UNIVERSITY OF CAPE COAST

PRODUCTION OF BIODIESEL FROM *Parkia biglobosa* OIL USING HETEROGENEOUS BI-FUNCTIONAL CLAY CATALYST

BY

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Thesis submitted to the Department of Environmental Science of the School of Biological Sciences, University of Cape Coast, in partial fulfillment of the requirements for the award of Master of Philosophy Degree in Environmental Science

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DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this university or elsewhere.

Candidate's Signature: ………………………………. Date: …………….

Name: Rogers Kipkoech

Supervisor's Declaration

I hereby declare that the preparation and presentation of the thesis was supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast.

Supervisor's Signature ………………………………. Date: …………….

Name: Dr. Mohammed Augustine Takase

ABSTRACT

The aim of this study was to produce biodiesel from non-edible *Parkia biglobosa* oil using heterogeneous bi-functional Na_2CO_3-clay catalyst. Soxhlet extraction method was used to extract the oil from *Parkia biglobosa* seeds and the percentage yield of oil determined to be 16.5 %. The oil contained 0.61% w/w free fatty acid (FFA) and 191.65 (mgKOH/g) saponification value, determine the suitable catalyst used for producing biodiesel. Subsequently the oil was subjected to transesterification to biodiesel using the H_2SO_4 and bi-functional clay mineral or catalyst. The properties of the biodiesel were analysed using gas chromatography mass spectrometry (GC-MS). Catalyst synthesized from clay was slightly acidic with the PH of 4.88. The prepared catalyst was characterised by means of FTIR, SEM, UV Spectrum, EDS, and XRD. The efficiency of the catalyst for production of biodiesel was proven by the results of the transesterification study. The percentage weight of yield of biodiesel produced were 93.4 % and 94.7 % at optimal parameter of 6:1 and 12:1 methanol to oil molar ratio, 3 wt % and 2 wt % catalyst concentrations, 65°C and 60°C reaction temperature, 1.5 hrs reaction time for H_2SO_4 and bi-functional Na_2CO_3-clay catalyst transesterification. The biodiesel produced were within the limits of specification given by the American standard, test method (ASTM D6751), European Standard (EN 14241**)** and Ghana Standard Authority. Among the recommendation, the study suggest further research on ways of reducing iodine value and water content which were the only properties beyond accepted limit.

KEYWORDS

Biodiesel

Catalyst

Parkia biglobosa

Reaction

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DEDICATION

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LIST OF ABBREVIATIONS

AOAC	American Oil Analytical Chemists
ASTM	American Society for Testing and Materials
B_X	Biodiesel blended with petro diesel at x percent biodiesel
CaO	Calcium Oxide
CI	Combustion injection
CO_2	Carbon dioxide or Carbon (IV) oxide
DG	Diglyceride
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography Mass Spectrometry
Hrs	Hours
SEM	Scanning Electron Microscope
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

Background of the Study

Petroleum-based fuel performs crucial function in the energy sector. Petroleum is used principally in the transport sector, specifically in motor engines to run vehicles and power plants. This resource is however, running out(Othman *et al.*, 2017). During the depletion, global warming is becoming a concern mainly due to anthropogenic activities such as emission of greenhouse gas resulting from burning of fossil fuel. There are however, significant efforts to search for renewable, sustainable and energy-friendly fuel sources (Unglert *et al.*, 2020; Yu *et al.*, 2020). Research by Yu *et al.* (2020) reveals the depletion in global fossil fuel reserves. There is no doubt that renewable energy sources could provide the much-needed reprieve from the over utilisation of petroleum products.

Research has been extensively carried on new, renewable energy sources in the quest of fulfilling the world's ravenous energy demand. The new substitute sources of energy include solar, wind, biomass, and so forth.

Biodiesel has become one of the most preferred forms of liquid fuel. Biodiesel can be compared in terms of characteristic to conventional petroleum diesel. It is renewable and produces minimal emissions after combustion as compared to petroleum diesel. It could revolutionise into a sustainable fuel source (Demirbas, 2009b).

Biodiesel is produced through chemical processes such as transesterification with alcohol that are short-chain for example methanol, butanol and ethanol using vegetable oil, animal fat or organism (example, algae and cyanobacteria).

The choice of an alcohol is due to consideration of many factors which include performance and cost-effectiveness. Ethanol and methanol are primarily used as alcohol. Methanol is cheap and has desirable physical and chemical properties, ethanol is friendly to the environment. It is obtained from renewable source through agricultural materials, making the process of transesterification entirely independent of petroleum-based alcohol (Mujeeb *et al.*, 2016).

Kinematic Viscosity of the vegetable oil is supposed to be lowered in order to enhance its utilization in diesel engine. There are methods that have been developed to reduce oil's viscosity. The methods are; blending with diesel, transesterification, pyrolysis and micro emulsification. Other process for example conventional, microwave, non-catalytic supercritical heating and ultrasound-assisted are also applied in production of biodiesel (Axelsson *et al.*, 2012; Borugadda & Goud, 2012). Blending and transesterification however, remain the most popular methods. Meanwhile, among the two, transesterification remains a more superior and efficient method of reducing vegetable oil’s viscosity and yielding fuel with similar diesel properties(Refaat & Refaat, 2010).

Transesterification entail the use of catalysts such as alkali, acids, or enzymes in nature. Homogenous catalyst exists in the same phase (either gas or liquid) as the reactants for example sulphuric acid, sodium hydroxide and many others. Alkali catalysts are mostly preferred due to its practical and industrial feasibility. They are also less costly, unlike enzymes. Glycerol as a by-product of the process is essential component in soap-making and cosmetic industries.

Heterogenous solid catalysts have however, been developed to substitute homogenous catalysts and they easily be recovered and reuse after reaction. Heterogeneous catalysts include clay minerals, eggshells, zeolites, snail shells and many others(Etim et al., 2020).

A bi-functional heterogeneous catalyst aims at efficient production of biodiesel and its efficiency has been tested using various feedstock(Mardhiah *et al.*,2017). Many studies have been undertaken using bi-functional heterogeneous catalyst for producing biodiesel using feedstocks such as of low-cost (M. Ali, 2015; Pereira *et al.*, 2014). Bi-functional heterogeneous catalysts possess both acidic and alkaline characteristics. They can perform esterification of free acid and transesterification of triglycerides concurrently. Bi-functional heterogeneous catalyst can be subjected to easy modification to introduce a desirable physicochemical property to prevent the free fatty acid or the existence of water from negatively affecting reaction steps in the transesterification process of (Al-Saadi *et al*., 2020; Ali *et al*., 2018).

Several feedstocks for producing biodiesel are from edible agricultural resources. Using edible oils to produce biodiesel is currently of great concern because of competition between oil to be used as fuel and oil used as food. This has necessitated research to discover alternative non-edible and cheap feedstock. Currently, non-edible feedstock oil used for producing biodiesel are derived from the seed of plants for example jatropha, castor, neem, moringa, croton and many others. A search for more of resources for producing biodiesel has led to the discovery of *Parkia biglobosa* seeds which has received recognition in medicinal and pharmaceutical industry but less or no attention in biodiesel production because it is widely spread among the west African countries and there is growing interest for the use of the medicinal plants more than production of biodiesel especially in the low-income countries.

Parkia biglobosa is a tree that is a perennial deciduous and produce the fruits which are in shape of pod that contains pulp which are yellow and powdery with seeds implanted in it. It belongs to *Fabaceae* family. *Parkia biglobosa* grows to a height of 7 to 20 meters though sometimes it can grow to 30 metres (Janick & Paull, 2008). *Parkia biglobosa* tree is found mostly in Africa, including Ghana. The tree is classified as spermatophytes and vascular plants. It is a halophyte-type, fire-resistant tree characterized with dark gray-brown bark (Abioye *et al.*, 2013). *Parkia biglobosa* pods are known as locust bean and appear pink initially and later changed to dark brown when they fully mature. On average, the pods are about 30 to 40 centimetres long, while some can attain 45 centimetres in length. A pod is made up of 30 seeds. The fermented *Parkia biglobosa* seeds are used in seasoning traditional foods in Ghana and some West African countries (Ojewumi, 2016). Preliminary research on the oil yield and physicochemical characteristics revealed that *Parkia Biglobosa* seed can yield oil of 11.41% in average. However, it is below the oil yield for castor seed which is 33.2% (Olowokere *et al.*, 2018). *Parkia biglobosa* oil could serve as among the main additional oil sources used for producing biodiesel.

This aim of the study was to investigate the feasibility of producing biodiesel from *Parkia biglobosa.*

Problem Statement

The rise in demand for fossil fuels is due to growth of industrialization and modernization. The finite nature of fossil fuel reserves in the world compared with ceaseless demand has resulted in a constant shortage in supply and continuous spiralling of prices. These threats coupled with food insecurity have drawn researchers' attention to the quest for a substitute fuel produced from resources that are renewable. Research has established biodiesel as the promising substitute especially, in engines that uses diesel. Presently it is made from typically grown edible oils like rapeseed, soybean, sunflower, and palm. Using the edible feedstock oils has worsened the existing situation of the unfortunate competition between oil for food and fuel, leading to food scarcity. Currently, commercial production technology of biodiesel via homogenous transesterification is associated with a lot of limitations including toxicity, corrosion and production of a large amount of wastewater that needs extra processing. The limitations make the cost of biodiesel production economically unfeasible.

Available literature indicates that there is little or no work on *Parkia biglobosa* seed oil for biodiesel. The use of bi-functional heterogeneous catalysts such as clay mineral has also not been applied to *Parkia biglobosa* for biodiesel.

Main Objective

The main objective of the study was to investigate biodiesel production from *Parkia biglobosa* seed oil using heterogeneous bi-functional Na_2CO_3-clay catalyst.

Specific Objective

i. To produce biodiesel from *Parkia biglobosa* oil via transesterification using sulphuric acid catalyst.

ii. To synthesize and characterize bi-functional heterogeneous catalyst from clay and sodium carbonate for biodiesel production from *Parkia biglobosa* oil.

iii. To optimize reactions conditions for the production of biodiesel from *Parkia biglobosa* oil via transesterification using a bi-functional heterogeneous catalyst and evaluate the properties of biodiesel.

Hypothesis

i. Biodiesel can be produced from *Parkia biglobosa* oil via transesterification using sulphuric acid catalyst.

ii. Bi-functional heterogeneous catalyst can be synthesized from clay and sodium carbonate for biodiesel production from *Parkia biglobosa* oil

iii. Bi-functional heterogeneous catalysts can be used to optimize reactions conditions for the production of biodiesel from *Parkia biglobosa* oil and evaluate the properties of biodiesel.

Significance of the Study

Due to limitations in estimating the remaining fossil fuel reserve, renewable energies have taken centre stage in providing fuels for the future. It is expected that the result of this research will lead to the cultivation of the *Parkia biglobosa* plant.

The research is also expected to reduce greenhouse gas emissions and develop social structures for sustainable fuel development, particularly in developing countries. The balance between agriculture, environment and the economic development can be feasible through the study. Moreover, biodiesel being a good lubricant (almost 66% superior to petrodiesel), will reduce the long-term wear of the engine common in diesel engines by improving the lubrication properties of the diesel fuel blend.

Organisation of the Study

The study is arranged into five major parts in the form of chapters.

Chapter one deals with the general introduction of the study. This is made up of background to the study, problem statement, hypothesis and significance of the research and the objective (s) of this study. Chapter two focus on the literature review. Chapter three entails the materials used and the research methodology applied. Chapter four consists of analysis and discussion of the results. Chapter five deals with the conclusions and recommendations.

CHAPTER TWO

LITERATURE REVIEW

Present-day Energy Scenario

There is a rise in the utilization of energy globally. Coupled with this, is the decrease in the abundance of natural resources while the amount of Chlorofluorocarbons (CFCs) being emitted is threatening the ecosystems. The majority of the energy produced at the moment is through fuel from fossil sources which include coal, oil and natural gas, and this has exacerbated the fossil fuels depletion. Furthermore, there is a rise in fuel prices and the threat of negative environmental impact occasioned by global warming and photochemical smog and ozone depletion. The rise in consumption of energy combines with limitation of fuels derived from fossils sources has occasioned the search for a substitute source of energy that can be efficient and less expensive with social equity and friendly to the environment. The two major sectors contributing to the rise in the energy demand include; transport industry from the basic level that consumes the most significant energy amount. The transportation sector is the largest user of petroleum fuels globally. Petroleum fuels used include diesel, compressed natural gas(CNG) gasoline and liquefied petroleum gas (LPG) (Demirbas, 2006).

Transportation sector is estimated to consume about 60% of the entire earth's fossil fuel energy demand (Vasanthakumar, 2013). Based on International Energy Agency (IEA), the number of cars and trucks owned by people has increased from 700 million in 2006 to 947million in 2019. It is expected to reach 2 billion in the year 2050 globally(Cuevas *et al.*, 2021). Explicitly, this will result in a significant rise in greenhouse gas release, particularly carbon dioxide. Besides, efficient bioenergy technologies are also being designed and are expected to suffice the future energy demand from renewable sources (Graaf, 2012).

Forms of Energy

Energy is categorized into two main forms. These include and non-renewable and renewable energy.

Non-renewable energy is a form of energy that cannot be replaced within a short human cycle once used. For instance, oil, soil, coal, and specific metallic mineral deposited may undergo formation once again after thousands to hundreds of millions of years. Contrastingly, the rate at which these resources are renewed is very slow when compared with how they are exploited. Yet, they are not renewable within human existence or cycle. Sources of non-renewable energy include; fuel obtained from fossil materials, for example oil, natural gas and coal. Fuel from fossils materials is primarily utilised in industries, agriculture, automobiles, household usage, and commercial purposes. The use of fossil fuels has risen rapidly over recent times (Refaat *et al*., 2008).Switching from non-renewable energy sources to renewable sources that are favourable to the environment such as bioenergy is a critical concern globally (International Energy Agency IEA, 2010).

Renewable energy is the energy that is replaced continuously by nature. They convert the fuels into helpful energy types. Renewable energy includes hydropower, wind energy, biomass etc (Söderholm, & Sundqvist, 2007).

Forms of Renewable Energy

Biomass Energy

The term biomass generalizes the material derived from plants that grow or the manure from animals. It is simply a term for referring to all the organic materials whose origin is plants, algae, animals and crops. It is obtained from parts of plant and animal for example natural forest, animal or human waste, agricultural or industrial wastes. Solar energy is absorbed by plants and use for photosynthesis which allows them to survive. The biomass's original energy from the plant matter is through solar energy, derived from the process of photosynthesis. Energy which is stored in the plants and animals or contained in the wastes they generate is referred to as biomass energy. The combustion of biomass fuel leads to the recovery of this energy. Combustion emits heat from biomass and gases such as carbon dioxide. The process of photosynthesis is essentially being reversed through the use of biomass energy. Therefore, biomass energy is a renewable form of energy which is chiefly obtained through the utilization of carbon containing materials. The process of using biomass can be direct or indirect. Direct methods involve burning wood for household use or indirectly through methods such as conversion to liquid or gaseous form of fuel such as alcohol, or biogas from animal wastes (Anadon *et al*., 2016).

Biomass is applied in the same process as fossil fuels through combustion and at a rate that is constant in the boiler furnace for heating water and producing steam. The biofuel produced from plants such as wheat, sunflower oil, sugar root, and rapeseed are at the moment being utilized in certain countries which are members of the European Union. Clean energy and renewable sources are obtained from biomass and improve the environment and economy (Fantini, 2017). Biomass energy releases fewer emissions as compared to fossil fuels. Moreover, biomass energy utilization decreases the quantity of waste taken to landfills and reduces the dependency on imported foreign oil. It is projected that thousands of employment opportunities are created through biomass energy and can revamp rural households' economic status (Briens *et al*., 2008).

Biofuels

Biofuel carries the energy obtained out of biomass which is obtained from plants, organic wastes, animals, and microorganisms. Biofuels exist in various forms which include solid, liquid, or gaseous. The fresh supplies of biofuel can re-grow and therefore, it is a renewable energy source. Biofuel is the potential alternative source for fossils fuels. The advantages of using biofuel depends on the classification of the particular biofuel, certain feedstock and technique of the technology used to produce energy (Gomez *et al.*, 2008).

