UNIVERSITY OF CAPE COAST

BIODIESEL PRODUCTION FROM TROPICAL ALMOND

(*Terminalia cattapa* L.) SEED OIL

BY

HAYFORD KWADZO DZAMESI

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of Biological Science, University of Cape Coast, in partial fulfilment of the

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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: Hayford Kwadzo Dzamesi

Supervisor's Declaration

I hereby declare that the preparation and presentation of the thesis were 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 work was to produce biodiesel from oil of tropical almond (*Terminalia catappa*) seed using response surface method (Box-Behnken design). Tropical almond seed oil was extracted using the Soxhlet extraction technique, and the yield was 58.24%. The free fatty acid value was 1.48 mgKOH/g. A bifunctional heterogeneous catalyst of NaOH (20%)/kaolin was synthesized to convert tropical almond (*Terminalia catappa* L.) seed oil into biodiesel. NaOH and modified bifunctional kaolin were used as catalysts via transesterification process to turn the oil into biodiesel. The transesterification study findings demonstrated the effectiveness of the catalyst for producing biodiesel. At modelling conditions of methanol-oil ratio (6:1), catalyst amount (1.0 g), temperature (65 ^{o}C), stirring speed (600 rpm) and time (30 minutes), the RSM predicted and validated biodiesel yields using NaOH as catalyst were 96.38%, and 96.81% respectively. The synthesized bifunctional catalyst (NaOH(20%)/kaolin) was characterised by means of XRD, FTIR, SEM, and TGA. The yield of biodiesel generated using the NaOH(20%)/kaolin catalyst was 95.94% at optimal parameter of catalyst amount (2 g), temperature (65 °C), methanol-oil ratio (8:1), time (90 minutes). For the forward response, a second-order kinetic process employing second sections was suggested. The process of converting triglycerides to diglycerides served as the rate-determining step for the whole NaOH (20 %)/kaolin catalysed transesterification. The rate constant saw an increment from 0.014 to 0.037 min^{-1} as temperature was elevated from 50 to 65 ^{o}C. Based on how well the physical and chemical characteristics of the produced biodiesel compared

to ASTM D6751 standards, tropical almond seed oil was deemed to be

suitable feedstock for producing biodiesel.

iv

KEY WORDS

Biodiesel

Response surface method

Heterogeneous catalyst

Almond seed

Terminalia catappa

v

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vi

DEDICATION

To my wife Anastasia Baah and children, Esmond S. K Hayford, Eliana S. A

Hayford.

TABLE OF CONTENTS

x

xi

xii

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOAC	American Oil Analytical Chemist
ASTM	American Society for Testing and Materials
CO_2	Carbon dioxide
DG	Diglyceride
FAME	Fatty acid methyl ester
FFA	Free fatty acids
FTIR	Fourier Transmission Infrared Spectroscopy
GSA	Ghana Standard Authority
MG	Monoglyceride
SEM	Scanning Electron Microscope
TG	Triglyceride
XRD	X-ray diffraction
RSM	Response Surface Method
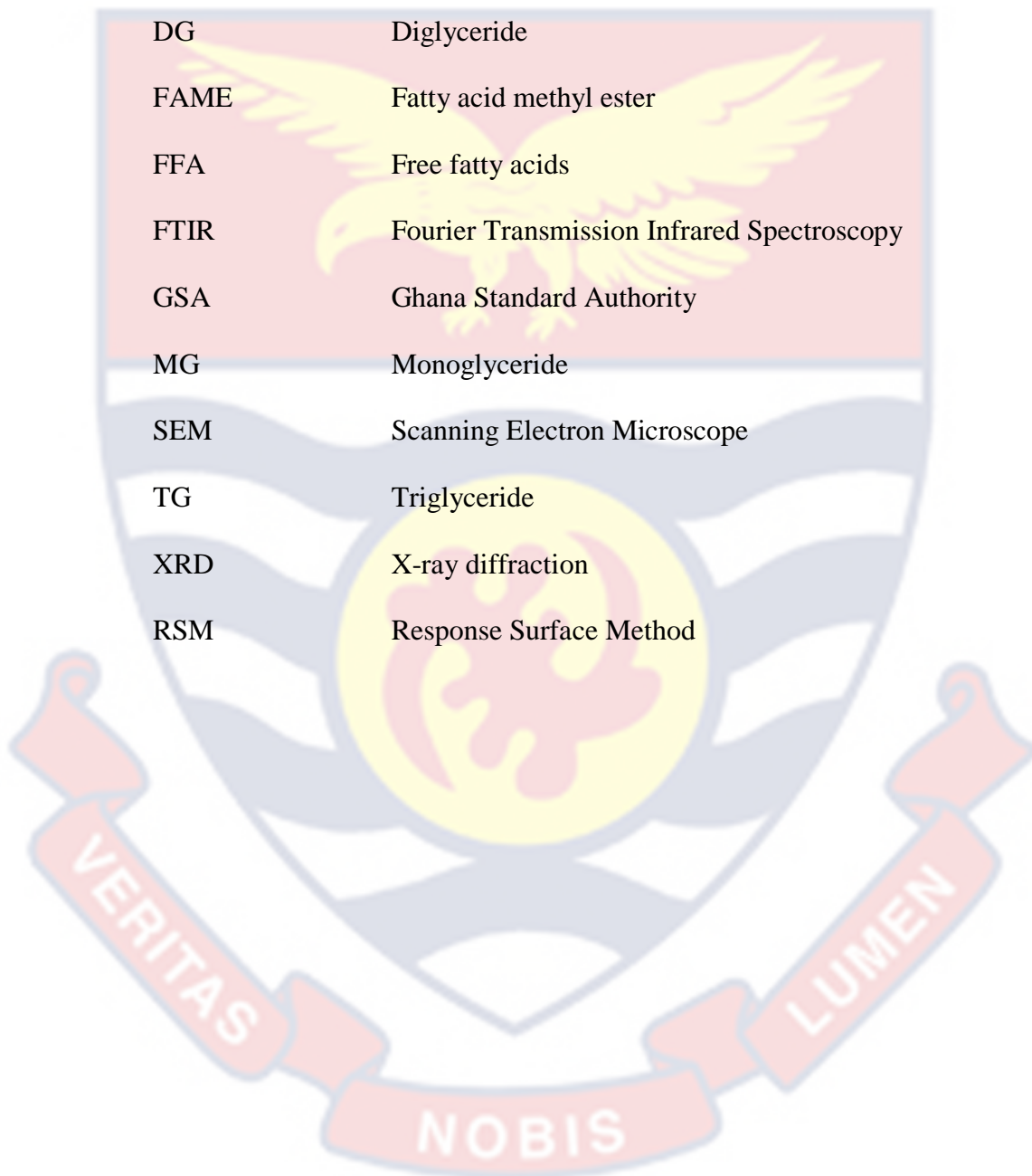
CHAPTER ONE

INTRODUCTION

Background to the Study

The current rate of fossil fuel consumption is unsustainable given the expanding global population. As a result, it is anticipated that humans will quickly run out of this non-renewable resource on Earth and the rising fossil fuel demand has other implications, such as rising fuel costs, environmental issues regarding pollution from crude oil by-products, and the impacts of global warming, all of which are pushing researchers to investigate various alternative fuel sources. Therefore, it is crucial to provide affordable, sustainable, and alternative fuels.(Escobar-nin, 2014). In addition to rising costs, the finite supply of fossil fuels is also declining. As a replacement for fossil fuels, renewable energy sources made from biomass are more environmentally friendly and can take their place. Biodiesel is one of these sustainable energy sources (Jigajinni & Meti., 2021).

Biodiesel is a composition of mono-alkyl esters that are generated from oils of vegetable waste cooking oil, , fats of animal, algae, and greases (Paintsil, 2013). Four alternative methods, including direct usage or oil mixing, micro emulsion, pyrolysis, and transesterification reaction, can be used to refine crude oils of animal fats and vegetable such that it may be utilised as appropriate replacement for diesel engines fuels (Babajide *et al.*, 2011). Transesterification of oils from vegetables to create biodiesel is currently the most widely used process (also known as ethanolysis or

1

methanolysis). Alkali, acid, biocatalysts, and heterogeneous catalysts can all be used to execute the transesterification process, but only the alkaline method is now used on an industrial application since it is very effective and affordable (Escobar-nin, 2014)

The manufacturing of biodiesel is known to employ a variety of feedstocks, comprising non-edible, edible oils, leftover cooking oils, animal fat, and waste oils. Although the preferred feedstocks for producing biodiesel in developed nations are edible oils like soybean and rapeseed oil, this is not the case globally since poorer nations lack access to affordable sources of these oils for human use (Abdulla *et al*., 2011). The world is now moving towards exploring non-edible oil feedstocks as alternative to edible oils for biodiesel production.

Statement of the Problem

Energy as a key resource is running out. The over exploitation of fossil fuels coupled with environmental deterioration are issues that the entire globe is currently dealing with. Due to the world's limited fossil fuel supplies and the unending demand, there is a continuing lack of supply and a cascading price hike (Mohammed *et al*., 2021; Vicente *et al*., 2004). These dangers together have made researchers focus on the search for an alternative fuel derived from sustainable sources. Biodiesel has been identified by researchers as a possible replacement, particularly for diesel-powered engines. Now, it is commonly produced using known cultivated vegetables oils such rapeseed, soybean, sunflower, and palm. Using edible oils as raw material has made the unwanted

2

struggle between oil for fuel and food worse, which has culminated into food shortages.

The homogeneous transesterification method used for commercial biodiesel synthesis currently has several drawbacks, including corrosion, toxicity, and the creation of a significant volume of effluent that requires further processing. The constraints render the expense of producing biodiesel commercially unviable.

Currently, statistical techniques like Response Surface Methodology (RSM) have been employed to model and optimize transesterification processes for methyl ester production. For instance, Mohammed *et al*., (2021) utilized RSM to model biodiesel production from *Jatropha* seed oil, achieving an optimal yield and conversion rate of 96% through the use of a Face Centered Central Composite Design. Santos *et al*., (2014) also applied RSM to optimize biodiesel production from soybean oil, employing a Central Composite Design. In a related study, Agu *et al*., (2022) combined artificial neural networks and RSM with a Central Composite Design to model biodiesel production from *Terminalia catappa* kernel oil. Additionally, Solomon, (2022) employed RSM to enhance *Jatropha* biodiesel yield by optimizing process variables using the Box-Behnken method. Various experimental designs, including the central composite design (CCD), face-centred composite design (FCCD), and Box-Behnken design (BBD), are readily accessible for research purposes. Among these, the BBD stands out as a notably efficient option, requiring less time and fewer experimental runs. It is particularly favoured in industrial research settings, particularly when three

3

process variables are known to impact the system's response (Kaiser *et al*., 2013). Prior to achieving large-scale development and efficient optimization of biodiesel production, numerous challenges and factors demand attention. These critical concerns encompass the utilization of cost-effective feedstocks like non-edible vegetable oils, enhancing production efficiency through meticulous process parameter optimization, reducing catalyst expenditures by means of catalyst regeneration, and optimizing process parameters to maximize biodiesel yield. This study seeks to tackle these challenges via the utilization of RSM with the Box-Behnken design specifically for modeling methyl ester yield through the transesterification of *Terminalia catappa* seed oil.

Main Objective

The primary aim of this work has been to produce biodiesel from oil of tropical almond (*Terminalia catappa* L.) seed using heterogeneous bifunctional catalyst NaOH/kaolin via response surface method.

Specific Objectives

1. To produce biodiesel with tropical almond seed oil using homogeneous catalyst, NaOH by response surface method (Box-Behnken design).

2. To model biodiesel yield from tropical almond seed oil by response surface method.

3. To characterise bifunctional heterogenous catalyst prepared from kaolin and NaOH to produce biodiesel from oil of tropical almond seed.

4

4. To optimize biodiesel production using bifunctional heterogeneous catalyst, NaOH/Kaolin and evaluate the properties of the biodiesel.

5. To study the kinetics of the process at the optimum reaction condition.

Hypothesis

1. H_0: Biodiesel cannot be produced from tropical almond seed oil by transesterification using NaOH as catalyst.

   H_1: Transesterification with NaOH as a catalyst can be used to make biodiesel from oil tropical almond seed.

2. H_0: Heterogeneous bifunctional catalyst cannot be synthesized from NaOH and kaolin to produce biodiesel from oil of tropical almond seed.

   H_1: Heterogeneous bifunctional catalyst synthesized from NaOH and kaolin can be used in producing biodiesel from tropical almond seed oil.

3. H_0: The heterogeneous bifunctional catalyst cannot be employed in optimizing process conditions for producing biodiesel from oil of tropical almond seed.

   H_1: The heterogeneous bifunctional catalyst can be employed to optimize process conditions for producing biodiesel from oil tropical almond seed.

5

Significance of the Study

Because of the difficulties in forecasting the future reserves of fossil fuel, sustainable energy has assumed the lead in delivering future fuels. It is envisaged that the findings of this study would lead to the growing of the tropical almond (*Terminalia catappa*) plant.

Additionally, this study is anticipated to lower emissions of greenhouse gases and provide societal frameworks for the development of sustainable fuels, especially in developing nations. Through this study, it will be possible to strike a balance between economic development, environmental protection, and agriculture. Furthermore, because biodiesel is a superior lubricant to fossil diesel, it will minimize long-term engine wear in combustion engines by enhancing the lubricating qualities of blended diesel fuel.

Organization of the Study

There are five chapters in this thesis. The introduction, which is covered in Chapter one, comprises the background, problem statement, hypotheses, significance of study, and objective (s). Second chapter is devoted to literature review on biodiesel. The third chapter is on materials and methods employed. The analysis and discussion of the findings are in chapter four. Conclusions and recommendations are covered in chapter five.

6

CHAPTER TWO

LITERATURE REVIEW

Introduction

In recent decades, the need for energy has risen globally. According to 2017 report from the United States Energy Information Administration's (EIA), there will be a 28% increase in global energy use between 2015 and 2040, indicating that this trend will continue. In 2018, global primary energy consumption increased by 2.9%. A total of 32% in terms of global final energy consumption in 2017–2018 came from the transportation sector, and fossil fuels accounted for 96.7% of this total. Global greenhouse gas emissions tied to energy account for over a quarter of all emissions in 2019 were attributed to the transportation industry. The surge in petroleum and other fuel use worldwide is mostly being driven by the transportation and industrial sectors. Even though there are less fossil fuel reserves, they still provide the majority of the energy used in the transportation industry (Johnston & Holloway, 2007; Razzaq *et al*., 2022).

Governments and reseachers are under pressure to find substitute fuel sources for traditional ones as a result of the rising worries about the environmental impact and energy needs. Liquid biofuels made from biomass may be the greatest short-term replacement for fossil fuels, yet they are also contributing to an increase in oil prices (Hickey, 2017; Ingeborgrud, 2019; Mutezo & Mulopo, 2020).

7

Fossil fuel still comes out on top in Africa, the Americas, and Europe, but in the Gulf region and the Commonwealth of Independent States, natural gas is dominant. The most prevalent fuel throughout the Asia-Pacific region is coal. It is becoming more and more crucial to switch from fossil fuels to more environmentally friendly ones and maximize the usage of renewable ones to aim at decreasing greenhouse gases emission and increase the security of the energy supply (Atabani *et al*, 2012). Increasing the utilization of biofuels as an alternate form of energy is one strategy to reach the suggested goals.

The benefits of biodiesel, such as its affordability, reusability, safety, and low pollution level, have led to an increase in its use in recent years. Due to its identical physicochemical features to petroleum diesel, it may be used in vehicle engines without endangering the environment (Alajmi *et al*., 2017; Wakil *et al*., 2015).

Sources of Renewable Energy

Renewable energy sources, widely referred to as alternative sources of energy, are sources that have the potential to produce energy repeatedly. Examples include wind, solar, geothermal and biomass energies. It is possible for renewable energy sources to deliver required energy with virtually minimal or no air pollution or releases of greenhouse gases when they are used to address home energy needs. Improvements in energy supply dependability and organic fuel efficiency are two of the most pressing issues that may be solved with the development of renewable energy systems (Panwar *et al*., 2011).

8

Biofuel

An eco-friendly replacement for fossil fuels are biofuels, which are fuels produced from biomass. Many of them may be utilized in the transportation industry, including biodiesel (a fatty acid methyl ester of diesel specification created from oils of animal fat, vegetable, or waste cooking oils,), bioethanol (ethanol derived from biodegradable or biomass portions of garbage), biogas, bio-methanol, and biohydrogen are fuel generated using biomass or the organic fraction of trash that may be refined to purity of gas and oil and used as biofuel or wood gas, methanol, and hydrogen, respectively (Ramos *et al*., 2019). The two biofuels that are most used in this industry are bioethanol, which may be used to replace gasoline, and biodiesel, which can be used to replace diesel. There are other biofuels that are utilized as well, although they have less market access.

Biodiesel

For the transportation sector, biodiesel offers a probable reduced-carbon and sustainable substitute for fossil diesel. Biodiesel is completely miscible, allowing it to be used either alone or in mixture with fossil diesel. The notation Bxx is used to identify biodiesel blends, with xx standing for the mixture's composition. B$_{100}$ denotes 100% biodiesel, whereas a B$_{80}$ mixture is composed 20% petrol diesel and 80% biodiesel.

In order to produce biodiesel, a variety of feedstocks can be used. Vegetable oils notably palm oil, rapeseed and soybean dominate the global biodiesel market to this day. Soybean oil makes for the majority (52% of all

9

biodiesel feedstocks) used in the United States, followed by 13 % each of maize and canola oils. In 2017, rapeseed oil accounted for 45% of the overall production in Europe and was the primary feedstock used. Waste cooking oil was in second place with 21 %, followed by palm oil in third place with 18% (Phillips *et al*., 2018). Because it is more expensive than petroleum-based gasoline, biodiesel has a limited market. About 70–95 % of the overall manufacturing costs are made up of the price of raw materials (Bankoviˊc-Iliˊc, 2014).

Advantages and disadvantages of biodiesel

Major advantages and disadvantages of utilizing biodiesel as replacement for diesel fuel are in Table 1 below.

Table 1*:* Advantages and disadvantages of biodiesel (Islam & Ravindra, 2016; Mahmudul *et al*., 2017; Romano & Sorichetti, 2011)

Advantages	Disadvantages
• Biodegradable	• Higher cloud and pour point
• Safer to handle	
• Non-flammable and low toxicity	• Lower calorific value
• Emissions of CO_2, SO_2, CO, particulate matter and hydrocarbons, as compared to diesel are lower	• Less oxidative stability and high viscosity
	• Higher emissions of nitrous oxide (NOx) in some cases
• Higher combustion efficiency, availability, and renewable	• Biodiesel corrodes copper and brass
• Higher flash point and cetane	• It causes excessive engine

10

number	wear
• Excellent properties as a lubricant	• Usage in pure form degrades natural rubber and plastic gaskets and hoses
• Easy to blend with diesel fuel in any ratio	
• Engine modification not required up to B20	

Properties of Biodiesel Fuel

Any fuel designed for use in an engine must typically satisfy a variety of checks and adhere to specific standards in order to maintain their quality (Babajide *et al*., 2011). The feedstock used for producing biodiesel has a considerable impact on the content and properties. Below are few indicators according to the most recent biodiesel requirements noted and explained. Biodiesel properties including melting point, viscosity, cetane number, and heat of combustion have been seen to rise with an increase unsaturation degree and carbon number, demanding improvement by supplementing source oil crops with appropriate fatty acids by genetic modification (Lee *et al*., 2009).

Flash point

It denotes temperature at which the vapour above a fuel ignites. With a flashpoint range of 50 to 80 ^{o}C, diesel fuel made from petroleum is safe and reliable. When compared to other commonly used diesel fuels, biodiesel poses a significantly lower danger of fire due to its flashpoint of more than 160 ^{o}C (Babajide *et al*., 2011).

Cetane number

It assesses a fuel's self-igniting ability after injecting it into a diesel engine. Most refineries generate diesel with cetane values between 40 and 45, which is necessary for diesel fuels to attain a cetane value greater than 40. The higher the cetane number of biodiesel, depending on the raw material utilized, which varies from 46 to 60, the shorter the engine's ignition lag and better the burning properties (Babajide *et al.*, 2011).

Viscosity

In contrast to diesel fuel, waste and plants oils have greater viscosities; nevertheless, when turned into biodiesel by transesterification significantly lowers the viscosities. As one of the requirements to meet when generating biodiesel, viscosity measurement is a fundamental characteristic that reflects the extent of the reaction. It also serves as one indication to assess the efficiency and thoroughness of the conversion process because it is connected directly to the methyl ester content of the product of transesterification (Babajide *et al.*, 2011).

