive and less efficient in removing fatty acid composition in biodiesel. Also, the biodiesel produced through this route has high viscosity which results in engine problems such as incomplete combustion, high carbon deposit on the combustion chamber, valve seat and injector nozzle. (Karmakar *et al.*, 2018). Therefore, there is a need to find alternative catalysts for biodiesel production in order to reduce viscosity in biodiesel production.

Various research including but not limited to banana peels as biomass precursor for biodiesel production has been conducted. For instance (Betiku *et al.*, 2016), conducted research on cocoa pod husks as a catalyst alongside NSO with 43 mm²/s viscosity and minimizes to 5.6 mm²/s and produced 98.5% of biodiesel for 69 minutes reaction time with 2 wt% catalyst dosage. Similarly, (Gohain *et al.*, 2017) used banana peel as a catalyst alongside waste cooking oil with 46 mm²/s viscosity and minimizes to 5.8 mm²/s using calcined banana ash (CBA) and produce 98.3% of biodiesel for 60 minutes reaction time with 7.6 wt% catalyst dosage. Not only that, (Singh *et al.*, 2010) study on eggshells/Snail shells against waste cooking with 47 mm²/s viscosity and minimizes to 5.7 mm²/s, produces 94.1% of biodiesel for 120 minutes reaction time with 10 wt% catalyst dosage. According to Betiku *et al.* (2016) researched on Napoleon's plume oil with viscosity 42 mm²/s minimizes to 4.9 mm²/s using CBA as catalyst produce 98.5% of biodiesel for 69 minutes reaction time with 2.75 wt% catalyst dosage. This study of blends Li-CaO/Fe₂(SO₄)₃ in calcined banana ash as a bio base catalyst minimizes viscosity for biodiesel production from neem seed oil (NSO) with kinematic viscosity 37 mm²/s to 3.8 mm²/s. These reactions took 53 minutes for biodiesel yield with 1.7 wt% catalyst dosage and it yields 98.88% of biodiesel. This route is anticipated to be more economical as a possible substitute of fuel raw material.

Production of biodiesel goes through the transesterification process as described in the reaction equation below Fig.1.

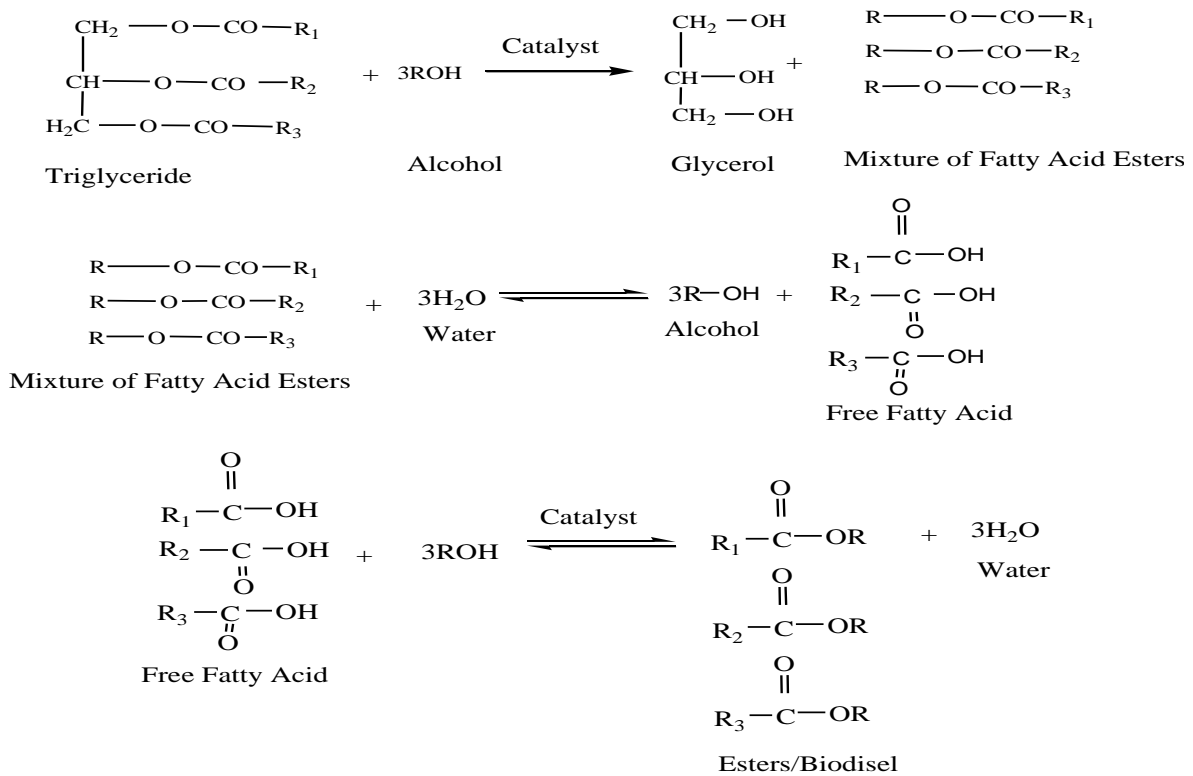


Figure 1: Chemistry overview for biodiesel production

1.2 Statement of the Problem

According to Singh and Singh (2010) investigated that most of the biofuel is often associated with high kinematics viscosity about 50.3 mm²/s. This leads to incomplete combustion, high carbon deposit in the combustion chamber, valve seat and injector nozzle. Although the current commercial catalysts have been used in the transesterification process they are chemically aggressive and less efficient in reducing viscosity and removing fatty acid composition in biodiesel (Leung *et al.*, 2010). High viscosity problems can be reduced by using an effective biomass catalyst (Zhang *et al.*, 2007).

1.3 Rationale of the Study

This study utilized non-edible neem seed oil together with banana peels as a catalyst. The use of these precursors will address energy and environmental challenges by planting neem trees that have a long-life span about 200 years.

1.4 Objectives of the Study

1.4.1 General Objective

The general objective of this research is to produce biodiesel from neem seed oil by using banana peels ash / $\text{Li-CaO/Fe}_2(\text{SO}_4)_3$ blends as a bio base catalyst.

1.4.2 Specific Objectives

The objective of the study was accomplished by three specific objectives:

- (i) To produce and characterize bio-catalyst derived from banana peel.
- (ii) To determine the effect of temperature and time in the production of biodiesel.
- (iii) To determine important properties of biodiesel derived from neem seed.

1.5 Research Questions

- (i) What are the physical-chemical properties of CBA catalyst produced from banana peels?
- (ii) What are the physical-chemical properties of neem seed oil and its effects after using catalyst derived from calcined banana peel ash loaded with $\text{Li-CaO/Fe}_2(\text{SO}_4)_3$?
- (iii) What are the parameters of produced biodiesel?

1.6 Significance of the Study

As an alternative to petroleum fuel, biodiesel will reduce dependence crude oil from foreign countries which is highly depleting at a fast rate. Biodiesel helps to reduce the emission of greenhouse gasses emission such as CO_2 which protect the environment from further heating up, many people have adopted the use of biofuels as agreed by the Kyoto Protocol agreement. The negative effects of emissions of biodiesel are less than diesel fuel, for this case it is suitable to areas with large car congestion like large cities. Not only that biodiesel can be used in existing Diesel Engines with little or no modifications at all and can replace crude oil to become the choicest preferred energy source.

On top of that Biodiesel can be used in blends with petroleum or diesel fuel and also it improves engine lubrication and increases engine life since it is virtually Sulphur free. However, biodiesel can produce, clean burning, renewable substitute for petroleum diesel. Using biodiesel as a vehicle fuel increases energy security, improves air quality, environment and provides safety benefits. Biodiesel can be grown, produced and distributed locally; it can be produced in local refineries which reduce the need to import expensive finished product from other countries. Biofuel refineries, which mainly convert vegetable and animal fat into biofuel releases less toxic chemicals, if spilled or released to the environment. Biodiesel is biodegradable and non-toxic they are burnt; they produce significantly less carbon output and few pollutants. As compared to petroleum diesel, biodiesel produces less soot (particulate matter), carbon monoxide, unburned hydrocarbons, and sulfur dioxide. Flashpoint for biodiesel is higher than 150 °C whereas the same is about 52 °C for petroleum diesel, which makes it less combustible. It is therefore safe to handle, store and transport. Better Fuel Economy, vehicles that run on biodiesel achieve 30% fuel economy than petroleum-based diesel engines which means it makes fewer trips to gas stations and run more miles per litre. Positive economic Impact on biodiesel produced, thousands of people may be employed in biofuel production plant. Since biodiesel is produced from crops, an increase in demand for biodiesel leads to increase in demand for suitable biofuel crops. Moreover, it creates less emission by reducing the amount of suspended particles in the air. This reduces the cost of healthcare products.