Biodiesel

Biodiesel is used as a fuel and it replaces diesel and is obtained from biomass’s source. It is a long chain fatty acid which is monoalkyl esters. Biodiesel must conform to the specific requirements of ASTM (American Standards for Testing Materials), European standards, and other international and national standards. For the biodiesel to be used, it must be consistent with the stringent quality standards. The nature of biodiesel's combustion is similar to diesel when used in the same engine and petroleum-based diesel produced domestically. The procedure for producing biodiesel by means of vegetable oil or animal fat is shown in the summary in the following general equation in figure 1:

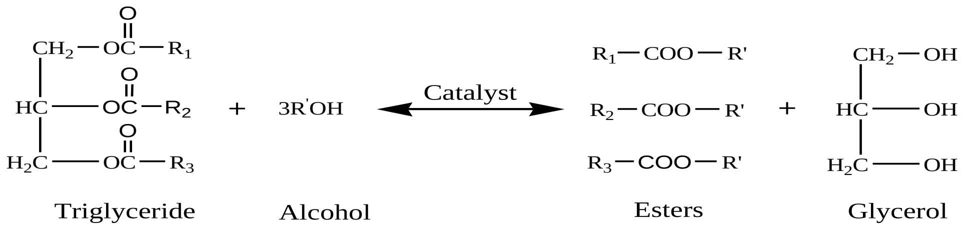


Figure 1: Process of producing biodiesel from vegetable oil or animal fat(Kulkarni & Dalai, 2006)

Biodiesel is applied in raw form or can be blended together with petroleum diesel in varying proportions, and the commonly used blending is B20, which contains 20% biodiesel. Addition of only 20% of the biodiesel to the diesel magnifies the cetane number, rating point of the diesel by about 3 points, which eventually increases the engine's efficiency(Ammous, 2011). The popular process of biodiesel production is transesterification by using edible and non-edible oil from various feedstock. Some of the edible oils are obtained from soybeans, coconuts, rapeseeds and many others while other sources of vegetable oils are from feedstocks such as *Parkia biglobosa*, castor seeds, croton, jatropha etc. Producing biodiesel in the coming times will be expected to be obtained from non-edible feedstock oil and edible feedstock oils from the feedstocks whose supply will be in excess(Kulkarni & Dalai, 2006)

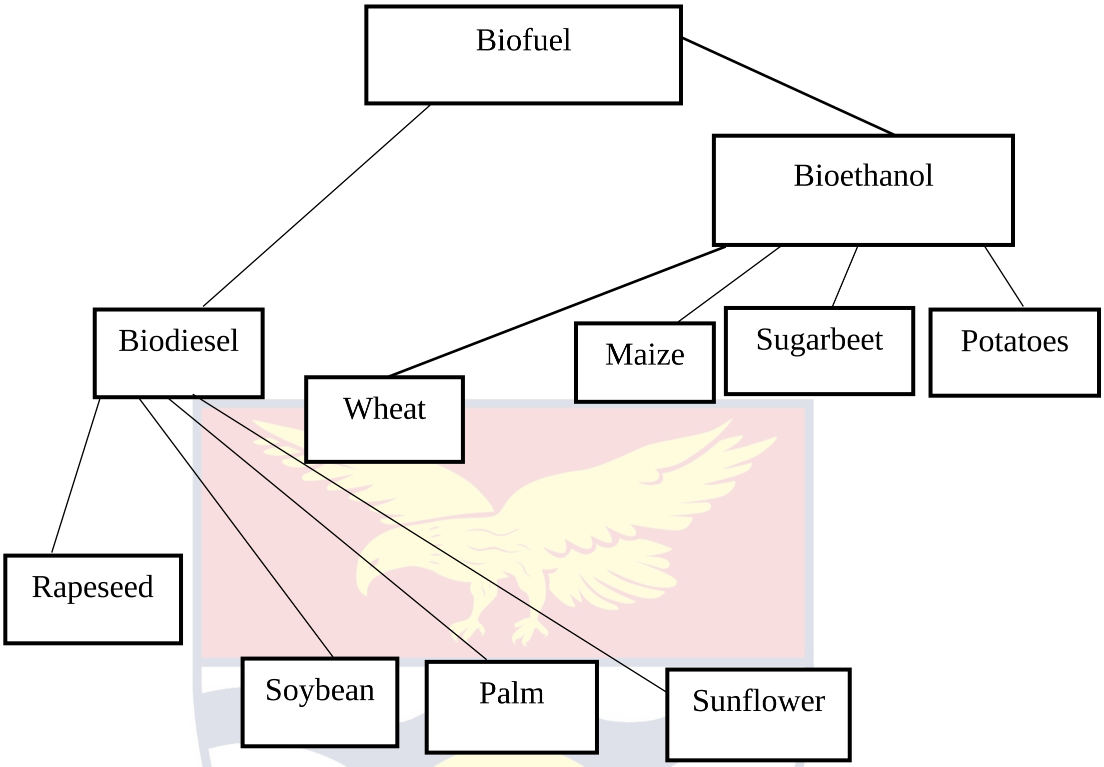


Figure 2: Major sources of liquid biofuels for automobiles (Demirbas, 2001)

History of Biodiesel

The origin of biodiesel can be traced back to the diesel engine's invented by Dr. Rudolf Diesel (Songstad *et al*., 2009). Dr. Rudolf Diesel (1858-1913) came up with discovery of a diesel engine that operated on a number of fuels, among them coal dust which was suspended in water, colossal mineral oil, and vegetable oils. There were failures with the initial engine, however at the time of the exhibition at World Exhibition in Paris in 1900. The operation of engine relied on 100% on the oil produced from peanut. Following the sudden death of Dr. Diesel in 1913, the engine had undergone improvement to operate using the petroleum fuel referred to as diesel. Nonetheless, his ingenuity in agriculture and his discovery laid a foundation for an engine in a society that operated using locally made fuel that is clean and renewable. As early as 1920, research was being done on many vegetable oils including palm oil, castor oil and soyabean oil. The initial research gave an excellent performance of the biodiesel obtained from vegetable oil on the diesel engine (Knothe, 2010).

Importance of biodiesel

Biodiesel possesses properties that are almost similar to that of fossil fuel. It is either applied as a substitute to fossil fuel or often in the form of diesel blend. It goes along with a plethora of advantages: high cetane number, flash point (making it convenient and safe for usage), and high lubrication power. Lubrication power enhances the engine's longevity and reduces the frequency of replacement of the engine parts (Ammous, 2011). Biodiesel has approximately 10% oxygen, leading to combustion and hydrocarbon emissions reduction. Biodiesel that has been blended with petroleum diesel is usually labelled by letter "B" and the biodiesel's percentage volume in the fuel blend follows. For instance, B20 comprises 20% biodiesel volume while the remaining 80% is petroleum diesel fuel. The most available blend is B5 and B20 which can apply in an engine that has not been modified.

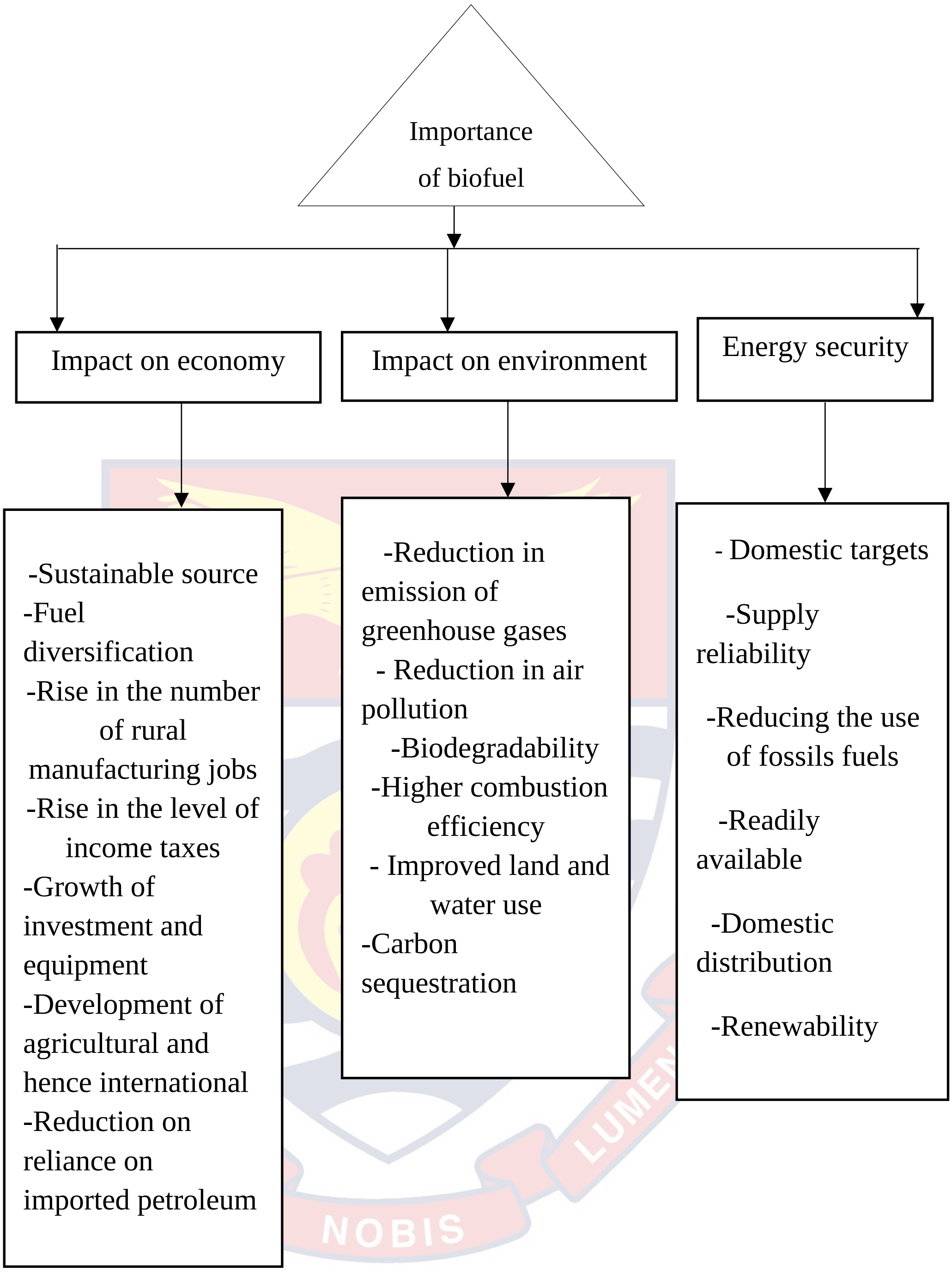


Figure 3: Major advantages of biodiesel (Demirbas, 2009)

Biodiesel Specification

Biodiesel B100 has the specification of ASTM D6751-02 as per the standards of the American Society for Testing Material (ASTM). These standards are summarized in table 1; (biodiesel versus conventional diesel). The test procedures outlined in it indicate more than one function. These procedures guarantee the fuel performances are similar as they were designed for combustion injection (CI) engines. Every property and the method of testing for measurement are described in table 1; In-depth explanations of its property are required, and particular procedures in the literature (Hadjali *et al.*, 2009).

Table 1: Specifications for Biodiesel and Diesel (Hadjali *et al.*, 2009; Suwannakarn *et al.*, 2008)

ASTM-6751		**Biodiesel EN 14214**			**Diesel EN 14214**	
Property	**Units**	**Limits**	**Test methods**	**Limits**	**Test methods**	**Limit**
Kinematic Viscosity(40^{0}C)	MM^2/s	1.9-6.0	D445	3.5-5.0	EN ISO 3104	1.9-4.1
Density(15^{0}C)	Kg/M^3	N/S	N/S	860-900	EN ISO 3675	-
Ester content	Mass%	N/S	N/S	96.5 min	EN 14103	-
Cetane number	-	47 min	D 613	51 min	EN ISO 5165	40-55
Flash point	^{0}C	130 min	D 93	120 min	ISO/CD 3679	60-80
Water content	Volume%	0.050 max	D 2709	500 max	EN ISO 12937	0.05
Sulphated ash	Mass %	0.020 max	D 874	0.02 max	ISO 3987	0.05
Copper Corrosion	Grade	No.3 max	D130	No.1	EN ISO 2160	-
Acid number	Mg KOH/g	0.80 max	D 664	0.5 max	EN 14104	-
Free glycerol	Mass %	0.02 max	D 6584	0.02 max	EN 14105	-
Total glycerol	Mass %	0.240 max	D 6584	0.25 max	EN 14105	-
Phosphorous content	Mass %	0.001 max	D 4951	10 max	EN 14107	-
Iodine number	-	N/S	N/S	120 max	EN 14111	-
Oxidative stability (110 ^{0}C)	H	N/S	N/S	6 min	EN 14112	-
Monoglycerols	Mass %	N/S	N/S	0.8 max	EN 14105	-
Diglycerols	Mass %	N/S	N/S	0.2 max	EN 14105	-
Triglycerols	Mass %	N/S	N/S	0.2 max	EN 14105	-
Methanol	Mass %	N/S	N/S	0.2 max	EN 14110	-
High calorific value	MJ/kg	N/S	N/S	N/S	N/S	-
Low calorific value	MJ/kg	N/S	N/S	N/S	N/S	-

Table 1 continued

Composition		FAMEb (C_{12}-C_{22})				HCa (C_{10}-C_{21})
Oxygen Content	%	N/S	N/S	N/S	N/S	0
Boiling point	^{0}C	182-338	-	-	-	188-343
Cloud point	^{0}C	-3 to 12	-	-	-	-15 to 5
Pour point	^{0}C	-15 to 16	-	-	-	-15 to 16
Carbon	Wt%	77	-	-	-	87
Hydrogen	Wt%	12	-	-	-	13
Stoichiometric air/fuel ratio	AFR	13.8	-	-	-	15
HFRRc	Dm	314	-	-	-	685
BOCLEd scuff	G	>7000	-	-	-	3600
Life-cycle energy balance (energy units produced per unit energy consumed		3.2/1	-	-	-	0.831

Biodiesel Properties

Kinematic Viscosity

This is the ability of fluid to resist the flow under gravity. This property has been designed specifically to be used in fuel injectors which are in diesel engines. It is a faster way to determine the degree of completing a series of reactions (Giakoumis, 2013).

Flashpoint

Flashpoint is lowest temperature which is equated to a barometric pressure of 101.3kPa (760mmHg) at the point when ignition results in vapours of specimen to ignite within the specific conditions of testing. In biodiesel, it accounts for the residual alcohol and is used in determining and classifying the flammability of the materials (Giakoumis, 2013).

Water and Sediment

Water and sediment testing involve determining the quantity of free water and the sediment in distillation with the viscosity range of 1.0 to 4.1 mm^2/s at 40 °C. This type of test ensures the fuel is clean. Water and sediments is used to determine the existence of free droplets of water or particles that form sediments (Giakoumis, 2013).

Sulphur content

It entails determining the entire amount of sulphur in the liquid hydrocarbon, having the boiling points estimated to be 25 to 400 °C. Viscosity assessed between 0.2 and 20 cSt (mm^2/s) at room temperature. Normally biodiesel feedstock is known to contain a small amount of sulphur. However, test indicates contamination of material that contains protein, or excess catalyst from the reaction or the material that causes neutralization of sulphur in the production process (Giakoumis, 2013)

Acid Number

Acid number refers to the amount of acid represented in milligrams of a specimen. This amount is needed during titration of a sample to a specific endpoint. The acid number is the measurement of the free fatty acids directly in B100. The corrosion of the engine parts usually happens because of presence of the free fatty acids and is signified by the presence of water content in the fuel (Giakoumis, 2013)

Cetane Number

It tests the ignition of diesel produced through comparison with other fuels of reference which had been tested using a standardized engine. It examined the ease of ignition of the fuel in an engine. In biodiesel, it is rarely a serious matter since all the common fatty esters are estimated to be having cetane numbers close to or more than 47 (Giakoumis, 2013).

Cloud Point

Cloud point is the point of temperature where a cloud of wax crystal initially occurs in the liquid in cooling down with specified conditions. This property is crucial in the weather with low temperatures and applies to all diesel fuels. Cloud point for biodiesel is higher as compared to the cloud point of conventional diesel. Formation of the crystal might be slowed down in B100 by incorporating additives using various mechanisms. Furthermore, another technique involves making a blend of feedstock oil with high fatty acid and low fatty acid content (Giakoumis, 2013).

Free Glycerine

Free glycerol is the glycerol that occurs in the form of glycerol in the fuel. It is produced when esters and glycerol products are not entirely separated after a subsequent transesterification reaction. It is caused by imperfect washing with water or using other methods which cannot efficiently detach glycerol from the biodiesel (Suwannakarn *et al.*, 2008).

Total Glycerine

Total glycerine refers to the summation of the free and bonded glycerol. Glycerol portion with mono, di, and triglyceride molecules are the bonded glycerol. When the values for total glycerine are high, it shows that the process of the esterification was not complete, and it predicts extra deposition of carbon in the engine (Suwannakarn *et al.*, 2008).

Feedstock for Biodiesel Production

Biodiesel is obtained through vegetable oils or fats from animal and green microalgae using short-chain alcohol. Lipid and alcohol are significant in determining the properties and the procedure to be used in producing biodiesel. Feedstock with lipids consists of vegetable oils and fats from animals (Ehimen *et al.*, 2010). Climate is the factor that vegetable oil available depends on. The utilisation of rapeseed is common in European countries and Canada while oil from soybean is used for biodiesel mainly in the United States of America.

Table 2: Oil Yield of Major Non-Edible and Edible Oilseed(Lapuerta *et al*., 2009)

Type of oil	Oil yield (kg oil/ha)	Oil yield(wt%)
Non-edible		
Jatropha	1590	Seed: 35-40
		Kernel: 50-60
Rubber seed	80-120	40-50
Castor	1180	53
Pongamia pinnata	225-2250	30-40
Sea mango	N/A	N/A
Edible oil		
Soybean	375	20
Palm	5000	20
Rapeseed	1000	37-50

Parkia Biglobosa (African Locust Bean)

African locust bean tree (*Parkia biglobosa)* is locally referred to as "Dawadawa." It is from the Fabaceae family and is a deciduous and perennial tree whose growth is between the height of 7 metres to 20 metres. The tree is dominant in Africa and comprises of pods, which have sweet pulp and valuable seeds. *Parkia biglobosa* seeds are mainly used in manufacturing medicinal substances. The plant is categorized into spermatophytes and vascular. The bark of *Parkia biglobosa* tree is thick and is grey-brown. The pods of *Parkia biglobosa* tree known as locust bean are pink in colour initially. When they mature, the pods turn dark brown. They have an average length of 30-40 centimetres while some grow up to 45 centimetres. Every pod is made up of 30 seeds per pod. The seeds are fermented and are used to season traditional food in Ghana and the Western Coast of Africa (Adolf *et al.*, 2018).

Traditionally, parkia species are of enormous value commercially and are used as food and agents for making medicines. The fruit's pulp is edible while stem bark is used for curing wound and wood for canoes and planking. Ojewumi *et al.* (2017) researched on the protein and amino content level in seeds of different parkia species varieties. The results showed sixteen amino acids in the *Parkia biglobosa*, contains a considerable glutamic acid level. Additionally, the efficiency ratio of protein and net utilisation and digestibility of *Parkia biglobosa* can be compared to one of groundnut and palm kernel. As per composition of an Indian variety of *Parkia biglobosa* that was earlier reported, it was established that the oil contained oleic acid, which is 39.4%, stearic acid (13.3%), palmitic acid (8.8%), and behenic acid (39.4).

Figure 4: Parkia biglobosa pods (a) and seeds (b*)*

In West Africa, *Parkia biglobosa* performs a vital role in agriculture of the rural areas. *Parkia biglobosa* trees are individually undergoing preservation on the compound garden or fallow land as minor edible fruits through their pods and seeds for livestock and humans. Flowering takes 3-8 weeks and fruiting occurs at end flowering season and ripening is before the first rain and continues over the most seasons and therefore producing several seeds per pod(Okpara & Ugwuanyi, 2017).