Sulphur content

Sulphur concentration of fossil diesel, since 2005 has been required to be less than 50 parts per million (ppm), because higher Sulphur concentration in fuels is linked to harmful health impacts and increased in vehicle servicing frequency. Waste vegetable oil derived biodiesel may include some levels of sulphur and must be tested to ensure it is below permissible limits whereas

12

new vegetable oil derived biodiesel is considered primarily to be sulphur-free (Mittelbach and Remschmidt, 2006).

Heat of combustion

The source of oil influences the heating of combustion of biodiesel, often termed as heat of combustion. Since it is denser than petroleum diesel, biodiesel has a calorific value that is 13% greater on bases of mass but only 8% fewer in terms of volume. As a result, engines using biodiesel have less torque and power for same volumes injected (Babajide *et al*., 2011). By changing the injection volume for biodiesel, almost equivalent power and torque may be generated. The motors of flexi-fuel cars incorporate intelligence that can recognize fuel type being used (conventional diesel, blend or biodiesel), and it instantaneously modifies its injection specifications (Mittelbach and Remsmidt, 2006). Whenever applying biodiesel, increasing the injection volumes results in somewhat greater specific fuel usage. It is vital to remember that the parameters listed above are for pure biodiesel. If biodiesel is mixed with petroleum diesel as low as 5 % or 10 %, the qualities of the petroleum diesel are not significantly altered (Babajide *et al*., 2011). Even at extremely low proportions, the biodiesel's lubricity property, which makes it an excellent supplement for diesel fuels is the only one that has an impact.

Feedstock for biodiesel production

Oils from vegetable (both non-edible and edible), algae, waste cooking oil and animal fat, are all possible feedstocks for synthesising biodiesel.

13

Animal fats and vegetable oils have identical composition chemically, with triglycerides dominating and a lower proportion of diglycerides and monoglycerides. A triglyceride is created by joining three molecules of either unsaturated or saturated fatty acid with one molecule of glycerol. Biodiesel may be divided into three groups according to their feedstock: 1st, 2nd, and 3rd generation (Ramos *et al*., 2019).

The term "first generation" describes biodiesel made from edible oils including palm, sunflower, soybean, rapeseed, coconut, and peanut oils which are the most widely utilized. Using vegetable oils to produce biodiesel is very simple and generally available. However, using edible vegetable oils to make biofuel presents several ethical considerations. From agricultural crops come edible vegetable oils. Using of fertilizer, arable lands, and water in "producing fuel" rather than food impacts both sustainability concerns and the price of food. Additionally, even if all edible oils were utilized to make biodiesel, it would not be sufficient to fulfil the need for diesel today. These worries combine with the fact that waste-derived biofuels are doubly counted, which has increased interest in more environmentally friendly feedstocks (Knothe & Razon, 2017; Ramos *et al*., 2019).

The term "second-generation" refers to biodiesels produced using non-food plants or bioproducts that were previously used for food, such as used animal fats, cooking oil, or oily refinery streams. Non-edible plants can be planted more economically because they are usually grown on land that cannot be used for plants that require less water and fertilizer to grow. Waste cooking oils refer to animal and vegetable oils that have been used to cook various

14

kinds of food. Various chemical reactions, including oxidation, hydrolysis and polymerization take place throughout the cooking process, altering the physical and chemical characteristics of fat and oil. Recycled fat can be classified as yellow fat or brown fat based on free fatty acid contents. While brown greases have free fatty acid level greater than 15 %, yellow greases have less than 15 %. Utilizing these less expensive feedstocks lowers production costs and allows for the recycling of trash without entering the food market (Ramos *et al*., 2019; Živkoviˊc *et al* 2017).

Biodiesels made from algal biomass are third generation. The chemical and physical characteristics are the same for biodiesel regardless of the kind of feedstock utilized (Ramos *et al*., 2019).

Tropical Almond Plant

The tropical almond (*Terminalia catappa* L.) tree, of the family *Combretaceae*, is mostly found in the subtropical and tropical climates (Anand *et al*., 2015). In Ghana, it is known as "Abrofo Nkatie" or tropical almond or Indian almond.

The tree may reach a height of 20 to 45 meters and can withstand wind, salt, and drought. It bears fruits with a huge fibrous nut that encloses the seed and a thin fleshy ring around it. The *Terminalia catappa*'s fruit is a seedpod with a mushy mesocarp and a hardened endocarp that resembles a stone which contains the kernel. It is reported that Malaysia is where the plant originated. Tropical Asia is the natural home of *Terminalia catappa*. In order to decorate the cities, it was brought to Cote d'Ivoire during colonialism

15

(Biego *et al*., 2012). The fruit ranges in size from 3.05 to 5.84 cm, is fleshy and delicious, and has a single seed within. When the fruit is unripe, it is greenish, and when it is mature, it becomes yellow or red. The fruit contains a husk, a hard endocarp that envelopes an edible nut, a pericarp that is spongy and fibrous, an outermost layer that is relatively thin and smooth, and all these structures are present (Thomson and Evans, 2006).

The fact that the nuts are generally tiny and challenging to remove may have led to their widespread lack of usage. Sun-dried seeds produce 38 to 54 % yellow, tasteless oil which can be consumed, but which turns cloudy when left undisturbed. In some regions of South America, the oil is utilized in cooking. As for the nuts, they can either be eaten right away after being removed from the shell, or they can be dried or smoked and eaten up until a year after. The bark, leaves, fruit shells, roots, and trunks of the plant are among the other components utilized for medicinal and other non-food reasons. Tropical almond seeds, for example, have a large quantity of oil that may be used to make biodiesel as replacement for petroleum-based fuel (Orhevba *et al*., 2016).

The oil output from tropical almond seed is around 60.0 % (Esonye *et al.*, 2016). Since biofuels can be derived from sustainable resources, establishing technologies to manufacture them should guarantee both a sufficient supply of fuel for transportation in the future and provide security against the uncertainties surrounding the timing for the discovery of new petroleum resources. Seeds of tropical almond trees, having high content of

16

oil, can be utilised to make almond oil (Abu-Hamdeh & Alnefaie, 2015; Davis & Iwahashi, 2001).

Economic and health benefits of oil from tropical almond seed

Tropical almond is nutritional powerhouse with its oil packed with several of helpful nutrients that had contributed to its economic and health importance. Some health benefits are as follows: anti-hepatotoxicity and inflammatory effects, its omega-3 fatty acid content helps improve memory, acts as good skin moisturizer, anti-fungal properties, its antibacterial and vitamin A content treat acne. Some of the economic importance include the following: its application in the pharmaceutical and cosmetic industry (soap, hair cream, massage oil), food industry (food flavour, cooking oil) and bioenergy industry for producing biodiesel (Akubude *et al*., 2020).

Biodiesel Production Process

Biodiesel is being promoted as a viable, sustainable, and less-carbon for the transport industry as alternative to fossil diesel (Ramos *et al*., 2019). Because it is completely miscible with petroleum diesel, biodiesel may be utilized either alone or in combination with petroleum diesel. The following procedures are used in producing biodiesel;

Direct blending

For usage in diesel engines, oils from vegetable are utilized as fuels or combined with petroleum diesel. The fact that these oils often exhibit 10 to 20 times more thicknesses than that of conventional diesel presents a number of

17

challenges, though. This characteristic results in poor fuel atomization, inefficient combustion, and a propensity for thermal and oxidative polymerization, which causes deposits to accumulate on the injector nozzles. Only by tailoring the gasoline to the engine and vice versa can this problem be resolved (Babajide *et al*., 2011).

Additionally, if sufficient atomization is to be performed, vegetable oil between 0 – 34 % would be needed when combining petroleum diesel with vegetable oil. It is possible to utilize biodiesel in its purest state, commonly referred to as tidy biodiesel or B_{100}. This method offers the greatest decrease in carbon monoxide, unburned hydrocarbons, and exhaust particles. Additionally, it is the ideal technique to use biodiesel when its biodegradability and lack of toxicity are crucial. Even though it wouldn't be envisaged that pure biodiesel would present any functional challenges, because some elastomers are incompatible with it, difficulties with varnish deposits in fuel tanks and fuel line deterioration might arise due to its solvent qualities, which are at their peak. It could result in paint fading close to gasoline fill ports (Babajide *et al*., 2011).

Micro-emulsification

Replacement for diesel engines fuels have been proposed in different forms of variations, including microemulsions or mixtures of different vegetable-based oils with regular diesel. As one of the four potential options for reducing vegetable oil viscosity, the creation of microemulsions (co-solvency) has been researched, and several researchers have shown that straight vegetable oil and alcohol micro-emulsions is not advised to be utilised

18

in diesel engines over a lengthy period for the same reasons. These fuels can burn inefficiently, accumulate combustion by-products, and have their lubricating fluid viscosity increase (Mittelbach and Remschmidt, 2006).

Pyrolysis

Fat pyrolysis has been used for more than a century, mostly in regions of the world without access to fossil fuels. Pyrolysis refers to heat degradation processes that typically take place without oxygen. Alkenes, alkanes, alkadienes, aromatics, and carboxylic acids are produced as a consequence of this process, which is comparable in many ways to diesel fuel made from hydrocarbons but with higher cetane numbers for the utilized oils and acceptable quantities of sulphur, water, and silt. But by today's standards, the fuels' viscosity is excessively high, their ash and carbon residues are much higher than those found in fossil diesel, and the resultant fuel has poor cold flow characteristics (Babajide *et al*., 2011; Knothe and Steidley, 2005). One main advantage of oxygenated fuel for the environment has been said to be negated during this process by the oxygen removal.

Transesterification

Transesterification of triglycerides (TG) is done with alcohol, most often methanol, to yield biodiesel in the company of an alkaline or acidic catalyst. It may also be made using a variety of various procedures, which will be discussed more below. As illustrated in Figure 1, three sequential reactions occur with the synthesis of diglycerides and monoglycerides intermediaries during transesterification processes of source triglyceride, leading to three

19

moles of fatty acid methyl ester and one mole of glycerol production from one mole of triglyceride (Babajide *et al.*, 2011).

$$
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - O - COR^2 \\
CH_2 - O - COR^3
\end{array}
+ CH_3OH \rightleftharpoons
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - O - COR^2 \\
CH_2 - OH
\end{array}
+ R^3 - COOCH_3
$$

(1)

$$
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - O - COR^2 \\
CH_2 - OH
\end{array}
+ CH_3OH \rightleftharpoons
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - OH \\
CH_2 - OH
\end{array}
+ R^2 - COOCH_3
$$

(2)

$$
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - OH \\
CH_2 - OH
\end{array}
+ CH_3OH \rightleftharpoons
\begin{array}{l}
CH_2 - OH \\
CH - OH \\
CH_2 - OH
\end{array}
+ R^1 - COOCH_3
$$

(3)

$$
\begin{array}{l}
CH_2 - O - COR^1 \\
CH - O - COR^2 \\
CH_2 - O - COR^3
\end{array}
+ 3CH_3OH \rightleftharpoons
\begin{array}{l}
CH_2 - OH \\
CH - OH \\
CH_2 - OH
\end{array}
+ 3R - COOCH_3
$$

(4)
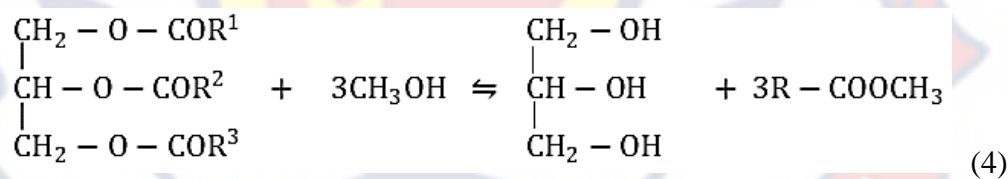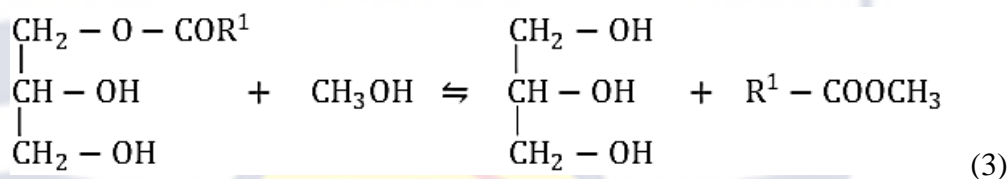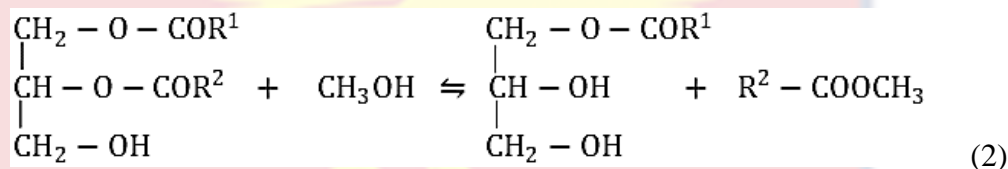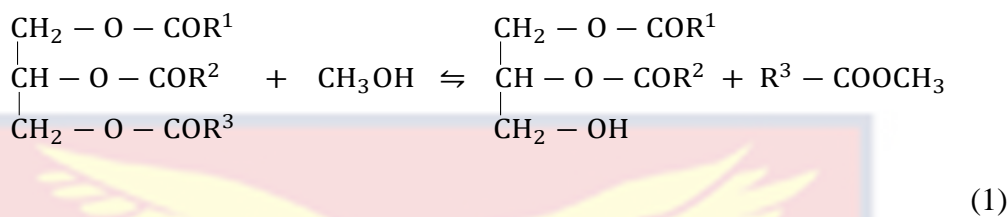
Triglyceride (TG)   *Alcohol*   *Glycerol*   *Methyl ester*

Figure 1: Process diagram for triglyceride transesterification with methanol (Babajide *et al*., 2011; Maa & Hanna, 1999)

Reaction parameters influencing the transesterification process

To make vegetable oils less viscous and more suited for use as fuel, transesterification has been frequently employed. However, various

20

parameters including alcohol-to-oil ratio, temperature, stirring speed, free fatty acid level, presence of water, catalysts, and time all have a substantial impact on the transesterification reaction.

Reaction temperature

Biodiesel yield is affected by reaction temperature, which is a significant component (Leung & Guo, 2006). Higher reaction temperatures, for example, accelerate the reaction rate while time is reduced owing to viscosity decrease. However, increasing the temperature above the recommended range reduces biodiesel yield as higher reaction temperature increases triglyceride soap formation. Alcohol evaporation can be avoided by keeping transesterification temperature less alcohol's boiling point. Based on the oils or fats employed, between 50 °C and 60 °C is the optimum temperature range (Mathiyazhagan & Ganapathi, 2011).

Reaction time

Fatty acid esters are converted more quickly as reaction time increases. The reaction takes longer than expected at initially stage when alcohol and oil are integrating and dispersing. The response then moves along quickly. However, it took just around 90 minutes to reach the maximal ester conversion. Further extending the time does not increase the methyl ester yield (Alamu *et al*., 2007; Leung & Guo, 2006). Additionally, extended time of reaction decreases final biodiesel yield as transesterification reaction is a reversible one that causes ester loss and soap production (Mathiyazhagan & Ganapathi, 2011).

21

Alcohol-to-oil ratio

An essential variable in biodiesel production is alcohol-to-oil ratio (Leung & Guo, 2006). Typically, three moles of alcohol to one mole of triglyceride are needed to undergo the transesterification process to produce three moles of methyl ester and one mole of glycerol. Utilising alcohol in excess speeds up the process by which lipids form esters. As a result, up to a specific percentage, the production of biodiesel increases as the concentration of alcohol increases. However, further boosting the alcohol level decreases biodiesel production and add up to the recovery cost of alcohol (Leung & Guo, 2006). Additionally, the alcohol concentration may change depending on the kind of catalyst being used; for example, when using an alkali catalyst, 6:1 ratio of alcohol-oil is necessary for fats or oils transesterification. Base catalysts will not be suitable to catalyse reaction of oil samples with higher free fatty acids (FFAs) concentrations. In this situation, an acid catalysis will be effective for the reaction because it involves more alcohol than a base catalyst does. This is so because both water and FFAs are tolerated by the acid catalyst when used with oil samples. After being subjected to an acid catalyst reaction, used cooking oil, for instance, a greater alcohol ratio, such as 15:1, is needed (Leung & Guo, 2006; Mathiyazhagan & Ganapathi, 2011).

Water and free fatty acid content

Water and free fatty acids (FFAs) contents play significant part in the transesterification process. Feedstocks with low acid value (<1) and the absence of water are required for base-catalysed transesterification for biodiesel production (Demirbas, 2009). Base catalysts greater than one percent

22

are required to neutralize oil samples with high FFAs levels. Since water results in soap production and foaming, which increases viscosity, its presence has a more detrimental impact than FFAs do. Glycerol extraction from biodiesel is further complicated by the development of gels and foams. During transesterification, free fatty acids and water generally have an adverse effect by reducing methyl ester production leading to the creation of soap and catalyst consumption, which lessens the catalyst's effectiveness (Kusdiana & Saka 2004). The supercritical methanol approach, which was compared to acid and base-catalysed methods and required 623 K, 43 MPa, and four minutes treatment time, was presented as a solution to this issue. It should be emphasized that the supercritical methanol approach is less affected by water (Mathiyazhagan & Ganapathi, 2011).

Reaction speed

The production of the final product (mono alkyl ester or biodiesel) depends significantly on the reaction's speed since stirring the oil and catalyst mixture speeds up the process. For instance, while keeping all parameters constant, the mixing intensities used were 200, 400, 600, and 800 rpm for 60 min. A greater conversion of the finished product was attained at 400 rpm. lower stirring speed indicates reduced product production, for this reason. On the other side, increased stirring speed promotes soap production. This is a result of the transesterification process acting in reverse (Mathiyazhagan & Ganapathi, 2011)

23

Catalyst type and amount

Transesterification requires catalysis to quicken the reaction rate. A catalyst is anything that speeds up a process without being consumed. A homogeneous catalyst is one that operates within identical phase as the medium of the reaction. However, if the catalyst functions in distinct phases, the catalyst is referred to as heterogeneous (Borges & Díaz, 2012: Shahid & Jamal, 2011). The two interface is where the chemical reaction takes place in this situation. (Ramos *et al*., 2019).

The nature of the catalysts determines whether they are basic, acidic, or enzymatic. Compared to the heterogeneous ones, homogeneous catalysts provide better yields and conversions in less time. Sodium hydroxide (NaOH) as well as potassium hydroxide (KOH), which are both highly dissolvable in methanol, are now the most often used homogeneous basic catalysts in the biodiesel sector (Ajala *et al*., 2017). The benefit of homogeneous basic catalysts over homogeneous acid ones is the higher biodiesel yield produced in a limited time and under comparatively mild working conditions. The use of such catalytic systems with poor grade fat raw materials, which have high moisture and percentage of FFA, is not recommended since high purity feedstocks are necessary.

Homogeneous catalyst process

Acid-catalysed process

Transesterifications with acid as the catalyst progress more slowly than those with alkali processes, necessitating increased temperatures, pressures,

24

and alcohol concentrations, but they have the benefit of converting free fatty acids found in fat and oil. Therefore, this method is particularly well adapted for transesterification of fatty substances that are extremely acidic, such as used cooking oil. Additionally, it facilitates the synthesis of long and branched chain esters, which is challenging for alkaline catalysis, while water in the reaction mixture is utterly unfavourable in acid catalysis (Babajide *et al*., 2011). Acids such as sulfuric or sulfonic can catalyse transesterification. Alkyl esters are produced in extremely high amounts by these catalysts, despite the reactions being slow and frequently take longer than three hours to complete (Paintsil, 2013). Carbonyl protonation leads in the production of a carbocation in the very first step. In the subsequent phase, alcohol is subjected to a nucleophilic attack, resulting in a tetrahedral intermediate that removes glycerol to create new ester IV and renewing the H^+ of the catalyst. Water and carbocation II in the reaction mixture react via this process, which can lead to the production of carboxylic acids. Accordingly, it is recommended that transesterification using acid-catalyst be undertaken without the presence of water to avoid producing of carboxylic acids in a competitive environment, which would otherwise lower methyl ester yields (Meher, 2006).

