SYNTHESIS AND CHARACTERIZATION OF BIO-BASED CATALYSTS DERIVED FROM PALM KERNEL AND SNAIL SHELL IN THE PRODUCTION OF BIODIESEL

BY

OLAIYA AYOMIDE EPHRAIM

ENG1703906

DEPARTMENT OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

UNIVERSITY OF BENIN

BENIN-CITY

DECEMBER, 2022

SYNTHESIS AND CHARACTERIZATION OF BIO-BASED CATALYSTS DERIVED FROM PALM KERNEL AND SNAIL SHELL IN THE PRODUCTION OF BIODIESEL

BY

OLAIYA AYOMIDE EPHRAIM

ENG1703906

A PROJECT WORK SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF ENGINEERING [B.ENG] DEGREE OF THE UNIVERSITY OF BENIN.

DECEMBER, 2022

CERTIFICATION

This certifies that **OLAIYA AYOMIDE EPHRAIM** with **MATRIC NO: ENG1703906** of the Department of Chemical Engineering of the University of Benin, Benin-city, Edo State, under the supervision of Mr. C.A Osagiede, has carried out this research project in partial fulfilments of the requirements for the award of Bachelor of Engineering Degree in Chemical Engineering.

……………………………… ……...………………………
ENGR.(MR.) C.A OSAGIEDE Date
Project Supervisor

……………………………… ……...………………………
ENGR. DR. O.U OSAZUWA Date
Project Coordinator

…………………………..... ………………………………
ENGR DR. (MRS.) E.A OYEDOH Date
(Head of Department)

……………………………… ……...………………………
External Examiner Date

DEDICATION

This project work is humbly dedicated to God Almighty for his grace, guidance, protection and the successful completion of my university program. Also, to my mum Mrs. Olaiya Janet for her unending financial, prayers and emotional support towards my academics.

ACKNOWLEDGEMENTS

I want to express my profound gratitude to God Almighty for making this project a huge success and for his unending love, grace, kindness and numerous blessings in my life generally and throughout my stay in the university, my utmost appreciation for his everlasting faithfulness.

My unreserved gratitude goes to my project supervisor, Mr. C.A Osagiede for his tireless efforts and patience towards the successful completion of my research work. I also want to thank Mr. Fred for his consistent direction and guidance during the course of this project work.

To my mother, Mrs. Janet Olaiya, my heartfelt gratitude and a million thanks for her love, encouragement, moral value, financial and emotional support and commitment throughout my course of study.

Special thanks to Dr. Andrew for his help and guidance on report writing. I also wish to thank my friends and colleagues who have always pushed me to do my best in everything.

Table of Contents

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The study investigated the use of palm kernel shells and snail shells in the synthesis of a bio-based bifunctional heterogeneous catalyst. Using impregnation methods, palm kernel shells (PKS) biochar was functionalized with calcined snail shell doped with copper sulphate. The catalytic activity of the resulting catalyst was tested through the simultaneous esterification and transesterification of palm kernel oil (PKO). The characteristics of the catalyst were examined using X-ray diffraction spectroscopy (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray fluorescence (XRF). The results showed that catalyst formulation with 90wt% CaO catalyst and 10 wt% activated PKS biochar generates the greatest biodiesel yield of 93.2%; this was reached with 3 wt% catalyst loading, 12:1 methanol to PKO molar ratio at 60 C within 1 hour and 30 minutes of reaction time. The bifunctional heterogeneous catalyst is chemically stable and can be reused up to five times, producing 72.6% biodiesel in the final cycles. The results show that the biodiesel produced meets the worldwide standards. The use of waste material to create an effective bifunctional catalyst for biodiesel synthesis from palm kernel oil (PKO) has significant commercialization potential in the future.