Parkia biglobosa grow in different agro-ecological zones that ranges from tropical forest with a lot of rain distributed well and also grow in arid regions. The average rainfall could be less than 400 mm per year. Several authors have suggested optimum rain per year for *Parkia biglobosa* to vary from 500-700 mm to 600-1200 mm. *Parkia biglobosa* can resist dry periods because of its intense tap root system and its capacity to restrict transpiration (Amusa *et al.*, 2014; Ndamitso *et al.*, 2020).

Table 3: Physical Properties of the Vegetable Oils (Lapuerta *et al*., 2009)

Oil	**Kinematic viscosity at 20℃** (X $10^{-6}m^2s^{-1}$)	**Kinematic viscosity at 40℃** (X $10^{-6}m^2s^{-1}$)	**Kinematic viscosity at 70℃** (X $10^{-6}m^2s^{-1}$)	**Density (kgm^{-3})**	**Acid value (mgKOH/g)**	**Glycerol (wt%)**	**Miscible**
Cotton seed	85.0	43.7	23.2	951	7.073	18.40	0-100%oil
Moringa oil	53.7	41.4	27.6	942	3.185	5.43	0-100% oil
Castor	961	268	61.9	993	0.022	4.12	Between 70% and 100% oil
Rubber seed	44.0	39.9	33.0	920	10.814	4.00	Insufficient oil
Soya bean	74.1	35.8	30.7	950	0.669	5.50	0-100% oil
Sunflower	78.9	45.6	24.7	953	2.124	7.64	0-100% oil
Groundnut	91.8	41.4	27.6	942	3.185	5.43	0-100%oil
Petroda Diesel	22.8	12.3	8.53	879	4.17×10^{-4}	0.70	-
ASTM Standard	-	19-6.0	-	-	0.8max	0.02max	-

Uses of *Parkia biglobosa*

Parkia biglobosa oil as a feedstock for biodiesel production

In comparison to other sources of vegetable oil, oil from *Parkia biglobosa* can be used for many purposes. However, very limited research has been carried out in production of biodiesel using this particular feedstock. *Parkia biglobosa* takes a short time to produce fruits and many times within different season and therefore can potentially supply adequate oil for biodiesel production.

Parkia biglobosa oil as food

Parkia biglobosa oil acts as a flavour besides being protein to a diet that is deficient in protein. Kwashiorkor being a syndrome makes a victim have the characteristic of a belly that is swollen. The swelling is caused by the extra fluid that pools the abdominal cavity due to poor diet. Kwashiorkor arises from the weaning of a child from breast milk rich in protein and instead feeding the child with a plant-derived diet (Ndamitso *et al.*, 2020). *Parkia biglobosa*, is best used as a protein additive to most stews and soup which is the staple food in most west African countries. In Togo for example, tribe called Cabrais of the northern region has 90% of their meal made up of *Parkia biglobosa* additives. In the northern part of Ghana, about 10% of the food eaten daily for a meal in different households have *Parkia biglobosa* as additives while in the north of Nigeria, it constitutes 1.4% of the calorie of the daily food intake (Olowokere *et al.*, 2019).

Medicinal use of *Parkia biglobosa* oil

Medicines produced from *Parkia biglobosa* are valuable to village community who cannot purchase or have the accessibility of conventional medicine. The significance of the *Parkia biglobosa* tree and its product is synonymous with the name given "Dawadawa" Apart from the *Parkia biglobosa* tree being food additives different part of the *Parkia biglobosa* tree is used to treat another ailment (Ndamitso *et al.*, 2020) (Table 4;).

Table 4: Medicinal use of *Parkia biglobosa* (Igoli *et al*., 2003; Ndamitso et al., 2020)

Source material	Preparation	Medicinal use
Bark	Gum extract	Toothache Diarrhea Ear complaints Mouthwash
	Macerated in bath	Leprosy, skin infection, sores, ulcers Bronchitis, pneumonia Colic Schistosomiasis Rheumatism Circumcision wounds and general wound
Leaves	Lotion preparation	Sores eyes Burns
	Crushed	Haemorrhoids Toothache Bronchitis
Flowers Flower bud	Grilled and macerated infusion	Hypertension Lumbago Leprosy prophylactic
Pulp		Diuretic, purgative Fever
Seeds	Pounded with salt Fermented Decoction	Tension Mouth ulcers Skin infections Wasp and bee stings
Roots	Decoction	Diarrhea, dysentery, eye infections Guinea worm

Methods of Biodiesel Production

Vegetable oil from various seed oil has variations in fatty acid compositions. The majority of the vegetable oil has high energy content, but there is a need for processing to ensure fuel is used in internal combustion engine. Formulation of biofuel from diesel can be through blending of vegetable oil in petro-diesel or through transesterification and micro-emulsion in alcohol (Atabani *et al.*, 2013).

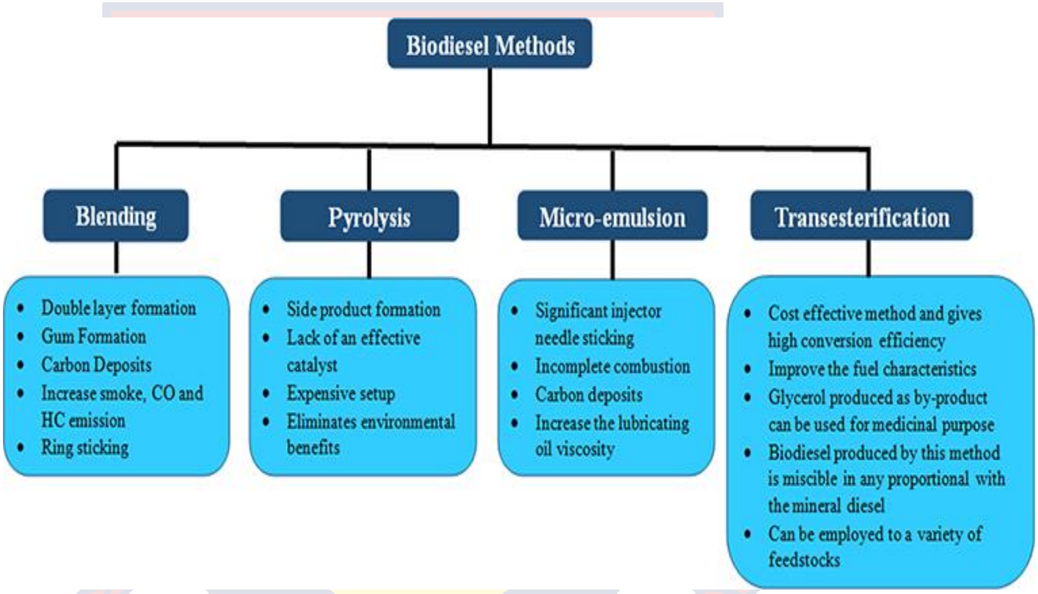


Figure 5: Methods for biodiesel production (Ramli *et al.*, 2017)

Biodiesel can be obtained from pure vegetable oil. For example, oil from peanut plant was used in 1893 in a prototype diesel in Augsburg, Germany, by Dr. Rudolf Diesel (Biodiesel & Reactions, 2014). Despite biodiesel's success from peanut oil, carried out by Rudolf Diesel, it was impossible to use direct application due to its high viscosity. It had a range of 10 to 20 times more than the petrol diesel. Because of being too viscous, poor atomization of vegetable oils happens in the combustion chamber, which causes the engine's key problems such as nozzle cooking and blockage by deposit (Fukuda *et al.*, 2001).

Blending

The solution to these engine hitches is by blending diesel directly from vegetable oil and petrol diesel. Besides, microemulsion in alcohol, pyrolysis and transesterification of oil using alcohol is also used. Blending vegetable oil directly in petrol-diesel and microemulsion in normal alcohol is not sustainable because of engine fouling. Technical challenges that include gumming piston rings sticking together and engine cooking are persistent (Balakrishna, 2012). Improved spray characteristics and combustion of the fuel are the only way to enhance biodiesel by blending directly and microemulsion (Boggavarapu & Ravikrishna, 2019).

Pyrolysis

Pyrolysis is a catalytic process that entails splitting huge molecules into smaller elements without using oxygen (Bulushev & Ross, 2011). While using vegetable oil, pyrolysis, triglycerides are broken down to form small molecules by combining catalysts with heat (Li *et al.*, 2019). Alternatively, through the cracking of sodium salts of fatty acids, the process generates a lot of output compared to triglyceride cracking (Demirbas, 2008).

Pyrolysis of vegetable oils occurs at the heat of about 300-500 ℃ in when a catalyst for example SiO_2/Al_2O_3 and SO_4^{2-}/ZrO_2 is present (Eterigho *et al.*, 2011). The product obtained is alkanes in nature and is the same as the one found in petro-diesel. Pyrolysis is important in addressing gumming challenges related to pure vegetable oil and its blends, coking, and high viscosity. Although fuels are produced by cracking, it is made up of total acid value above the standard of 0.50 $mgKOHg^{-1}$ for pure biodiesel (Demirbas, 2008).

Transesterification

Transesterification is a chemical procedure that entails triglyceride reaction which is the major component of vegetable oil or animal fats. The reaction is performed with short-chain primary alcohol, specifically, methanol which produced biodiesel (Fatty Acid Methyl Esters, FAME) and glycerol production as the secondary product using three stepwise reversible procedures that involve removing fatty acid moieties from the triglyceride (Reza *et al.*, 2012; Todorovic *et al.*, 2008).

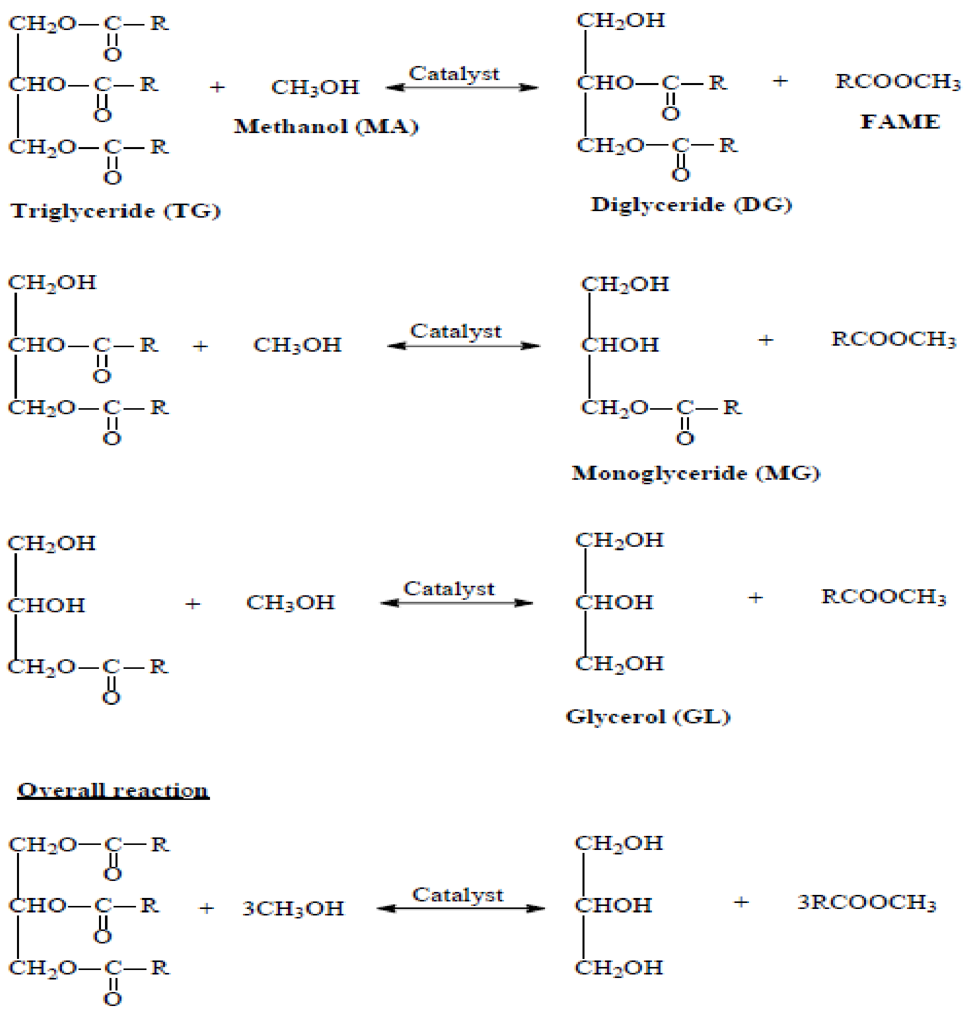


Figure 6: Step-wise transesterification reactions (Todorovic *et al.*, 2008)

The transesterification rate for each step of the reaction is affected by; temperature of the reaction, molar ratio of methanol to oil, type and concentration of the catalyst. The conventional transesterification method is normally performed out of temperatures ranging between 25℃˚–65℃, as the amount of biodiesel produced increases with temperatures (Todorovic *et al.*, 2008). For example, biodiesel produces output estimated 25% at 25℃, 84% at 40℃ and 92% at 60℃ as reported within 20 minutes of reaction time in a transesterification which uses the ratio of 6:11 molar ratio of methanol to sunflower's oil and 0.5 wt% of NaOH as per the weight of oil (Bambase *et al*., 2007).

Temperature for the conventional transesterification reaction is usually lower as compare to the boiling of methanol to stop the development of bubbles which prevents mass transfer on the phases interface (Liu *et al.*, 2007). Extra methanol is required for shifting the equilibrium to favour products for the producing biodiesel. Thus, methanol to oil molar ratio which is bigger than stoichiometric requirement (3:1) is needed. The methanol to oil molar ratio of 6:1 in an experiment was reported as the optimal condition for acid-catalyzed transesterification (Eze *et al*., 2018).

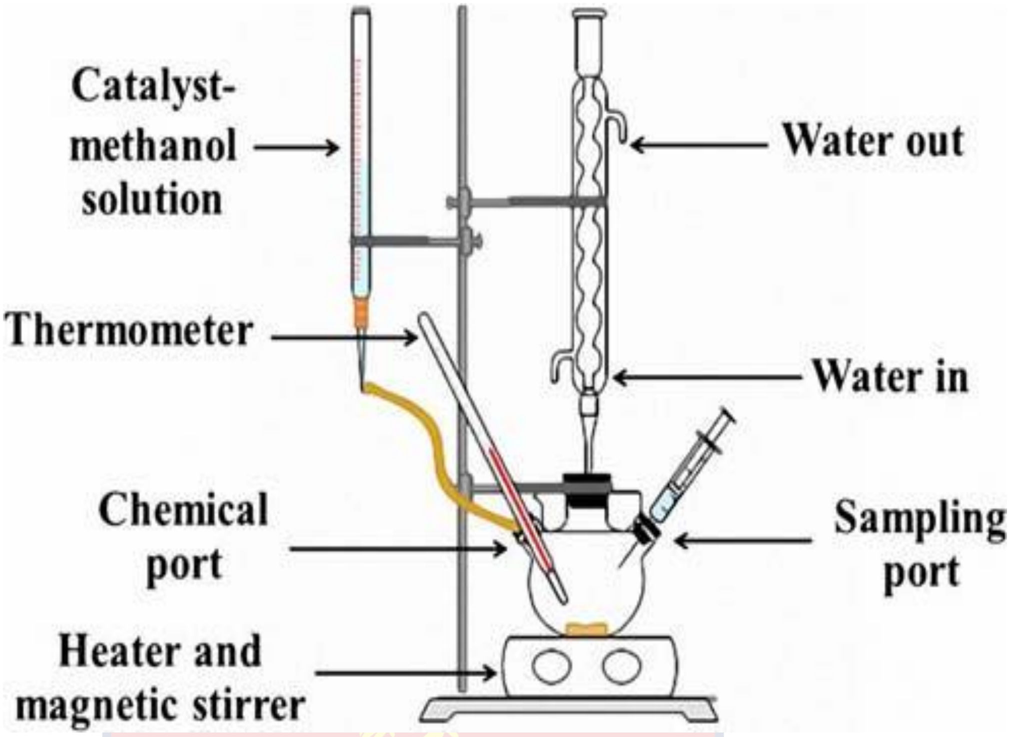


Figure 7: Schematic experimental set up of the transesterification process (Gandure *et al*., 2017)

Factors Affecting Transesterification Reaction

The variables which affect the fatty esters' production, comprise of the following:

The Molar Ratio of Alcohol to Oil

It is a crucial factor that has an effect on the biodiesel yield obtained from oil. According to stoichiometry reaction, three moles from alcohol are supposed to carry out transesterification of a triglyceride molecule and result in fatty acid alkyl esters containing three moles and one mole of glycerol. Normally, between 100 to 200% of extra alcohol is applied (Musa, 2016).

High molar ratio of alcohol to oil must be shunned because it may result in interference of separation of the phases of the biodiesel from the glycerol after completion of the transesterification process. Besides, using large molar ratios leads to backward reactions favourable to low yield of esters.

Effect of Temperature

The rate of reaction and percentage of conversion oil to biodiesel is affected by the temperature. In a particular study, transesterification process was done using molar ratio of methanol to oil in of 6:1; methanol to oil molar ratio, 1%(wt) sulphuric acid under three different reactions temperature (ASTM). The yield of biodiesel was determined after 6 minutes and was 94%, 87%, and 64% at 60℃,45℃ and 32℃ respectively. Nevertheless, the yield was similar after 60℃ and 45℃, it lowers slightly only at 32℃ (Ahmad *et al*., 2019; Musa, 2016).

Effect of Reaction Time

Production of biodiesel through the conversion of oil increases as the reaction time is extended. From similar research, the effects of reaction time on conversion of oil to biodiesel was also studied. The research used cottonseed, soybean, sunflower, and transesterified peanut with methanol to oil molar ratio of 6:1, 0.5%(wt) sodium methoxide (catalyst), and reaction temperature at 60℃. An estimated yield of 80% of biodiesel was produced within one minute with oil from sunflower and soybeans plants. The yield was (93%-98%) for the same four oil under the study after 60 minutes (Ahmad *et al*., 2019; Marques Cardoso *et al*., 2019).