Base-catalysed process

Vegetable oil transesterification that is base-catalysed occurs more quickly than processes that are acid-catalysed. Industrial processes often choose base catalysts, such as hydroxides and alkoxides of alkaline metal as well as carbonates of potassium of sodium, since they are less corrosive than acidic compounds. Figure 2 is a description of the base-catalysed

25

transesterification mechanism (Paintsil, 2013). An alkoxide is produced in the

first stage by the reaction of a base with alcohol using a protonated catalyst.

$$ROH \quad + \quad B \quad \rightarrow \quad RO^- \quad + \quad BH^+ \tag{1}$$

$$\tag{2}$$

$$\tag{3}$$

$$\tag{4}$$
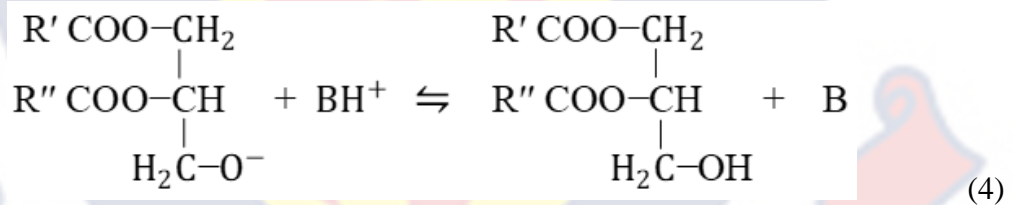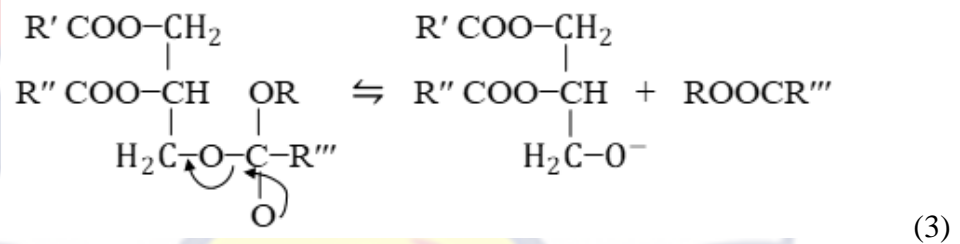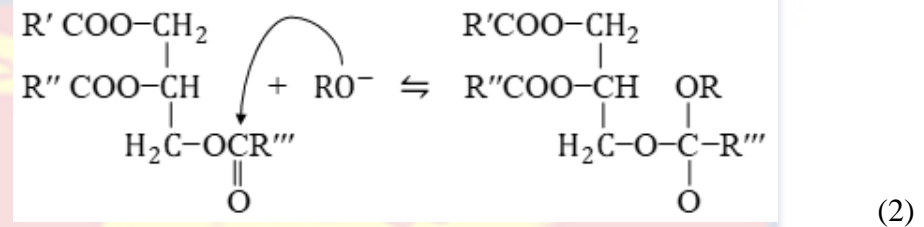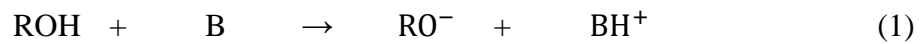
Figure 2: Base-catalysed oil transesterification mechanism

An alkyl ester and its associated anion are produced in a second step,

which involves the alkoxide ion attacking the carbonyl carbon of the

triglyceride through a nucleophilic attack. In the final stage, the catalyst is

deprotonated, which regenerates the free radical and enables it to interact with

an additional alcohol molecule to initiate a fresh cycle. The same technique is

26

used to convert diglycerides and monoglycerides into a mixture of alkyl esters and glycerol.

The most effective catalysts for methanolysis are alkaline metal alkoxides like CH_3ONa because they provide extremely high yields (up to 98 %) in a short amount of time (30 min), even when used at low molar concentrations (0.5 mol %). However, they are unsuitable for standard industrial procedures since they need the absence of water. Although less active than metal alkoxides, alkaline metal hydroxides (NaOH and KOH) are less expensive. They are still an excellent option, though, as they can produce biodiesel with the same high conversion rates by simply raising the concentration of catalyst to 1.0 or 2.0 mol %. The alcohol and hydroxide reaction results in the production of some water in the system, even when an alcohol-oil mixture devoid of water is utilized. Water causes some of the generated ester to hydrolyse, which leads to the creation of soap (Paintsil, 2013).
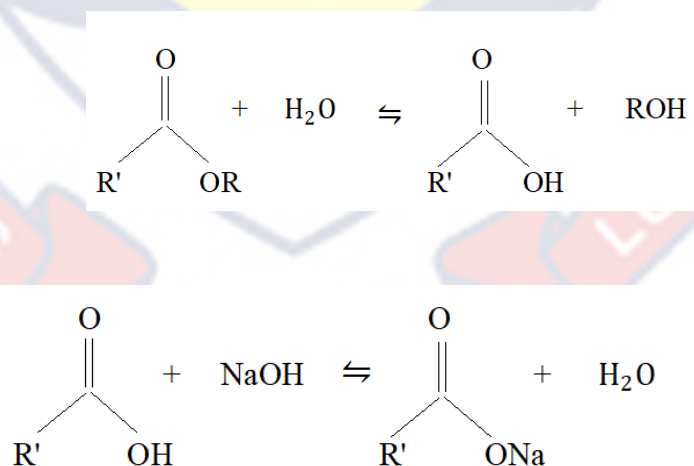
R = alkyl group of the alcohol R' = carbon chain of fatty acid

Figure 3: Ester hydrolysis and further reactions to form soap

27

The amount of diffused methyl esters in the glycerol phase is reduced when KOH is utilized instead of NaOH as the catalyst in during transesterification. This phenomenon lowers the propensity for soap production and hence lowers ester losses. In contrast to the higher percentage of methyl esters (around 6 %) inside the glycerol phase for the NaOH-catalysed process, Vicente *et al*. (2004) found that KOH-catalysed transesterification of sunflower oil revealed just 3% methyl ester dissolves in the glycerol phase. Significant benefit of this technique is the quick segregation of the glycerol phase, which allows for the simple removal of majority of the catalyst from the reaction medium as the first formed esters will scarcely come into contact with the hydroxide. KOH has a favourable behaviour when employed as catalyst in place of NaOH, a larger molecular weight than NaOH, which speeds up phase segregation by making the glycerol layer increase in density. The ability to produce potassium dihydrogen phosphate, a fertilizer, by adding phosphoric acid to the alkaline glycerol phase is another benefit. The addition of fertilizer increases the value of the by-products, while sodium salt produced when NaOH is used as a catalyst is regarded as a waste product. (Mittlelbach and Remschmidt, 2006). As a last point, it should be noted that transesterifications catalysed by sodium hydroxide tend to be performed more quickly and at a lower cost than those catalysed by potassium hydroxide. The result of the reactions using homogeneous alkaline catalysts to produce biodiesel requires centrifugation and water washing to remove contaminants, which is a significant disadvantage.

28

Enzyme-catalysed process

Lipase-catalysed reactions, for example, provide benefits over the techniques already stated, such as the production of no waste products, simplicity of product recovery, lenient reaction settings, catalyst recycling, and resistance to water content and FFAs in used frying oil (Babajide *et al*., 2011). Substantial yields and mild temperatures are achieved by enzyme-based transesterification, but this process is not currently employed on larger scale because of the high enzyme cost and issues with their deactivation brought on by feed contaminants. However, utilization will be feasible if prices of enzyme are decreased, as used for dairy products, detergents, leather, and textile processing. Enzymes can be used heterogeneous catalyst by adsorbing on a support. Pure triglyceride enzymatic alcoholysis has been extensively documented in literature both with and without the use of a solvent (Jigajinni & Meti., 2021; Kumari *et al*., 2009; Panichikkal *et al*., 2018).

Heterogeneous catalyst process

While traditional homogeneous catalysis has a lot of benefits, one significant drawback is that homogeneous catalysts cannot be recycled (Babajide *et al*., 2011). Additionally, the ester product must have the catalyst residues removed, which necessitates many washing procedures and produces an unnecessarily large volume of waste water. These elements contribute to higher manufacturing costs in this procedure. The ability to be recycled and easily segregated from the reaction medium are two benefits of heterogeneous (solid) catalysts. Therefore, heterogeneous catalysis is viewed as a green process. An intriguing possibility to lower the expenses associated with

29

isolating and cleansing of reaction products is the heterogeneous transesterification of oils. High yields of methyl esters are produced, greatly simplifying the purification processes of the products (Cao *et al*., 2008). The efficiency of heterogeneous catalysts has been observed to be relatively low compared to frequently used homogeneous catalysts because heterogeneous catalysed transesterification processes often demand more harsh operating conditions such as relatively increased temperatures (Refaat, 2010).

Another significant issue with heterogeneous catalysts is the gradual loss of activity that results from a variety of potential processes, including, leaching, coking, and poisoning (Sivasamy *et al*., 2009). A deeper comprehension of the variables that control their reactivity is necessary for the application of solid catalysts in producing biodiesel. The chosen catalysts must, in general, have a certain characteristic that includes, able to catalyse both esterification and transesterification, does not leach, be stable, not being affected by water, have a high degree of selectivity and be active at low temperatures (Di Serio *et al*., 2008). Understanding the relationships between catalytic activity and basic and acidic strength is critical for improving the efficiency of catalysts. Additionally, it is apparent that the surface of these heterogeneous substances needs to have certain hydrophobic properties to encourage the preferred deposition of triglycerides and prevent inactivity of catalytic sites by significant accumulation of by-products which are polar like glycerol and water (Babajide *et al*., 2011).

Zeolites

The general name used to designate a group of minerals known as the tectosilicates is zeolite. Their typical formula is M x/ n [(AlO$_2$)xSiO$_2$)y], and they are composed of oxygen-bonded tetrahedral SiO$_4$-4 and AlO$_4$-5 molecules. The anion charge of the framework in zH$_2$O is balanced by an extra frame work cation. These minerals have a vast surface area due to their small pores. By varying the composition, pore size, silica-to-alumina ratio, and density of zeolites, unique materials may be created. To get certain catalytic capabilities, other metals can be added into zeolites (Lee *et al*., 2007).

Transesterification processes have also been investigated using zeolite catalysts (Georgogianni *et al*., 2009; Xie and Huang, 2007) which have garnered a lot of attention when solid base catalysts were being made. Due to their micro - porous architectures, ordinary zeolites are limited in their ability to transfer mass, but zeolite-X, one of the most fundamental zeolites, has gained interest for use in the biodiesel synthesis process. Through the degradation oxides of alkali metal in zeolite framework and the alkali ion exchange, the catalytic activity and basicity of these zeolites may be altered. It has been observed that adding alkali oxides to pore cavities and exchanging bigger monovalent cations like K with Na-X can significantly boost its basic strength (Lee *et al*, 2009). Elemental structure, pore size distribution, and charge carrier capacities of zeolites contribute to their varied catalytic activity. The ratio of Si/Al of the primary framework of zeolite, the types and amounts of cations charge carriers, determine the acid-base characteristics of zeolites. Two methods often used to adjust the basicity of zeolite are: impregnating

31

basic materials on the internal layer of the zeolite pores and alkali metal ion exchange (Kim *et al*., 2004).

Metal oxides

Oxides of alkali earth metals, mixed metals, transition metals, and supported metals are only a few of the metal oxides that have been researched for oil transesterification. Due to their acidic/basic characteristics, of transition metal oxides such as titanium oxide, zirconium oxide, and zinc oxide, have drawn interest for the generation of biodiesel. (Zabeti *et al*., 2009). When utilized to catalyse esterification and transesterification at the same time, these catalysts demonstrated good catalytic activity and high stability. However, they are not widely utilized in industrial production processes, mostly due to the expensive cost of the catalysts and the challenges associated with filtering the tiny catalyst particles. Due to its poor solubility in methanol, calcium oxide has a comparatively high basic strength and minimal negative environmental effects. Comparing calcium oxide to KOH or NaOH will likely result in equivalent efficiency with the added benefits of simple recovery of products, better treatment, and an ecologically friendly method. (Refaat, 2010). According to Kouzu *et al.* (2008), homogeneous catalysis employing sodium hydroxide and calcium oxide (CaO) were both used to transesterify soybean oil with methanol. Results obtained showed that FAME was converted absolutely in both situations. According to Takase *et al*. (2014), the production of biodiesel from oil of *S. marianum*, a prospective new non-edible feedstock that might benefit the biodiesel business since its biodiesel can be evaluated as

32

a viable alternative fuel, can be catalysed by zirconia modified with KOH (32%KOH/ZrO2-5).

Kaolinite

Clay catalysts are widespread, eco-friendly, inexpensive, and reusable. Clay substance known as kaolin has several industrial uses, including cement, paper coatings, plastic fillers, paint extenders, decolorization, photocatalysis, decolorization, adsorption, and ceramics. (Abd El-Aal *et al*., 2022).

The clay mineral kaolinite has the formula $Al_2Si_2O_5(OH)_4$, and it has a two-layered crystalline structure made up of alternating layers of alumina octahedral layers and silicon-oxygen tetrahedral layers. $Al (O, OH)_6$ and SiO_4 octahedral and pseudo-hexahedral sheets with pseudo-hexagonal symmetry make up the 1:1 sheet structure of kaolinite. The planes that are occupied as O_6-Si_4-O_4-$(OH)_2$-Al_4-$(OH)_6$ generate the sheets (Ramirez-Ortiz *et al*., 2012).

Because of its drawbacks, including impurities, poor surface area, acidity and porosity, kaolinite is not employed as a catalyst directly. There are several ways to increase kaolinite's catalytic activity. Chemical activation, heat and mechanochemical treatment are the three main alteration techniques. (Abd El-Aal *et al*., 2022; Alaba *et al*., 2015).

Chapter Summary

The biodiesel sector must constantly improve on elements that will boost its prospects of production technologies and greater market penetration considering the reviews and discussions offered in this chapter. A brief

33

summary of the manufacture of biodiesel, the feedstocks that are utilized, the

transesterification process, contributing factors, and the various catalysts used

in the transesterification of oils is provided in the review.

CHAPTER THREE

MATERIALS AND METHODS

Biodiesel Production from Tropical almond seed oil by Response Surface Method using NaOH as catalyst

Reagents and Materials

Methanol (99.8 %) purity level and sodium hydroxide (NaOH) were sourced from Department of Laboratory Technology laboratory and kaolin was sourced from the Technology Village in the University of Cape Coast. All reagents used were analytical reagent grade.

Experimental procedure

Sample collection and preparation

Matured ripened fruits of tropical almond were gathered from different locations at Abura Dunkwa in the Central region, Ghana, located between latitude 5°05N and 5°25N and longitude 1°5W and 1°20W. The outer pulp of the fruits was removed manually and they were sun-dried. After that, the dried shells were manually cracked open and the seeds removed. The seeds were thoroughly screened to remove dirt and bad seed and then oven dried at 60 ^{o}C for 12 hours to significantly reduce the moisture content (Agu *et al*., 2022).

35
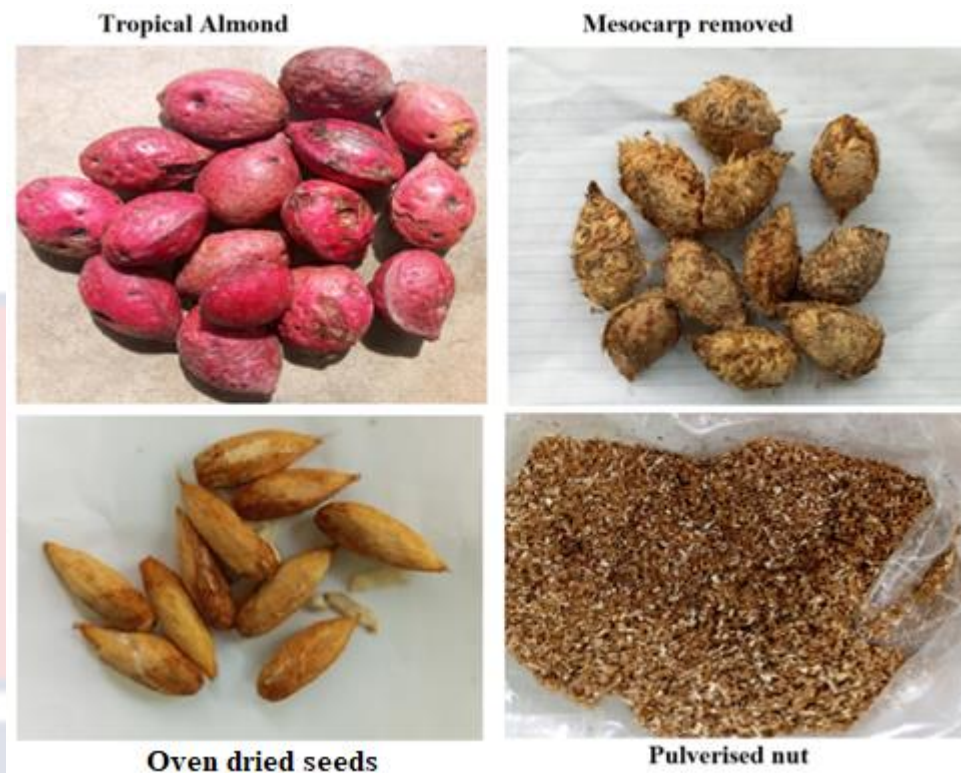
Figure 4: Processing of Tropical almond fruit into pulverised form

Moisture content of seed

Tropical almond seed samples were weighed and recorded as M_1, before being placed in a hot air oven and dried at 60 ^{o}C. The samples were removed after every 12 hours and then weighed until constant mass were determined and recorded as M_2. Using the formula below, the percentage moisture content in the seed was determined:

Moisture content (%) $= \dfrac{M_1 - M_2}{M_1}$ x 100   (5)

Oil extraction from almond seed

Tropical almond seed oil was extracted using a solvent extraction technique. *Terminalia catappa* (tropical almond) seeds that had been oven

36

dried were pulverized using mortar and pestle into tiny pieces. The powdered seed sample was then placed in a filter paper, which was used to wrap the sample as tightly as possible before being neatly stapled. The samples were then carefully placed inside a Soxhlet extractor along with a thimble, and a round bottomed flask fitted to the Soxhlet apparatus was carefully filled with 300 ml of n-hexane before being placed on a heating mantle connected to electrical source. The solvent's temperature was raised to boil, and the regulator was set such that the solvent stood at a temperature range of 50 to 60 ^{o}C where n-hexane could not escape for approximately 4 to 6 hours. (Orhevba *et al*., 2016). The oil was obtained with a rotary evaporator after extraction. The pulverized almond seeds amount utilized was 3640 g. The equation below was utilised determined oil yield.

$$\text{Oil yield } (\%) = \frac{\text{Mass of oile xtracted}}{\text{Mass of crushed seed}} \text{ x } 100 \qquad (6)$$

Tropical almond seed oil and biodiesel characterization

Free Fatty Acid Value and Acid Value

The acid value is a figure that represents how much potassium hydroxide is needed for neutralizing the free acids present in one gram of a material. It is expressed in milligrams. Here, direct titration is carried out using the ASTM D664-06 technique with a neutralized combination of equal volumes of ethanol (95%) as solvent and phenolphthalein as indicator.

10 grams of almond seed oil were diluted in ethanol and titrated with 0.1 moldm^{-3} KOH solution using a few drops of phenolphthalein as an

37

indicator. Titration was carried out three times. Calculated are the mean and standard deviation. The following formulae were used to calculate the acid value and the free fatty acid:

$$\text{Acid value} = \frac{C \times V \times 56.1}{m} \qquad (7)$$

$$\text{Free fatty acid value} = \frac{C \times V \times 28.05}{m} \qquad (8)$$

Where, V is volume (ml) of KOH consumed, m is mass of oil sample (g), molecular weight of KOH (g/mol) is 56.1 and concentration of KOH (mol/ dm^3) is C.

Density

The mass of any liquid per unit volume at a specific temperature is known as density. The term "specific gravity" refers to a liquid's relative density to that of water. This feature is crucial because it affects how well the fuel is atomized and is crucial for calculating cetane number of oil sample (Srivastava & Prasad 2000). Following the ASTM D4052-96 standard of techniques, three replicates were performed to test density of oil sample at 15 °C, and the mean and standard deviation were computed.

Iodine value

Iodine number or value refers to how much gram of iodine is consumed per 100 grams of fat. Larger iodine value is a sign that there is more unsaturation present. Saturated fatty acids are produced when unsaturated ones are hydrogenated. Depending on how unsaturated they are, the fatty acids can

38

react with oxygen or halogens to produce saturated fatty acids. Therefore, it is necessary to understand how unsaturated a fatty acid is. Analysing the iodine content of lipids is one way to assess the degree of unsaturation of fatty acids.