1.7 Delineation of the Study

The study was based on the experimental investigation of the calcined banana ash loaded with metal oxide $\text{Li-CaO/Fe}_2(\text{SO}_4)_3$ as a catalyst for fast rate production of biodiesel from neem seed oil. The first part of this experimental work concentrated on producing catalyst derived from ripen banana peel ashes. This was done by drying ripen banana peel under the sun for 7 days, followed by oven dried 100 °C for 6hrs. Then the ashes obtained was finally calcined in a box muffle furnace at temperature ranges at 100 °C intervals from 550 °C to 1100 °C for 3hrs in the presence of air and finally milled and sieved to a fine powder. Thermogravimetric analysis (TGA) was done on banana ashes to determine the suitable range of calcination temperatures. Based on the TGA results, different temperatures were considered for the production of catalyst, from which elemental analysis justified the optimal calcination temperature with high potassium composition. Not only that BET analysis was

done to determine the specific surface area by which the catalyst showed high surface area about 411 m²/g. Scanning Electron Microscope (SEM) was done to see morphology of particle size distribution in CBA. X-Ray Diffraction pattern (XRD), was done, to identify CBA crystal structure and crystalline phases of compound present in CBA material and to reveal their chemical composition information. Fourier-Transform Infrared Spectroscopy (FT-IR) was done to identify the functional group of compound present in CBA by measuring their absorption of infrared radiation over a range of wavelengths from 500-4000 cm⁻¹. The second part of this study was to extract oil from neem seed, production of biodiesel from neem oil through transesterification reaction and finally identification of fuel properties in accordance with ASTM D- 6751 and EN 14214 standards. The catalyst produced showed high efficiency to biodiesel production and fuel produced showed similar properties with standards.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Biodiesel with physical properties that conform to International standards and suitability for diesel engines have been synthesized from various precursors. Singh and Singh (2010) reported that biofuel often results in high kinematic viscosity of about 50 mm²/s, low vitality and polyunsaturated characters. There are three categories of catalysts used for biodiesel production such as alkali catalysts, acidic catalyst and enzyme catalysts. Alkali and acidic catalysts are mostly used (Leung *et al.*, 2010). They are further categorized into homogeneous and heterogeneous catalysts. Commercial (homogeneous) catalysts have advance negative effects such as shorter reaction time, chemically aggressive, expensive, and sensitive to FFA content which leads to saponification that decreases in biodiesel yield (Atadashi *et al.*, 2013).

Heterogeneous catalysts derived from biomass have become more attractive recently because they do not undergo soap formation processes and have a simple purification process (Ruddy *et al.*, 2014) Biomass-derived catalysts have not only been evaluated as effective catalysts to convert vegetable oil to methyl ester (Boey *et al.*, 2011) but they can also be reused up to ten times without degrading their efficiency (Wei *et al.*, 2009). Nakatani and his coworkers realized that applying 25 wt% catalyst dosage of calcined biomass waste at (700 °C) using 6:1 methanol: oil molar ratio, the yield of biodiesel production is over 70% and purity of 98.4% was achieved in a 5 hrs reaction time (Gabriëls *et al.*, 2015). Biocatalyst has several advantages such as faster reaction rate than acid catalysts, relatively lower energy, long catalyst lifetimes, easy to separate from product environmentally friendly, abundantly, noncorrosive, recyclable and higher selectivity (Fukuda *et al.*, 2001).

Banana peels has already been investigated as a bio base catalyst to remove high free fatty acid (FFA) content from content from Bauhinia monandra seed oil (BMSO) as shown in Table 1. It should be noted that it is comparatively time-consuming to incorporate Fe₂(SO₄)₃ into bio base as the reaction time for the production of biodiesel was 69 minutes. Not only that ripen plantain fruit peels researched by (Etim *et al.*, 2018) is an eco-friendly biomass catalyst in producing biodiesel was been used but the free fatty acid was reduced to 0.9%

using biocatalyst and $\text{Fe}_2(\text{SO}_4)_3$ for 85 minutes reaction time in two-step transesterification process. On top of that Various research including but not limited to banana peels as biomass precursor for biodiesel production has been conducted. For instance (Betiku *et al.*, 2016), conducted research on cocoa pod husks as a catalyst alongside NSO with 43 mm²/s viscosity and minimizes to 5.6 mm²/s and produced 98.5% of biodiesel for 69 minutes reaction time with 2 wt% catalyst dosage. Similarly, (Gohain *et al.*, 2017) used banana peel as a catalyst alongside waste cooking oil with 46 mm²/s viscosity and minimizes to 5.8 mm²/s using CBA and produce 98.3% of biodiesel for 60 minutes reaction time with 7.6 wt% catalyst dosage. Not only that, (Singh & Singh, 2010) study on eggshells/ Snail shells against waste cooking with 47 mm²/s viscosity and minimizes to 5.7 mm²/s, produces 94.1% of biodiesel for 120 minutes reaction time with 10 wt% catalyst dosage. According to Betiku et al. (2016) researched on Napoleon's plume oil with viscosity 42 mm²/s minimizes to 4.9 mm²/s using CBA as catalyst produce 98.5% of biodiesel for 69 minutes reaction time with 2.75 wt% catalyst dosage. This study utilized calcined banana ash (CBA)/ Li-CaO/ $\text{Fe}_2(\text{SO}_4)_3$ blends as an economical bio base catalyst and tends to reduce biodiesel production time.

Table 1: Performance of different biocatalyst catalysts for biodiesel production through transesterification process

Bio-catalyst type	Oil type	Surface Area (m ² /g)	A load of catalyst added (wt %)	Ratio methanol to oil	Temp (°C)	Reaction time (Min)	Production (wt %)	Reference
Rubber seed shell	Rubber seed oil	352.51	2.2	0.2	60	60	60	(Onoji <i>et al.</i> , 2017)
Cocoa pod husks	Neem oil	2.76	0.65	0.73	65	57	99.3	(Betiku <i>et al.</i> , 2017)
Ostrich-egg shell	Waste cooking oil	71.00	1.5	12	65	120	96	(Tan <i>et al.</i> , 2015)
Chicken-egg shell	Waste cooking oil	54.60	1.5	12	65	120	94	(Tan <i>et al.</i> , 2015)
Unripe plantain peels	Yellow oleander oil	NR	2.8	0.3	60	75	94.97	(Betiku <i>et al.</i> , 2014)
Banana peels	Napoleon's plume oil	4.442	2.75	7.6	65	69.02	98.50	(Betiku <i>et al.</i> , 2016)
Banana peels	<i>Bauhinia monandra</i> seed oil	180	5	10	60	85	96.5	(Etim <i>et al.</i> , 2018)
Banana peels	Waste cooking oil	14.036	2	6	60	180	100	Gohain, M. <i>et al.</i> , 2017)
Coconut husk	Jatropha oil	—	7	12	45	78	99.86	(Vadery <i>et al.</i> , 2014)
Torrey leaves ash	Jatropha oil	9.622	9	65	5.0	300	89.43	Chouhan, A.P.S. and Sarma, A.K., 2013)
River snail shells	Palm oil	3.495	5	12	65	90	98.50	(Roschat <i>et al.</i> , 2016)
Waste chicken bones	Waste cooking oil	98.54	5	15	65	240	89.33	(Farooq <i>et al.</i> , 2015)
Sea sand	Soybean oil	4.60	7.5	12	60	360	97.50	(Mucino <i>et al.</i> , 2014)
Pyrolyzed rice husk	Waste cooking oil	4.00	5	20	110	900	87.57	(Li <i>et al.</i> , 2014)
Coal fly ash-derived sodalite	Soya oil	10.00	4	12	65	120	95.50	(Manique <i>et al.</i> , 2017)
Eggshells/ Snail shells	Waste cooking oil	220	10	15	60	120	94.1	(Singh & Singh, 2010)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials and Reagents

The ripe banana peels were sourced from Tengeru market in Arusha, Tanzania. The reagents used were Methanol (CH_3OH) 99.8%, ethanol ($\text{C}_2\text{H}_5\text{OH}$) absolute, Iron (III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$), Lithium metal (Li), Calcium oxide (CaO) and Phenolphthalein (POP) indicator, hydrochloric acid (HCl) 37%, Wijs and iodine solution. All chemicals were supplied by Sigma Aldrich and used without further modification.