CHAPTER ONE
INTRODUCTION

1.1 BACKGROUND TO THE STUDY

The search for alternative renewable and sustainable fuels with efficiency comparable to the current conventional fuels is being driven by the drastic depletion of fossil fuels and ongoing global greenhouse gas emissions. In this light, sustainable and renewable biofuels had been considered as an alternative to cut back on the use of fossil fuels. Typically created from biological material or living things, such as plants, animal byproducts, or microorganisms, biofuels are defined as liquid or gaseous fuels that are produced from renewable sources. The biofuel sector has seen tremendous expansion over the last ten years, with Europe, Brazil, and the United States being the biggest contributors. Currently, liquid transportation fuel is where biofuels are most commonly used. According to the raw materials utilized, biofuels can be broadly classified into four generations. The majority of first-generation biofuels come from crops used for food. Biomass or lignocellulosic crops are the source of second-generation biofuels. The biorefinery industry benefits from this material source because it is abundant, affordable, and sustainable. Notably, the usage of lignocellulosic crops results in low environmental impact and zero net carbon dioxide emissions (Alptekin et al., 2014). The third generation of biofuels come from algae-sources. Avoiding the problem of food competition is the advantages of the type of raw resources needed for the creation of second and third generation biofuels. Additionally, there are several benefits to making biofuels from algae, as the amount of triglyceride-based oil that can be recovered from microalgae is 15 to 300 times greater than that from conventional crops in terms of area. The fourth generation of biofuels are those produced from genetically engineered algae. Fourth-generation biofuel use is gaining popularity as a means of reducing environmental impact, particularly with regard to the use of land for agricultural plantations.

Biodiesel and bioethanol are two liquid-based biofuels that are commonly used in transportation. Bioethanol is created through starch or sugar fermentation, whereas biodiesel is created through the transesterification of oil crops.Diesel is replaced by biodiesel, and petrol is replaced by bioethanol. Notably, biodiesel accounts for 76% of all biofuel consumption, with bioethanol making up the remaining 20%. With little to no modification, biodiesel is frequently used in engines with compression ignition. Biodiesel shares several traits with conventional diesel, but they are not the same. Because biodiesel has a high flash point, it is secure to handle and store. Direct use of biodiesel as engine fuel is possible (B100), as is blending it with diesel in a specific ratio (B20, B50, etc.). It is noteworthy that bioethanol has a high-octane number with anti-knocking capabilities in engines, while biodiesel has a lower octane number with a lower cetane number. Earlier research found that biodiesel outperformed bioethanol in engine performance because bioethanol has a higher miscibility to water and organic solvents, that ends up contaminating automobile lubricant components and causing engine corrosion.

1.2 AIM AND OBJECTIVES

The aim of this study is to modify the catalyst by doping with conventional metal in order to introduce active sites to the catalyst using snail shell, to improve the reaction time of the production of biodiesel. The specific objectives of the study are;

- Synthesis of bi-functional heterogeneous catalysts by modified impregnation method.
- Study of physicochemical properties of synthesized catalysts by analytical techniques.
- An economical biodiesel production from palm kernel oil.

- Study of physicochemical properties of synthesized biodiesel.

1.3 SCOPE OF STUDY

In order to achieve the objectives stated above, the research scope encompasses;

- Collection of palm kernel shell from site
- Preparation of catalyst from the palm kernel shell
- Modifying the catalyst prepared by doping with a convectional metal and snail shell

1.4 PROBLEM STATEMENT

Biodiesel is a diesel engine alternative fuel that is sustainable, renewable, and kind to the environment. Using the appropriate catalyst, transesterification of vegetable oil, animal fats, or algal oil in the presence of methanol is a viable process for producing biodiesel. Free fatty acids (FFAs) in the feedstock and the biphasic (immiscible) nature of the reactants, such as methanol oil, create certain challenges for transesterification reactions. Effective and inexpensive catalysts with an environmentally friendly process are needed to address the problems with biodiesel manufacturing. Heterogeneous catalysts have recently demonstrated a promising potential over homogeneous catalysts for the manufacture of biodiesel from third generation feedstock like microalgae, notwithstanding some challenges. Catalyst activity and selectivity need to be increased for more efficient catalytic processes.

Waste shell materials high in calcium are a commonly available low-cost green resource. The use of the modified waste shell catalyst offers the biodiesel industry great potential. On a larger industrial scale, there are still obstacles to overcome. This is a result of the CaO catalyst's instability, which frequently has Ca2+ leaching issues. The use of CaO catalysts generated from discarded shells has been hampered by additional issues like poor surface area, water sensitivity, leaching of active sites by glycerol, and competition with soap-forming side reactions.