Reacting iodine with fatty acid results in the addition of iodine to the carbon-carbon double bond position to generate iodine monochloride which then reacts with the double bonds in the process to form a single bond of di-halogen, of which an iodine atom is attached to one carbon. When the reaction is finished, the amount of iodine that has reacted is calculated by mixing the reaction result with a potassium iodide solution.

$$ICl \; + \; KI \; \rightarrow KCl \; + \; I_2 \qquad\qquad (9)$$
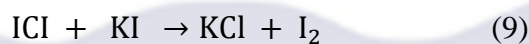
As a result, the remaining unreacted ICl becomes molecular iodine. After the I_2 has been freed, it is titrated using a standard solution of sodium thiosulphate in 0.1N.

$$I_2 \; + \; 2Na_2S_2O_3 \; \rightarrow 2NaI \; + \; Na_2S_2O_4 \qquad\qquad (10)$$
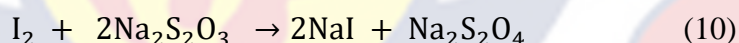
Saturated fatty acids will not undergo the halogenation process. Iodine values between 0 and 70 indicate that it is a fat, and it will be an oil if the value is greater than 70. The freed iodine will react with starch to produce a product that is blue-black in colour, serving as an indication for the reaction so that the endpoint may be seen.

Accurately weighing 0.2 grams of the oil, 20 millilitres of Wijs solution, and 10 millilitres of tetrachloromethane (CCl_4) were combined. Then it was darkened for 30 minutes. The combination was then given 10 ml of

39

deionized water and 15 ml of a 10 % potassium iodide solution. This is then titrated three times against a 0.1 M sodium thiosulfate (VI) solution. Three drops of starch indicator solution were added, and the titration was maintained until the blue colour had almost completely vanished after the yellow colour had nearly completely vanished. 12.69 g of iodine are included in 1 ml of 0.1 M sodium thiosulphate solution. The mass of iodine absorbed by the oil is calculated by multiplying the difference between the control titration and that of titration values with the presence of fat by this factor.

This adhered to the ASTM D5554-95 Standard Methods for Analysis (2006). The iodine value was evaluated using the equation below:

$$\text{Iodine value} = \frac{(B-S) \text{ x N x } 12.69}{Mass\ of\ Oil\ sample\ (g)} \qquad (11)$$

Where S is volume of titration of sample (ml), B is volume of titration of blank (ml), N is normality of $Na_2S_2O_4$ solution.

Saponification

The amount of potassium hydroxide (KOH) required to thoroughly hydrolyse a gram of oil or fat is referred to as saponification value. An excess of a standard alcoholic potash solution is refluxed with a known amount of oil, and the unused alkali is titrated against a standard acid (AOAC, 2000).

2.0 g of the oil was precisely weighed into a conical flask. To dissolve the oil in the flask, 25 ml of alcoholic potassium-hydroxide (0.5 M) solution was then added. For around 30 minutes, the reaction mixture was refluxed

40

using a water condenser on a water bath. The resultant solution was chilled and titrated using 1.0 ml of phenolphthalein indicator against a 0.5 M HCl solution. The amount of acid in millilitres (ml) needed to stop the reaction was recorded as (A). The amount (ml) of hydrochloric acid needed was calculated after performing an identical blank experiment without the oil (B).

$$\text{Saponification value (mgKOH/g)} = \frac{(B-A) \text{ x Concentration of HCl x 56.10}}{\textit{Mass of Oil sample (g)}} \quad (12)$$

Where A = volume of titration of sample (ml), B = volume of titration of blank (ml). Concentration of HCl (mol/ml^3)

Viscosity

The most crucial physical characteristic of a lubricating oil is its viscosity, which affects both how quickly it flows and how much load it can support. Any form of lubricant used requires maintaining the ideal balance between low viscosity for simple circulation and high viscosity for load bearing. The typical way to check the quality of a machine is to measure kinematic viscosity, which describes how a fluid flows while gravity is at work. Kinematic viscosity is evaluated at 40 °C in the industry for crude oil exploration and production. It is computed by dividing the dynamic viscosity by density, which is represented by the following equation and is defined as mass per volume:

$$V = \frac{\eta}{\rho} \qquad \rho = \frac{m}{V} \qquad (13)$$

Where V is Kinematic velocity (m^2/s) , η is dynamic velocity, ρ is density oil (g/cm^3), *m* is mass (g) and V is volume of oil (ml).

The ASTM D445-06 was used to determine the kinematic viscosity. The sample was injected into the digital automated viscosimeter analyser Anton Paar Stabinger SVM 3000 in three replications and temperature set at 40 °C. The means and standard deviations of the Kinematic velocity were calculated.

Flash Point and Fire Point

The critical temperature of lubricating oil at which it produces sufficient vapours to spark but not burn when a little fire is placed close to it is referred to as flash point. The term "fire point" refers to the smallest temperature at which oil vapours persistently burn for at least five seconds when a small flame is placed close by. Important lubricating oil characteristics that affect their volatility and fire resistance are their flash point and fire point. Most of the time, fire points are 5 to 40 ^{o}C higher than flash points. To prevent fire dangers while the oil is being used, a suitable lubricating oil should have a flash point well above temperature at which it will be utilized.

The ASTM D93-07 standard test procedure was used to estimate the flash and fire point. Before the test began, all components of the Pensky-Martens closed cup tester were properly cleaned and dried. The cup has enough almond seed oil in it to reach the target. In order to create a closed system, the lid was put on the cup. All was properly fixed, including the thermometers, which were within the prescribed range. After that, the oil

42

sample was heated. The test flame was ignited and set up such that the bed size is 4 mm in diameter. At a rate of 5 to 6 ^{o}C per minute, the sample was heated. The sample was swirled at a rate of around 60 revolutions per minute while it was being heated. Till the temperatures at which the oil displayed flash and fire signs were observed, the test flame was applied at intervals of one minute.

Determination Fatty Acid Composition

In accordance with the AOAC (2005), 963.22, 969.33 standard method, determination of fatty acid composition was done using Agilent HP-6890 GC-MS by Agilent Technologies, Palo Alto, CA, USA with an HP-5MS 5% phenylmethylsiloxane capillary column (30 m x 0.25 mm i.d., film thickness 0.25 m). The carrier gas helium, with a flow rate of 1.0 mL/min. A split ratio of 30:1 was used to inject one litre of oil sample into each column. The GC operation protocol was used to complete the temperature ramp programming of the oven. With AMDIS-Chromatogram (GC-MS system) software, the resulting mass spectra were compared with data from the NIST05.LIB and NIST05s.LIB (National Institute of Standards and Technology) libraries to identify the fatty acids. In this work, all results are reported as mean values and standard deviations of experimental and GC measurements performed in triplicate (Takase *et al*., 2014).

Cloud and Pour Points

The temperature at which dissolved materials are no more entirely soluble and precipitate as a second phase, making the oil appear hazy, is

43

known as the cloud point of a fluid. Pour point refers to the lowest temperature, stated in multiples of 3 ^{o}C, at which oil is seen to flow when cooled and studied under specific circumstances. The lowest temperature at which petroleum products are still useful is indicated by the cloud and pour points. The temperature at which oil may be handled safely without worrying about congealing or filter clogging is roughly indicated by the term cloud point. Throughout its cooling process in the pour and cloud point device, the sample is frequently inspected. The temperature below which oil stopped flowing is known as the pour point, whereas the temperature beyond which haziness first appeared is known as the cloud point.

According to ASTM D2500, respectively, the cloud and pour points were calculated. The oil sample was initially added to a test jar until it was about halfway filled. The jar was sealed with a cork that had a thermometer attached. The bulb of the thermometer was set up to rest at the jar's base. The complete test subject was then positioned on top of a gasket in a cooling solution of constant temperature to prevent overcooling. The sample was removed, checked for cloudiness or haziness, and rapidly replaced after every 1°C drop in temperature. The temperature at which cloudiness was noticed was reported as the cloud point. The cooling process was carried out three (3) times. The pour point was determined to be the temperature at which the oil did not flow for 5 seconds while the test jar was held horizontal.

44

Transesterification of Almond seed oil

Experimental design

Modelling of biodiesel yield using response surface method

The process variables under consideration were optimised using the Box-Behnken Design (BDD). The response surface method develops an experiments design using least amount of data feasible in order to get reliable ANOVA models. Because BBD designs lack axial points, all design points must comply with operational constraints, necessitating the usage of a BBD to create a design matrix (inputs). It calls for fewer treatment alternatives to be available. A number of combinations of the input factors alcohol-oil ratio, time and catalyst amount together with a constant temperature and speed, were chosen to give yield as outcome (Tosin, 2022). Three factors and 3 centre points were employed in this work. Table 2 shows the coded and non-coded factor notation. The design was randomised (Table 3) to eliminate any potential association. The quantity of BBD experiment runs is drastically decreased. In order to represent the impact of yield as an output response factor, a model was also created based on the BBD. Each run was done twice, and the associated yield calculated.

45

Table 2: Independent factors of the transesterification process

Symbols	Factors	Level		
		Low	Centre	High
		-1	0	1
A	Methanol-oil ratio	4:1	6:1	8:1
B	Catalyst amount (g)	1	1.5	2
C	Time (minutes)	30	60	90

Table 3: Randomised Box-Behnken Design

STANDARD ORDER	RUN ORDER	BLOCK	FACTORS		
			A	B	C
9	1	1	8:1	1.5	30
10	2	1	4:1	1.5	90
12	3	1	6:1	1.5	60
8	4	1	6:1	1.0	90
4	5	1	4:1	1.0	60
1	6	1	6:1	1.0	30
2	7	1	6:1	2.0	30
5	8	1	4:1	1.5	30
7	9	1	4:1	2.0	60
3	10	1	8:1	1.5	90
11	11	1	6:1	1.5	60
14	12	1	6:1	1.5	60
6	13	1	8:1	1.0	60
15	14	1	8:1	2.0	60
13	15	1	6:1	2.0	90

Experimental Setup for Transesterification Process
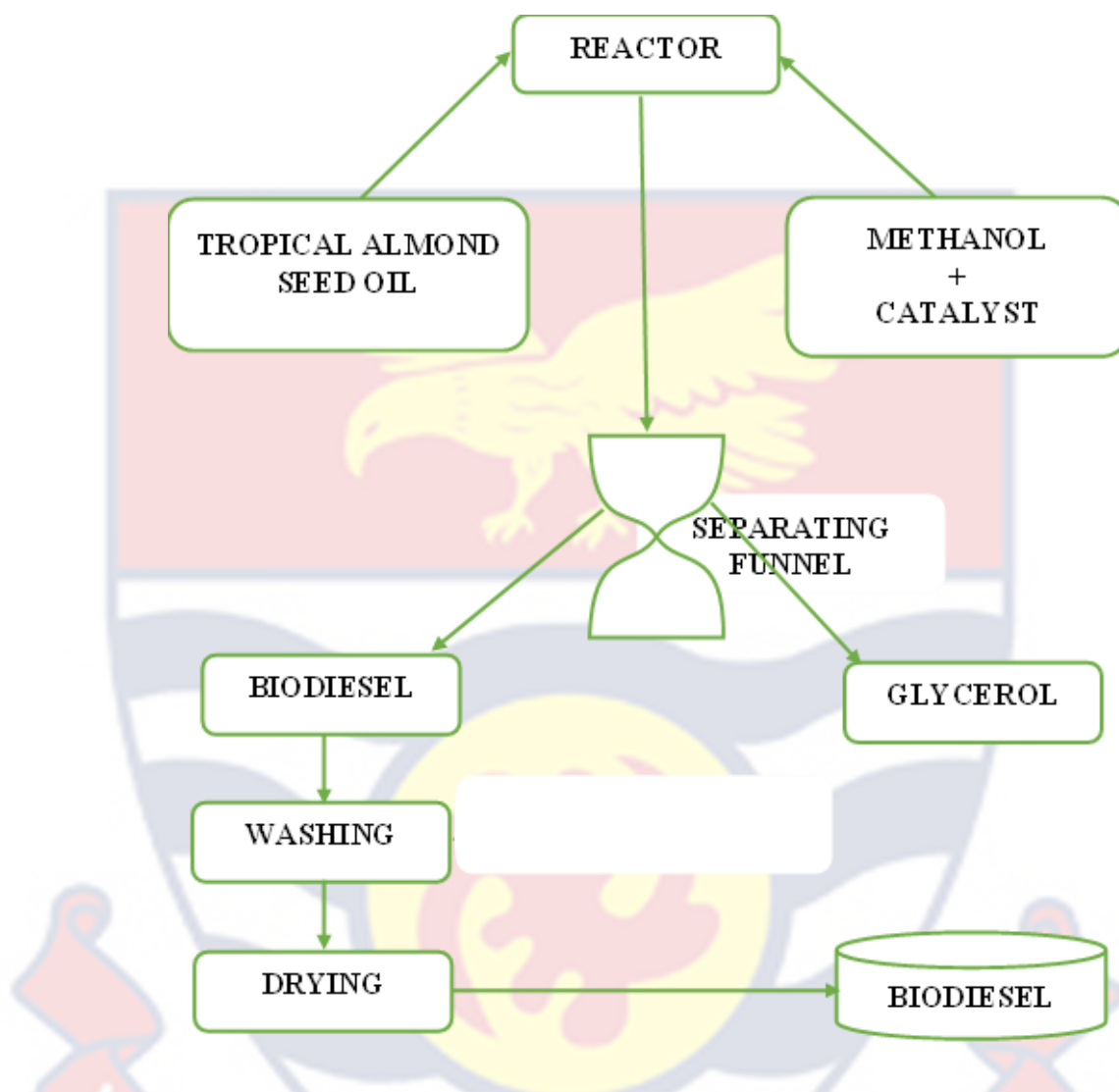
Figure 5: Schematic diagram of components used in biodiesel synthesis process from tropical almond seed oil in a batch reactor.

Homogeneous base catalysed transesterification reaction

Exactly 50 g of tropical almond oil was weighed and transferred into a 250 ml Erlenmeyer flask, which was then heated to 65 ^{o}C on a hot plate with a magnetic stirrer. To make a uniform sodium methoxide solution, a blend of methanol and NaOH catalyst was stirred on a stirrer plate for five minutes.

47

After that, the sodium methoxide was added to the warmed oil and the mixture agitated using a magnetic stirrer at 500 rpm. The methanol-oil ratio (4:1-8:1), NaOH catalyst amount (1-2 g), and time (30-90 minutes) were adjusted in the process to assess their effects on the yield. Following transesterification, glycerol and other residues were separated from the reaction mixture using a separating funnel for up to 12 hours. The biodiesel produced was then rinsed with warm (60-80 ^{o}C) distilled water to flush out excess NaOH catalyst and methanol. The washed biodiesel was then dried with a rotary evaporator. Equation 14 was used to estimate the biodiesel yield.

$$\text{Biodiesel yield (\%)} = \frac{\textit{Mass of methyl ester obtained (g)}}{\textit{Mass of sweet almond oil used (g)}} \, x \, 100 \qquad (14)$$

Data Analyses

Analyses of mean, standard deviation, RSM and ANOVA were carried out at confidence interval of 95 % in Minitab® 20.2 software. Analysis was done on the characteristics of the biodiesel and oil that was extracted. The important findings of the study were presented, and were compared with similar qualities of Tropical almond oil found in previous research. The causes of changes in the physicochemical composition were outlined. Additionally, key biodiesel characteristics were compared to ASTM D6751, EN 14214 and Ghana Standard Authority requirements.

Production of biodiesel from Tropical almond seed oil using heterogeneous bifunctional NaOH/kaolin as catalyst.

Catalyst preparation

By employing the incipient wetness impregnation approach, the catalysts were created. The raw kaolin was calcined for 5 hours at 700 °C in a muffle before being impregnated. The calcined kaolin, also called metakaolin, was progressively added to various concentrations of NaOH aqueous solution, and it was left for 24 hours. The catalyst was impregnated, dried at 110 °C for six hours and calcined for four hours at 600 °C in a muffle furnace. 20% NaOH was actually impregnated for 24 hours in 100 ml of deionized water containing 15 g of calcined kaolin (Takase *et al*., 2014).

Characterization of catalyst

By using the Hammett indicator technique, the base strength of the catalysts was characterized. For this procedure, 300 mg of the sample are normally kept in one millilitres of Hammett indicators before being diluted with 10 ml of methanol. After 2.5 hours, equilibrium was finally established, as shown by colour stability. As a result, base strength is characterized as being less powerful than the strongest indicator, that does not cause colour change, but more powerful than the weakest indicator, which does. 2,4-dinitro-aniline (H_15), 4-nitroaniline (H_18.4), bromothymol blue (H_7.2), and phenolphthalein (H_9.8) were the Hammett indicators utilized. The base strength of the solid catalysts was subsequently evaluated by a titrimetric

49

process using benzene carboxylic acid, 0.02 mol/L anhydrous ethanol solution Hammett indicator (Takase *et al*., 2014).

The catalyst samples were subjected to Fourier transform infrared examination using an AVATAR 360, Nicolet, Madison, USA FTIR spectrometer with a resolution of 2/cm in the 500–4000/cm range. An average was found after at least 32 scans (Takase et al., 2014).

An X-ray diffractometer (D8, Bruker-AXS, Germany) reflection scan using Cu, Ka radiation that has been nickel-filtered was employed to analyse intermediary substances in the produced catalyst complexes. The $2h^{\theta}$ results for the XRD were taken within the 20^{θ} to 80^{θ} range (Qiu et al., 2011; Takase et al., 2014). At a 20 kV accelerating voltage, the samples' forms and surface properties were scanned using a field S-4800, HITACHI Corp., Tokyo, Japan, emission scanning electron microscope.

Thermogravimetric analysis was executed on a Netzsch instrument (STA 449C, Netzsch, Seligenstadt, Germany). In a nitrogen environment, the instrument was programmed to a heating rate of 10 °C/min and range from ambient temperature to 800 °C. Samples weighing 5–10 mg was used for the measurement. Using an analytical instrument called the NDVA2000e (Qunta-chrome Corporation, USA), the nitrogen desorption and adsorption isotherms were measured at -196 °C (Takase *et al*., 2014).

Transesterification of tropical almond seed oil

Transesterification reaction of *Terminalia. catappa* seed oil was performed utilizing 50 g of extracted oil with varied methanol-oil molar ratio

50

(4:1 - 10:1) and catalyst amounts (1- 4%,); with respect to the molecular weight of the oil. At different temperature (50–65 °C) and periods (1–2.5 hours), the mixture was put into a 250 ml Erlenmeyer flask on a heated plate with a magnetic stirrer while stirring speed was maintained at 500 rpm. Fatty acid methyl esters (FAMEs), which had been absorbed by the solid catalyst, were removed from the mixture by washing it with n-hexane after process was completed. In order to assure segregation of the liquid layer comprising the n-hexane and biodiesel from the catalyst, mixture was further centrifuged for 15 minutes at 5000 rpm. In order to purify the biodiesel of n-hexane and any other residues, the transferred liquid part was then moved to a rotating vacuum evaporator. Following a 24-hour stand time, each biodiesel sample was placed in a separating funnel, after washed at least three times with water, and dried. Equation 14 was used to calculate the biodiesel yield:

Catalyst reuse

The reactions were run repeatedly under optimal conditions, involving 3 hours of reaction time, methanol-oil of 4:1, and a 7 wt.% catalyst, to assess the viability of catalyst reusing. The catalyst was collected by vacuum filtering and used again after each of the five (5) successive reaction cycles. It was next cleaned with methanol and thereafter n-hexane to eliminate any potential glycerol and oil adhering to the surface of the catalyst, and dried for four (4) hours in an oven at 110°C.

Kinetics model of transesterification of Tropical almond seed oil

The transesterification of triglycerides (TG) in the presence of a catalyst with methanol produces methyl esters and glycerol (GL) in a reversible process. The intermediaries are monoglycerides (MG) and diglycerides (DG). The equations below contain the reaction stages, where forward rate constants are as follows k_1, k_3, and k_5 and the backward rate constants are k_2, k_4, and k_6.

$$TG + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} DG + R_1COOR \qquad (15)$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MG + R_1COOR \qquad (16)$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} GL + R_1COOR \qquad (17)$$

Overall reaction

$$TG + 3ROH \overset{Catalyst}{\rightleftharpoons} GL + 3RCOOR \qquad (18)$$

The Arrhenius equation provides the connection between reaction temperature and rate constant:

$$\log_{10}K = -\frac{E_a}{2.303\ R} \ \mathrm{x} \ \frac{1}{T} + C \qquad (19)$$

The rate constant is K, R = ideal gas constant (8.314 Jmol^{-1}K^{-1}), T = absolution temperature (K), Ea = activation energy (J.mol^{-1}), and a constant C. The slope (-Ea/2.303R) is obtained by plotting log 10 k in terms of 1/T.