3.2 Preparation of Calcined Banana Ash (CBA)

Figure 2 shows steps for the preparation of the Calcined Banana Ash (CBA). Ripe banana peels were sliced into small pieces to accelerate the drying process. After washing with distilled water, banana peels were sundried for 7 days followed by oven-drying at 100 °C for 6 hrs. Then, the dried banana peels were ashed in a Box Muffle Furnace in the presence of air and finally milled and sieved to a fine powder. The resulting fine ash was annealed in varying temperatures of 550-1050 °C for 3 hrs to remove impurities. Finally, the CBA was ground and kept in a bottle and sealed for further analysis.

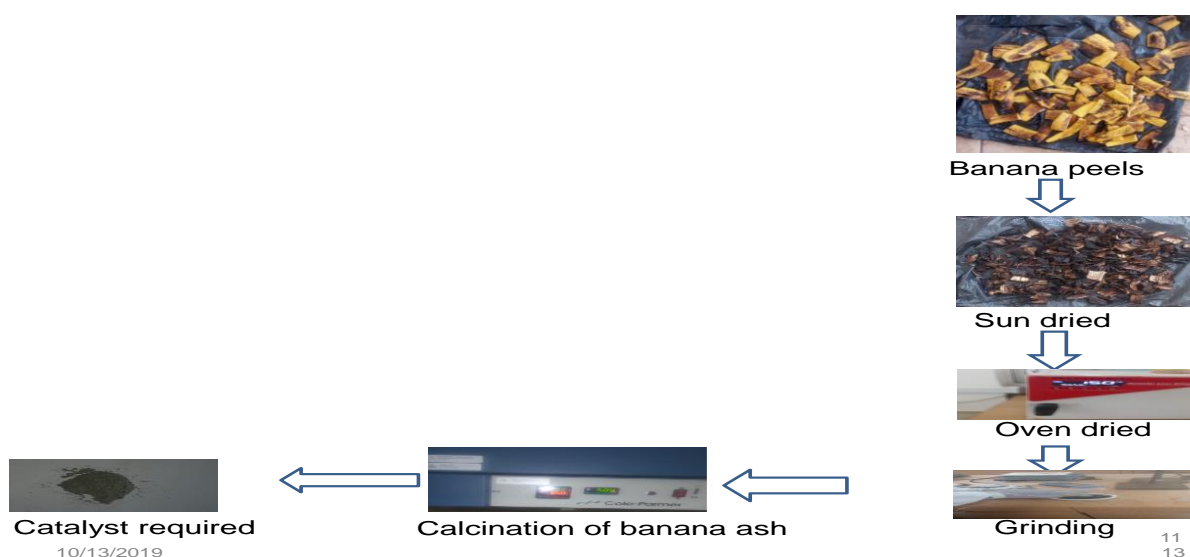


Figure 2: Steps for the preparation of the calcined ripe banana peel ash

3.3 Neem Seed Oil Preparation

Neem seed was purchased from Dar es salaam (Bagamoyo), Iringa and Singida regions in Tanzania. Steps for the preparation of neem seed oil (NSO) as shown in Fig. 3. Initially, the seeds were washed with distilled water and sundried for five days whereas other solid dirty impurities also were removed by handpicking and winnowing processes. Seeds were soaked in water for 24 hrs to remove husks followed by sun-drying for five days. Finally, Neem seeds were pressed using a hydraulic pressing machine to obtain Neem Seed Oil (NSO).

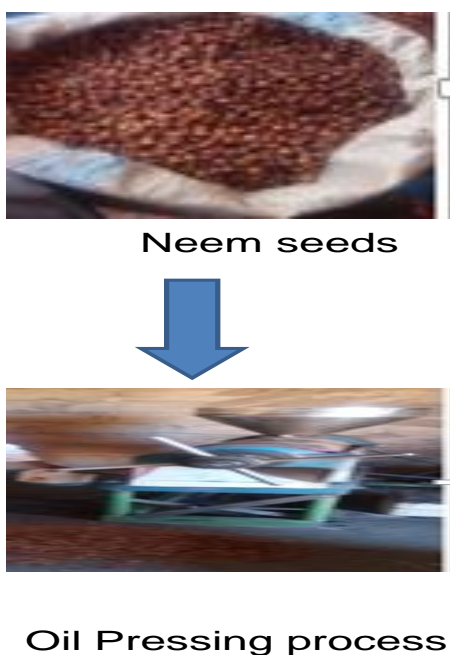


Figure 3: Shows steps on the preparation of neem seed oil

3.4 Preparation of Heterogeneous Catalyst

1.5 wt% of lithium metal, 1.3 wt% of Calcium oxide (CaO), 1.3 wt% of Iron (III) sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and 1.7 wt% of CBA/Li-CaO/ $\text{Fe}_2(\text{SO}_4)_3$ blends was used in the preparation. The blended catalyst was dissolved in 80 mL of methanol with continuous stirring of 2700 rpm for five minutes. The solution of the blended catalyst was finally covered with aluminium foil waiting for further experiments.

Micrometric Instrument [ASAP 2020] was used for nitrogen sorption studies. Functional groups in calcined banana ash were analysed by using Fourier Transform Infrared (FT-IR) instrument in the wavenumber ranging from 4000-1000 cm^{-1} , X-Ray Fluorescence (XRF) was used for elemental composition, XRD analysis for Crystallographic Identification and SEM for morphological analysis. Thermogravimetric Analysis (TGA) was used to study the decomposition profile of the sample. Approximately 0.24 mg of the sample was subjected to a temperature range from 29 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ in a time interval of 5.38 to 78.4 minutes. The ground catalyst precursor was subjected to heat treatment in a Box Furnace for 3hrs at 650 $^{\circ}\text{C}$.

3.5 Biodiesel Production through Transesterification Process

Transesterification of (NSO) to methyl esters was carried out using CBA/Li-CaO/ $\text{Fe}_2(\text{SO}_4)_3$ blends solution. 800 mL of Neem Seed Oil was poured in 2000 mL conical flask, and then warmed to 40 $^{\circ}\text{C}$ while stirring followed by addition of catalyst (1.7 %wt calcinated banana ash and 1.3 %wt Li-CaO / $\text{Fe}_2(\text{SO}_4)_3$) which was mixed with 100 mL of methanol followed by stirring for 53minutes. The conical flask was covered with aluminium foil and temperature was monitored by a thermometer under constant temperature of 60 $^{\circ}\text{C}$. The experiment was carried in a water bath till two immiscible layers of biodiesel (top layer) and glycerol (bottom layer) were formed as shown in Fig. 4. Both separating funnel and filtration method were employed to isolate the catalyst from the reaction mixture and finally, the filtrate was washed and dried with anhydrous sodium sulphate. The process was repeated using the same filtrate catalyst up to the fifth run. The transesterification process was repeated by varying catalyst dosage from 1-1.7 wt% and methanol to oil molar ratio varies from 2:1 to 16:1. The percentage of biodiesel yield was calculated using Eq. (1).

$$\text{Percentage biodiesel yield} = \frac{\text{Weight of biodiesel obtained}}{\text{Weight of oil used}} \times 100 \quad (1)$$