1.5 RELEVANCE OF THE STUDY

Natural waste shells are a rich source of calcium, which may be converted into a Ca-based catalyst for the transesterification and esterification of biodiesel. In most cases, the calcium is present as calcium carbonate (95–99%), and additional processing is necessary to expose the calcium active phases (such as oxide or hydroxide phases) for additional reaction. CaO or Ca(OH)2 generated from waste shells has similar properties to the traditional form, such as basicity and surface area. Both of these characteristics, particularly the high basicity density and strong basic strength of the catalyst, were found to significantly increase the transesterification rate for the synthesis of biodiesel.

CHAPTER TWO

LITERATURE REVIEW

Renewable energy has emerged as one of the most appealing alternative energy sources for the future, owing to the depletion of fossil fuel resources and growing environmental concerns. Biodiesel and bioethanol are two liquid transportation fuels generated from biomass that have the potential to replace gasoline and diesel on a worldwide scale. Demirbas (2009). Transportation is one of the most energy-intensive industries, and bioethanol and biodiesel will almost certainly replace gasoline and fossil fuels, respectively. Because they recycle the same carbon atoms, biomass-based energy sources for heat, power, and transportation fuels are carbon dioxide neutral.

Due to the fact that biomass resources are widely available, biomass-based fuel technology has the potential to employ more people than fossil fuel-based technology. As traditional energy sources such as coal, petroleum, and natural gas become depleted, the daily need for energy increases due to the rapid urbanization and population growth. Biomass is becoming one of the most promising environmentally friendly energy sources.

2.1 BIOFUELS

Any fuel derived from biomass materials, such as plant or algal material or animal waste, is referred to as biofuel. In contrast to fossil fuels such as petroleum, coal, and natural gas, biofuel is regarded a renewable energy source due to the simplicity with which it may be provided. Biofuel is widely promoted as a cost-effective and environmentally benign alternative to petroleum and other fossil fuels, particularly in light of growing petroleum prices and increased concern about the effects of fossil fuels on global warming. Many critics are concerned about the proliferation of some biofuels due to the possibility of large-scale use of agricultural land from food production and the associated environmental and economic implications of the refining process. (Morshed et al., 2011).

Some biofuels, such as wood, can be used directly as the fuel for a fire to generate heat. In a power plant, heat is utilized to power generators, which in turn produces electricity for the plant.

Today, many power plants burn wood, grass, and other forms of biomass. Given the infrastructure in place to use them, liquid biofuels are critical, particularly for transportation. The most widely produced liquid biofuel is ethanol, which is produced by fermenting starch or sugar. Brazil and the United States are two of the world's largest ethanol producers. In the United States, ethanol biofuel is frequently blended with gasoline to produce "gasohol," a 10% ethanol-based fuel. Sugarcane is the principal source of ethanol biofuel in Brazil, where it is frequently used as a 100 percent ethanol fuel or in gasoline blends with 85 percent ethanol. In contrast to "first-generation" ethanol biofuel, "second-generation" cellulosic ethanol is produced from low-value biomass with a high cellulose concentration, such as wood chips, crop residues, and municipal waste. Cellulosic ethanol is typically made from sugarcane bagasse, a byproduct of sugar production, or from other grasses that may be grown on poor soil. Because of its lower conversion rate compared to first-generation biofuels, cellulosic ethanol is mostly used as a gasoline additive.

The second most extensively used liquid biofuel is biodiesel, which is mostly made from oily plants (such as soybeans or oil palm) it is also gotten from other oily sources (such as waste cooking fat from restaurant deep-frying). Biodiesel is routinely mixed with petroleum diesel fuel in varying amounts in diesel engines. Europe has demonstrated the most tolerance. Despite difficulties in commercialization, the utilization of algae and cyanobacteria as a source of "third-generation" biodiesel shows promise. Up to 40% of the weight of certain algae species is made up of lipids, which can be used to make biodiesel or synthetic petroleum. Algae and cyanobacteria may produce 10 to 100 times more fuel per unit area than second-generation biofuels, according to some estimates.

Other biofuels include methane gas and biogas, which can be generated from the decomposition of biomass in the absence of oxygen, as well as the in-development biofuels methanol, butanol, and dimethyl ether.

Biofuels contain oxygen levels ranging from 10 to 40%, whereas petroleum has virtually none, resulting in vastly differing chemical characteristics. However, all biofuels have very low sulfur levels and many have low nitrogen levels.

Biomass can be turned into liquid and gaseous fuels through thermochemical and biological processes. Biofuel is a fuel derived from renewable sources that is non-polluting, easily available, economical, sustainable, and dependable. (Zhang et al., 2010).