52

Depending on the circumstances, forward reactions often seemed to be second-order or pseudo-first order. With both alkaline and acidic catalysts, the forward and reverse were of the pseudo-first and second order respectively kinetics processes with a 30:1 butanol to soybean oil molar ratio. For both forward and reverse processes, the alkaline-catalysed reactions showed substantially higher rate constants than the acid-catalysed ones. The forward and reverse processes that were catalysed by alkaline, on the other hand, had second order kinetics for a 6:1 molar ratio. FAME was shown to increase quickly in the event of methanolysis at a 6:1 molar ratio, but neither diglyceride nor monoglyceride showed a matching increase in speed (Freedman *et al*., 1986). This work used a pseudo-second-order kinetic model developed by Darnoko & Cheryan (2000) for the first phase of the process.

53
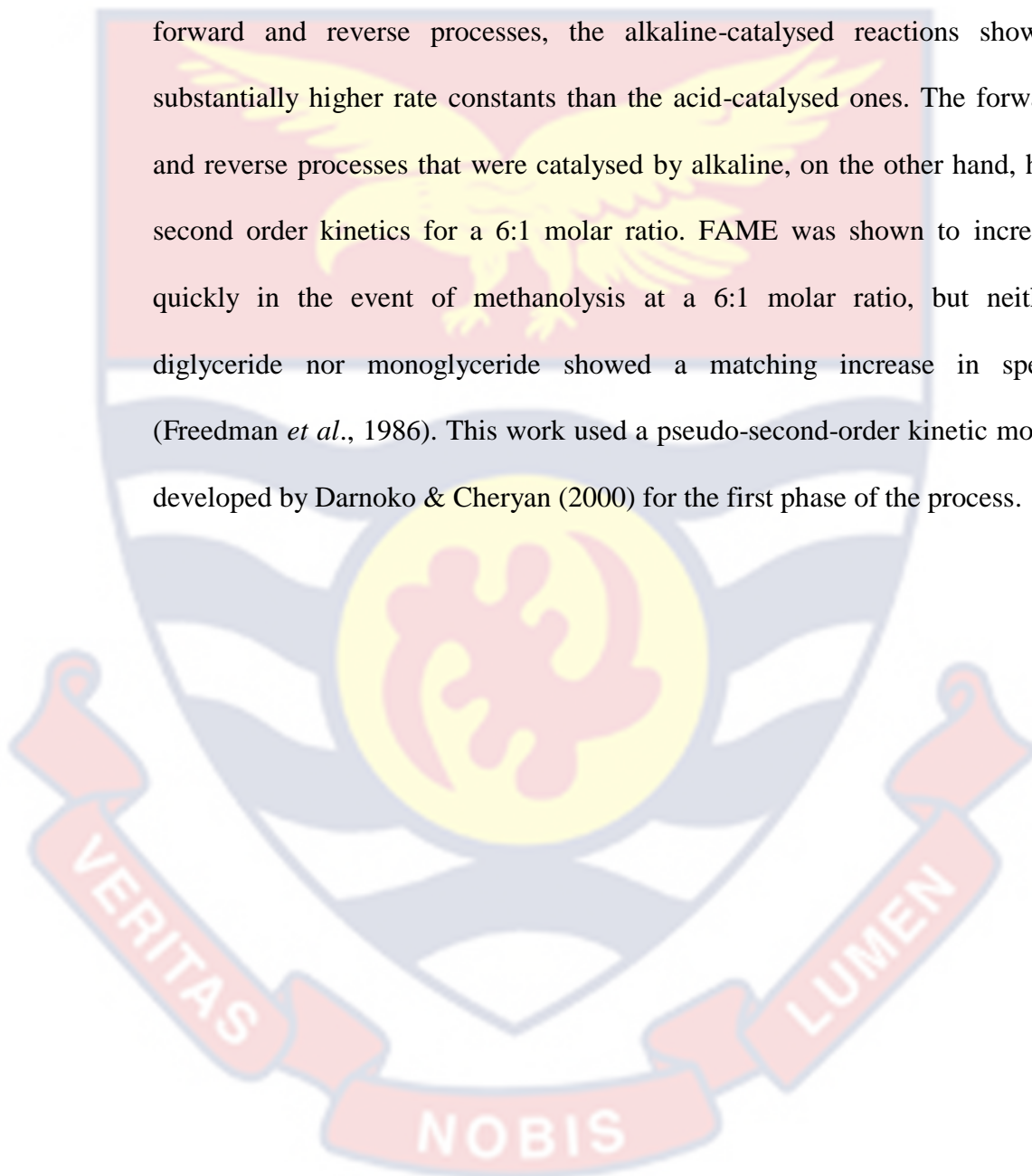
CHAPTER FOUR

RESULTS AND DISCUSSION

Physicochemical properties of extracted oil and biodiesel

Table 4 shows the fuel characteristics of the extracted tropical almond oil and the biodiesel generated from this study under optimal parameters. The biodiesel characteristics were in line with the requirements set out by ASTM D6751, EN 14214 and Ghana Standard Authority standards for the manufacturing of biodiesel.

The almond seed's moisture content was 2.30 %, which is greater than the 2.04 % reported by Orhevba *et al*. (2016) and lower than 4.13 % reported Matos *et al*. (2009). This may be as a result of climatic conditions hence removal of some moisture by the sun could not be achieved. The percentage yield of tropical almond seed oil after the extraction was 58.24%, which was higher than 50.33% reported by Orhevba *et al*. (2016), 51.80% published by Matos *et al*. (2009) and 52.11% obtained by Barku *et al*. (2012). Though the oil yield appeared high, it was marginally lower than the 60.57% reported by Giwa & Ogunbona (2014). The difference in yield may be linked to the oil extraction process employed, the time of oil extraction, cultivation climate, variance in plant type, stage of ripeness and the timing of seed harvesting. Because the oil extracted being liquid at normal temperature, makes it suitable to be used for biodiesel production.

54

Table 4: Physicochemical properties of extracted almond seed oil and biodiesel produced using base catalyst.

Properties	Extracted oil	Biodiesel	ASTM Std. D6751-12	EN 14214-12	Ghana Standard Authority
Moisture content of seed (%)	2.30 ± 0.05				
Oil yield (%)	58.24	96.38			
Colour	Yellow	Light yellow			
Odour	-	-			
Acid value (mgKOH/g oil)	2.97 ± 0.02	0.47 ± 0.07	≤ 0.5	≤ 0.5	1.0 max
Density (g/cm^3)	0.92 ± 0.01	0.89 ± 0.04	0.86 - 0.90	$0.86 - 0.90$	-
Iodine value (gI$_2$/100g oil)	96.2 ± 0.15	53.41 ± 0.10	≤ 120	≤ 120	-
Free fatty acid value (mgKOH/g)	1.48 ± 0.01	0.24 ± 0.21	-		
Kinematic viscosity (m^2/s)	13.4 ± 0.1	5.4 ± 0.4	1.9 - 6.0	3.5-5.0	1.5-6.5
Saponification value (mgKOH/g)	200.25 ± 2.15	185.30 ± 0.34	-		
Flash point	160	176	≥ 93	≥ 120	66 min
Cetane number		56	≥ 47	≥ 51	47 min
Pour point	5	-3	-15 to 10	-	15 max
Cloud point	3	-2	-3 to 12	-	-

Data represents the mean and standard deviation of triplicate analyses

The extracted oil has density of 0.92 g/cm^3 which is slightly above 0.90 g/cm^3 reported by Orhevba *et al*., ((2016) and 856.10 kg/m3 reported by Esonye *et al*., (2016). Density of the biodiesel was 0.89 g/cm^3 and this result is within the ASTM D6751, EN 14214 and GSA standard specified range of 0.86 – 0.90 g/cm^3. Both the specific gravity of the oil and the biodiesel are determined by density.

At 40 °C, the kinematic viscosity of the oil was 13.4 m^2/s. This value is similar to viscosities reported as 14.1 m^2/s by Orhevba *et al*., (2016), 43.0 m^2/s (Matos *et al*., 2009), and 20.29 m^2/s (Agu *et al*., 2022). The difference in viscosity between these *Terminalia catappa* oil samples might be attributable to the varying extraction temperatures. This is because temperature fluctuations have a substantial impact on viscosity. The kinematic viscosity of the biodiesel was 5.4 m^2/s and was within the ASTM D6751 standard.

The tropical almond seed oil recorded free fatty acid value of 1.48 mgKOH/g which is lower than 1.68 mgKOH/g obtained by Orhevba *et al*., (2016). The sacid value was found to be 2.98 mg KOH/g oil which was less than 3.37 mgKOH/g (Orhevba *et al*., 2016), and 4.73 mg KOH/g (Agu *et al*., 2022) but was slightly higher than 2.156 mgKOH/g reported by Ogunkunle *et al*. (2017). This acid value disparity could be attributed to the extraction method adopted, length of fruit storage before processing into oil and activities of microbes (Tagoe *et al*., 2012). Acid value indicates the type of catalyst to use for the transesterification process. Acid value of 0.47 mgKOH/g of the produced biodiesel was within the ASTM standard.

The extracted oil has a lower iodine value of 96.2 gI_2/100g; as opposed to 98.0 gI_2/100g (Orhevba *et al*., 2016) and 121.19 gI_2/100g (Barku *et al*., 2012) and the biodiesel had a value of 53.41 gI_2/100g which is within the ASTM D6751 standard of ≤ 120 gI_2/100g.

The saponification value was 200.25 mgKOH/g, which is greater than 199.19 mgKOH/g (Orhevba *et al*., 2016) and 168.27 mgKOH/g (Barku *et al*., 2012) for tropical almond seed oil. The technique by which the oil was extracted and the procedure used to obtain the saponification value may have accounted for the differences. This indicates that more alkali is needed to neutralize the obtainable free fatty acid generated by the oil. The ease with which an oil can be utilized to make soap increases with its saponification value.
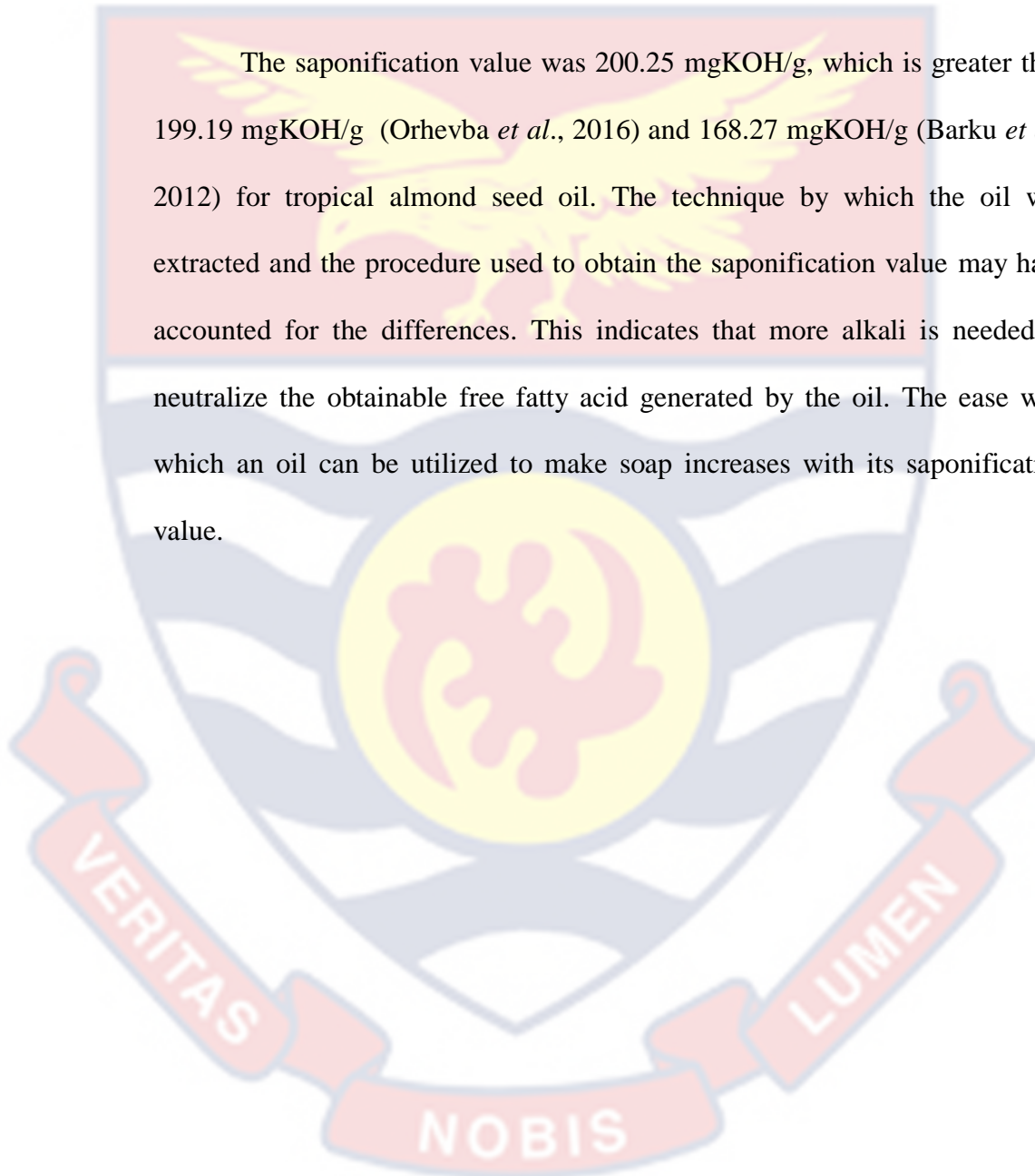
57

Table 5: Tropical almond seed oil fatty acid profile

Total fatty acids (%)	Almond seed oil
Mysristic acid, $C_{14:0}$	0.24 ± 0.02
Palmitic acid, $C_{16:0}$	29.13 ± 0.14
Palmitoleic acid, $C_{16:1}$	0.49 ± 0.10
Stearic acid, $C_{18:0}$	6.69 ± 0.01
Oleic acid, $C_{18:1}$	40.97 ± 2.01
Linoleic acid, $C_{18:2}$	21.47 ± 0.01
a-linolenic acid, $C_{18:3}$	0.09 ± 0.02
Arachidic acid, $C_{20:4}$	0.92 ± 0.01
Σ SFAs	36.06
Σ UFAs	63.94
Σ MUFAs	41.46
Σ PUFAs	22.48
Total	100.00

Data presented as mean $\pm$ standard deviation of triplicate analyses. SFAs = Saturated fatty acids, UFAs = Unsaturated fatty acids, PUFAs = Polyunsaturated fatty acids, MUFAs = Monounsaturated fatty acids.

The *Terminalia catappa* seed oil fatty acid profile displayed the prevalence of unsaturated fatty acids (63.94 %), represented mainly by oleic acid as major proportions of fatty acids in the oil sample constituting (40.97 %), followed by palmitic acid (29.13 %), linoleic acid (21.47 %) then stearic acid (6.69 %) as shown in Table 5. Additionally, the fatty acid profile of *Terminalia catappa* is in agreement with literature. Santos *et al*. (2022) reported that the oil from *Terminalia capatta* kennel from purple and yellow varieties extracted by Soxhlet solvent extraction presented similar fatty acid composition and the major proportions are oleic acid (39 %), palmitic acid (33 %) and linoleic acid (up to 26 %). Also, Janporn *et al*. (2015), in their work found that the oil from *Terminalia catappa* had the major proportions of

58

fatty acids to be oleic acid (31.7 %), followed by palmitic acid (up to 31.4 %), then linoleic acid (up to 23 %).

Optimization of Base-catalysed transesterification by response surface method (RSM)

The transesterification process was optimized using a response surface design, Box-Behnken Design (BBD), which required 15 runs. Table 6 shows the experimental and predicted biodiesel yields determined as a reaction to the design points using BBD experimental designs. The obtained biodiesel yield ranged from 87.84 to 96.38 %. Table 7 illustrates the RSM analyses of variance, which revealed that all the linear variables methanol, catalyst amount, and time, two-way interaction (methanol*catalyst amount and catalyst amount*time), and three squared terms, $(methanol-oil)^2$, $catalyst^2$ and $time^2$ at 95 % confidence level were all significant model variables, as established by $p < 0.05$. The term methanol-oil ratio*time was determined to be insignificant ($p > 0.05$). With $p < 0.0001$, the effects of the linear terms methanol-oil ratio, catalyst amount, and time as well as that of methanol-oil $ratio^2$ and catalyst $amount^2$ were the most significant.

59

Table 6: Box-Behnken design for almond oil biodiesel production process optimization by responds surface method.

Run	Factors			Biodiesel Yield (%)	Predicted Yield (%)	Std. Residual	Conf. Interval
	Methanol-Oil ratio	Catalyst Amount (g)	Time (Minutes)				
1	8:1	1.5	30	95.35	95.22	0.64	(94.313, 96.125)
2	4:1	1.5	90	89.72	89.85	-0.64	(88.945, 90.757)
3	6:1	1.5	60	93.60	93.71	-0.32	(93.103, 94.311)
4	6:1	1.0	90	91.62	91.67	-0.23	(90.760, 92.572)
5	4:1	1.0	60	89.18	89.00	0.87	(88.096, 89.909)
6	**6:1**	**1.0**	**30**	**96.38**	**96.81**	**-2.12**	**(95.905, 97.717)**
7	6:1	2.0	30	91.38	91.33	0.23	(90.428, 92.240)
8	4:1	1.5	30	92.71	92.46	1.25	(91.550, 93.362)
9	4:1	2.0	60	87.84	88.14	-1.47	(87.234, 89.046)
10	8:1	1.5	90	92.23	92.48	-1.25	(91.578, 93.390)
11	6:1	1.5	60	93.64	93.71	-0.20	(93.103, 94.311)
12	6:1	1.5	60	93.88	93.71	0.52	(93.103, 94.311)
13	8:1	1.0	60	94.14	93.84	1.47	(92.934, 94.746)
14	8:1	2.0	60	88.52	88.70	-0.87	(87.791, 89.604)
15	6:1	2.0	90	91.57	91.14	2.12	(90.233, 92.045)

60

Table 7 displays the analysis of variance, which indicates that the model has a high level of significance with a model F-value of 58.06 and a $p < 0.0001$. An acceptable value for the coefficient of determination, R^2, which reflects how well the model fits should be more than 0.80 (Guan & Yao, 2008). Only 0.0095 percent of the overall variance is not accounted for by the model, according to the R^2 value of 0.9905, which shows that the model could account for 99.05% of the variation in the biodiesel yield. It shows how well-fit the model is. The adjusted R^2 of 0.9735 was reasonably comparable to the predicted R^2 of 0.8556, signifying that the model may be utilized to analyse response patterns. When contrasting models with various number of terms, the R^2 adjusted value is very helpful (Uzoh *et al.*, 2019). Apart from coefficient of determination, the lack of fit was insignificant relative to pure error (F-value 11.37, $p > 0.05$). This is similar to work reported by Sarve *et al*., (2015), which shows that the model is significant and indicates that the model equation is adequate for predicting biodiesel yield under any sets of combination of the variables

61

Table 7: Analysis of variance for response surface model of tropical almond seed oil transesterification

Source	Degree of freedom	Sum of Squares	Mean Square	F-value	P-value
Model	9	86.5732	9.6192	58.06	0.000
Linear	3	46.8408	15.6136	94.25	0.000
A	1	14.5530	14.5530	87.84	0.000
B	1	18.0300	18.0300	108.83	0.000
C	1	14.2578	14.2578	86.06	0.000
Square	3	29.0229	9.6743	58.40	0.000
A^2	1	14.0741	14.9297	90.12	0.000
B^2	1	12.5462	11.6440	70.29	0.000
C^2	1	2.4026	2.4026	14.50	0.013
2-Way Interaction	3	10.7094	3.5698	21.55	0.003
AB	1	4.5796	4.5796	27.64	0.003
AC	1	0.0042	0.0042	0.03	0.879
BC	1	6.1256	6.1256	36.98	0.002
Residual	5	0.8283	0.1657		
Lack-of-Fit	3	0.7825	0.2608	11.37	0.082
Pure Error	2	0.0459	0.0229		
Total	14	87.4015			

Std. Dev.	0.41	R^2	99.05%
AICc	109.12	Adj. R^2	97.35%
BIC	28.91	Predicted R^2	85.56%
PRESS	12.62		

A = Methanol-oil ratio, B = Catalyst amount (g), C = Time (Minutes). Source: Laboratory analysis

Equation 15 represents a multiple regression model for tropical almond seed oil transesterification that took a second-order polynomial equation form and provided the most accurate explanation of the process parameters in terms of the methanol-oil ratio (A), catalyst amount (B), and time (C) values.