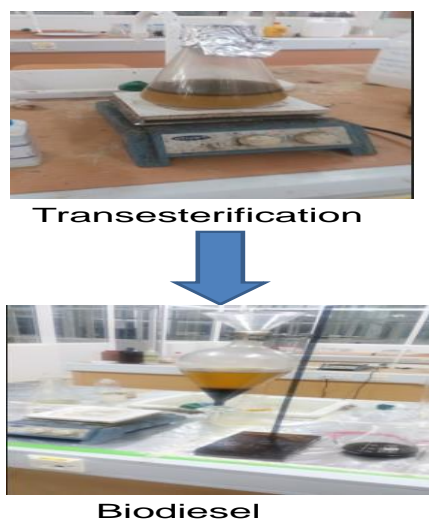


Figure 4: Production of biodiesel through transesterification process

3.6 Characterization of Biodiesel Properties

Fatty acid composition analysis for NSO was done using Gas Chromatography-Mass Spectrometry (GC-MS), Anton Parar Stabinger Viscometer instruments were used to determine the Density at 15.5 °C DMI 4500 and Kinematic Viscosity at 40 °C in accordance with ASTM D7042 standards, cloud point and pour point were determined by Test Cabinet Instruments (Setaflash Tester NCM 440) using ASTM D2500 and ASTM D97, and recommended agency of American Oil Chemists Society (AOCS) CD1-25 were used to respectively. The flashpoint was determined with the aid of Pensky-Martin Flash Point Tester PMA 5: Anton-Paar. Com Instruments as per ASTM D93 standards. The approximation of various values of the acid, iodine and saponification was done through the titration method.

3.7 Recyclability of the Catalyst

Heterogeneous catalysts have gained fame as compared to homogeneous catalysts because of their reusability. Therefore, the recyclability of the catalyst synthesized in this study was determined as follows. Methanol was used to wash the catalyst used in the biodiesel production to remove the contents of glycerol and oil. Since water is a product of transesterification process, the catalyst was later oven-dried for 2 hrs at a temperature of 110 °C. After drying and cooling, the spent catalyst was successfully used to produce biodiesel for the next successive run. Biodiesel yield produced was calculated after every successful run till the fifth run.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterization of the Catalyst

4.1.1 Thermogravimetric Analysis (TGA)

Figure 5 shows the TGA graph with plateaus at 650 °C, a clear indication that all the impurities have been lost and mostly only the metal oxides such as CaO, K₂O, MgO and Na₂O remained which increase the performance of the catalyst. Above 740 °C most of the metal oxide like potassium was decomposed and decrease its composition which leads to decrease in basicity finally, catalyst performance

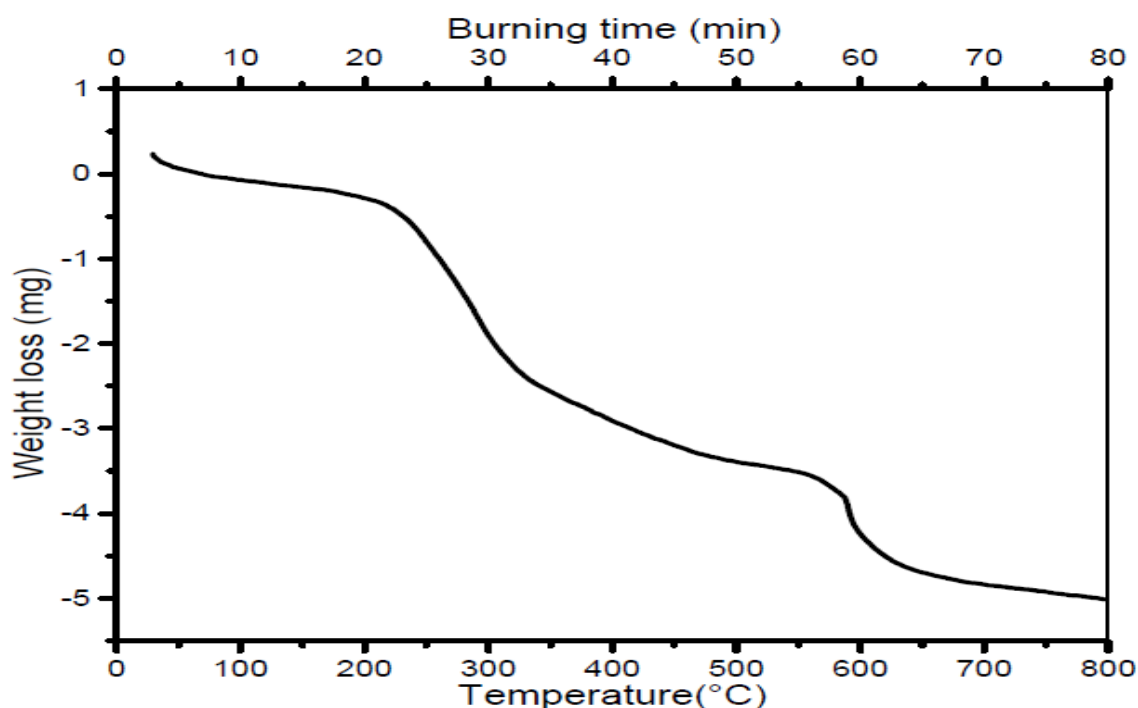


Figure 5: Decomposition profile of catalyst between 29 and 800 °C

4.1.2 Textural Properties of Calcined Banana Ash (CBA)

Brunauer–Emmett–Teller (BET) method was used to determine the surface area, while Barret-Joyner Halenda (BJH) method was used to determine pore sizes and pore volume of CBA. CBA possesses a BET surface of 411 m²/g, pore diameter was 3.0 nm and pore volume of 0.628 cm³/g. This implies that the high specific surface area, as well as the pore volume, have a significant contribution in the performance of the catalyst.

4.1.3 Fourier-Transform Infrared Spectroscopy Analysis

Fourier-Transform Infrared Spectroscopy of banana ashes (BA) calcined at different temperatures are illustrated in Fig. 6a-c. The broadband at 3303 cm^{-1} (Fig. 6a) shows the stretching vibration of the O-H group and in Fig. 6b-c, the O-H group disappeared due to burning in air and calcination at $650\text{ }^{\circ}\text{C}$. The sharp peak and small peak observed at 2920 cm^{-1} (Fig. 6a) and $2900\text{--}3150\text{ cm}^{-1}$ (Fig. 2b-c) respectively shows the stretching vibration of the C-H. Bands observed at $1350\text{--}1380\text{ cm}^{-1}$ have been associated with stretching vibrations of C-O. The bending vibrations observed at $500\text{--}1020\text{ cm}^{-1}$ show some elements of interest since the peaks are associated with CaMgSiO_4 . It is worth mentioning that a well-pronounced peak of K_2CO_3 located at 1376 cm^{-1} it comes with a number of advantages such as increased catalyst performance, surface area, reusability and prevents leaching also was reported by (Betiku *et al.*, 2016).