2.2 RENEWABLE ENERGY RESOURCES

2.2.1. Alcohols (Bio-Ethanol)

Bioethanol is an attractive alternative fuel to fossil fuels because it has the potential to boost both energy security and environmental safety. The production of bioethanol from sugars, starch, and lignocellulosic biomass are the three primary forms of biomass that have been researched extensively up until this point. However, depending on the type of feedstock, the amount of biomass that may be converted into ethanol might vary greatly. This is mostly due to differences in the biochemical composition of the feedstock. As a direct consequence of this, only a limited number of feedstocks have been successfully exploited in commercial settings. In spite of the fact that the vast majority of these innovations have not yet been implemented in a plant that is used for commercial purposes, the process of converting biomass has undergone a significant amount of development, in recent years. Sugar fermentation is a standard phase in the conversion of all different types of biomass, and microorganisms have a substantial influence on all of the primary processes that take place during this step. In the production of ethanol, it is common practice to make use of the yeast strain Saccharomyces cerevisiae and the bacterium species Zymomonas mobilis. The production of ethanol is subject to the effect of a number of different variables, and the optimal conditions for each of these components have a direct bearing on the total amount of ethanol produced.

Carbohydrates are the most important fermentable components of a bioethanol feedstock. Carbohydrates come in a variety of forms, including starch, soluble sugars (including mono- and disaccharides), cellulose, and hemicellulose. The bulk of the feedstocks that are based on sugar are soluble sugars, even though starch is the primary source of carbohydrates in crops that are classified as starchy. Cellulose and hemicellulose are the two primary varieties of carbohydrates that can be found in lignocellulosic biomass. The amount of carbohydrates that can be found in renewable sources might vary substantially depending on the type of biomass, the botanical sources used, and the crop hybrids used. Some of the plant parts that are utilized as ethanol feedstocks are the stalks, grains, tubers, roots, leaves, stems, fruits, and straws of the various crops. Other plant parts that contain carbs and are used include the stems.

The primary fermentable sugars found in biomass, particularly sugar-based raw materials, are glucose, fructose, and sucrose. Glucose is the most common of these three sugars. In the absence of any further processing, yeasts or other fermenting microorganisms are able to convert these soluble sugars into ethanol through the process of fermentation. In contrast to soluble sugars, yeasts and bacteria that feed on glucose in their natural forms are unable to digest starch in its polymeric state since it is a glucose polymer. Because of this, in order for fermentation to occur, the starch first needs to be hydrolyzed into glucose, a process that requires amylolytic enzymes. This process is known as hydrolysis.

2.2.2. Vegetable Oils as Fuels

Vegetable-derived fuels have been utilized for many years; Dr. Rudolf Diesel used peanut oil for his engine more than a century ago. The first diesel engine was really created by Dr. Diesel to run on vegetable oil. Up to the 1920s, diesel engines were powered by vegetable oils. However, throughout that decade, diesel engine producers altered their specs to make them better suited for the mineral diesel's viscosity rather than the previously utilized vegetable oils. Vegetable oils have a number of benefits over mineral diesel, including biodegradability, portability, quick availability, renewability, higher heat content, reduced sulfur level, and lower aromatic content. (Gondra, 2010a).

2.2.2.1. Constituents and properties of vegetable oils

Oils and fats are actually blends of various liquids. The principal constituents of raw oils are triacylglycerols, diacylglycerols, monoacylglycerols, and free fatty acids, with triacylglycerols accounting for more than 95% of the total (FFA). This sample may contain phospholipids, free sterols and sterol esters, triterpene alcohols, hydrocarbons, and fat-soluble vitamins.

The primary distinction between animal fats and vegetable oils is that animal fats are often saturated, meaning they lack double bonds and are therefore solid at room temperature. Vegetable oils, on the other hand, are often liquid at room temperature. Vegetable oils have a different chemical makeup than mineral diesel. As many as three fatty acids can be joined to a glycerol molecule in the case of vegetable oils by employing esters as linkers. These molecules are the triacylglycerols, which are the primary component stated above. Diacylglycerols and monoacylglycerols are used to describe situations in which only two or one fatty acids are connected to a glycerol molecule, respectively. The fatty acids in the various oils will vary from one another.