Intensity of Mixing

Among the factors that influence transesterification, mixing intensity is one of the crucial factors. Alcohol such as methanol and ethanol have low molecular weight, and cannot mix with oil at the room temperature. Therefore, the reaction is subjected to mechanical agitation to allow massive movement of alcohol into the oil. In a previous research, the influence of mixing intensity in transesterification process of beef tallow was investigated (Encinar *et al*., 2010).

The results established that the process of reaction could not continue in absence of the two reactants being mixed together. But on the addition of NaOH-Methanol into the beef tallow that has melted placed in the reactor as mixture is continuously mixed as it proceeded, the speed of stirring was discovered to be not significant, which suggests the speed of mixing speeds being investigated were beyond the threshold required for mixing (Meher *et al*., 2004).

Type of Catalyst used and the Concentration

The production of biodiesel is through the transesterification process using catalyst that acidic, basic, or enzymes in nature. Transesterification can also be done using a supercritical fluid process without a catalyst. Transesterification of vegetable oil by applying supercritical alcohol and enzyme catalysis has not been applied for commercial production because of the high cost. Synthesis of biodiesel using enzyme catalysis is still expensive for industrial production due to the enzymes being costly in terms of price, deactivation of enzymes, and the slow rates of reaction (Borges & Díaz, 2012; Lotero *et al*., 2005).

Homogenous catalysts are usually acidic or alkaline. The homogenous acid-catalysed biodiesel production process, a two-step process; acid-catalyzed esterification of the FFA, preceded by base-catalysed transesterification process. Acid-catalysed transesterification is recommended for feedstocks that contains high levels of FFAs (≥ 0.5wt%) or water (≥ 0.3wt%). The most frequently used acids during the homogenous biodiesel production include sulphuric, hydrochloric, and organic acid, phosphoric and sulphonic acids (Lotero *et al*., 2005).

Heterogeneous Catalysis

The need for effective technology for producing biodiesel has resulted in massive research interest in heterogeneous catalysis reactions for producing biodiesel. Application of heterogeneous catalyst removes the downstream processing step and results in high-quality glycerol as the by-product. Catalysis reaction of various solid catalysts were studied in the production of biodiesel. Based on this research, solid catalysts are classified into two groups according to the action's manner. These groups are the conventional heterogeneous catalyst and non-convention heterogeneous catalysts (Sivasamy *et al*., 2009; Thangaraj *et al*., 2019).

Clay

Clays are promising catalysts that are generally hydrated aluminium silicate which has a very fine particle size, normally less than 2 µm made up of a layered structure which has been formed through tetrahedral sheets bound by sharing apical oxygen to an octahedral sheet. Smectite group are the best-known clay minerals, which are commonly used because of their high cation exchange capability, ability to swell, and large surface area in different industries. Clay contains many cations that make it capable of ion exchange processes, such as Na, K, Ca, Fe, and Mg in the form of calcium carbonate, clays often contain calcium oxide (CaO) (CaCO3) (Azzouz *et al*., 2006).

Bi-Functional Heterogeneous Catalyst

Bi-functional heterogenous catalyst exudes both acid and base characteristics and gained a huge attention for organic reactions in the last ten years. Bi-functional heterogeneous catalysts simultaneously perform esterification of free fatty acids and the efficient transesterification of triglyceride that exists in the oil. At the same time, water content that exists or is formed in the process of producing biodiesel does not affect its performance. The existence of both acidic and basic sites as the active site within the catalyst's surface lowers biodiesel production.

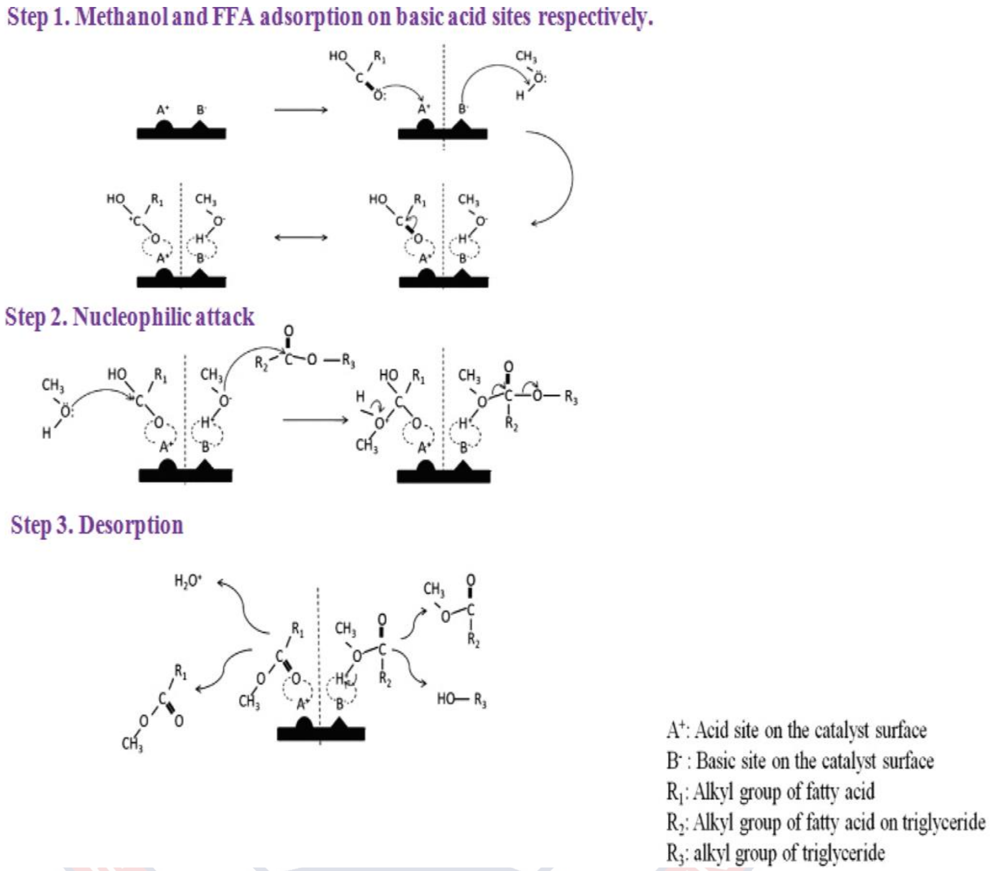


Figure 8: The general mechanism for simultaneous esterification and transesterification reactions on the bi-functional heterogeneous catalyst(Wan Omar & Amin, 2011)

Product Yield

Product yield refers to the percentage weight of the end product in relation to the oil’s weight at the start):(Daniel *et al*., 2010; Faisal *et al*., 2018).

$$\text{Yield }(\%) = \frac{\text{Weight of } the\ biodiesel}{\text{Weight of the raw oil/fat}} \quad \text{X } 100$$

Equation 1: Calculation of the product yield

The product yield indicates the competition's final results among the major reaction (transesterification) to produce biodiesel and the side reactions such as saponification.

CHAPTER THREE

MATERIALS AND METHOD

Biodiesel Production from *Parkia biglobosa* oil using Sulphuric acid (H_2SO_4) as Catalyst

Instrument

The instruments used in the experiments were; soxhlet extractor, 250 ml round bottom flask condenser, heating mantle, oven (DGH-9140A, YIHENG), furnace, Gas Chromatograph Mass Spectrometry (GC-MS,7890A Agilent Technology Inc. USA), rotary evaporator (BÜCHI rotavapor), 7890B GC-MS (Agilent Triple Quad, Agilent Technology Inc. USA), Fourier Transform Infrared Spectroscopy (FTIR, An AVATAR 360, Nicolet (Madison, USA), S-4800, HITACHI (Corp., Tokyo, Japan) SEM instrument, UV–vis spectrometer (UV2450,shimadzu, Japan), Microcalorimeter Energy-dispersive X-ray spectrometry (EDS), and Powder X-ray Diffractometer.

Reagents and Materials

Laboratory equipment and chemicals that were applied to the experiment included; petroleum ether purchased from the certified chemical shops in Accra, electric grinder, 250 ml round bottom flask, reflux condenser, magnetic stirrer, methanol of purity 98%, 5%(w/w) H_2SO_4, anhydrous Na_2CO_3 obtained from School of Biological Science Store at the University of Cape Coast, and clay obtained from the school farm at the Technology Village in the University of Cape Coast.

Experimental Protocol

Sample Collection and Preparation

Collection of the *Parkia biglobosa* seeds were done during the harvest season at Abura Dunkwa Town 5° 20' 16.4436" N and 1° 10' 16.6764" W in the Central part of Ghana. The samples of the seed were screened and thoroughly cleaned to ensure the elimination of dirt and seed that have been destroyed for example by insect. Dehulling, was carried through removal of the outer covering of the seed, washing, and sun-drying were subsequently done before grinding. The seeds were then grinded using an electric grinder into particle size and put into an airtight Teflon-lined container before extraction.

Oil Extraction and Determination of Percentage Yield

The *Parkia biglobosa* oil was extracted using petroleum ether (40-60℃) by adopting the method described by Olowokere *et al.* (2019). Extraction of the oil was performed using a soxhlet apparatus and petroleum ether as the solvent of extraction. A ratio of 10:1 of solvent to seed was applied for extraction. 250 ml of the petroleum ether was poured into a round bottom flask while ground *Parkia biglobosa* seed weighing 25 g was put into a filter. The filter containing the seeds was then carefully placed inside the thimble, fixed to the round bottom flask on top of the heating mantle, and connected to the condenser. The heating mantle was switched to heat the solvent.

As the solvent was heated in a round bottom flask connected to soxhlet apparatus it began to boil and change to vapour rising through the vertical tube into the top's condenser. The vapour was condensed and dripped back into the thimble in the centre. The extractor solvent seeped through the thimble pores and fill up the siphon tube and from there it flow back down into a round bottom flask (Olowokere *et al*., 2018). The extraction process was extended to 5 hours, (Suwari, Kotta, & Buang 2017). Extracted *Parkia biglobosa* oil was first dried, recorded, and subjected to the degumming procedure by treating hot water to eliminate hydrates, gums, phosphate, and other impurities.

$$\text{Oil content }(\%) = \frac{\text{Weight of } Parkia\ biglobosa \text{ oil}}{\text{Weight of grounded } Parkia\ biglobosa \text{ seed}} \quad \text{X } 100$$

Equation 2: Percentage yield of oil(Hoekman *et al*., 2012)

Composition and characterization of the feedstock (*Parkia biglobosa* oil**)**

The analysis of the content of the oil sample extracted was done by means of a 7890B Gas Chromatography-Mass Spectrometry (GC-MS) Agilent Technology Inc. USA) using ASTM D6751 method. A thermal conductivity detector (TCD) was with fitted to GC-MS and a high-polarity general purpose column recommended for Free Fatty Acid and Phenols (15% FFAP, Chromosorb W, A/W 80/100, Length of 2m). Helium at high purity 99.9999% functioned as the carrier gas. Column operation temperature range of 50ºC-250℃ and sample inlet temperatures of 200℃ were used. The temperature of the oven was initially kept at 60℃ for 5 min and thereafter it was raised to 220℃ at 10℃/min for 10 min. Sample inlet pressure (Carrier gas 20mL/min) and total pressure with makeup (Carrier gas and makeup 21mL/min) were used. The temperature of the detector was 250℃.

Analysis and characterization of *Parkia biglobosa* oil were based on American Standard for Testing Material (ASTM D6751) methods and Association of Official Analytical Chemists (AOAC,2005), to identify the following properties density at 15℃ (ASTM D4052-96), kinematic viscosity (ASTM D445-06), acid value (ASTM D664-06), saponification value (ASTM

D4052-96), FFA (AOAC 940.28) water/moisture content (AOAC 984.20-90) and average molecular weight (ASTM D445-06).

Transesterification Reaction

The process of transesterification reaction of triglyceride to biodiesel was done using 20 g of the extracted *Parkia biglobosa* oil by initially filling into a 250 ml three-necked round bottom flask in a heating mantle reflux condenser and magnetic stirrer. The oil weight was measured and recorded before heating to the standard temperature of 60°C as the oil's magnetic stirring continued. Methanol was mixed with 4wt.% of catalyst (H_2SO_4) and added to the oil. The conversion of triglyceride to biodiesel was done using methanol to oil ratio variation between 5:1,5.5:1,6:1, and 6.5:1. The time of reaction was from 0.5 hrs,1 hr, 1.5 hrs and 2 hrs, the temperature of the reaction from 55°C, 60°C, 65°C, and 70°C, and the amount of catalyst from 1%, 2%, 3% and 4% (making reference to the weight of the oil). Determination of highest yield of biodiesel was done through consideration of the optimum parameters of molar ratio of methanol to oil, reaction temperature, catalyst concentrations and the reaction time. All the experiments conducted were under standard conditions for temperature and pressure. The speed of rotation of the magnetic stirrer was maintained at constant speed of 600 revolutions per minute (RPM). Transesterification experiment performed was composed of treatment sample and then two replicates for every treatment sample. The yields of the biodiesel samples were determined using equation 1.

Determination of Biodiesel Properties

The samples of biodiesel were analysed using a 7890A gas chromatograph (Agilent Technology Inc. USA) and 7890B gas chromatography-mass spectroscopy (GC-MS) (Agilent Technology Inc. USA) according to ASTM D6584 and conditions as stated in the section of (Composition and characterization of the feedstock).

Properties of biodiesel were analysed through the following standards; ASTM 6751 Standard, and Europe Standard (14214) and included; density at (20℃) (SH/T0248), kinematic viscosity (ASTM D445-06), acid value (ASTM D664-06), water/moisture content (ASTM D6304), flash point (ASTM D93-07), pour point (GB/T3535), cloud point (GB/T510), cetane number (ASTM D6890-07), ash content (GB/T508), sulfur content (ASTM D4294), free glycerine (EN 1405), total glycerine(SH/T0796), Oxidative stability 110°C (h)(EN 14112), Cold filter plugging point (℃)(GB/T 2540), Iodine value g/100(EN 14111), Copper strip corrosion (50 ℃; 3 h) (ASTM D 130-94)were determined.

Results and Discussion

Characterization of *Parkia biglobosa* oil

The properties of the oil analysed using the methods and procedure given in section of (Composition and characterization of the feedstock). The key properties of the oil obtained from the analysis are discussed and comparison were made with the same properties of *Parkia biglobosa* oil in different studies. The reasons for variations in the physicochemical composition were explained.

Optimization of the Reaction Conditions

Results from the experiment on producing biodiesel through transesterification *Parkia biglobosa* oil by using sulphuric acid as a catalyst were presented in tables and figures. Four reactions conditions that affects the transesterification process are discussed. The conditions of reactions taken into consideration were; molar ratio of methanol to oil, reaction temperature, catalyst concentrations and the time of the reaction.

Biodiesel production from *Parkia biglobosa* oil using bifunctional heterogeneous clay catalyst

Synthesis of clay catalyst

(a) Experimental procedures

The clay sample was crushed in a mortar and sieved using 200 mesh (75 µ) to obtain powdered clay (0.075 mm as the size of the particle) and store in sample bottles. About 500 g of the clay was dried using a hot air oven at the temperature of 120°C for 12 hrs. 100 g of the dried powdered clay was subjected to calcination process in furnace at the temperature of 450°C for 4 hrs to produce fine clay, which was then kept in a desiccator to cool and was then removed on expiry of 24 hrs. The sealed container was used to keep the mixture to avoid contamination. 27 g of the sodium carbonate was dissolved in 100 millilitres of deionized water. Impregnation was carried out by pouring 9 ml of the solution of sodium carbonate into 22 g of the calcined clay support. The resulting mixture of clay and sodium carbonates was stirred and then mixture in a pasty form was dried using an oven for 12 hrs before subsequent calcination in a furnace at the temperature of 600°C to obtain clay catalyst.

(b) Characterization of clay catalyst

Fourier Transform Infra-Red (FTIR)

The Fourier Transform Infrared **(**FTIR) spectroscopy was applied in ascertaining functional groups present in the catalyst after conducting catalyst synthesis and testing. An AVATAR 360, Nicolet (Madison, USA) was used in

4000-400 cm^{-1}. A resolution of 2 cm^{-1} was employed. The identification of functional groups was made by subjecting the sample to IR radiation.

Scanning Electron Microscopy (SEM)

The catalysts' morphology was studied by means of SEM analysis. The SEM was undertaken using S-4800, HITACHI (Corp., Tokyo, Japan) SEM instrument at a working distance of 10 mm. Voltage of 15 kV magnification at 10000 and a spot size of 20 mm was used

Ultra Violet Spectrum

UV-vis spectrum measurements were done for the determination of the characteristic of the clay catalyst after calcination. Prior to the measurement of UV transmission, the clay sample was ground to<63μm and a sample of clay weighing 22 g was impregnated with 9 ml of a solution of sodium carbonate. The mixture was stirred to a pasty form and calcined for 12 hours at 600 ℃ .

The characteristics of UV- transmission for the calcined clay catalyst were carried out using AnalytikJenaAG SPECORD 50 photometer, connected to a UV lamp as light source and operated at an electric potential of 483 V, a current of 0.3 A, and a frequency of 200 Hz. The sample was placed a distance of 10cm from the source of light. Measurement was done at room temperature and 0-900nm wavelength. The measurements were done repeatedly to obtain average value and data were expressed in terms of transmission and values plotted in a graph and the peak was calculated and interpreted.

Energy-dispersive X-Ray spectroscopy (EDS)

Microcalorimeter Energy-dispersive X-ray spectrometry (EDS) was used. Largest condenser aperture and spot size 1 was used. The sample and the detector were placed at a distance of 170mm. The rate of counts, time and total counts for the analysis of the raw clay catalyst were determined and represented in a figure.