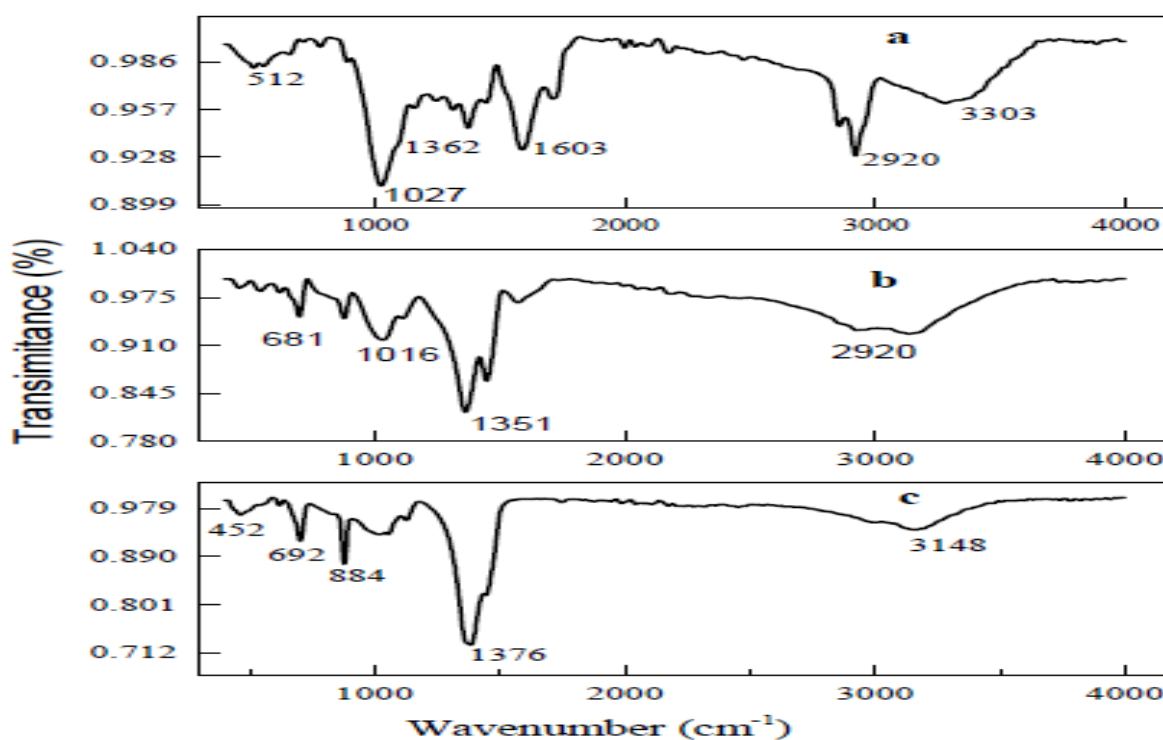


Figure 6: FT-IR peaks of Banana Peels (a) Fresh (b) Burnt (c) After Calcination at $650\text{ }^{\circ}\text{C}$

4.1.4 Morphological Analysis

Scanning electron microscope displays images at magnification of $5000\times$. The micrographs have shown in Fig. 7(a), (b) and (c) represent fresh banana ash, burnt banana ash and calcined

banana ash. The surface microstructure of Fig. 3(a) shows a smooth and flat nature of fresh banana ash while Fig. 3 (b) has a mix of small flake-like aggregates, and lastly Fig. 3(c) displays interestingly spongy-like microstructure a clear indicator of increased surface area which is proportional to the catalyst activity. This is in line with the argument of Sharma and his group that heat treatment hinders leaching of potassium therefore increases the life of the catalyst (Sharma *et al.*, 2012)

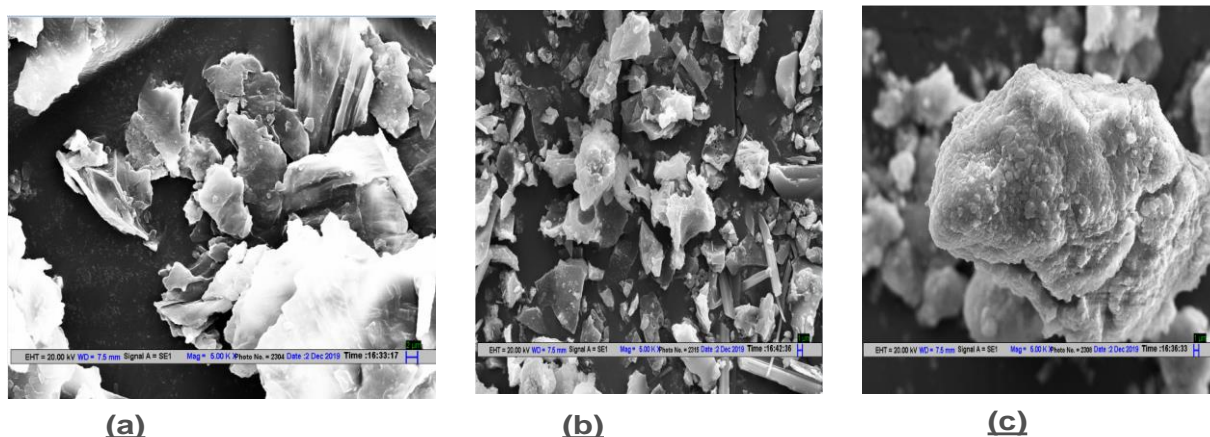


Figure 7: Images of SEM (a) Fresh banana ash (b) Burnt banana ash (c) Calcined banana ash

4.1.5 X-ray Diffraction Analysis

For crystallographic identification, X-ray Diffraction analysis was carried out on CBA, BBA and fresh BA as shown in Fig. 8(a-c). There was a significant increase in potassium compounds with an increase in calcination temperature up to 650 °C. Figure 8 (3a). Sharp pronounced peaks at 2θ:29 degrees correspond to K_2CO_3 whereas peaks at 2θ:33 and 43 degrees correspond to $CaMgSiO_4$ and $KNaSO_4$, respectively. Remarkable crystallinity of the materials can be observed from the fact that the peaks are narrow with high intensity. Additionally, weak unmarked peaks may be attributed to trace elements which as reported elsewhere have a significant contribution to basicity and consequently optimizing the catalyst performance (Betiku *et al.*, 2017).

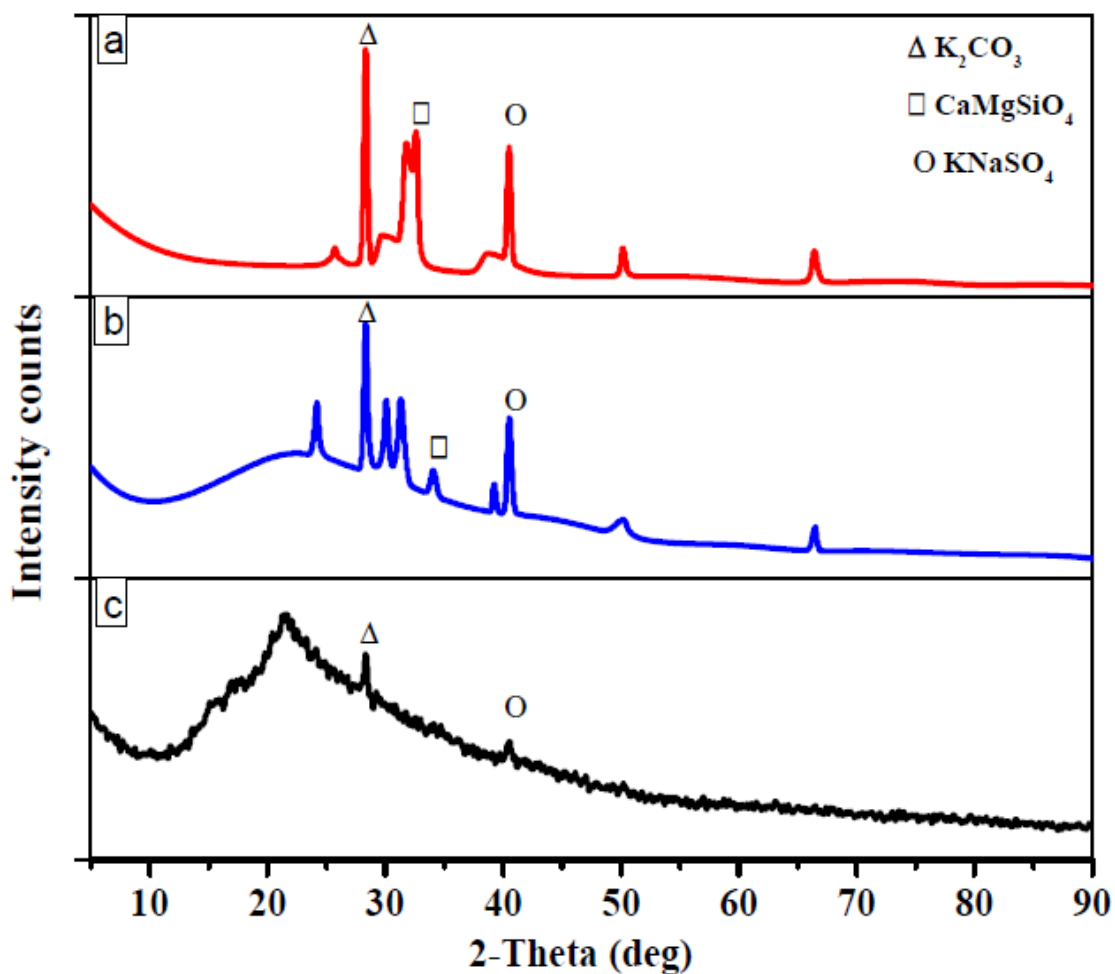


Figure 8: X-ray Diffraction Pattern of (a) Calcined banana ash (b) Burnt banana ash (c) Fresh banana ash

Table 2 shows the results of the XRF analysis of CBA at different calcination temperatures ranged to 100 °C from 550-1050 °C. These results show that the calcination temperatures influence the decomposition of various elements to metal oxide in banana ash. Main elements present in banana ash are K, Na, Ca, Mg, Fe, Al, Si, S, P and Cl. Potassium as the main element of interest showed highest percentage (74.4%) composition after calcination at 650 °C, therefore the ash produced at 650 °C was used as catalyst for rapid production of biodiesel.