62

Biodiesel Yield (%) = 63.58 + 8.344 A + 19.78 B - 0.2726 C - 0.5027 A^2

$\quad$ - 7.103 B^2 + 0.000896 C^2 - 1.070 AB - 0.00054 AC + 0.0825 BC   (15)

Similarly, Equation (16) shows the model equation after the insignificant terms have been deleted. The p-values in the table of analysis of variance were the basis for the exclusion of the insignificant terms, as shown in Table 7. The terms with p-values > 0.05 were removed because they were statistically insignificant.

Biodiesel Yield (%) = 63.58 + 8.344 A + 19.78 B - 0.2726 C - 0.5027 A^2

$\quad$ - 7.103 B^2 + 0.000896 C^2 - 0.00054 AC + 0.0825 BC   (16)

Equation (15) was chosen to predict the optimal values for the required process conditions because it was statistically significant for obtaining optimum biodiesel yield from the transesterification of tropical almond seed oil. The optimum conditions required were methanol-oil ratio (6:1), time (30 min) and catalyst amount (1 g). The theoretically biodiesel yield was 96.81 % based on the optimum conditions and was experimentally validated as 96.38 % by performing two replicates of independent experiments and the average value was calculated thereafter. The competence and the validity of the model were established on the basis that the validated and predicted biodiesel yields were close. Similar findings were reported for *Anacardium occidentale* kernel oil transesterification which obtained optimum yields of 94.70 % (Matthew, *et al*., 2022a) and Kusum *(Schleichera triguga)* oil, with optimum methyl ester yields 98.14 % (Sarve *et al*., 2015).
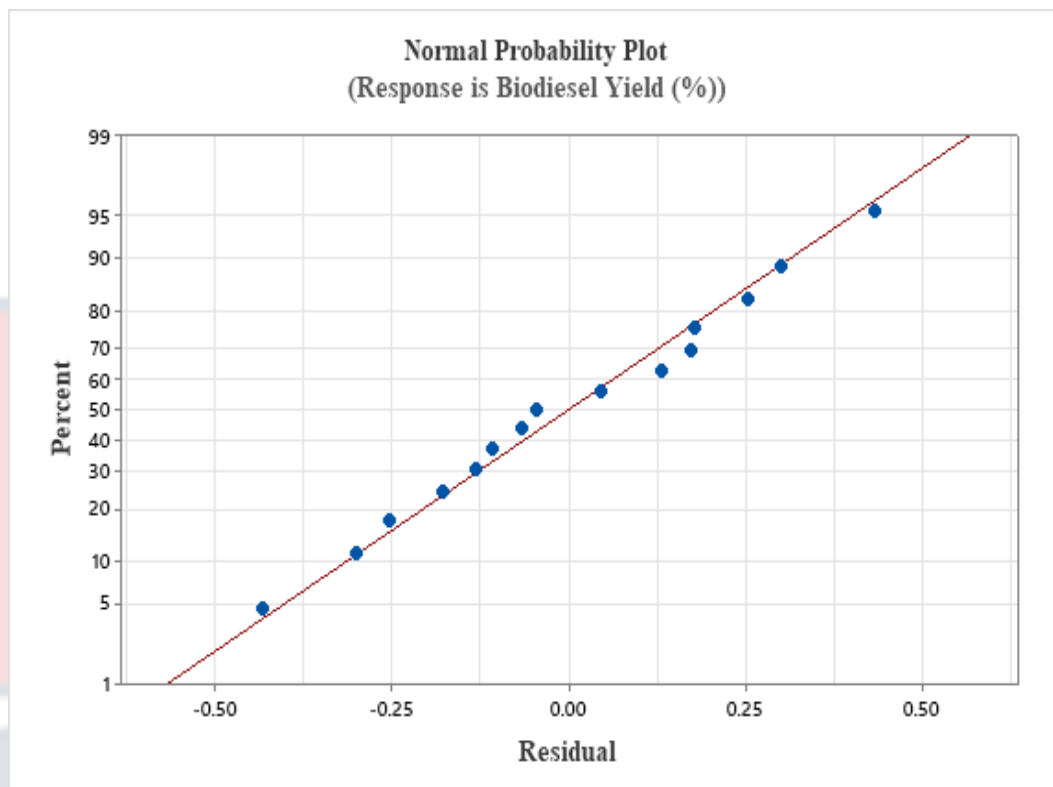
63

*Figure* 6: Residuals plot for biodiesel production from transesterification of tropical almond seed oil
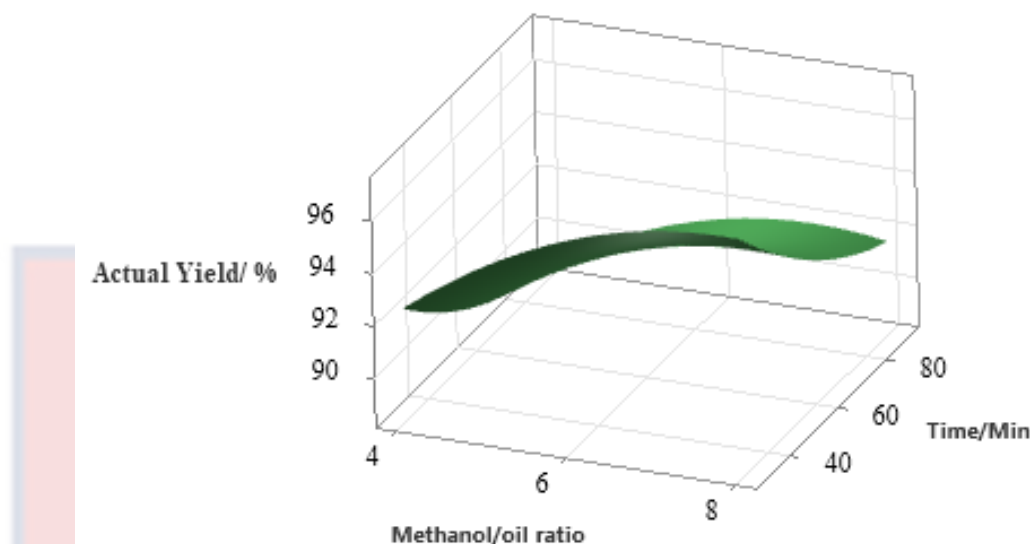
Figure 6 illustrates the residuals normal probability plots of biodiesel yield from tropical almond seed oil transesterification. The results of the predicted response from the model and experimental response agreed with the selected range of reaction parameter of time, catalyst amount, and methanol-oil ratio.

(A)

(B)

65
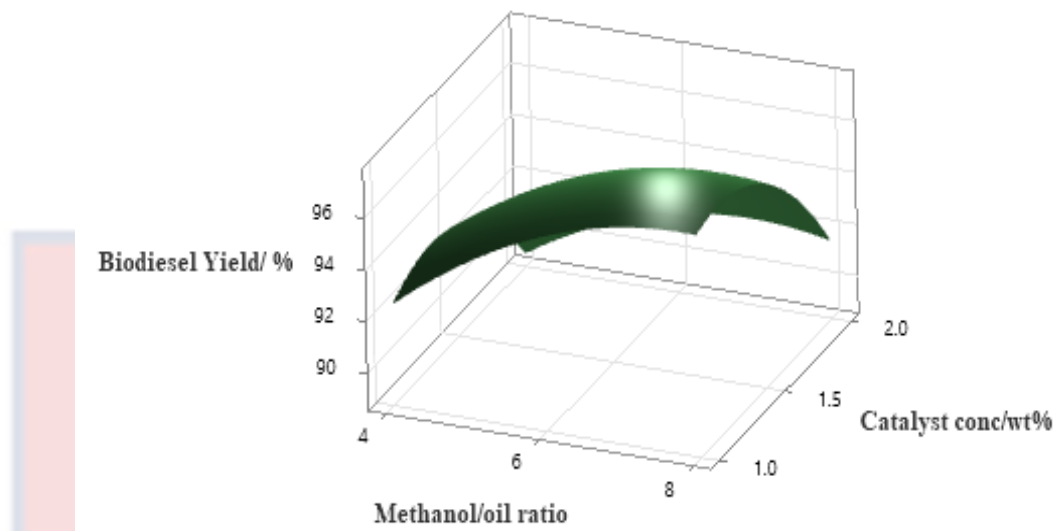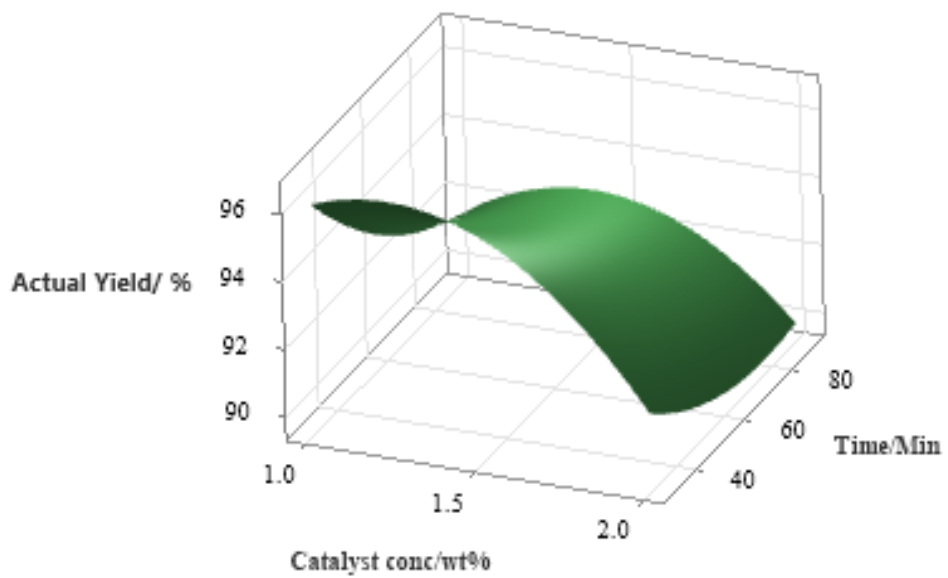
(C)

Figure 7: A 3D surface plot illustrating effects of process factors on biodiesel production. (A) The interaction of the catalyst amounts and methanol-oil ratio; (B) The interaction of the catalyst amount and time; and (C) The interaction of time and methanol-oil ratio.

Figure 7 shows the response surface plot which demonstrates very well the interactions and effect of the three considered operating variables on yield of biodiesel. The optimal biodiesel yield of 96.38 % was reached when the methanol-to-oil ratio and catalyst concentration were increased nearly to their centre-point as these factors positively influence the response as illustrated in figure (7A). Slightly increasing the values of these variables above the centre point however, led to a drop in biodiesel yield. The decline was noted in methanol-oil ratio, as a result of the negative sign of the quadratic term. Therefore, as observed by Constantinou *et al*., (2010 and Santos *et al*., (2014), it is because there are more active sites, the rate of converting triglycerides to fatty acid methyl ester has increased. However, too much catalyst can disrupt

66

the of methanol-oil, and catalyst combination and result in a phase separation, which, for discussion purposes, limits the reaction.

The process of transesterification is reversible by nature, therefore adding more methanol to the reaction medium causes the equilibrium to move to the right and produces more methyl ester. Separating the glycerol and methyl ester layers becomes more challenging when the reaction is conducted at high methanol-oil ratios. Thus, methanol, glycerol, and methyl ester phases can be homogenized by monoglycerides and diglycerides, favouring the reverse reaction and lowering the yield of biodiesel (Santos *et al*., 2014).

The methanol-oil ratio and catalyst amount as functions of time is illustrated in figures 7(B) and 7(C). As observed, the optimal biodiesel yield was attained by increasing the values of each parameter, time, methanol-oil ratio, and catalyst amount, to around the centre of the respective examined range. This demonstrates that giving the transesterification process enough time might favour it. The catalyst amount at the lowest point, the molar ratio raised to nearly the centre point, and the time of 30 minutes produced the maximum biodiesel yield. Because the process of making biodiesel is reversible, using too much time results in a reverse reaction that actually generates a saponification reaction, which lowers the yield of methyl ester.

Table 8: Constraints for tropical almond seed oil optimization

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
A: Molar ratio	Minimise	4:1	8:1	1	1	3
B: Catalyst	Minimise	1	2	1	1	3
C: Time	Minimise	30	90	1	1	3
Yield (%)	Maximise	87.84	96.38	1	1	3

Table 9: Result for the tropical almond seed oil optimization scenario

Solution	Molar ratio	Catalyst concentration	Time	Biodiesel yield	Desirability
1	7.19:1	1.02	30	97.56	1 .00
2	6:1	1.39	30	96.38	1.00
3	5.69:1	1	30	96.38	1.00
4	5.9:1	1.61	30	95.12	0.852

Tables 8 and 9 display desirability functions for three distinct conditions with varying inputs (methanol-oil ratio, catalyst concentration, and runtime) at constant temperatures and speeds. Table 9 displays the optimization solutions generated premised on the optimization of biodiesel scenario. The optimization solution with molar ratio (7.19:1), time (30), and catalyst amount (1.02) yielded biodiesel of 97.56% with an overall desirability of 1.00 using catalyst amount (1.0 wt%, 1.5 wt%, and 2.0 wt%), methanol-oil ratio (4:1, 6:1, and 8:1) and a fixed time of 30 minutes. Catalyst amount, time, and methanol-oil ratio were all important variables in biodiesel production, according to the analysis of variance results.

Catalyst preparation and screening

For the transesterification of *Terminalia catappa* oil, the activity of kaolin loaded with various concentrations of NaOH (10%, 15%, 20%, and 25%) was screened. The outcomes are shown in Table 10. Same process conditions were applied to the catalysts in all of the transesterification process to assess their performances. It was discovered that pure kaolin lacked any catalytic activity, making the deposition of NaOH on it necessary. The incipient wetness impregnation method was used to produce NaOH with different loading levels (10 %, 15 %, 20 %, and 25 %) on kaolin with the calcination temperature set at 600 °C. Pure kaolin and catalysts made from NaOH/kaolin were tested for their basic strength using the Hammett indicator method. According to Table 10, pure kaolin had the lowest basic strength $(H\_ \leq 7.2)$, which is consistent with research by (Jalalmanesh *et al*., 2021). The basic strength of the created catalysts did, however, completely increased after loading with NaOH. It is important to note that catalysts generated with loading levels of 15, 20, and 25 weight percent of NaOH exhibited basic strengths $(9.8 \leq H\_ \geq 15)$ that were higher than catalyst produced with loading level of 10 wt.% of NaOH.

The yield increased from 85.37% to 88.82% as a result of the increase in NaOH loading (from 10% to 20%). This may have been caused by the catalyst's base strength becoming stronger as NaOH loading increased. Increasing the loading quantity also improved the catalytic activity at the

69

active sites. After the peak was attained, the basic strength might have lowered

the active sites, resulting in a dip in the activity of the catalyst to a yield of

86.51% with an additional rise in the quantity of loaded NaOH to 25%. This

may have happened as a result of too much NaOH covering basic sites on the

surface. At the 25% NaOH, these sites may then become inaccessible to

incoming reactants. In order to conduct additional study, 20% NaOH was

selected as the suitable loading level.

Table 10: Effects of NaOH loading amount, temperature, and calcination time
on the catalytic activity of kaolin

Catalyst concentration	NaOH loading amount (%)	Calcination temperature (°C)	Calcination Time (hrs)	Base strength (pK$_{BH+}$)	Biodiesel yield (%)
Kaolin		600	5	H_ < 7.2	54.46
NaOH (10%)/Kaolin	10	600	5	7.2-9.8	83.37
NaOH (15%)/Kaolin	15	600	5	9.8-15	85.46
NaOH (20%)/Kaolin	20	600	5	9.8-15	88.82
NaOH (25%)/Kaolin	25	600	5	9.8-15	86.51

Conditions for the reaction include 2.0 g catalyst, methanol-oil ratio (6:1),

time of 2 hours, and a temperature, 65 °C.

Catalyst characterization

Figure 8 displays the powdered XRD patterns of the kaolin and NaOH

(20 %)/kaolin samples. This was done in order to comprehend the example

structures. For both the modified and raw kaolin, the strongest characteristic

peak was visible at $2\theta = 25°$ linked with SO_2. By analysing the crystalline

structure of raw kaolin, XRD studies revealed that the primary constituents of

70

kaolin were Si and K, with trace amounts of Al, Mg, and Fe (Alencar *et al*., 2017).
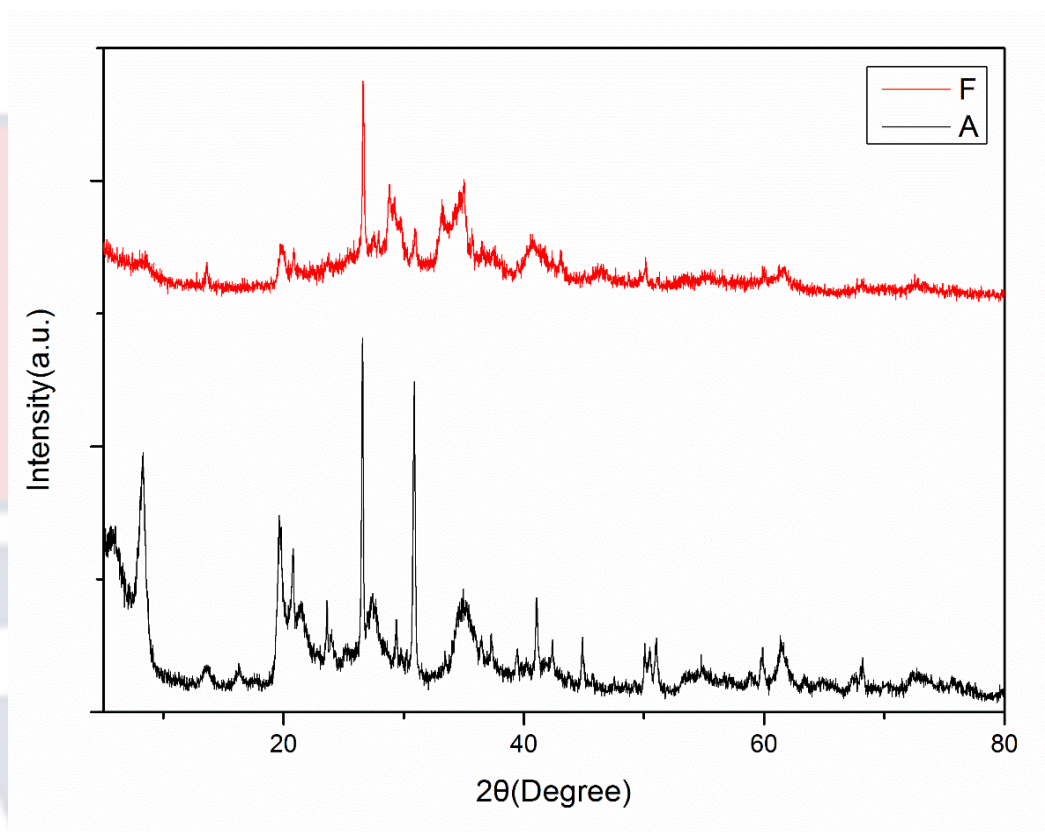

Figure 8: X-ray diffraction pattern of raw kaolin (A) and NaOH(20%)/Kaolin catalyst (F)