2.2.2.2. Disadvantages of vegetable oils when used as fuels

However, a number of issues have been discovered, chiefly relating to the increased viscosity of this type of oil in comparison to mineral diesel, which typically results in poor fuel atomization, incomplete combustion, carbon buildup on the injector, and fuel accumulation in lubrication lubricants. Finding better fuels has become necessary as a result of a number of physical characteristics, including their decreased volatility compared to mineral diesel and the reactivity of unsaturated hydrocarbon chains. (Gondra, 2010b).

2.2.3. Biodiesel

Biodiesel is a type of liquid biofuel that can be used in diesel engines alone or in conjunction with normal diesel oil. It is produced chemically by combining vegetable oils or animal fats with an alcohol (Romano & Sorichetti, 2011). Biodiesel is a combination of long-chain monoalkylic esters generated from renewable fatty acids that is intended for use in diesel engines. This definition was provided by ASTM International, formerly known as the American Society for Testing and Materials.

Long chain fatty acid mono alkyl esters are a type of alternative non-fossil diesel fuel that can be made from animal fat or vegetable oils. It is composed of long-chain alkyl esters and is produced when an alcohol lipid undergoes a reaction that results in the formation of esters of fatty acids.

The combustion qualities of biodiesel are remarkably comparable to those of petroleum diesel, notably the amount of energy it contains and the cetane ratings it has, despite the fact that diesel derived from petroleum contains completely different chemicals. Because of this, it is a viable alternative to diesel made from petroleum.

In most injection pump diesel engines, biodiesel can either be utilized in its unadulterated form (referred to as B100) or it can be blended with petroleum diesel at any percentage.

2.2.3.1 Historical Development of Biodiesel

In the 1890s, Rudolf Diesel devised the diesel engine (Van Gerpen, 2005). By the time he displayed his engine at the World Exhibition in Paris in 1900, it was powered entirely by peanut oil. However, because inexpensive petroleum fuels were widely available, few people were interested in alternatives.

Several countries used vegetable oil as fuel during World War II (1939-1945), when petroleum fuel supplies were disrupted. When the war ended and petroleum supplies became cheap and plentiful again, however, vegetable oil fuel was forgotten.

Many nations turned to vegetable oil as a potential fuel during the 1970s oil crisis, but the viscosity (thickness) of the vegetable oil damaged the engines. Then, scientists experimented with turning the vegetable oil into biodiesel. In or around 1984, the term "biodiesel" was likely first used. (Van Gerpen, 2005).

At an agricultural college in Austria, the first biodiesel manufacturing facility specifically created to manufacture fuel was launched in 1985. In Kansas City, Missouri, the first commercial production of biodiesel began in 1991. (Van Gerpen, 2005)

The development of standards to guarantee and provide excellent product quality and consumer confidence has resulted from the development and commercialization of biodiesel in various nations across the world. ASTM D6751 (American Society for Testing and Materials) and the European standard EN14214 are two frequently used biodiesel standards (Chitra, 2012).

2.2.3.2 Properties and Composition of Biodiesel

Biodiesel can be produced from various feed stocks, oils and fats of varying origin and quality. The diesel produced from these different sources are of different qualities and therefore need to meet the standard condition for biodiesel which is specified by ASTM D6751. The parameters which define the quality of biodiesel include the following:

2.2.3.2.1 Viscosity

A fluid's resistance to gradual deformation by tensile or shear stress is measured by its viscosity. It is also known as a measurement of the fluid's internal friction-induced flow resistance. Kinematic viscosity, which is calculated as the ratio of dynamic viscosity to density, is a fluid's natural resistance to flow in the absence of any external forces other than gravity.

Due to the fact that it primarily influences the engine's fuel injection system at low temperatures, viscosity is a crucial characteristic of biodiesel. Poor fuel atomization, partial combustion, and carbon buildup on the injectors are all effects of a highly viscous fuel. Because high viscosity also causes engine power loss, smoke to be produced, and operational issues like difficult engine starting, erratic ignition, and decreased thermal efficiency, biodiesel must have a low viscosity. Although the figures are similar, biodiesel has a little bit greater viscosity than regular diesel. Vegetable oils are not commonly employed as fuels due to their viscosity.