X-ray diffraction (XRD) pattern

Powder X-ray diffraction patterns of the samples were obtained with a Powder X-ray Diffractometer with CuKα radiation ($\lambda = 1.54018$ Å). This was performed to detect the composition of the samples. The Preparation of the samples was through pressing composite samples using a flat surface down the sample cells. Due to this, sample were packed densely and oriented randomly. A beam of x-rays hits the sample at a slow angle that increases while an electronic detector revolves around it as it is recording the x-rays bouncing off of the sample. The diffraction patterns were drawn from the data using MDI Data scan software in the PC, and data was then processed using MDI Jade and ICDD PDF minerals data base.

Optimization of Reaction Conditions

20 g of the *Parkia biglobosa* oil was initially placed into 250 ml round bottom flask. The weight was measured and recorded before being heated to the required reaction temperature of 60℃ while stirring at 600 rpm. 4wt.% of catalyst (Na_2CO_3-Clay) (reference to the oil's weight) was mixed together with the methanol and then place into the oil. The amount of clay catalyst (1 % ,2 %,3 % and 4 %) weight of the oil was mixed with specified amount methanol (prepared separately) and was then added to the oil being heated in the round bottom flask. The influence of methanol to oil molar ratio (10:1, 11:1,12:1 and 13:1), loading of the catalyst (1 % ,2 %,3 % and 4 %), the reaction temperature (50℃,55℃, 60℃, 65℃), and the reaction time (0.5,1,1.5 and 2.0) hours on converting triglycerides to methyl esters were determined. Every experiment

that was done under standard atmospheric temperature and pressure. The rotational speed of the magnetic stirrer was maintained at the constant speed of 600 rpm. Previous studies indicated that the rotational speed in the range of 400 to 1000 rpm does not affect biodiesel's yield (Mishra *et al.*, 2013). After the reactions, the products were decanted and separated within 24 hrs using a separating funnel for glycerol separation. After every cycle, catalyst that has already been used was isolated from the reaction mixture using centrifugation method and was then subjected to washing using n-hexane to facilitates the removal of any impurities. Unreacted methanol and water were then removed using a rotatory evaporator. The layers of biodiesel and glycerol separated easily since the two entities exhibited different densities of 0.86 g/cm^3 for biodiesel and 1.126 g/cm^3 for glycerol respectively. The methyl esters content of the decanted products was then weighed and analysed.

In the experiment there was treatment samples and then two replicates for every samples. The yields of the biodiesel samples were determined using similar method as in the equation 1.

Determination of Biodiesel Properties

Samples of biodiesel was analysed using a 7890A (GC-MS, Agilent Technology Inc. USA) and 7890B (GC-MS, Agilent Technology Inc. USA) according to ASTM D6584 and conditions as stated in the section of (Composition and characterization of the feedstock). Properties of biodiesel were analysed using the ASTM 6751 Standard and Europe Standard (14214). Properties that were analysed included; density at (20°C) (SH/T0248), kinematic viscosity (ASTM D445-06), acid value (ASTM D664-06), water/moisture content (ASTM D6304), flash point (ASTM D93-07), pour point (GB/T3535), cloud point (GB/T510), cetane number (ASTM D6890-07), ash content (GB/T508), sulfur content (ASTM D4294), free glycerine (EN 1405), total glycerine(SH/T0796), Oxidative stability 110℃ (h)(EN 14112), Cold filter plugging point (℃)(GB/T 2540), Iodine value g/100(EN 14111), Copper strip corrosion (50℃ ; 3 h) (ASTM D 130-94) were determined.

CHAPTER FOUR

RESULTS AND DISCUSSION

Percentage yield of *Parkia biglobosa* oil

Oil is the primary raw material while producing biodiesel (Fatty acid methyl ester). Oil's yield from *Parkia biglobosa* seed was 16.5%. The percentage yield of 16.5% is in accordance with the study by Adolf *et, al.* (2018), which show that *Parkia biglobosa* oil can be a possible source of oil for commercial purposes if exploited. However, based on Augustine, Okoro *et al.* (2013), *Parkia biglobosa* showed a higher oil yield of 33.97%. The yield of oil with that range can be subjected to a favourable comparison to particular vegetable oil used for commercial purposes, such as cottonseed (19.50%) and palm oil (48.65%).

Physicochemical Characterization of *Parkia biglobosa* Oil

From the result of the experiment of the study, the stearic acid for the analysed of *Parkia biglobosa* oil was 4.30 %, while the reported *Parkia biglobosa* oil was 5.3 %. The variation in the percentage of stearic acid is slight. Similarly, linoleic acid for both the *Parkia biglobosa* oil that was analysed and the one reported below was 65.42% and 63.5%, respectively. The composition of the fatty acid obtained from the analysed values of the extractions experiment of the study was almost same to the study as reported by Augustine *et al*. (2013) in table 5;. As indicated, there was a substantial variation on palmitic acid for the analysed oil which was 15.08% while from the reported literature by Augustine *et al.* (2013) was 5.0%.

Table 5: Fatty Acid Composition of *Parkia biglobosa* Oil

Fatty Acid Composition	**Analysed Value (%)**	**Reported by (%)** (Augustine *et al.*, 2013)
Palmitic acid (16:00)	15.08	5.0
Stearic acid(C18:0)	4.30	5.3
Oleic acid(C18:1)	7.90	12.5
Linoleic acid(C18:2)	65.42	63.5
Arachidic acid(C20:0)	5.21	-

Source: Lab analysis (2021)

The difference in palmitic acid in both oils agrees with the research by State (2020). In his research, State (2020) alluded that the differences in the chemical composition of similar oil were due to difference in locations where the oil was obtained. Some of the key factors such as soil type and climatic conditions were proven to affect the oil. Further, these findings are comparable with those in research by Lin & Lin (2012), which found out that palmitic acid (C16:0), linoleic acid (C18:2) and Oleic acid (C18:1) form the three main compounds. Furthermore, it was determined that individual kinetics for the three acids mentioned are useful, especially in situations where the composition of FFA is higher it will results in the biodiesel that has highest saturated fatty acid, and therefore huge thermal and oxidative stability, which will retards fuel from deteriorating in environments with high-temperature or during long-term storage. *(Gaurav et al.*, 2019). Though not mentioned by Augustine *et al.* (2013), Arachidic acid was 5.21% in the analysed oil.

Properties of *Parkia biglobosa* oil

Parkia biglobosa oil was analysed for physicochemical properties which include density, kinematic viscosity, water content, average molecular weight, and free fatty acid.

Table 6: Properties of *Parkia biglobosa* Oil Used as Feedstock for Biodiesel Production

Property	Testing procedure	ASTM Std.	Ghana Std. Authority	Determined value
Density at 20℃ (Kg/m^3)	ASTMD4052-96	860 - 890	870 – 900	916.2
Saponification value (mgKOH/g)	ASTMD4052-96	191-202	-	191.65
Kinematic viscosity at 40 ℃, mm^2/s	ASTMD 445-06	1.9 – 6.0	1.5 – 6.5	35.70
Water content (%) w/w	AOAC 984.20-90	0.05 max	0.05 max	1.93
Free fatty acid content (%) w/w	AOAC 940.28	-	-	1.61

Source: Lab analysis (2021)

Method used for analysis were as outlined by the Association of Official Analytical Chemists((AOAC,2005) (AOAC, 1997; Aransiola, *et al.*, 2010) and American Standard for Testing Material (ASTM). Based on the results, *Parkia biglobosa* oil has a high density of 916.2 Kg/m^3 and kinematic viscosity (35.70 mm^2/s) at 40℃.

Denser oil produces a higher amount of energy (Tabatabaei *et al.*, 2019). Biodiesel's relative density is important in mass to volume conversion and calculates the flow and viscosity properties. It is also helpful in the determination of the homogeneity of biodiesel tanks. The saponification value as per the analysis of the *Parkia biglobosa* oil was 191.65 (mgKOH/g). The value suggests the average amount of molecular weight fatty acids, (table 6;). The saponification value from the analysis still falls within the limit outlined by ASTM4052-96. *Parkia biglobosa* oil contained high FFA of 1.61 %, and the high-water content of 1.93(%) w/w.

Free fatty acid and moisture content are crucial parameters in determination vegetable oil if they are viable for transesterification process. Feedstocks containing high free fatty acid (> 0.5%) cannot be converted easily by base catalyzed transesterification, as a results of concurrent formation of soap, which potentially reduces the efficiency of the catalyst, and increasing viscosity, and making glycerol separation difficult. That challenge was avoided through, carrying out transesterification using sulphuric acid catalyst, which also acted as a test of establishing the visibility of oil in producing biodiesel (Mishra & Goswami, 2018; Suraj *et al*., 2020). From the results it was confirmed that *Parkia biglobosa* oil was ideal for biodiesel production.

Optimization of Reaction Conditions

Results from figure 9 shows there was a gradual increase in biodiesel yield from78.9 % to 90.7 % as the molar ratio of methanol to oil increased from 5:1 to 6:1, respectively. Optimization was carried out through the determination of the highest yield of biodiesel which was attained at the ratio of 6:1, and this molar ratio was used for the subsequent experiments. There was a reduction in the yield of the biodiesel to 88.7 % at the molar ratio of methanol to oil of 6.5:1. This was possibly due to an increasing molar ratio which leads to low separation glycerol and biodiesel due to high solubility. According to Lee & Saka (2010), molar ratio of alcohol to oil is the most crucial factor that affects the efficient conversion of oil to biodiesel and the cost of production. The transesterification stoichiometric molar ratio of alcohol to oil for the is 3:1. Greater molar ratios are needed since the reaction is reversible, for the purpose of increasing the miscibility for the enhancement of the contact among the molecule of alcohol and triglyceride (Miao & Wu, 2006).

Shifting the reaction to the completion side means the molar ratio is supposed to be greater than the stoichiometric ratios. Breaking the glycerine-fatty acid bonds in transesterification reaction of glyceride to form biodiesel needs extra alcohol (Miao & Wu, 2006). Thus, a greater molar ratio of alcohol to oil leads to converting the large amount of alkyl ester within a short period (Helwani *et al.*, 2009). Increasing the molar ratio of alcohol to oil leads to a rise in biodiesel and enhancement of purity in biodiesel. This is supported by study on vegetable oil by Eevera *et al.* (2009). Oil from sources that are not edible such as pongamia and neem needs lot of alcohol to produce maximum amount of ester, possibly because of the greater viscosity of the non-edible oil than edible oils (Eevera *et al.*, 2009).

Effect of methanol to oil ratio on production of biodiesel

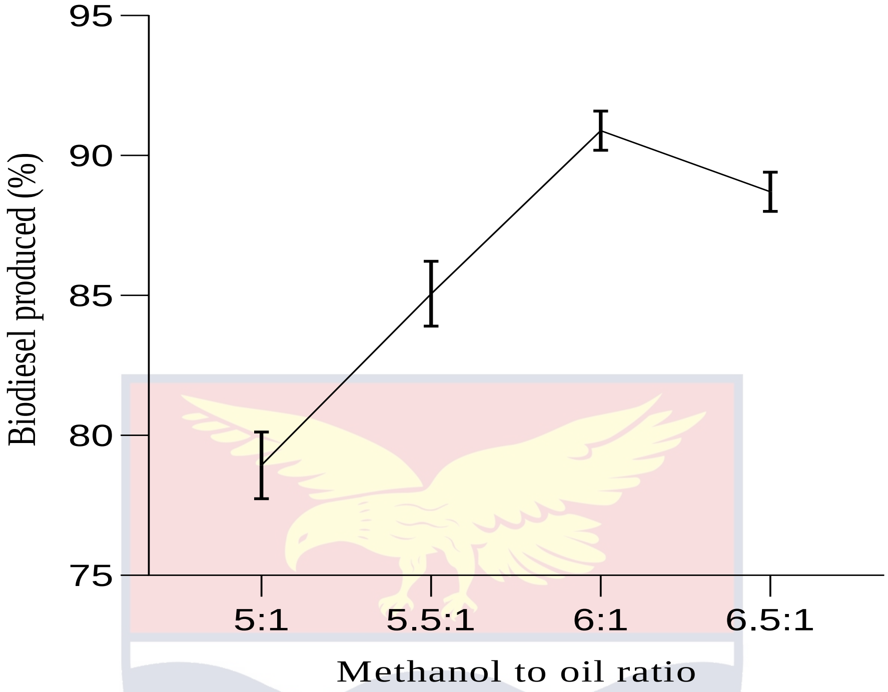


Figure 9: Effects of Methanol to Oil ratio on Production of Biodiesel (Reaction conditions: Reaction Temperature 60℃, Catalyst Concentration, 1%wt and Reaction Time, 1 hr) Mean with Standard deviation values were;78.93±1.18, 85.07±1.16, 90.90±0.7, and 88.70± 0.7

Effects of temperature on production of biodiesel

The effect of temperature was examined by keeping constant other factors: methanol to oil molar ratio, catalyst concentration and time at 6:1, 1wt %, and 1hr correspondingly. The synthesis of biodiesel through transesterification of *Parkia biglobosa* seed oil was achieved through variations of the temperature (55℃, 60℃, 65℃ and 70℃), (Figure 10). As the temperature was increased from 55℃ to 60℃, it resulted in a slight rise in biodiesel yield from 76.6 % to 77.0 %, respectively. However, a sharp rise in biodiesel yield from 77.0 % to 81.6 % occurred when temperature was increased from 60℃ to

65°C and decreases from 70°C to 76.5%. Therefore, the optimized temperature for transesterification of *Parkia biglobosa* oil was 65°C. The yield at temperatures below and above 65°C were low. At 55°C and 60°C, the reaction was not complete. At temperature above 70°C, the methanol starts to burn entirely as some vaporize and formed bubbles. Since methanol undergoes melting at a temperature between 60°C to 65°C reaction interface is inhibited. These findings are in line with those of Borugadda & Goud (2012) which noted similar observation about the vaporization of methanol at 70°C and the formation of bubbles. Furthermore, it was noted that at 70 °C the reaction was still not complete. The observation could be because of slightly increased in viscosity of the oil which results in to oil and catalyst mixing poorly (Liu *et al.*, 2008).

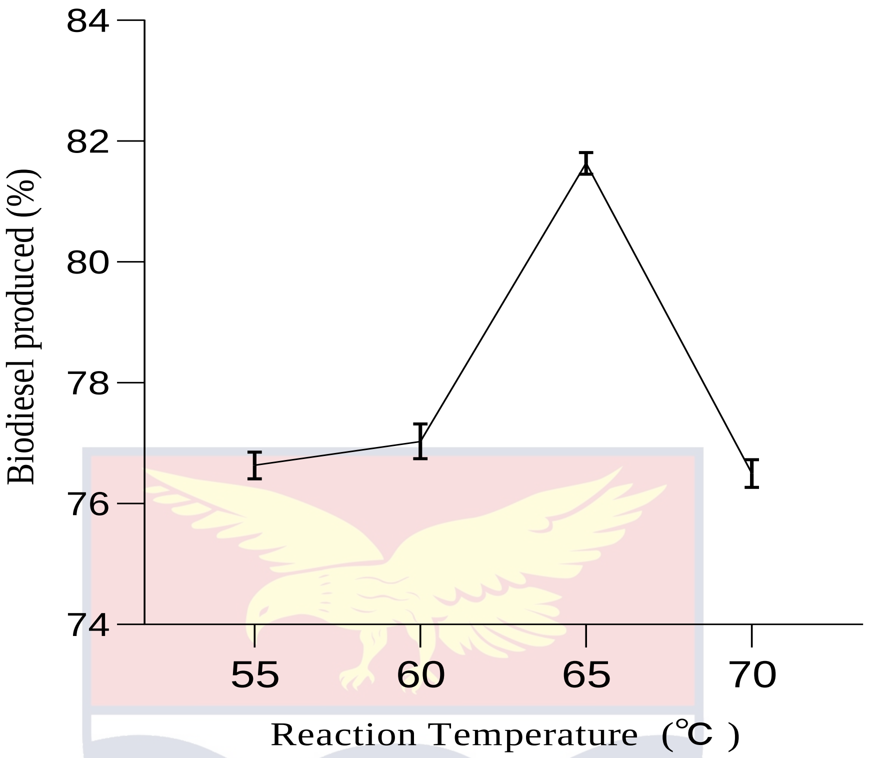


Figure 10: Effects of Temperature on Production of Biodiesel (Reaction Conditions: Molar ratio of Methanol to Oil, 6:1, Catalyst Concentration, 1 %wt, and Reaction Time,1 hr) Mean with Standard deviation values were; 76.63±0.38, 77.03±0.49, 81.63± 0.31, and 76.5±0.4

Effects of catalyst concentration on the production of biodiesel

1%, 2%, 3%, and 4% wt (weight) of the sulphuric acid catalyst concentration (with consideration of the oil's weight) was used (Figure 11). Initially, there was a sharp increase from 81.3 % to 93.4 % in the biodiesel yield as the concentration of catalyst rose from 1wt % to 3 wt %. A highest production of 93.4 % was attained by using 3 wt % of the catalyst. A sharp decline in the yield (88.5 %) of biodiesel was noted on additional increase in the concentration of catalyst to 4 wt %. Studies by Mathiyazhagan & Ganapathi (2011) showed similar trends. They highlighted that the rates of reaction in acid-catalysed transesterification reaction can lead to attainment of a higher yield of biodiesel by using a higher amount of catalyst. Increasing concentrations of catalyst results in more active sites for the reaction of available triglyceride and methanol. Moreover, addition rise in catalyst concentrations (beyond 4wt.%), leads to slightly lowered the yields. A development attributable to soap formation, thus the observed lowering of yields in Figure.11.