4.1.6 Elemental Composition of Calcined Banana Ash

Table 2 shows elemental composition of banana ash of the XRF results at different calcination temperatures ranged from 550-1050 °C. These results show that the calcination temperatures influence the decomposition of some elements. Main elements present in the CBA are K, Na, Ca, Mg, Fe, Al, Si, S, P and Cl. Potassium as the main element of interest showed highest percentage (74.4%) composition after calcination at 650 °C, therefore the ash produced at 650 °C was used as catalyst for rapid production of biodiesel.

Table 2: Elemental composition of banana ash

Temp °C	K	Cl	Si (%wt)	Na	S	P	Al	Mg	Ca	Fe
550	54.65	7.37	4.96	3.21	3.15	1.84	1.49	1.42	1.27	0.14
650	74.41	10.88	5.22	2.88	0.00	2.96	0.21	1.19	1.62	0.25
750	72.51	11.36	5.79	3.79	0.00	3.02	0.18	0.70	1.68	0.28
850	72.34	7.0	9.53	3.86	0.00	2.94	1.51	0.41	1.21	0.35
950	63.08	3.19	20.34	3.33	0.057	2.27	1.88	1.40	2.39	0.83
1050	67.06	0.92	16.15	4.49	0.39	3.17	1.11	1.55	3.22	0.64

4.1.7 Physico-Chemical Properties of Neem Seed Oil

The physico-chemical properties of NSO was shown in Table 3, also the amount of oil in neem seeds was 37% which was enough for high production of biodiesel. From Table 3, the concentration of acid value was reasonably high (6.7), suggesting that, there was a high level of free fatty acid contents that probably would results in soap formation as previously reported by (Atabani *et al.*, 2013). Oils with FFA contents higher than 1.1%, it is desirable to apply a biomass catalyst in order to maximize the yield of biodiesel production as this may prevent the reaction that results to soap formation.

Table 3: Physico-chemical properties of Neem Seed Oil

Property	Unit	NSO
Oil content	%	37.3
Acid- value	mgKOH/g	6.7
Iodine- value	gI ₂ /100 g	81.6
Saponification -value	mgKOH/g	134.8
Free fat acid- (FFA)	mgKOH/g	3.4

4.1.8 Fatty Acid Profile of Neem Seed Oil

Table 4 shows that neem oil was extremely unsaturated (67.62%) due to availability of linoleic acid, pentadecanoic acid, oleic acid, and linolenic acid as the major methyl esters as reported by Muthu and his groups, (Muthu *et al.*, 2010).

Table 4: Fatty acid composition of neem oil

Fatty Acid	Formula	Systematic Name	Structure	Wt (%)
Saturated fatty acids				
Palmitic	C ₁₆ H ₃₂ O ₂	Hexadecanoic acid	16:0	10.92
Stearic	C ₁₈ H ₃₆ O ₂	(E)-9-Octadecenoic acid	18:1	19.85
Arachidic	C ₂₀ H ₄₀ O ₂	Eicosanoic acid	20:0	1.35
Lignoceric	C ₂₄ H ₄₈ O ₂	Tetracosanoic acid	24:1	0.26
Total				32.38
Unsaturated fatty acids				
Pentadecanoic	C ₁₇ H ₃₄ O ₂	Pentadecanoic acid, 14	17:1	2.57
Oleic	C ₁₈ H ₃₄ O ₂	9-Octadecenoic acid	18:1	1.82
Linoleic	C ₁₈ H ₃₂ O ₂	9,12-Octadecadienoic acid,	18:1	52.51
Linolenic	C ₁₈ H ₃₀ O ₂	9,12-Octadecatrienoic acid,	18:1	10.71
Total				67.62

4.1.9 Characterization of Biodiesel

The properties of biodiesel produced from NSO using blends of CBA/Li-CaO/Fe₂ (SO₄)₃ catalyst is summarized in Table 5. Interestingly, these properties showed comparable similarities with the standard specifications of EN 14214 and ASTM D 6751. For instance, the close similarity in cloud pour points, viscosity, initial boiling points, final boiling points, and acid value were observed. With an exception of density which was slightly higher than the recommended range, all other properties were in accordance with the ASTM D6751 standards. However, this biodiesel displayed remarkable cold flow properties like cloud point, pour point and kinematic viscosity which can be used in cold areas and also its calorific value was high. It has been reported elsewhere in the literature that, both the molecular mass of methyl ester and its saturation level determine the density of biofuel, in short, the unsaturation level is directly proportional to the specific gravity (Ong *et al.*, 2013). The high density of biodiesel from neem oil seeds due to the high unsaturation level. Flashpoint is the important parameter in the diesel engine combustion which can define the minimum temperature at which fuel ignites. In this study, the minimum ignition temperature obtained was 150 °C which is in within the ASTM D6751 standards, and also will guarantees safety during storage and transportation.

The produced biodiesel and catalyst from this study shows higher yield compared to other studies as shown reported in Table 5.

Table 5: Physico-chemical properties biodiesel [neem] compared standards

Test/characteristics	Petrol diesel ASTM D975 limits	Biodiesel ASTM D 6751 limits	Biodiesel [Neem]
Density kg/m ³ at 15.5°C	850	860 - 900	863.8
Kinematics viscosity at 40°C mm ² /s	2-4.5	1.9 -6.0	3.8
Pour point °C	-35 to -15	NS	-30
Flash point °C	60-80	130 minimum	150
Cloud point °C	-15 to -5	NS	-40
Cetane index (minimum)	-	47	48.9
Initial boiling point °C	-	NS	86
Final boiling point °C	-	NS	86
Calorific value	42-46	-	43
Acid value (titration) mgKOH/g	-	0.5 max	0.12

4.2 Performance of Catalyst for Biodiesel Production

4.2.1 The Effect of Catalyst Loading

The production of biodiesel yield was done by evaluating the percentage performance of the CBA catalyst using Eq. (1), by changing the parameters conditions of the reaction like percentage by weight of the catalyst added, the reaction time-temperature set and the ratio of CH_3OH and Neem Seed Oil. The amount of produced biodiesel was affected by the amount of the catalyst. The excess ratio of 16:1 of methanol to oil was used during testing the performance of the catalyst. The amount of catalyst added varied with the amount of oil at an interval of 0.1 wt% from 1 to 2 wt%. The effect of catalyst added to the rate of production of biodiesel yield was increased from 1.1 to 1.7 wt% respectively whereby the percentage of conversion of biodiesel was increased. The highest production yields 98.8% of biodiesel was attained at catalyst to oil weight of 1.7 wt% as shown in Fig. 9. There were a number of factors which may contribute to the high production yield of biodiesel, for example, the high surface area of the catalyst, presence of alkali metals such as K, Na, Ca and Mg, which contributed to high basic strength 11.09 pH of the catalyst. Also the availability of higher oxygen compounds in $\text{Li-CaO/Fe}_2(\text{SO}_4)_3$ increases the oxidation rate for conversion of oil to biodiesel (Buchori *et al.*, 2016; Guo *et al.*, 2010).