2.2.3.2.2 Density

Density is defined as the mass per unit volume of a substance, it is defined mathematically as:

$$\rho = \frac{m}{v} \text{---------------------}(1)$$

The density of a material varies with temperature and pressure. Density is a very significant fuel property because it affects the mass of fuel pumped into the combustion chamber, thereby affecting the efficiency of the engine's air-fuel ratio. The density of biodiesel depends primarily on its ester content and the quantity of alcohol remaining, so the density of biodiesel is mainly influenced by the feedstock used to manufacture biodiesel.

2.2.3.2.3 Specific Gravity

Specific gravity is the ratio of a material's density to the density of a reference substance. Water is the reference substance for liquids, while air is the reference substance for gases. Mathematically, for a liquid, the specific gravity (SG) is given as:

$$SG = \frac{\rho liquid}{\rho water} \text{-----------------------(2)}$$

2.2.3.2.4 Flash Point

The flash point of a volatile material is the minimum temperature at which the substance will catch fire (flash) when a spark is applied. Minimum temperatures at the flash point are important for fuel safety and handling. Biodiesel has a higher flash point than diesel made from petroleum. This makes it a good fuel for cars because it makes explosions less likely.

Table 2.1: Standard Specification for Diesel and Biodiesel

(Prah, 2010)

Fuel Property	**Diesel**	**Biodiesel**	Unit
Fuel Standard	ASTM D975	ASTM PS 121	
Fuel composition	C10-21HC*	C12-22	Not applicable
Lower heating value	36.6x103	32.6x103	Calories
Kinematic viscosity@40°C	1.3-4.1	1.9-6	mm^2/s
Specific gravity @15.5°C	0.85	0.88	No units
Density @ 15°C	848	878	g/cm3
Carbon	87	77	Wt %
Hydrogen	13	12	Wt %
Sulphur	0.05	0.0-0.0024	Wt %
Flash point	60-80	100-170	°C
Cloud point	-15 to5	-3 to 12	°C
Pour point	-35 to -15	-15 to 10	°C

Cetane number	40-55	48-65	Not applicable
Stoichiometric air/fuel	15	13.8	

2.2.3.3 Advantages and Limitations of Biodiesel

2.2.3.3.1 Advantages of Biodiesel

It is possible to draw the conclusion that the research for biodiesel is truly useful to mankind because it has numerous advantages as a substitute. This is because biodiesel possesses features that are superior to those of petroleum diesel itself.

The advantages of biodiesel include:

1. Biodiesel is a renewable source of energy, which implies it has a constant source of supply, and it will minimize the country's dependence on imported petroleum. This is one of the primary benefits of biodiesel (Gondra, 2010a).
2. Biodiesel is non-toxic and biodegradable at the same time. It degrades approximately four times more quickly than diesel made from petroleum. This is made possible by the high oxygen level of the fuel, which is significantly higher than the oxygen content of mineral diesel (Igbokwe & Nwafor, 2014).
3. Because it has a higher cetane number than petroleum diesel, biodiesel ignites more quickly than petroleum diesel. The cetane number is an indicator that is utilized to determine the quality of diesel fuel, particularly the ignition quality. The purpose of this test is to determine whether or not the fuel is ready to self-ignite when it is injected into the engine (Igbokwe & Nwafor, 2014).
4. Due to the closed carbon cycle, the production of biodiesel does not contribute to the

warming of the planet. It lessens the amount of greenhouse gases like carbon monoxide (CO) and carbon dioxide that are released into the atmosphere (CO2). A life cycle analysis of biodiesel was found to have a 78% reduction in overall CO2 emissions, as determined by cycle analysis (Van Gerpen, 2005).

5. Compared to diesel, biodiesel has lower levels of sulphur and aromatic compounds, which results in reduced emissions of these pollutants (Gashaw & Lakachew, 2014).
6. It offers a market for the surplus production of animal fats and vegetable oils (Van Gerpen, 2005).
7. Because of its lubricating characteristics, it helps extend the lifespan of engines.

2.2.3.3.2 Limitations of Biodiesel

Even though biodiesel has various advantages, it also has certain downsides that should be mentioned:

1. Agricultural feedstock is required for the production of biodiesel, and its availability may be limited at times due to the requirement to generate food. This may limit biodiesel output (Gashaw & Lakachew, 2014).
2. To handle biodiesel, a modified refueling infrastructure is required, which increases the overall cost (Gondra, 2010a).
3. The kinematic viscosity of biodiesel is higher than that of diesel fuel.
4. Because biodiesel oxidizes more easily than diesel, it may generate compounds that are detrimental to car components when kept for lengthy periods of time (Gill et al., n.d.).