Sulphuric acid is among the many acid catalysts used because it exhibits the highest activity, and its performance is not influenced strongly by the existence of fatty acids in feedstock. Canakci & Van Gerpen (2001) carried out transesterification of grease with methanol using varied sulphuric acid amounts (1,3, and 4 % wt). Their study monitored the enhancement rate of an increased level of catalyst concentration and the yield of biodiesel. This resulted in rise of the biodiesel produced from 72.7% to 95.0% as the concentration of the catalyst was also raised. Sulphuric acid is more suitable than other acid catalysts used for the feedstock's transesterification with a reasonably high level of free fatty acid (≥ 0.5)

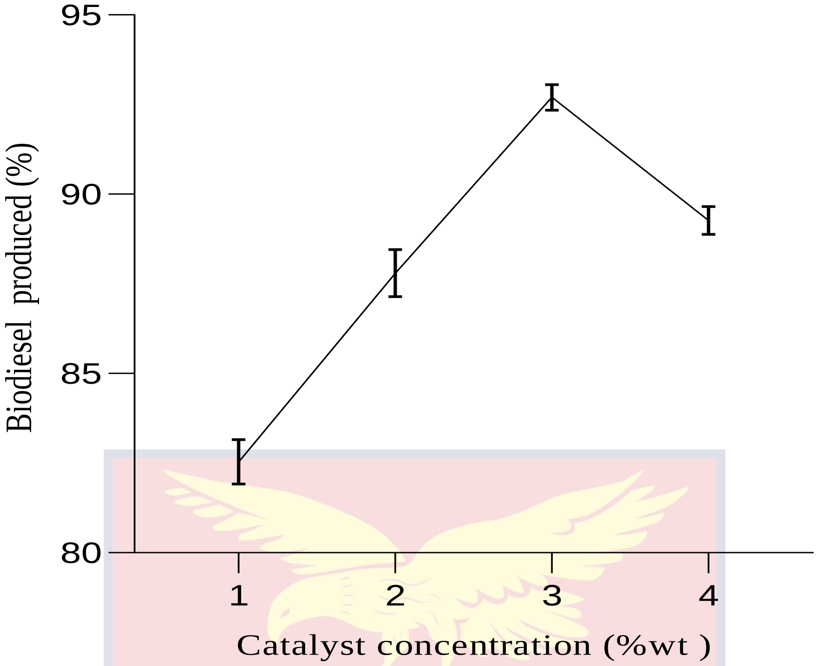


Figure 11: Effects of Catalyst Concentration on the Production of Biodiesel (Reaction Conditions: Molar ratio of Methanol to Oil, 6:1, Reaction Temperature 65℃, and Reaction Time,1 hr) Mean with Standard deviation values were; 82.53±1.07, 87.80±1.13, 92.70±0.61, and 89.27±0.67

Effects of Reaction Time on Production of Biodiesel

Transesterification reactions depend on time. At 0.5 hrs, the yield of biodiesel was 90.0 % (Figure 12). The reaction was however, slow and this could be attributed to insufficient stirring which could not enhance adequate mixing and dispersion of methanol and oil (Sharma *et al.*, 2008). Contrastingly, between 0.5 hrs and 1 hr, a constant rise in the amount of biodiesel obtained (90.0 % to 91.9 %). It was then preceded by a slight increase in biodiesel yield (93.0 %) at 1.5 hrs of the reaction time and this was an optimum yield.

As the time was prolonged from 1.5 hr to 2 hrs, biodiesel's amount decreased to 90.5 %. The reduction in the quantity of biodiesel obtained is as result from the occurrence of a reversible reaction. The findings are similar to Freedman *et al.* (1986) findings on the effect of time on acid- catalysed transesterification, which resulted in high amount of biodiesel produced up to a particular level as the reaction time increased. In the beginning, the slow rate of reaction could be due to poor mixing and dispersion of alcohol onto the alcohol-oil reaction interface. Nevertheless, optimum production of biodiesel was reached in less than 1.5 hr. This shows the optimum amount of biodiesel from *Parkia biglobosa* seed oil was attained after a considerable time while using H_2SO_4 catalyst as compared to other oil which can produce optimum yield of biodiesel within a short time and the yield is considerably lower as compared to yield of biodiesel from *Parkia biglobosa* oil. An additional increase in the time could not result into increased yield of biodiesel (Leung & Guo, 2006; Alamu, Jekayinfa, & Akintola, 2007). Increasing reaction time causes the lowering in the amount of biodiesel produced due to reversible reaction due to glycerol dissolving during the transesterification which causes in reduction of esters and formation of soap (Eevera *et al.*, 2009; Ma, Clements, & Hanna, 1998).

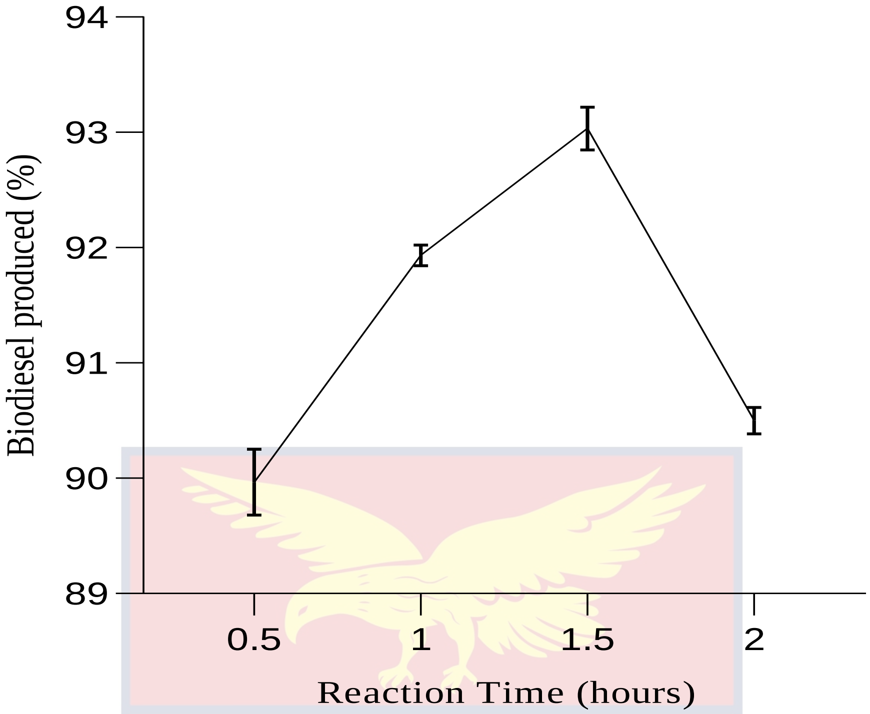


Figure 12: Effects of Time on the Production of Biodiesel (Reaction conditions: Molar ratio of Methanol to oil, 6:1, Reaction Temperature 65℃, and Catalyst Concentration, 3wt %) Mean with Standard deviation values were; 89.97±0.49, 91.93± 0.15, 93.03±0.32, and 90.50 ± 0.2

Summary of Optimum Reaction Conditions for the Production of Biodiesel from *Parkia biglobosa* oil using sulphuric acid catalyst

Table 7; shows the optimum reaction conditions for production of biodiesel from *Parkia biglobosa* seed oil through transesterification using sulphuric acid as a catalyst. Based on the results presented in the table 7; the methanol to oil molar ratio was 6:1; while the reaction temperature was 65℃, and the concentration of the catalyst was 3 wt % while the reaction time was 1.5 hrs. This experiment resulted in the highest amount of biodiesel yield of 93.4 %.

Table 7: Optimum Reaction Condition for the Production of Biodiesel

Factors	Optimum condition
Methanol to oil molar ratio	6:1
Reaction temperature (℃)	65
Catalyst concentration(wt%)	3
Reaction time (hrs)	1.5
Biodiesel yield (%)	**93.4**

Source: Lab experiment (2021)

Studies by Khan, Yan, & Chen (2019) on optimization, and analytical study of *Rhus typhina* non-edible oil for production of biodiesel discovered similar results. In their finding, the molar ratio of 6:1 of methanol to oil was identified as the best proportion with the temperature of 65℃. The catalyst concentration of 2.9 wt% produced a yield of biodiesel of 91.7 %. The yield was the highest compared to the methanol to oil ratio molar ratio of 7:1 with similar temperature and concentration of the catalyst which had a lower yield of 70% of the biodiesel.

Properties and application feasibility of biodiesel obtained through the sulphuric acid catalyst

Physical, chemical and fuel properties for the biodiesel produced from *Parkia biglobosa* seed oil using sulphuric acid as a catalyst are within the limits of international standards (Table 8). The international standards used were American Standard for Testing Material (ASTM D6751) and the European standard-EN14214 and Ghana Standard Authority which describe biodiesel's testing parameters and limits. Density and kinematic viscosity are crucial properties because they affect the performance of the engine. Fuel with higher density has greater mass and more viscous one has a low flow rate which influences the engine's output. Kinematic viscosity impacts the atomization of fuel during injection into the combustion engine. In this research, the transesterification using sulphuric acid, kinematic viscosity of oil was greatly reduced by 88.5% (from 35.70 to 4.1 mm^2/s) in the biodiesel obtained. The oil density was 916.2 Kg/M^3 and the biodiesel produced had a density of 868 Kg/M^3.

Iodine value represents the degree of unsaturation of biodiesel. There is a significantly high level of iodine value (137 g/100) in the biodiesel, which was above the limit for the international standard of both ASTM Std.D6751 and EN 14214. According to Costenoble *et al.* (2008), manufacturers of engine for a long time have been arguing that high value of iodine possibly causes polymerization and formation of deposits on the engine nozzles, piston rings and piston ring grooves during heating. There was 0.093%(w/w) water content in the oil, which was not within ASTM StdD6751 of 0.05 as maximum. Water content in biodiesel was 0.07 mg/kg which was slightly higher than ASTM Std.D6751 and EN 14214 standard as well as Ghana Standard Authority of 0.05 mg/kg maximum.

Other properties such as cetane number, kinematic viscosity, flash point and so forth were within the international standards.

Table 8: Comparison of Properties of *Parkia Biglobosa Biodiesel* to Standards of Europe, United States and Ghana Standard Authority

Property	Method	ASTM Std. D6751	EN 14214	Ghana Std. Authority	Determined value
Cetane number	ASTM D6890	≥47	≥51	47 min	51
Kinematic viscosity (mm^2/s; 40 °C)	ASTM D445	1.9-6.0	3.5-5.0	1.5 – 6.5	4.1
Oxidative stability 110 ºC (h)	EN 14112	≥3	≥6	-	3.1
Cloud point (℃)	GB/T510	-15 to 16	-	-	-1
Pour point (ºC)	GB/T3535	-3 to 12	-	+15 max	-1
Flash point (ºC)	ASTM D93	≥93	≥120	66 min	155
Sulfur content (%, w/w)	ASTM D4294	≤0.05	0.020	0.05 max	0.004
Ash content (%, w/w)	GB/T508	≤0.02	≤0.02	0.1 max	0.019
Acid value (KOH mg/kg)	ASTM D664-01	≤0.5	≤0.5	1.0 max	0.456
Water (mg/kg)	D6304	≤0.05	≤0.05	0.05 max	0.07
Density (20 ºC)	SH/T0248	-	860-900	-	868
Iodine value g/100	EN 14111	≤120	≤120	-	137
Copper strip corrosion (50 ºC; 3 h)	ASTM D 130-94	≤No.3a	≤No.1a	-	1 a
Free glycerine (%, w/w)	EN 1405	≤0.02	≤0.020	-	0.002
Total glycerine (%, w/w)	SH/T0796	0.24	≤0.25	-	0. 16

Source: Lab analysis (2021)

Optimizations of the Reaction Conditions for Production of Biodiesel from *Parkia biglobosa* using bi-functional Na_2CO_3-Clay catalyst

Influence of molar ratio of methanol to oil on the yield of biodiesel

Based on the stoichiometry theory of the process of transesterification reaction, 3 moles of alcohol are needed for each triglyceride mole to produce 3 moles of methyl esters and a mole of glycerol-by-product (Ashok *et al.*, 2020). To practically propel the reaction equilibrium to form more biodiesel, it requires a higher molar ratio of methanol to oil to be applied. In th research, the molar ratio of 10:1 to 13:1 was applied (Figure 13). There was a steady rise in biodiesel yield from 67.2 % to 90.7 % as the methanol to oil molar ratio was raised from 10:1 to 12:1. The optimum yield of biodiesel (90.7 %) was produced at a molar ratio of 12:1. From the molar ratio of 13:1, the output started declining to 87.6 % (Figure 13). This could be attributed to the catalyst dilution by extra methanol.

Excess methanol causes reversible reactions which lowers the oil being converted to biodiesel and increases glycerol solubility (Demirbas, 2005). The findings in this study are in line with study by Ofoefule *et al.* (2019) on use of response surface methodology for optimizing the production of biodiesel through transesterification of soybean oil using ethanol. Their studies indicated that 12:1 molar ratio of methanol to oil provided the best ratio for optimum yield for ester yield at 95%. The findings are similar to the research by Kondamudi (2010), who identified that varying methanol to oil ratio from the stoichiometric ratio of 3:1 to 15:1. Molar ratio greater than 15:1 results in challenges such as both biodiesel and glycerol dissolving which becomes a problem to separate

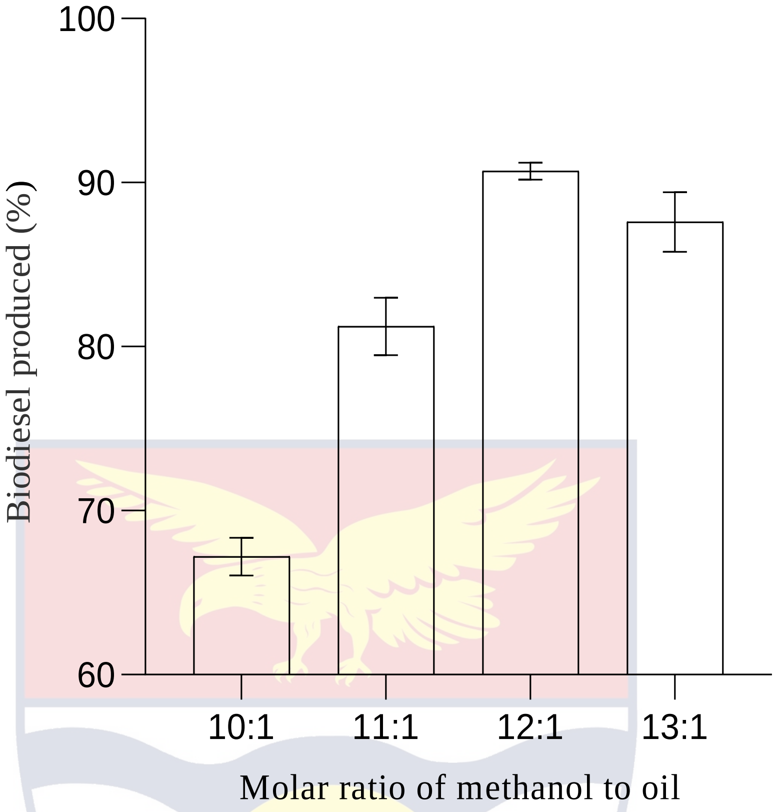


Figure 13: Effect of Methanol to Oil ratio on the Production of Biodiesel (Reaction conditions: Catalyst Concentration, 1wt %, Reaction Temperature 60°C, Catalyst Concentration, 1wt % and Reaction Time, 1 hr) Mean with Standard deviations values were; 67.20 ±1.44, 81.23±1.76, 90.67±0.55, and 87.60± 1.82

Influence of Temperature on the Yield of Biodiesel

Reaction temperatures was varied from 50°C, 55°C, 60°C, and 65°C, as other parameters were maintained at constant. The parameters kept constant were; time at 1 hr, molar ration of methanol to oil ratio at 12:1, and concentration of the catalysts at 1 wt %.

From figure 14; the amount of biodiesel produced rose from 87.6 % to 92.6 % as the temperature was raised from 50°C to 60°C, respectively. The optimum temperature was reached at 60°C with biodiesel yield of 92.6 %.

Increasing temperature leads to the rise in the rate of reaction during transesterification process and therefore, makes it more efficient. At 65℃, the yield sharply decreases to 86.7 %. The methanol turns into vapour from 60℃ and forms bubbles which inhibit the reaction surface. Gui, Lee, & Bhatia (2008), in their study found similar trends and found out that the reaction temperature should be less than the boiling point of the alcohol to stop leaking through vaporization and depending on the oil used, the optimal temperatures should be between 50℃ and 60℃.

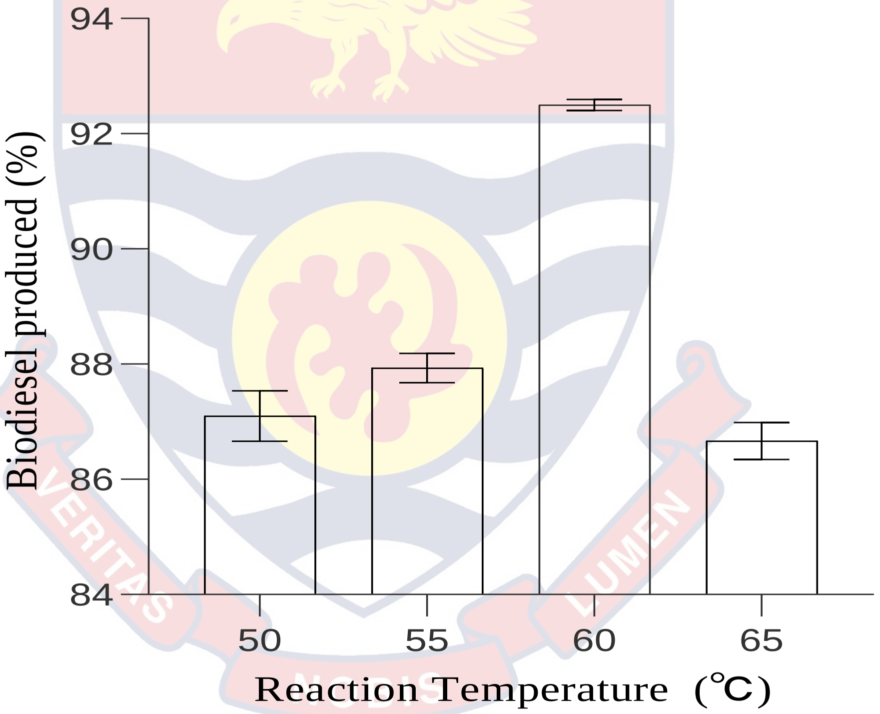


Figure 14: Effect of Temperature on Production of *B*iodiesel (Reaction conditions: Methanol to Oil ratio, 12:1, Catalyst Concentration, 1%wt and Reaction Time, 1 hr) Mean with Standard deviations values were; 87.10±0.44, 87.93±0.25, 92.5±0.1, and 86.67±0.32

Influence of Catalyst Concentration on the Yield of Biodiesel

There was a sharp increase in biodiesel produced from 88.8 % to 94.7 % as the concentration of the catalyst increased from 1% wt to 2% wt, (Figure 15;). It suggests the optimum loading of the catalyst on *Parkia biglobosa* oil was 2wt% with 94.6 % of biodiesel produced. However, biodiesel yield reduced from 92.2 % to 90.3 % as there was further increased in the concentration of the catalyst from 3% wt to 4% wt. Increase in the concentration of the catalyst leads to backward reaction being favoured. The observation was similar to Ataya, Dubé, & Ternan (2008), who found out that, triglyceride conversion to biodiesel rises as the concentration of catalyst increases to some point. Beyond the optimum yield, a reversible reaction occurs which decreases the yield of biodiesel.