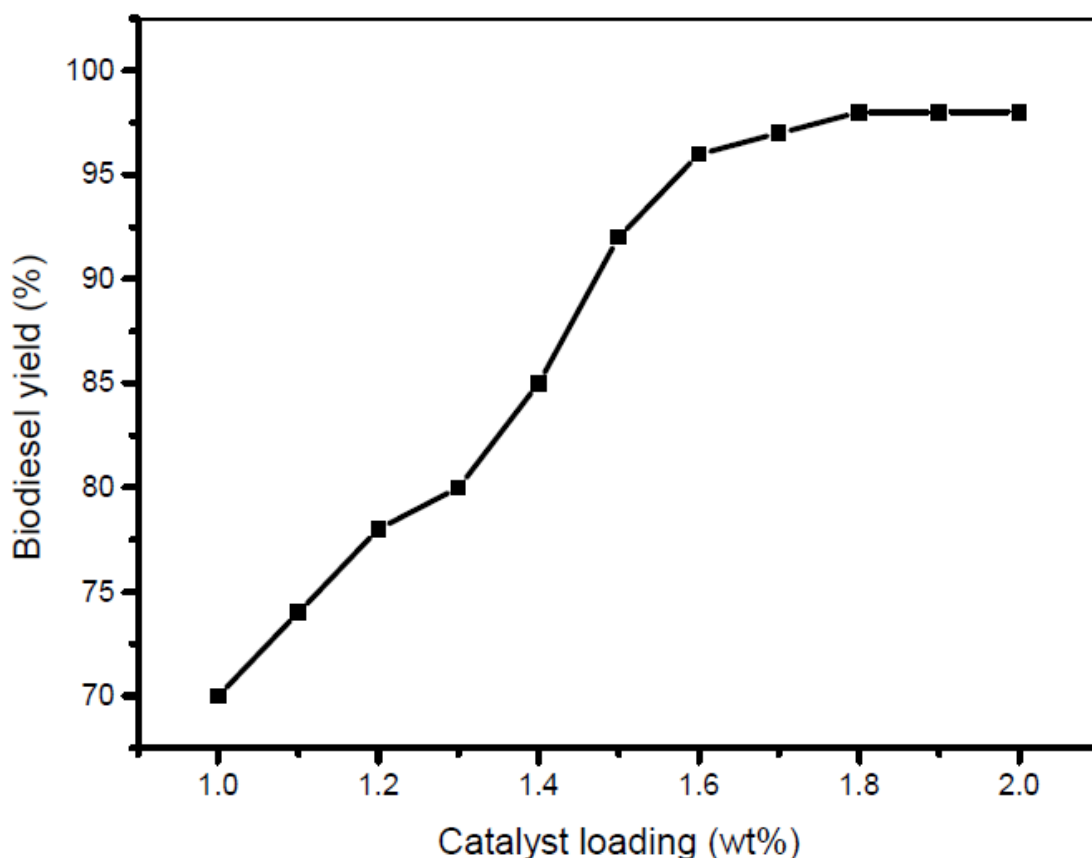


Figure 9: Effect of the amount of catalyst added to the production of biodiesel

4.2.2 Effect of Reaction Time

The production of biodiesel using NSO with 1.7 wt% catalyst loading and 8:1 excess methanol was done by changing the time of the reaction after every 10 minutes from 10 to 70 minutes while stirring at 2700 rpm and maintaining the temperature at 60 °C. Figure 10: Effect of reaction time to biodiesel yield shows the effects of reaction time in biodiesel yield. It is observed that the rate of production of biodiesel yield increases with time from 10 minutes to around 50 minutes. Above 50 minutes biodiesel yield remained constant. This is due to a reversible reaction caused by reduced and disappearance of esters resulting in soap formation associated with the fatty acid composition. It is observed that the prime time for the production of the highest yield of biodiesel is 53 minutes.

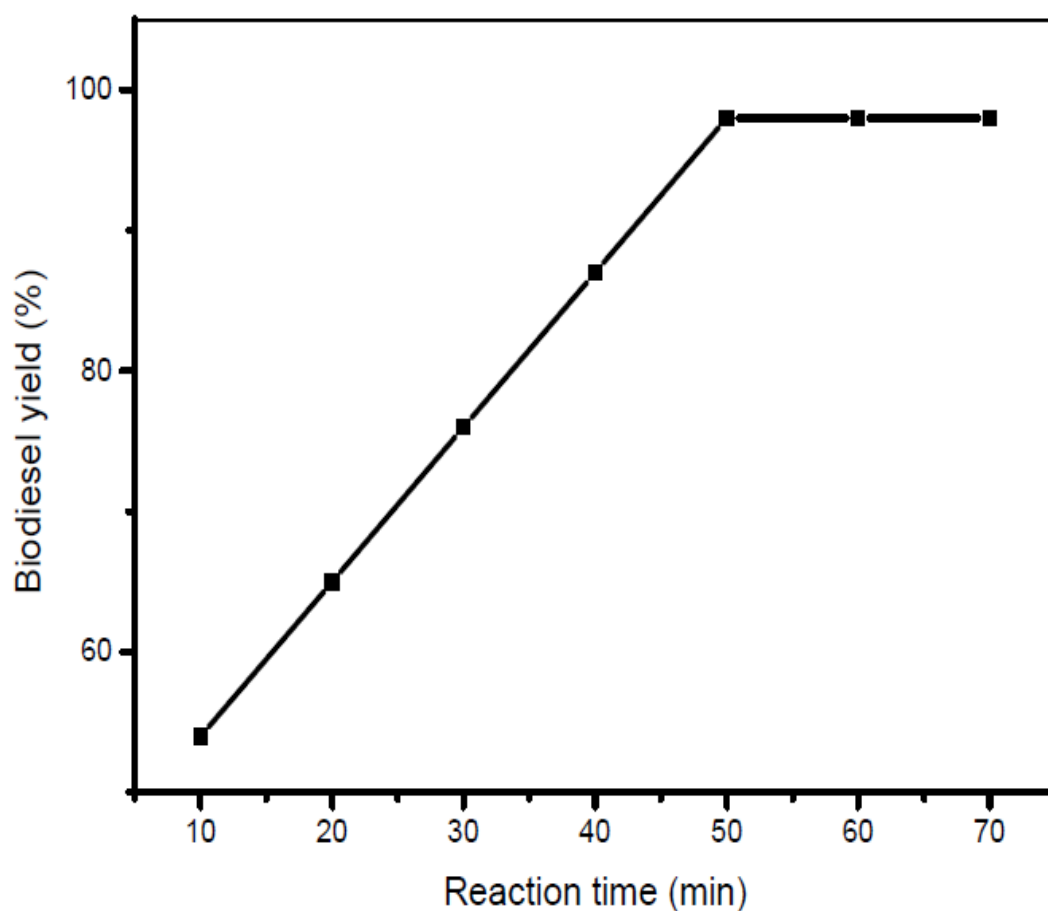


Figure 10: Effect of reaction time to biodiesel yield

4.2.3 The Effect of Methanol to Oil Ratio

Key factors for converting long fatty acid esters to methyl esters (biodiesel) is the ratio of methanol to oil. The relation between quantities of substance and the number of moles that can take part in a chemical reaction is needed in the process. This can result in the split of the mixture of reaction on the solubility of glycerol to methyl ester layer. Figure 11: Effect of ratio of methanol and oil in a yield of biodiesel yield, and the best ratio for the highest yield of biodiesel was 8:1.