NaOH(20%)/kaolin catalyst FTIR spectrum is presented in figure 9. The existence of chemical water and mineral breakdown in the Kaolinite structure are explained by a large band associated with the O-H that spans between 3500 and 3000 cm^{-1} in the spectrum. A second band between 2500 and 2000 cm^{-1} also relates to O-H low energy bond caused by the humidity and adsorbed water.
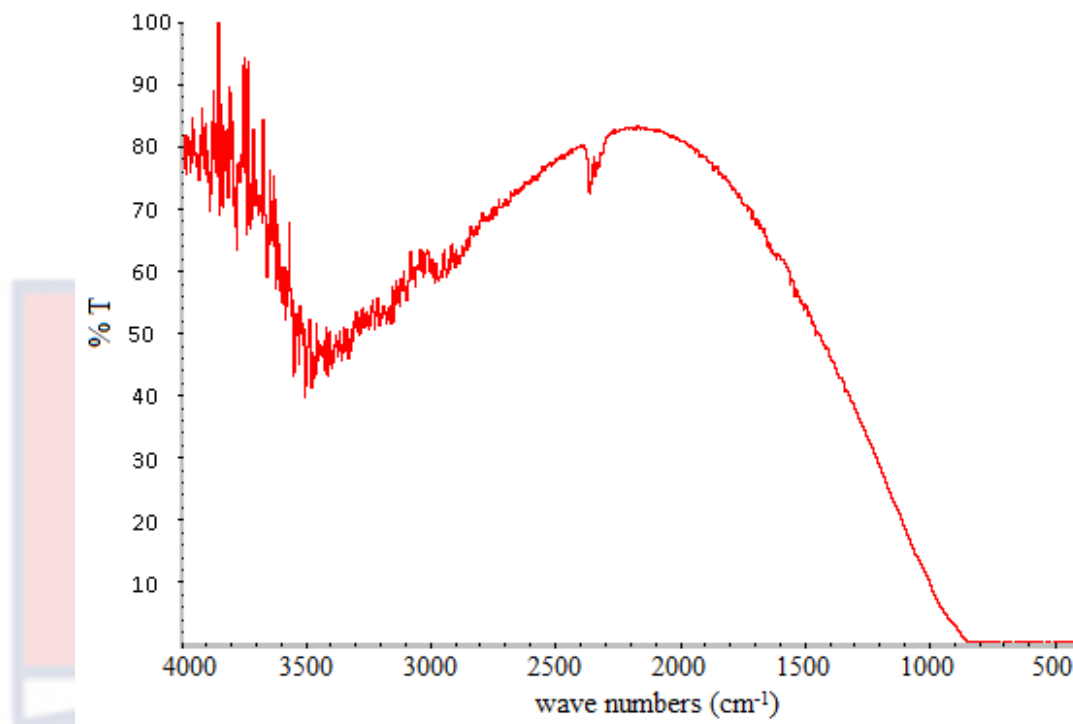
71

Figure 9: FTIR spectrum of NaOH (20%)/kaolin catalyst

Figure. 10 (A) and (B) illustrates the scanning electron microscope images of kaolin and NaOH (20%)/kaolin particles, respectively. The porous surface significantly decreased from 1 μm (A) to 100 μm (B) after modification. A clay's surface area is increased when the grain size is reduced. The increased surface area of the catalyst causes more collisions between the reactants and the catalyst during the transesterification process, increasing the reaction rate (El-Gendy *et al*., 2014). The structural characteristics of raw mineral clay makes it a charge carrier which serves as the foundation for cation interchange and its capacity to swell. The structural properties exist as surface charge or structural charge. Surface charge is pH dependent and relies

72

on Si-OH and Al-OH hydrolysis and bonds along the surface of the clay structure. This explains why the kaolin is acidic, with a pH of 4.88. Because of its ability to interchange cations with those in NaOH solution, it can replace unpaired cations in the interlayers. So, the modified kaolin clay now becomes a bifunctional heterogeneous catalyst with two active regions, basic and acid sites.
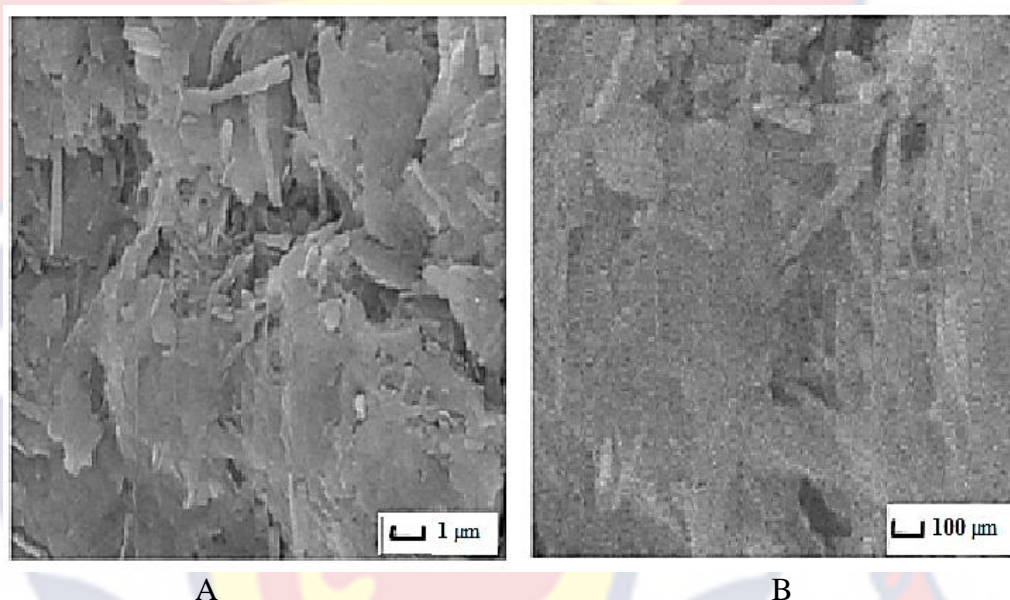

A   B

Figure 10: SEM image of kaolin (A) and NaOH (20%)/kaolin catalyst (B)

The thermal behaviour of NaOH (20%)/kaolin is shown in Fig. 11. At temperatures below about 140 °C, the first significant endothermic weight loss (5 %) was seen as a result of moisture loss. Between 300 and 900 degrees Celsius, least amount of weight was lost, which is attributable to endothermic dehydroxylation, which results in muddled metakaolinite, $Al_2Si_2O_7$ (Ramirez-

73

Ortiz *et al.*, 2012). This means that the NaOH absorbed on the kaolin has been
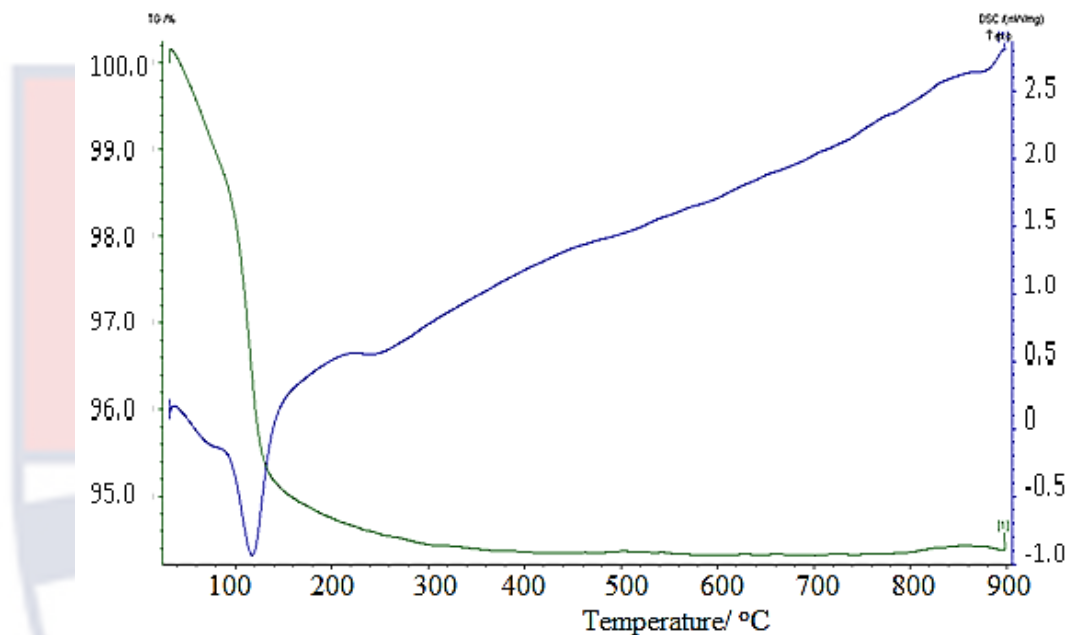
fully decomposed.

Figure 11: TGA of the NaOH (20%)/kaolin catalyst

Biodiesel production process optimization from Tropical almond seed oil using bifunctional NaOH(20%)/kaolin

Influence of methanol–oil ratio on biodiesel yield

Transesterification is based on the molar ratio principle, which states that to produce three moles of methyl esters and a mole of glycerol as a by-product, every mole of triglyceride requires three moles of alcohol to be added to it. A higher methanol-oil ratio must be utilized in order to push the

74

equilibrium to make more biodiesel. This study employed a ratio starting from 4:1 to 10:1 (Figure 12). The output of biodiesel increased consistently from 85.87 % to 95.40 % by raising the methanol-oil ratio from 4:1 - 8:1. A yield of 95.40 %, was obtained at an 8:1 molar ratio. The production began to decline at a molar ratio of 10:1 and reached 91.23 %. This can be a result of excess methanol diluting the catalyst.
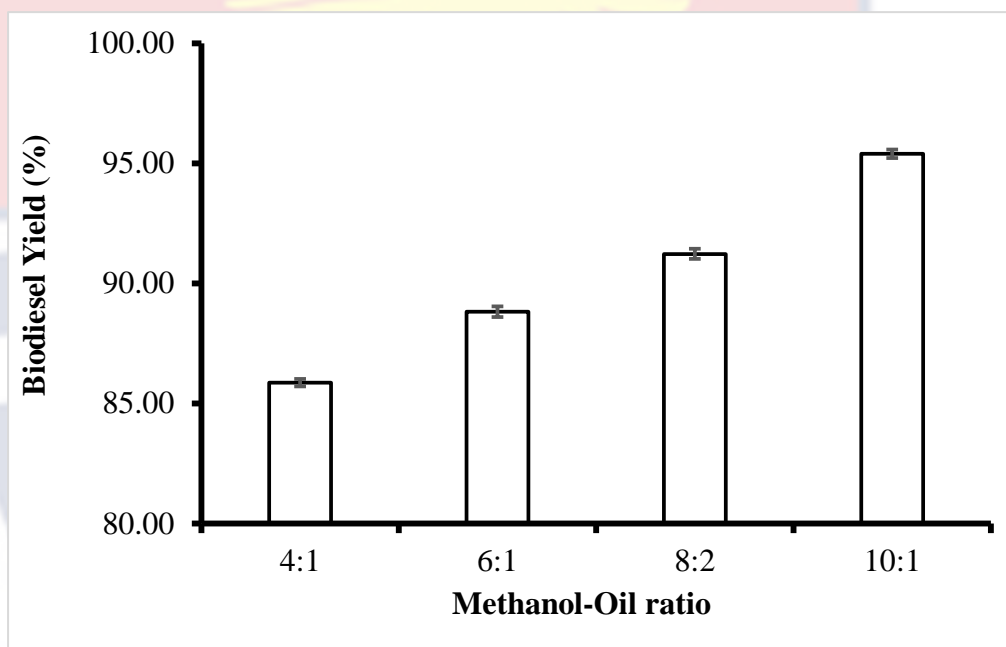
Figure 12: Effect of methanol-oil ratio on tropical almond seed oil transesterification.

The amount of oil being converted to biodiesel is reduced through reversible reaction by excess methanol, which also enhance the solubility of glycerol. The results are consistent with work by Ofoefule *et al*. (2019), which applied response surface approach to maximize biodiesel production using ethanol for soybean oil transesterification. They discovered that ethanol-oil ratio (12:1) as the optimum ratio produced 95 % methyl ester.

75

Influence of catalyst amount on yield of biodiesel

Biodiesel rose steadily to 95.4 % from 88.8 % when the catalyst amount was moved from 1 g to 2 g illustrated in figure 13. It implies that 95.4 % of biodiesel was generated at the optimal catalyst loading of 2 g on tropical almond oil. However, as the catalyst amount was raised from 3 g to 4 g weight, the biodiesel output decreased from 92.2 % to 90.3 %. Backward reactions are encouraged when the catalyst is present in higher concentrations. Converting triglyceride to biodiesel improves as catalyst amount increases up to a certain degree and beyond the yield that is optimal, a reversible process takes place that reduces the biodiesel yield.
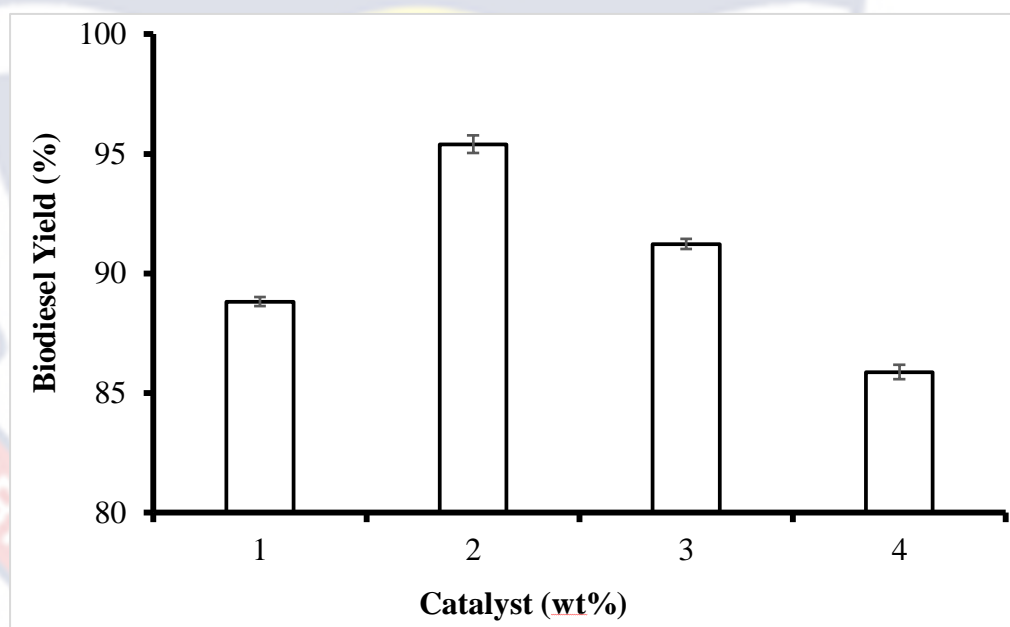

Figure 13: The effect of catalyst amount on biodiesel yield.

Influence of time on biodiesel yield

By employing a NaOH(20%)/kaolin heterogeneous bifunctional catalyst to optimize the process conditions, the reaction duration was changed from 1 to 2.5 hours to investigate the impact of time on the biodiesel produced. Within 1 hour to 1.5 hours of response time, the biodiesel output increased from 78.81 % to a high of 91.53 %. The short reaction time and insufficient mixing might be blamed for the initial low yield as well as the poor methanol dispersion over the oil. From 2 to 2.5 hours later, the biodiesel output gradually declined to 86.12 % 81.26 % respectively, as illustrated in figure 14.
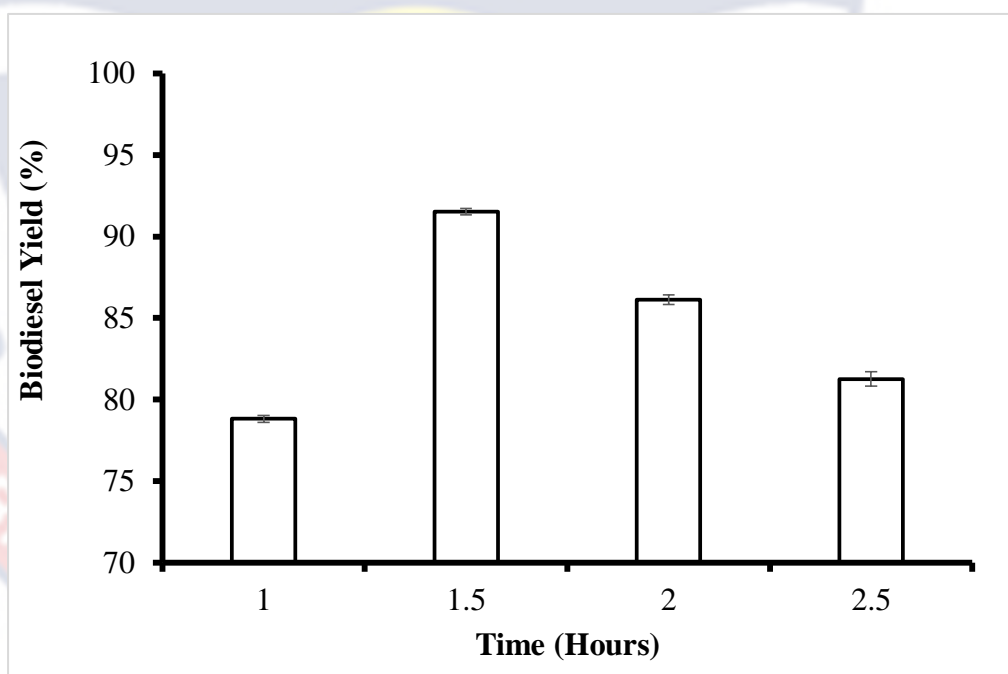

Figure 14: Effect of time on yield of biodiesel.

77

Influence of temperature on biodiesel yield

Other factors were kept constant as the response temperatures ranged from 50 °C to 65 °C. Time, methanol-oil ratio, and catalyst quantity were all held constant at 1.5 hours, 8:1, and 2 g, respectively. As presented in figure 15, increment in temperature from 50 °C to 65 °C, caused the quantity of biodiesel generated increase consistently from 84.71 % to 95.94 % respectively. The biodiesel production was 95.94 % at the optimal temperature of 65 °C. The transesterification process becomes more efficient as a result of rising reaction rates brought on by raising temperature. From 65 °C on, the methanol vaporizes and produces bubbles that obstruct the reaction surface. To prevent vaporization, temperature should be below the boiling point of methanol, with ideal temperatures ranging between 65 °C and 70 °C depending on the oil employed
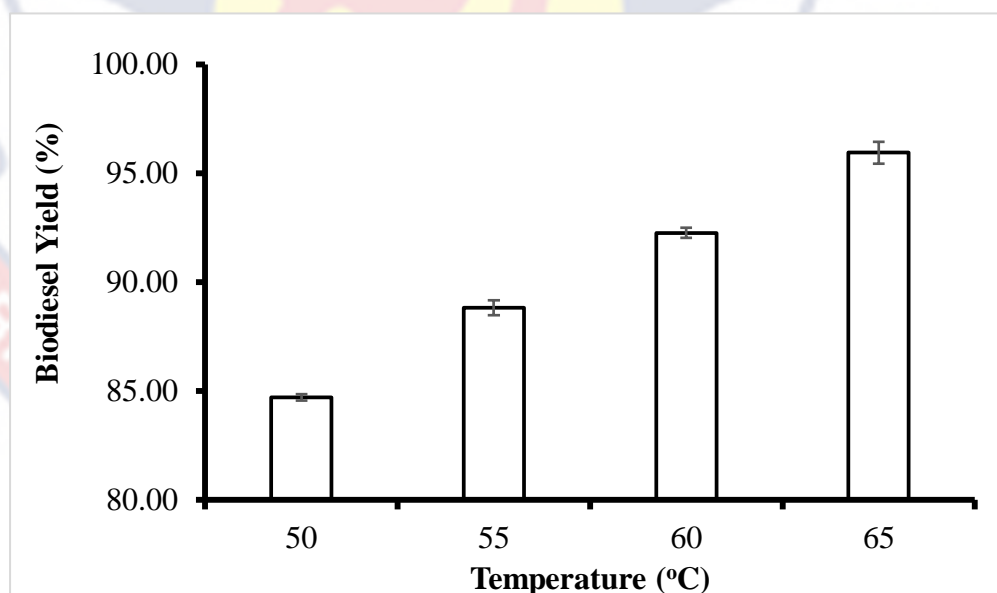

Figure 15: The effect of temperature on yield of biodiesel

78

Optimum reaction conditions

Table 11 displays a summary of the optimal process parameters for used for producing biodiesel from tropical almond seed oil by transesterification process utilizing a bifunctional heterogeneous catalyst of NaOH (20%)/kaolin. The optimal stoichiometric methanol-oil ratio was 8:1, time of 1.5 hours, catalyst amount was 2% by weight in reference to the oil, and temperature, 65 °C. The optimal biodiesel yield of 95.94%, was generated under these process conditions.

Table 11: Optimum process conditions for biodiesel production from Tropical almond seed oil

Variables	Optimum process conditions
Biodiesel Yield (%)	95.94
Time (Hours)	1.5
Temperature (^{o}C)	65
Methanol-oil ratio	8:1
Catalyst amount (wt%)	2

Physicochemical properties of biodiesel produced

Analyses were done on the produced biodiesel from tropical almond seed oil using a 20% NaOH/kaolin heterogeneous catalyst. In accordance with ASTM D6751 specifications, the physicochemical characteristics of the fuel were compared, and the results are shown in Table 12. Almost all the biodiesel's major characteristics fell inside the acceptable range set out by international standards.