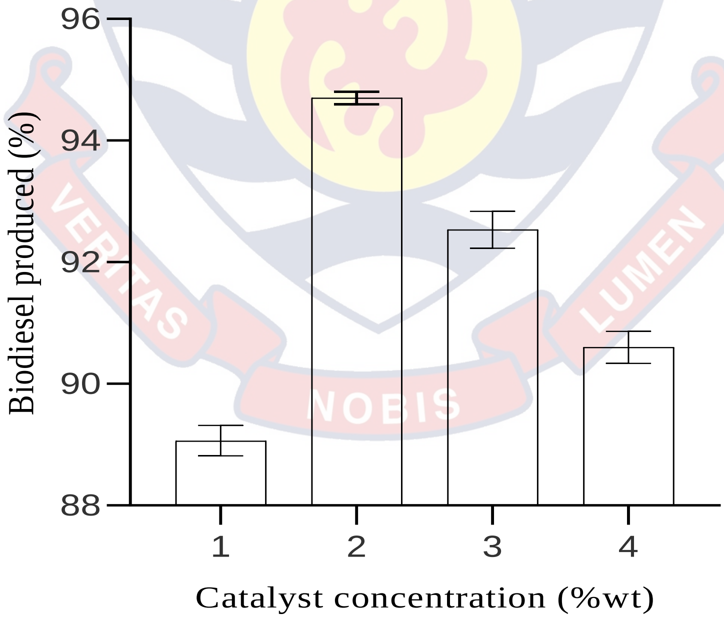


Figure 15: Effect of Catalyst Concentration on the Production of Biodiesel

(Reaction conditions: Methanol to Oil ratio, 12:1, Reaction Temperature,60℃

and Reaction Time, 1 hr) Mean with Standard deviations values were; 89.07±0.25, 94.60 ±0.1, 92.53±0.31, and 90.60±0. 26

Influence of Reaction Time on the Yield of Biodiesel

Time of reaction was varied from 0.5 hrs to 2 hrs to examine the effect of time on the production of biodiesel through optimization of reaction conditions using bi-functional heterogeneous catalyst.

The biodiesel yield rose steadily from 89.6 % to 90.3 % within 0.5 hr to 1 hr respectively, of the reaction time. The low yield at the initial (0.5) hr could be attributed to poor dispersion of methanol onto the oil due to inadequate mixing and short time of reaction. Thereafter, biodiesel yield progressively increased to optimum yield of 92.4 % within the next 1.5 hrs. After reaching the peak, the yield sharply decreases to 89.1 % in the next 2 hrs of the reaction time as shown in figure 16. Similarly, studies by Eevera, Balamurugan, & Chittibabu (2011) showed that the yield of biodiesel reduced as a result of reversible reaction. They attributed this to the reversible reaction to hydrolysis, which is enhanced by a long reaction time beyond; 1.5 hrs to 2.5 hrs. The respective time from 1.5 hrs had no crucial influence on conversion of the triglyceride to biodiesel but rather decreased the yield.

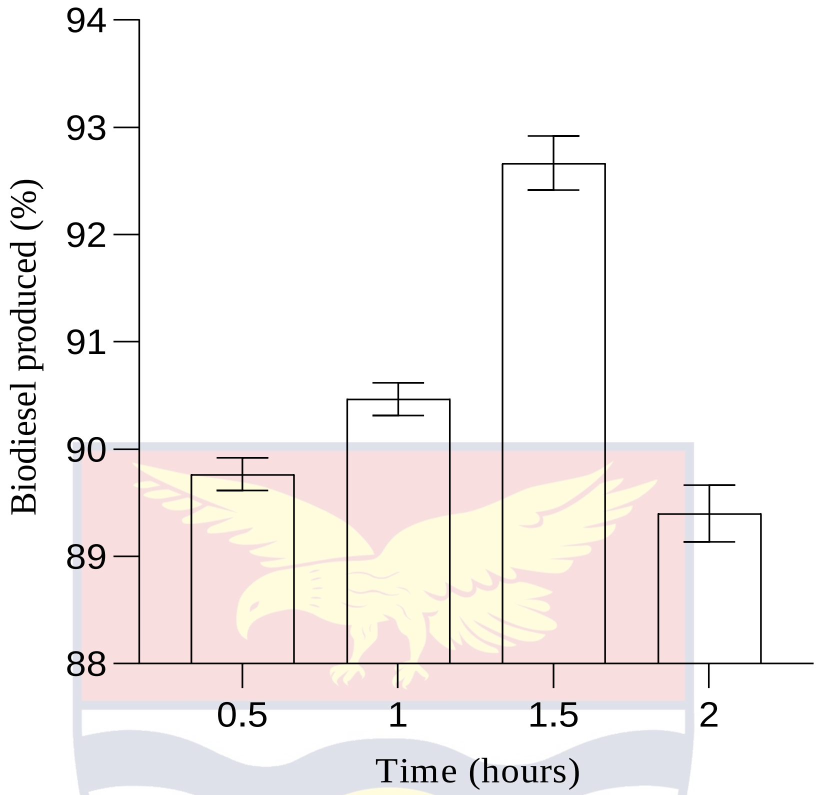


Figure 16: Effect of Reaction Time on the Production of Biodiesel (Reaction conditions: Methanol to Oil ratio, 12:1, Catalyst Concentration 2 % wt, and Reaction Temperature, 60℃) Mean with Standard deviations values were; 89.80±0.17, 90.47±0.15, 92.67±0.25, and 89.40±0. 26

Characterization of Catalyst

FTIR Analysis

Figure 17 represents the FT-IR spectra of Na_2CO_3-Clay catalyst. From the results, there was a peak around 2000 cm^{-1}. This could be attributed to the increasing intensity confirming the existence of oxides of clay. New peaks at about 1500 ,1200 and 800 cm^{-1} and are attributed to Si-O, K-O, and Mg-O bonds, respectively. The broad band between 3344 - 1663 cm^{-1} regions could partly be assigned to the stretching vibration of Si-O-K groups (Tetteh et al.,

2018) in which K ions could replace the protons of isolated hydroxyl groups to form Si-O-K groups in the activation process which was considered to be the active species of the catalyst. The vibration is well overlapped with the broad vibration band of OH groups which is ascribed to OH stretching vibration of the hydroxyl groups attached to the catalyst surface including molecules of water absorbed from the atmosphere. Na_2CO_3-clay catalyst band stretching from 3200-1700 cm^{-1} regions are endothermic peak possibly as a result of very weak bonding vibration of water molecules.

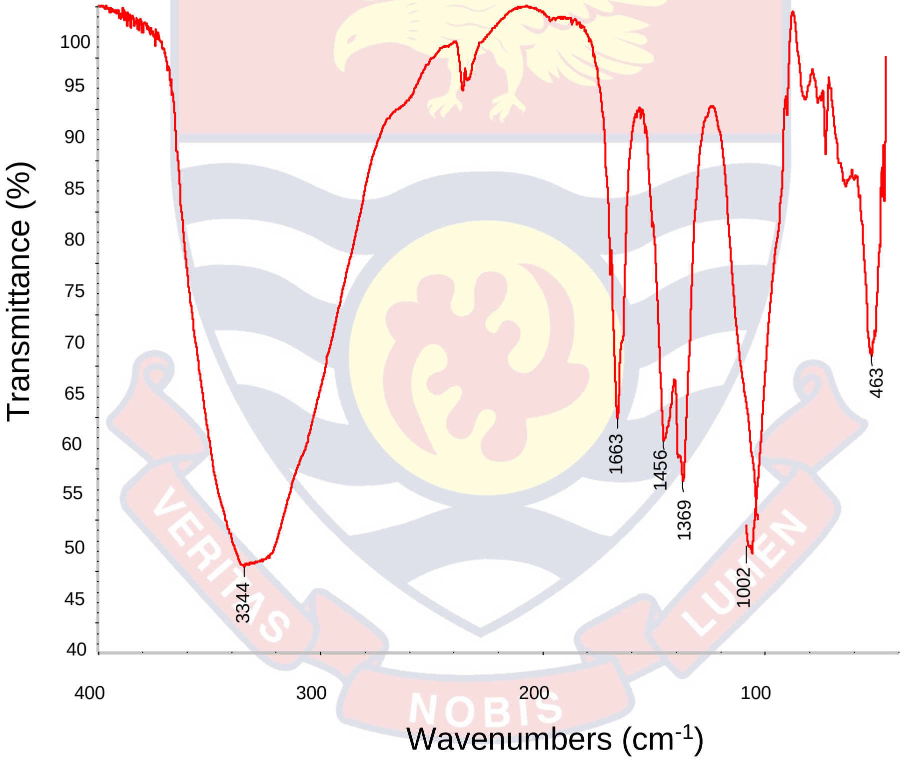
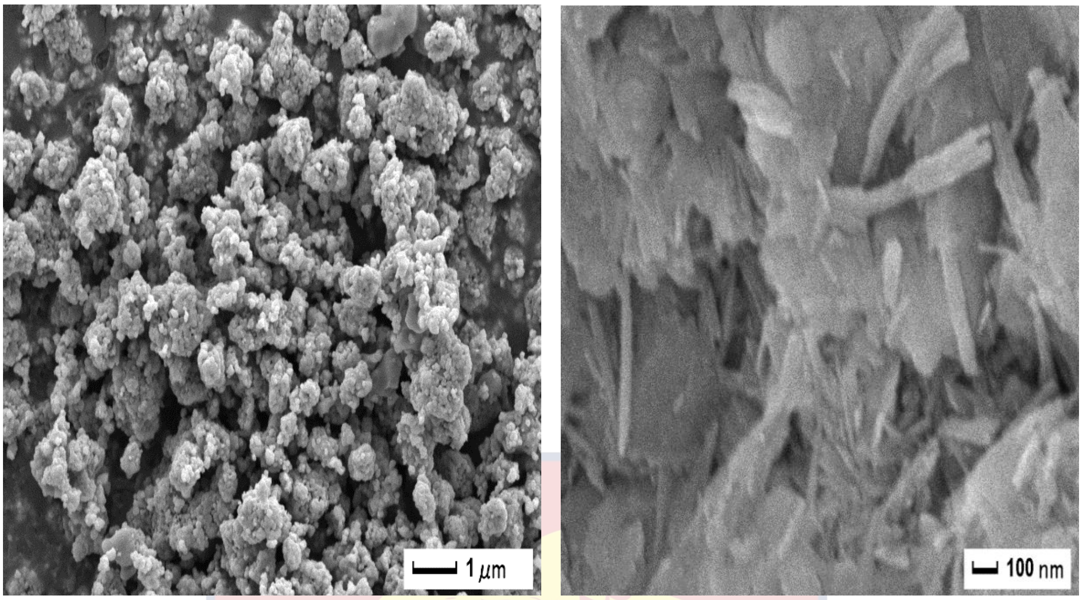


Figure 17: FTIR of the Na_2CO_3- Catalyst

SEM Analysis

Surface and surface morphology were examined for both calcined and raw clay through scanning electron microscopy (SEM) (Figure 18). After calcination, there was significant decrease in the porous surface to 100nm from 1μm before calcination (raw clay). Clay with smaller size particle has a higher surface area. During the transesterification process, there is more collision between the reactants and the catalyst by the higher surface area of the catalyst thereby enhancing the reaction rate in the transesterification (El-Gendy *et al.*, 2014).

Furthermore, structurally properties of the raw clay mineral ensure its suitability as a charge carrier and it acts as a basis of cation exchange and the swelling ability of the clay minerals. The structural charge exists as structural or surface charge. The structural charge exists in between the octahedral sheets and is permanent while surface charge depends on hydrolysis of Si-OH and Al-OH bonds along surface of the clay structure and is PH dependent. This explains PH of 4.88 of clay mineral(kaolin) making it weak acidic. Cation exchange capacity makes the clay mineral to substitute unfixed cations in interlayers for cations in solutions of Na_2CO_3. It therefore results in the calcined clay possessing two active sites; acid and alkaline sites hence bi-functional heterogenous catalyst.



(a) Raw clay powder (b) Calcined clay

Figure 18: SEM mages (a) and (b) of heterogenous clay catalyst

Ultra Violet Spectrum

Figure 19 represent the UV–vis spectrum of clay which shows a peak of absorbance of about 100 nm, which could be attributed to π=π charge transfer transitions in the Si-O group of SiO_2. This is an indication that Na_2CO_3 has been absorbed on the clay completely decompose at 600 °C (figure 19).

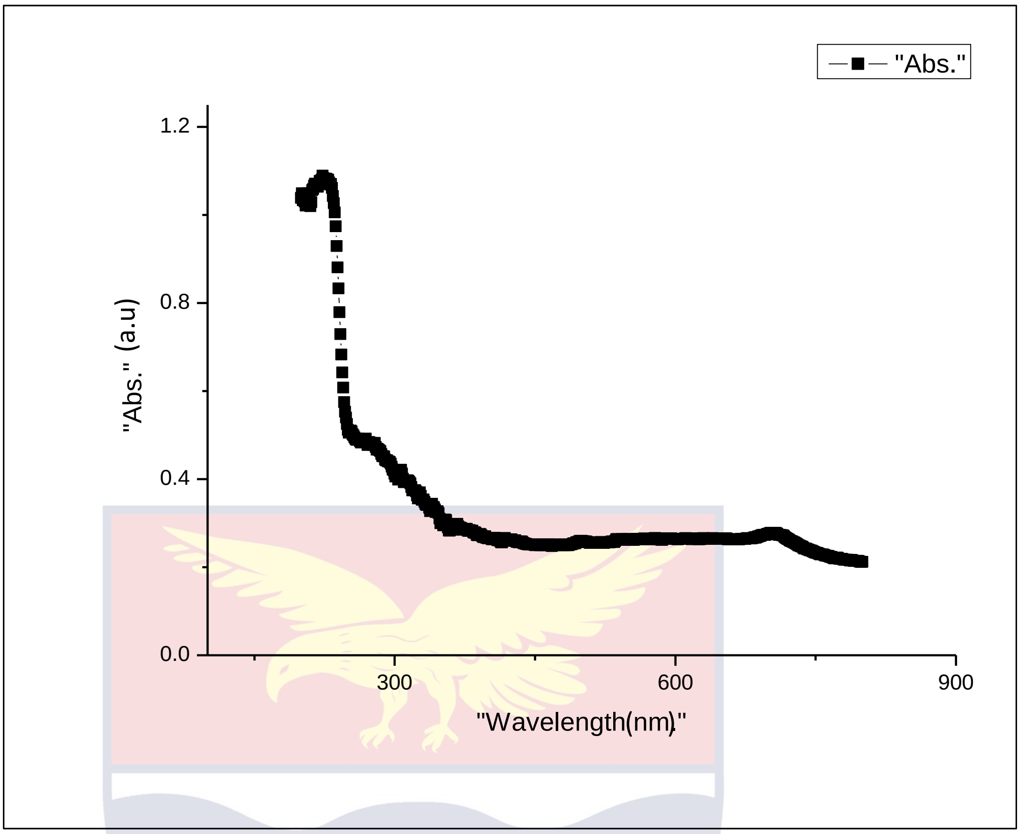


Figure 19: UV spectrum of clay catalyst

Energy-dispersive X-Ray spectroscopy (EDS)

The vital element present in the catalyst is silicon dioxide and oxide of potassium. These are the active materials for the conversion of triglyceride to biodiesel. Fe, Mg, and Al were found in trace amounts (Figure 20) (Faruque *et al.*, 2020).