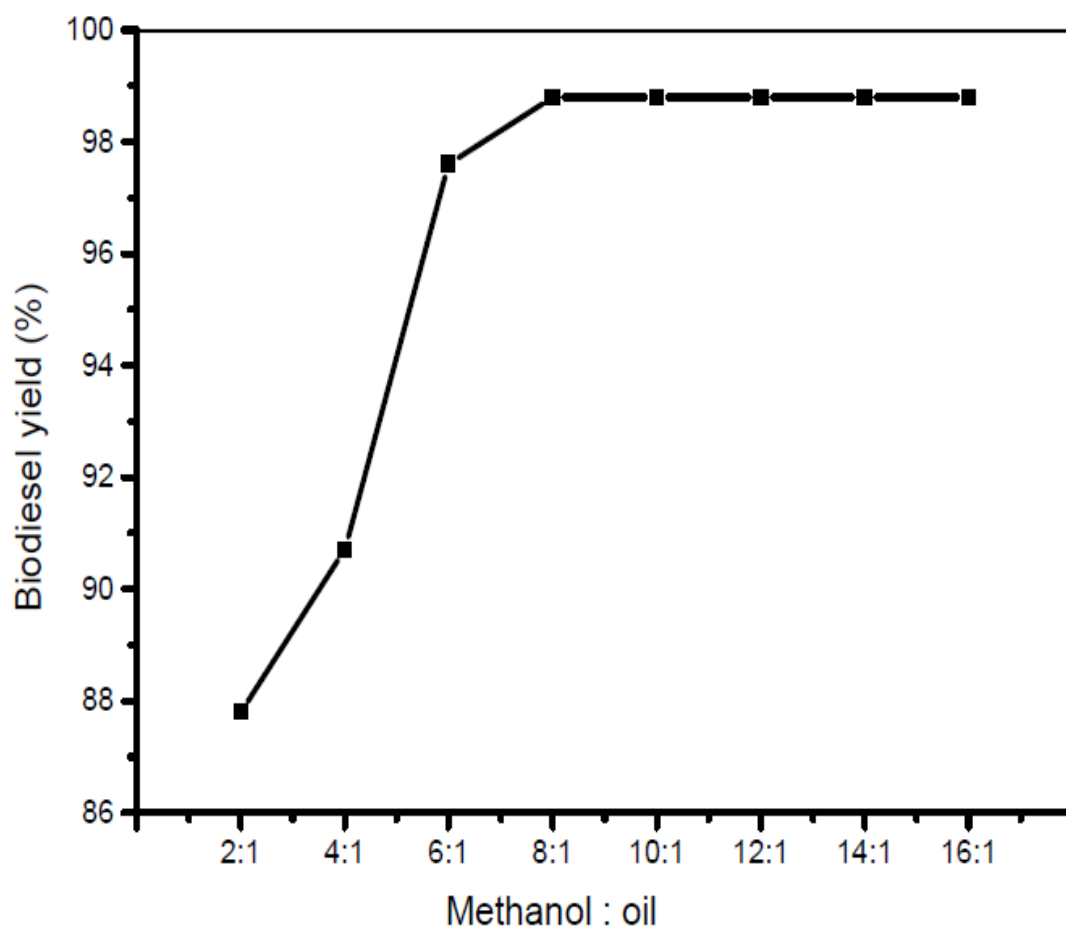


Figure 11: Effect of ratio of methanol and oil in a yield of biodiesel

4.2.4 Catalyst Recyclability

Bio base catalyst precursor prepared was reused up to the fifth run in the transesterification process. Under the optimum condition, 1.7 wt% catalyst fed, methanol to oil molar ratio 8:1, 53 minutes time of the reaction, 60 °C temperatures of the reaction and stirring rate of 2500 rpm. Figure 12 shows the results of catalyst reusability. Figure 12 the recyclability of the catalyst vs biodiesel production from the catalyst reusability.

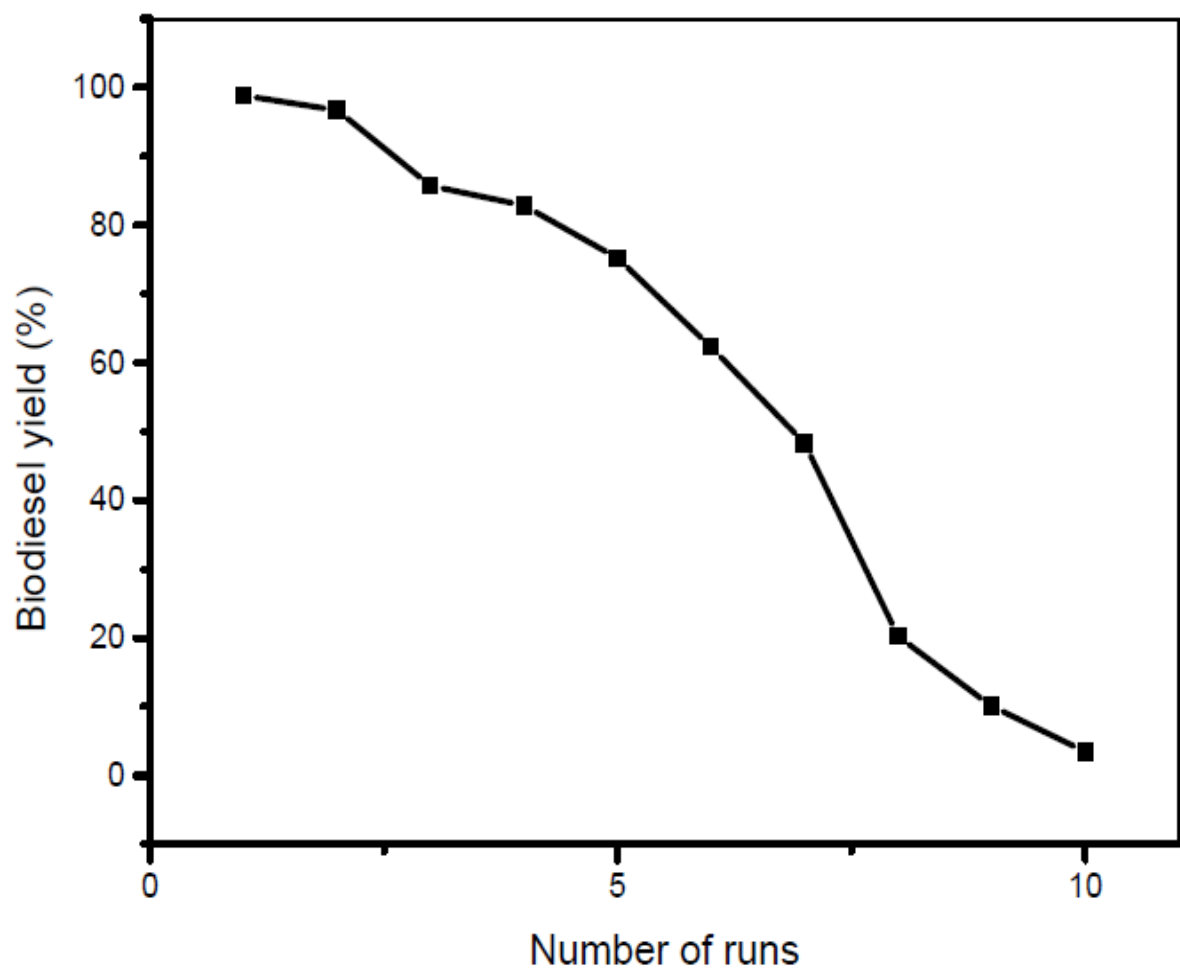


Figure 12: Number of runs vs % biodiesel production

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study presents the production of biodiesel from NSO and affordable solid catalyst synthesized by direct calcination of banana ash loaded with Li-CaO/Fe₂(SO₄). Calcined banana peels at 650 °C acquired good catalytic activity due to the presence of basic metal oxides of K, Ca, Na and Mg and basic strength of 11.09 pH. The performance was also attributed to its high specific surface area of 411 m²/g, and pore diameter of 3.0 nm. The optimum biodiesel production yield of 98.8% achieved at a low catalyst loading of 1.7 wt%, 8:1 methanol to oil molar ratio at a temperature of 60 °C. The produced biodiesel acquired physicochemical parameters within the recommended ASTM D6751 standards and it displayed remarkable cold flow properties that can be used in cold areas. The catalyst shows good reusability properties with a yield of approximately 75% after a fifth run. In conclusion the production of the CBA catalyst is affordable and minimizes waste disposal also is compatible catalyst to our environment.

5.2 Recommendations

To commercialize biodiesel from neem seeds, there is a need to maximize a wide range of factors. The following are recommendations for future work.

- (i) For high yield of biodiesel through transesterification the following factors must be considered concentration, reaction temperature, catalyst, stirring effects, and moisture. Among of these factors, the reaction temperature should not exceed the boiling temperature (64 °C) of methanol.
- (ii) Pressing and extraction of NSO must be done using a specific machine in order maximize the amount of oil extract, this is because neem seeds have sticky husks that interfere with oil production.
- (iii) The biodiesel from NSO is easily oxidized, it is recommended to carry further research on additives for maintaining biodiesel stability.

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