79

Table 12: Physicochemical properties of biodiesel produced using bifunctional heterogeneous catalyst

Properties	Extracted oil	Biodiesel	ASTM Std. D6751-12	EN 14214-12	Ghana Standard Authority
Moisture content of seed (%)	2.30 ± 0.05		-	-	-
Oil yield (%)	58.24	95.94	-	-	-
Colour	Yellow	Light yellow	-	-	-
Odour	-	-	-	-	-
Acid value (mgKOH/g oil)	2.97 ± 0.02	0.42 ± 0.03	≤ 0.5	≤ 0.5	1.0 max
Density (g/cm^3)	0.92 ± 0.01	0.88 ± 0.07	0.86 - 0.90	0.86 – 0.90	-
Iodine value (gI$_2$/100g oil)	96.2 ± 0.15	71.41 ± 1.20	≤ 120	≤ 120	-
Free fatty acid (mgKOH/g oil)	1.48 ± 0.01	0.22 ± 0.21	-	-	-
Kinematic viscosity (m^2/s)	13.4 ± 0.1	5.1 ± 0.6	1.9 - 6.0	3.5 - 5.0	1.5 – 6.5
Saponification value (mgKOH/g oil)	200.25 ± 2.15	179.30 ± 0.34	-		
Flash point	160	170	≥ 93	≥ 93	66 min
Cetane number		61	≥ 47	≥ 51	47 min
Pour point	5	-1	-15 to 10	-	15 max
Cloud point	3	-1	-3 to 12	-	-

80

Reusability of catalyst

Figure 16 shows that during the initial almond seed oil transesterification of five cycles using a NaOH(20%)/kaolin catalyst, fatty acid methyl ester yields of 95.94 to 84.28% were obtained, demonstrating that the catalyst may be recovered for at least five cycles with an 11% loss from the 95.94% biodiesel yield obtained with new catalyst.
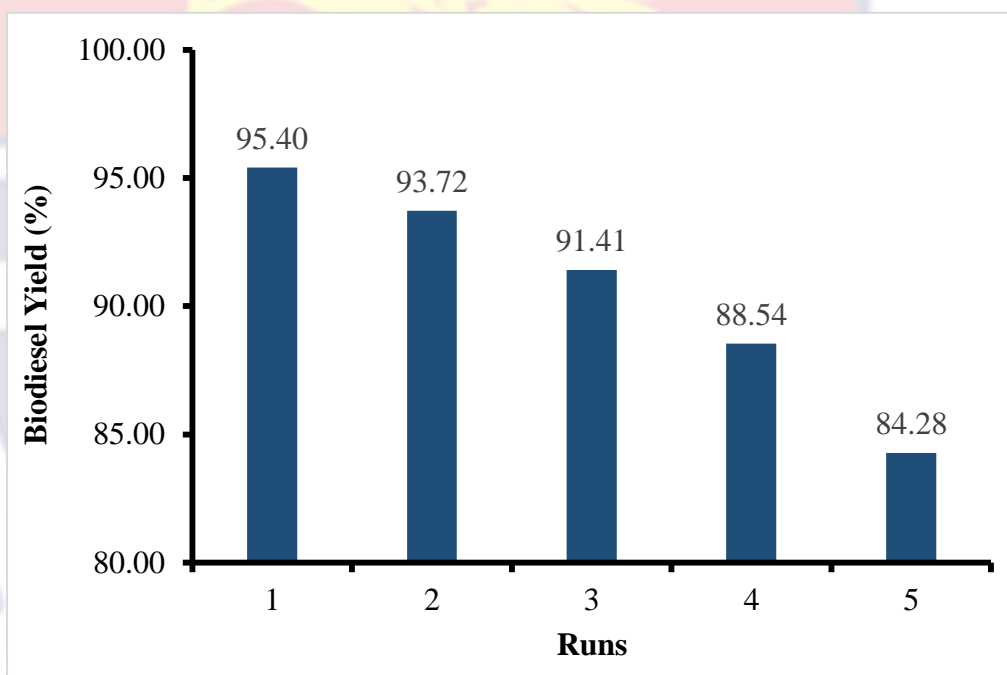

Figure 16: NaOH(20%)/Kaolin catalyst reusability.

The optimal parameters for the reusability analysis in this section were time of 1.5 hours, methanol-oil ratio (8:1), 2 g catalyst, , and temperature kept at 65 °C. It is possible that the partial sodium leaching into the mixture during

81

subsequent runs and the depositing of glycerol, methyl ester or unreacted oil, on the active sites located on the catalyst are the causes of the decline seen after each run in methyl ester yield (Jalalmanesh *et al*., 2021; Salmasi *et al*., 2020).

Kinetic model of transesterification of Tropical almond seed

The initial step of the forward reactions is represented by a pseudo second-order model in the kinetic model. In equation (15), the simple second-order rate of reaction for triglyceride (TG) is as follow:

$$\frac{-d[TG]}{dt} = k[TG]^2 \tag{20}$$

Integrating of equation (20) gives:

$$k_{TG}.t = \frac{1}{[TG]} - \frac{1}{[TG]_0} \tag{21}$$

Same procedure was applied to (16) and (17), and the result leads to the following equations:

$$k_{DG}.t = \frac{1}{[DG]} - \frac{1}{[DG]_0} \tag{22}$$

$$k_{MG}.t = \frac{1}{[MG]} - \frac{1}{[MG]_0} \tag{23}$$

Where, k represents the pseudo rate constant, $[TG]_0$ represents the initial triglyceride concentration, t is the time of reaction, $[DG]_0$ represents the first greatest diglyceride concentration, while $[MG]_0$ represents the initial highest monoglyceride concentration. A graph of 1/[TG] against time (t) will give a straight line if the model of equation (21) is accurate. The slope, k_{TG} is

82

shown in figure 17. Equation 15 (TG → DG) was used to get the rate constant of the conversion reaction.

The conversions of DG in equation (16) and MG in equations (17) was also accomplished using straight lines in figure 18 (A) and (B) respectively.
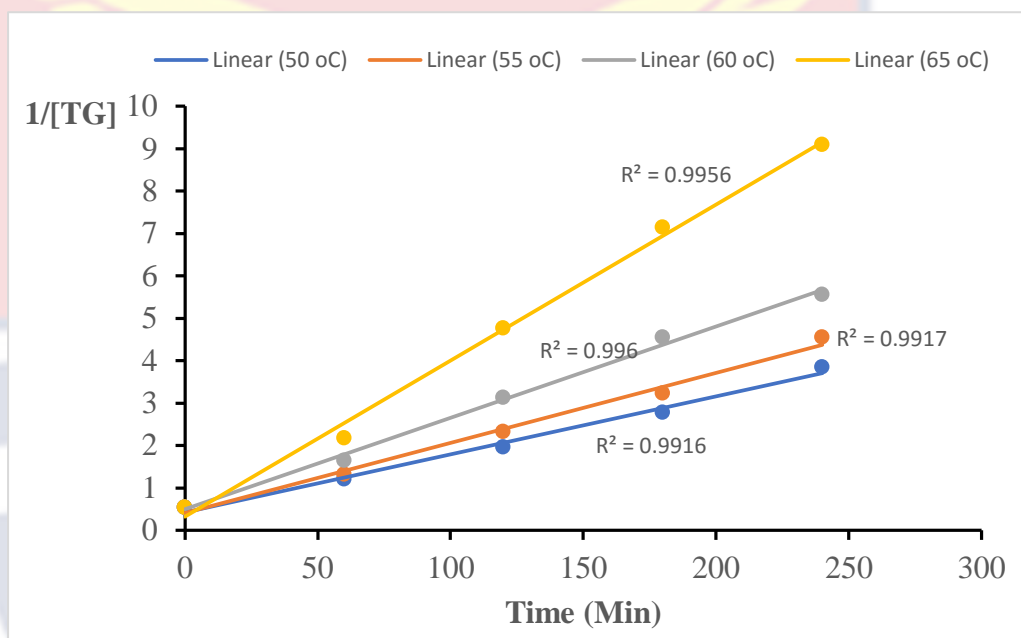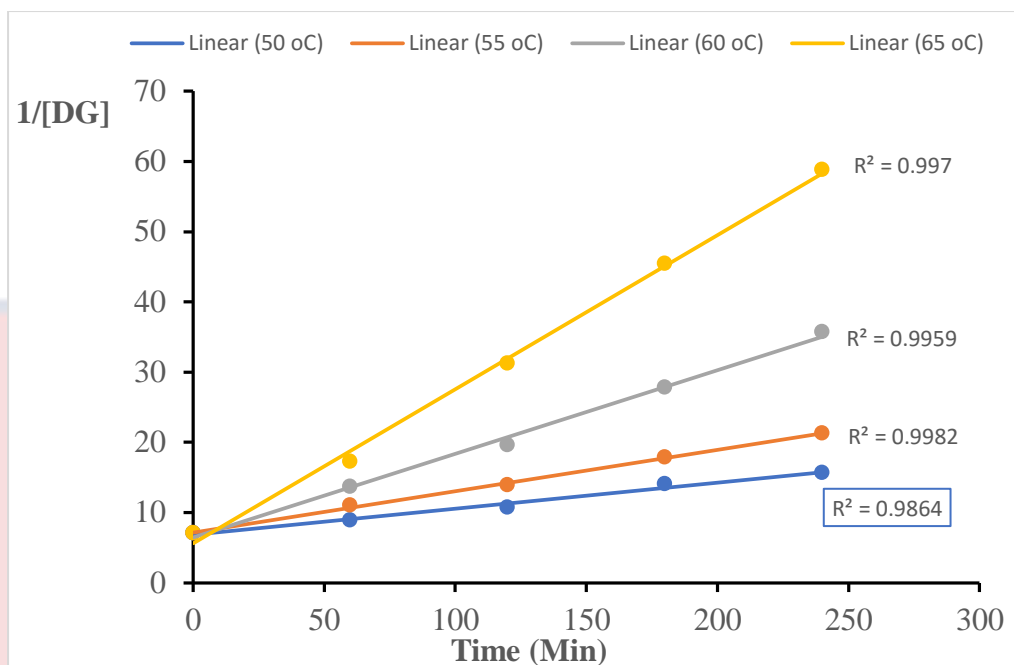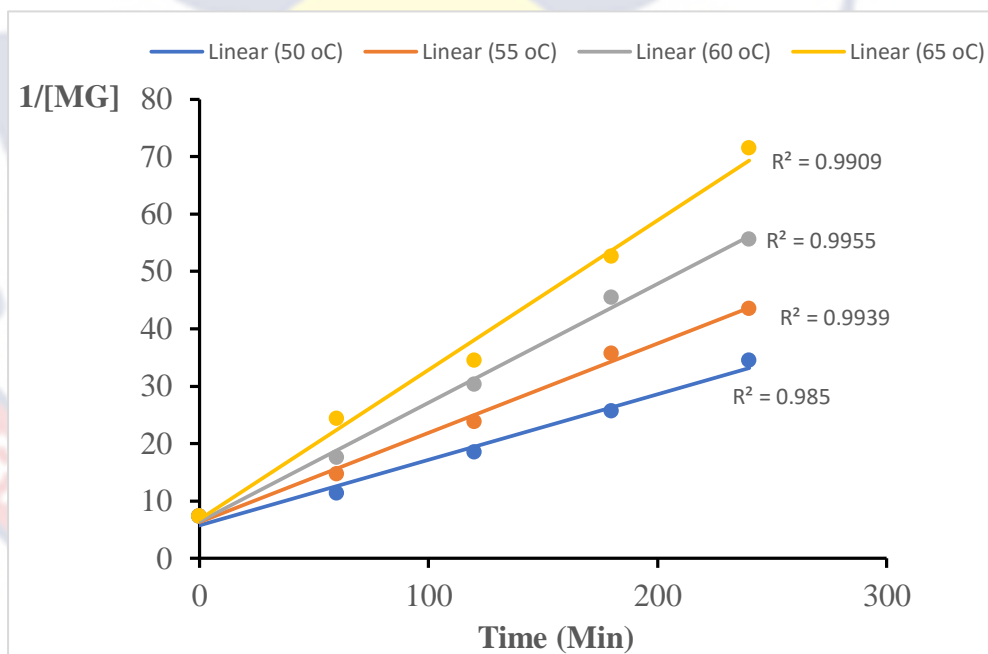

Figure 17: Rate constants for triglyceride to diglyceride conversion at different temperatures

(A)

(B)

Figure 18: Rate constants for converting diglyceride to monoglyceride (A) and monoglyceride to glycerol (B) at different temperatures

84

Table 13: Transesterification rate constants and correlation coefficients of tropical almond seed oil at various temperatures

Glyceride	Temperature (^{o}C)	Rate constant, k (min^{-1})	R-square
Triglyceride	50	0.014	0.9916
	55	0.017	0.9917
	60	0.022	0.9960
	65	0.037	0.9956
Diglyceride	50	0.037	0.9864
	55	0.059	0.9982
	60	0.119	0.9959
	65	0.220	0.9970
Monoglyceride	50	0.114	0.9850
	55	0.155	0.9939
	60	0.207	0.9955
	65	0.261	0.9970

Table 13 shows the k values and their conforming coefficient of determination for four distinct temperatures (50 ^{o}C, 55 ^{o}C, 60 ^{o}C, and 65 ^{o}C). The statistical data had a good coefficient of determination (> 0.99 %), indicating that the expected data for computing the rate constants was correct. The findings indicated that at methanol-oil ratio (8:1) and 2 g amount of NaOH(20%)/kaolin catalyst, the transesterification conversions of tropical almond seed oil using methanol exhibits the second-order kinetics.

It is worth noting that when temperature rises, the rate constants get larger and value of k increases in this sequence: $k_{TG} < k_{DG} < k_{MG}$. These findings matched the influence of temperature on composition change that were previously indicated. The rate-determining step for the whole NaOH(20%)/kaolin catalysed methanolysis of tropical almond seed oil is the

85

triglycerides to diglycerides conversion since it had the lowest rate constant. The rate constant rose from 0.013 to 0.037 min^{-1} when temperature went up from 50 to 65°C (Darnoko & Cheryan, 2000; Thi *et al.*, 2008).

86

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

Conclusion

Terminalia catappa (Tropical almond) seed oil has not garnered much attention as a potential substitute raw material for biodiesel production, primarily due to its established uses in medicine and as a food seasoning. The main objective of this study was to explore the production of biodiesel by means of transesterification applied to tropical almond seed oil, employing the response surface method along with NaOH and a heterogeneous bifunctional catalyst composed of NaOH(20%) and Kaolin.

Tropical almond seed oil was obtained from the seeds using the Soxhlet extraction method. The resulting oil exhibited a yield of 58.24%. The properties of the oil, including its acid value, iodine value, fatty acid composition, viscosity, saponification value, and various other requisite characteristics, all fell within acceptable limits for biodiesel production

Based on the study's findings, it can be concluded that the highest biodiesel yield of 96.38% from tropical almond seed oil was achieved through transesterification using the response surface method and NaOH as the catalyst. Utilizing the response surface method, a quadratic polynomial model was formulated and subsequently verified. An analysis of variance (ANOVA) was conducted on the quadratic model, revealing that the three (3) parameters

and their interactions, except for the interaction between methanol-oil and time, significantly influenced the process yield. This optimal result was obtained with a methanol-oil ratio of 6:1, a catalyst amount of 1 g, and a reaction time of 30 minutes.

Heterogeneous catalysts were successfully developed from natural kaolin clay material, loaded with varying amounts of NaOH species, and employed in the transesterification reaction of tropical almond seed oil with methanol for biodiesel production. Under the ideal conditions for catalyst preparation and reaction variables (methanol-oil ratio of 8:1, 2 g catalyst quantity, reaction time of 1.5 hours, and a reaction temperature of 65°C), the NaOH(20%)/kaolin catalyst (with 20 wt.% NaOH impregnation on kaolin) demonstrated its highest catalytic activity, reaching 95.94% due to its enhanced basicity.

Furthermore, the results showed that even after five cycles, the catalyst consistently achieved an acceptable methyl ester yield of 84.28%, indicating its reusability as a material for the transesterification reaction. Consequently, the prepared NaOH(20%)/kaolin catalyst proves to be a sustainable and promising catalyst for the production of biodiesel from tropical almond seed oil and methanol. Additionally, the kinetic model that was established indicated a pseudo-second order reaction.

88

Recommendations

Terminalia catappa (Tropical almond) seed oil has been noted to have capacity as a feedstock for biodiesel production. The suggestions from this work are as follows:

1. To evaluate the feasibility of tropical almond plant cultivation on a commercial scale to produce biodiesel.

2. To investigate the performance of the blends of conventional diesel and biodiesel made from tropical almonds.

3. Additionally, to test and evaluate the efficacy of the synthesized heterogeneous bifunctional catalyst using refined standard oils such as jatropha, castor, palm or soybean.

89
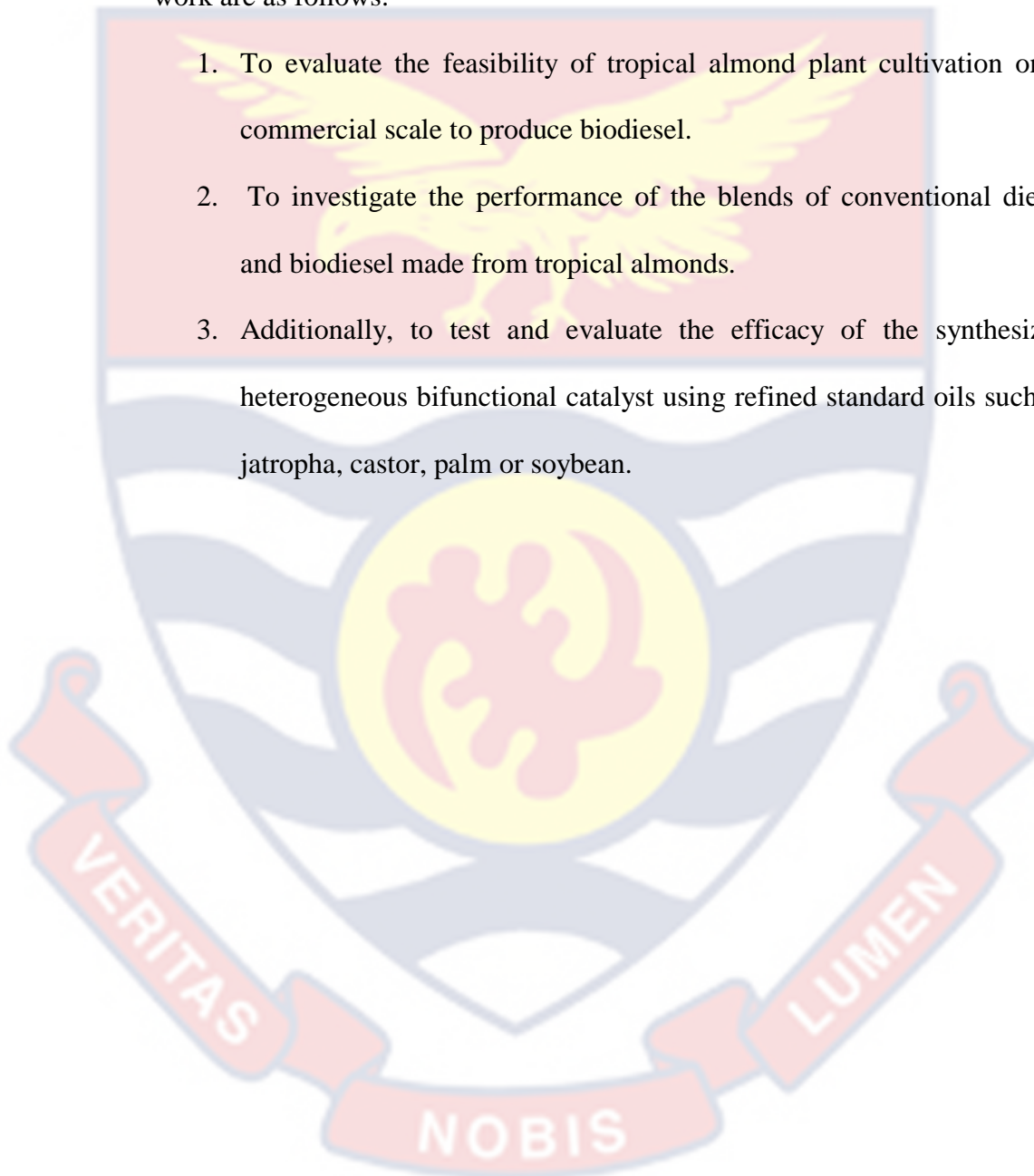
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