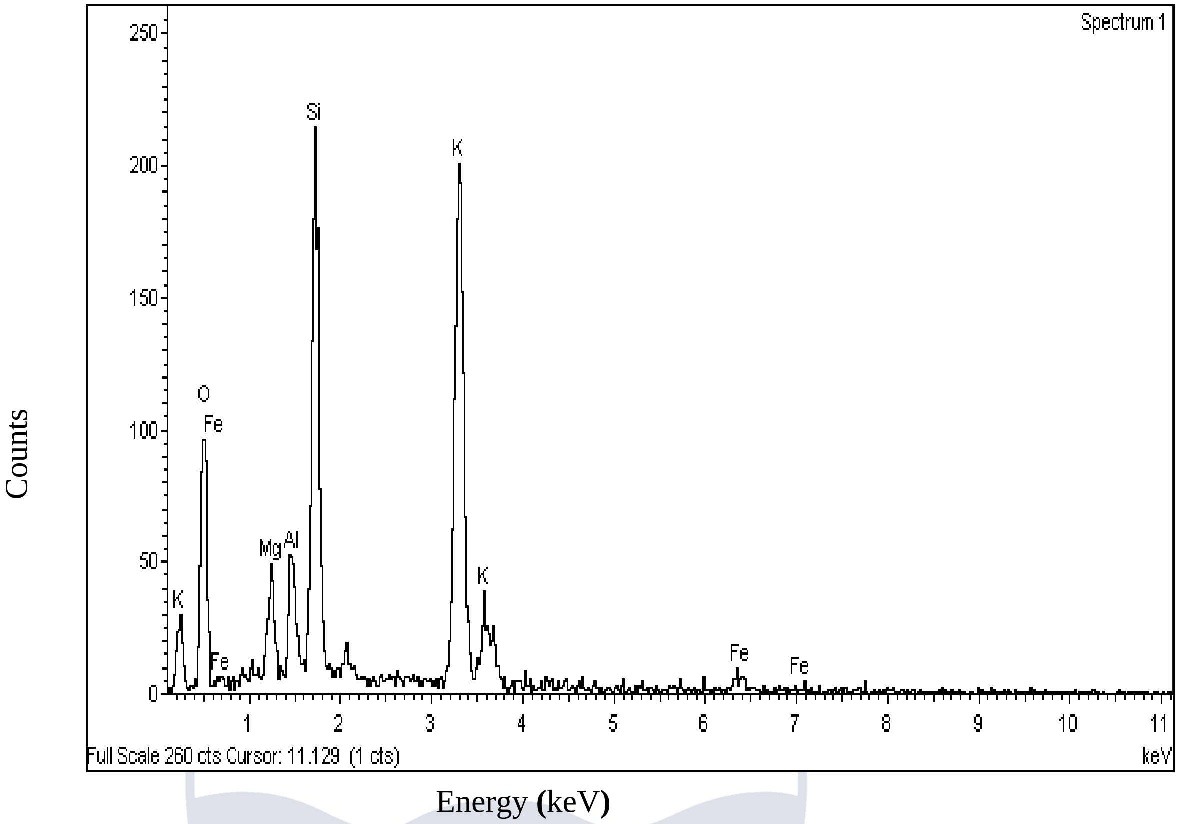


Figure 20: Energy-dispersive X- ray spectroscopy (EDS) of the clay catalyst

X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns of raw and modified clay material catalysts are shown in Figure 21. This was done to elucidate the composition of the samples. The highest patterns display the characteristic peak at 2θ =35° associated with silicon dioxide for the calcined clay, 2θ =25° associated with silicon dioxide for the raw clay. Other common peaks include 2θ =30° associated with potassium oxide for the calcined clay, 2θ =32° associated with potassium oxide for the raw clay, 2θ =20° associated with magnesium oxide for the raw clay. The crystalline structure of the raw clay identified by XRD measurements showed that clay was composed mainly of Si, and K, additionally Mg, Al, and Fe were present in traces (Alencar *et al.*, 2017).

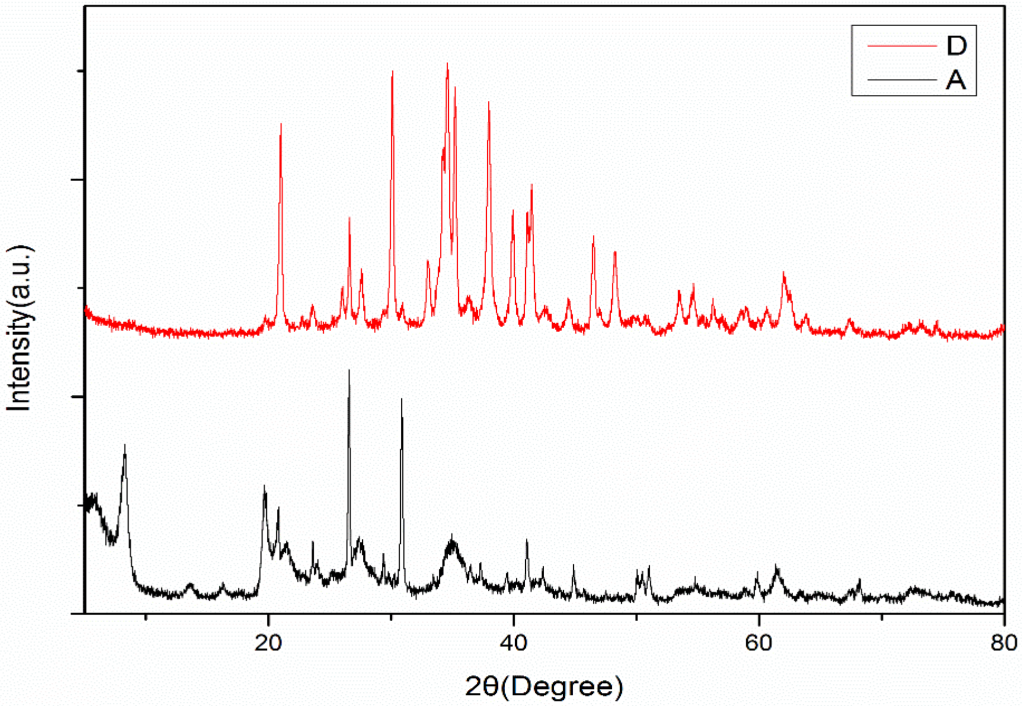


Figure 21: X-ray diffraction (XRD) of A (raw clay) D (calcined clay catalyst)

Summary of Optimum Reaction Conditions for the Production of Biodiesel from *Parkia biglobosa* oil using Bi-functional Heterogeneous Na_2CO_3- Clay Catalyst

Table 9; illustrates the summary of the optimum reaction conditions in the production of biodiesel from *Parkia biglobosa* seed oil through transesterification process using bi-functional heterogeneous clay catalyst. The optimum molar ratio of methanol to oil was 12:1, and catalyst concentration was 2wt %, the temperature of the reaction was 60 ℃, and the reaction time was 1.5 hrs. These optimum reaction conditions produced the highest yield of the biodiesel of 94.7 %. Though no research has been carried on production of biodiesel from *Parkia biglobosa* oil using bi-functional heterogeneous catalyst, several research have been done on biodiesel production from several non-edible oil plants using bi-functional heterogeneous catalysts. Gao, *et al.*(2010) performed research using almost similar reaction conditions in table 10. The reaction conditions Gao *et al.*(2010) used were the methanol to oil molar ratio of 12:1, concentration of the catalyst of 5 wt% using bifunctional heterogeneous (Ca-Al metal oxide), and reaction time was 3 hrs. The highest amount of biodiesel obtained from Gao, *et al.*(2010) experiment was 99.74 %. Similarly, Lee *et al.* (2015) researched on production of biodiesel from jatropha oil using a mixed oxide-based bifunctional heterogenous catalyst ($CaO-La_2O_3$). According to Lee, *et al.* (2015), the network of metal-metal oxide among Ca and La, led to CaO being dispersed sufficiently on the composite surface and therefore created more active sites which are acidic and basic. It resulted in enhanced catalytic activity. The largest biodiesel yield of 98 % was obtained at 160°C, 3hrs, 25:1 methanol to oil, molar ratio and concentration of catalyst of 3 wt%.

Table 9: Summary of Optimum Reaction Conditions for the Production of Biodiesel

Variable	**Optimum reaction condition**
Methanol to oil molar ratio	12:1
Catalyst amount (wt%)	2
Reaction temperature (°C)	60
Reaction time (hrs)	1.5
Biodiesel yield (%)	**94.7**

Source: Lab experiment (2021)

Physicochemical Characterization of the Biodiesel

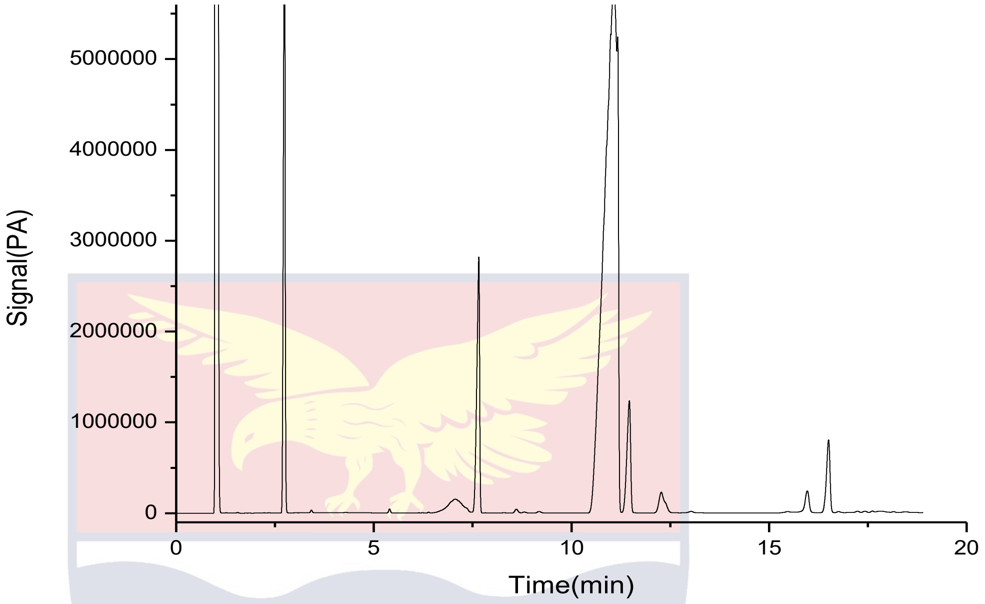


Figure 22: Chromatogram of compositions of the Biodiesel measured by GC–MS

Table 10: Composition of Biodiesel

Composition	**Analysed Value (wt%)**
Methyl palmitate	15.08
Methyl stearate	4.39
Methyl oleate	8.90
Methyl linolenate	65.42
Methyl Eicosadinoate	6.21

Source: Lab analysis (2021)

The chromatogram of biodiesel has been presented in Figure 22. Analysis in this study was mainly carried out to confirm the conversion of oil to biodiesel and the presence of the different methyl ester present in biodiesel from *Parkia biglobosa* oil qualitatively. The most predominant methyl esters observed are Methyl linoleate, 65.42 %; Methyl palmitate, 15.08 %; Methyl oleate, 8.90 %; Methyl Eicosadinoate, 6.21 %. Methyl stearate, 4.39 %; Table 10 reveals the percentages of esters present in biodiesel from *Parkia biglobosa* oil.

Properties and Application Feasibility of Biodiesel Obtained Through the Bi-Functional Heterogeneous Catalyst

Biodiesel obtained from *Parkia biglobosa* oil using bi-functional heterogeneous clay catalyst were analysed. Chemical, and physical fuel properties were matched with ASTM, EN Standard and Ghana Standard Authority requirements and presented in Table 11;

Nearly all the key properties of the biodiesel were within the required limit stipulated by the international standards. There was a reduction in kinematic viscosity and the density from 35.7 mm^2/s(oil) to 4.2 mm^2/s (biodiesel). Both properties are fundamental properties of fuel. Kinematic viscosity has an effect on fuel atomization in combustion chamber. In this study, transesterification significantly reduced oil's kinematic viscosity by 88.24 %, making it to be within acceptable international limit. Alternatively, the density of *Parkia biglobosa* oil was high, possibly due to the triglyceride molecules' higher molecular weight. However, in the transesterification of *Parkia biglobosa* oil using a bi-functional heterogeneous catalyst, the biodiesel density was reduced by 5.04 % (870(Kg/m^3)). Water content in the oil was 1.93w/w while after transesterification, the water content of the biodiesel obtained was 0.08 w/w. There was a significant reduction of water content by 13.98 % though it was still higher than the acceptable limits of $\leq$0.05 or 0.05 maximum as provided by EN 14214 and ASTM Std D6751 and the Ghana Standard Authority. All other parameters except water content were within the limit of

ASTM D6751, EN 14214, and the Ghana Standard Authority. Therefore, the biodiesel obtained from *Parkia biglobosa* seed oil through transesterification using a bi-functional heterogeneous clay catalyst is an appropriate fuel for the diesel engine's direct application.

Table 11: Comparison of Properties of *Parkia biglobosa* Biodiesel to Standards of Europe, United States, and Ghana Standard Authority

Property	Method	ASTM Std. D6751	EN 14214	Ghana Std. Authority	Determined value
Cetane number	ASTM D6890	≥47	≥51	47 min	50
Kinematic viscosity (mm2/s; 40℃)	ASTM D445	1.9-6.0	3.5-5.0	1.5 – 6.5	4.2
Oxidative stability 110℃ (h)	EN 14112	≥3	≥6	-	3.3
Cloud point (℃)	GB/T510	-3 to 12	-	-	-2
Flash point (℃)	ASTM D93	≥93	≥120	66 min	157
Sulfur content (%, w/w)	ASTM D4294	≤0.05	0.020	0.05 max	0.006
Acid value (KOH mg/kg)	ASTM D664-01	≤0.5	≤0.5	1.0 max	0.458
Water (mg/kg)	D6304	≤0.05	≤0.05	0.05 max	0.08
Density (20℃)	SH/T0248	-	860-900	-	870
Copper strip corrosion (50℃ ; 3 h)	ASTM D 130-94	≤No.3a	≤No.1a	-	1 a
Total glycerine (%, w/w)	SH/T0796	0.24	≤0.25	-	0. 18

Source: Lab analysis (2021)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

Conclusion

The depletion of the non-renewable energy sources such as fossil fuels is one of the most persistent challenges facing human society. There is also issue of global warming resulting from the fossil fuel combustion and their impacts on the future of energy systems globally. In the face of these, is the increase in population, there is a great drive from multiple players to provide alternative sources to conventional fossil fuel. Renewable energy resources can provide solutions to current and future global energy needs, ultimately contributing to sustainable development. Besides, the sustainable use of energy is a vital component in mitigating the adverse effects of anthropogenic climate change and variability.

Biodiesel; a renewable energy source that is alternative to fossil fuel has been widely accepted. It is obtained through edible plant oil such as soybean, sunflower, peanut, among many others. The use of edible oil jeopardizes food security. It is against the World Health Organization (WHO) recommendations and therefore the utilisation of non-edible oil such as jatropha, croton, moringa and so forth is gaining attention.

Parkia biglobosa oil has received very little attention as a substitute feedstock for producing biodiesel because of its uses for food seasoning and as medicine. The study's main aim was to investigate biodiesel production through transesterification of non-edible *Parkia biglobosa* seed oil using the heterogeneous bifunctional Na_2CO_3-Clay catalyst.

Parkia biglobosa oil was obtained by subjecting the *Parkia biglobosa* seed to the soxhlet extraction. The percentage yield of the oil was 16.5 %. Properties such as fatty acid compositions, water content, saponification value and many other properties of the oil as required were within acceptable limit for producing biodiesel. From the study, the following can be concluded:

1. The optimum yield of biodiesel from *Parkia biglobosa* oil through transesterification using sulphuric acid catalyst was achieved at the molar ratio of methanol to oil of 6:1, reaction temperature of 65℃, concentration of the catalyst at 3 wt % in 1.5 hrs. This optimum biodiesel yield was 93.4%.
2. The optimum yield of the biodiesel from the transesterification using bi-functional heterogeneous clay catalyst was achieved at the molar ratio of methanol to oil of 12:1, reaction temperature of 60℃, catalyst concentration of 2 wt % and within reaction time of 1.5 hrs. The optimum yield of the biodiesel was 94.7 %.
3. The properties of biodiesel produce from the two catalysts were with American Standard Testing Material (ASTM D6751), European Standard (EN14241), and Ghana Standard Authority.

Recommendations

Based on the conclusion of the study, *Parkia biglobosa* seed oil has potential as a feedstock for producing biodiesel. The following are the recommendations of this study;

1. Further research could be undertaken on reducing water content and iodine value since these properties exceeded the acceptable limit

2. Testing of *Parkia biglobosa* biodiesel should be carried out in a diesel engine to assess the engine performance and emissions characteristics.
3. To study the blends of *Parkia biglobosa* biodiesel with conventional diesel in order to assess the performance of the blends.
4. To apply the prepared heterogeneous solid catalysts to standard refined oils such as soybean, castor or palm to assess and compare the performances.

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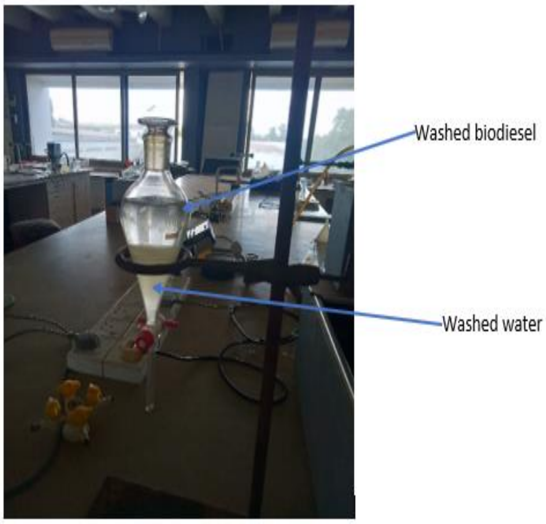
APPENDICES

APPENDIX A: Biodiesel Production images

Biodiesel production setup

Biodiesel – Glycerol separation

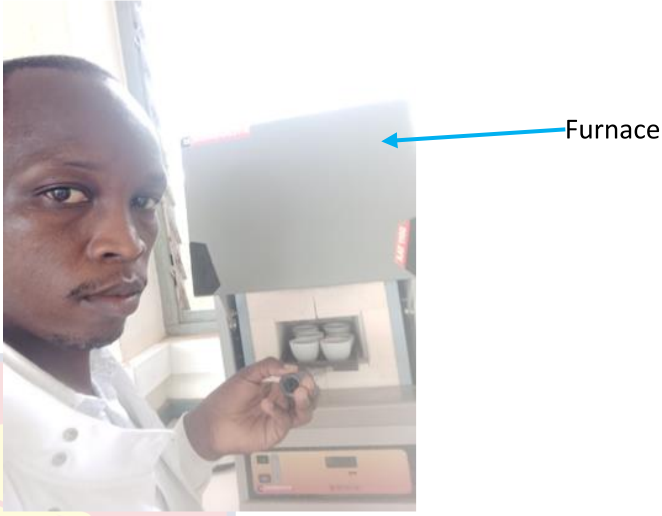


Washing of *Parkia biglobosa* biodiesel

Samples of biodiesel from *Parkia biglobosa* oil

APPENDIX B: Some of the instruments used

GC-MS



Muffle furnace