2.2.3.4. Feedstock for Biodiesel Production

There are many different kinds of raw materials that can be used to make biodiesel. This involves a variety of vegetable oils and animal fats. The majority of the starting components are first-century edible feedstock. "Prices and availability play a significant role in determining the different types of feedstock used for the manufacture of biodiesel in different parts of the world." (Adewale et al., 2015). Edible feedstock should not be used as it will not be cost effective and it is not feasible to be used in a larger scale. There will be fight over for sustainability and food for fuel production (Chitra, 2012).

Table 2.2: List of Biodiesel Feedstock

Source: (Gondra, 2010a)

Vegetable oils	**Non-edible oils**	**Animal fats**	**Other sources**
Soybeans	Almond	Lard	Bacteria
Rapeseed	Babassu	Tallow	Algae
Canola	Brassica carinata	Poultry fat	Fungi
Safflower	cardunculus	Fish oil	Micro algae
Barley	Jatropha curcas		Tapenes
Coconut	Jatropha nana		Latexes
Copra	Jojoba oil		Cooking oil
Cotton seed	Laurel		(Yellow grease)
Groundnut	Palm		Microalgae
Oat	Karang		(Chlorellavulgaris)
Rice	Tobacco seed		
Sorghum	Rubber seed		
Wheat	Rice bran		
Winter rapeseed oil	Sesame		
	Salmon oil		

Rapeseed oil, which is predominantly found in countries in the European Union, soybean oil is predominantly found in areas of Argentina and the United States, palm oil, which is mostly found in countries in Asia and Central America, and sunflower oil are the oils that are most often used to make biodiesel around the world. Other oils like peanut, linseed, and sunflower oil are also used. Also used are safflower, vegetable, and animal fats. Even though ethanol can be used, methanol is the alcohol most often used. Because of how much oil costs, cost is the most important thing to think about when making and selling biodiesel. For this reason, using vegetable oils that can't be eaten has been looked into for several years with promising results.

Not only does using non-edible oils to make biodiesel save money, but it also means that no food is wasted in the process. For these and other reasons, tests have been done in a number of countries to see if non-edible oils like castor oil, tung, cotton, jojoba, and jatropha can be used to make medium- and large-scale biodiesel. Animal fats are also a good option, although they need to be processed before they can be used since they are solid. This is especially true in countries with a lot of cattle. Grease from cattle, pigs, chicken, and fish that is very acidic can also be utilized.

Microalgae appear to be a critical alternative for future biodiesel production due to their extraordinarily high oil yield; however, it should be noted that only certain species are effective for biofuel production. Although the characteristics of the oils and fats used as raw materials may vary, biodiesel must have the same attributes in order to meet international organization criteria.

2.2.5. Typical Oil Crops Useful for Biodiesel Production

In the next few paragraphs, we'll go over the main qualities of oil crops that have been found to be useful for making biodiesel.

2.2.5.1 Rapeseed and Canola

Rapeseed grows best in soils that are low in nutrients and have a lot of sulfur. It can be planted as a winter cover crop and makes a lot of oil about (40–50%), it can be grown twice and allows for crop rotation.

It is the most important raw material used in Europe to make biodiesel. But some Central and South American countries didn't have the right technology to plant and harvest rapeseed because they didn't know enough about fertilization, seed handling, and storage (the seeds are very small and require specialized agricultural machinery). Also, its low yield per unit area and cheap prices compared to wheat, which is its main crop rotation competitor, have made it hard to use.

Rapeseed flour is more nutritious than soybean flour, and it is added to cow feed as a source of protein. Canola, also called "Canadian oil low acid," is made by changing the genes of rapeseed. In Canada, rapeseed has been changed to canola over the last 40 years to lower the amount of erucic acid and glucosinolates in rapeseed oil, which makes it hard for animals and people to eat.

Canola oil is highly valued for its high quality, and along with olive oil, it is thought to be one of the best cooking oils because it helps lower blood cholesterol levels.

2.2.5.2 Soybean

Soybean acreage is substantially higher than that of other oilseed crops, resulting in significant soybean oil output and availability as a biofuel feedstock.

Soybeans are a major crop throughout much of North America, South America, and Asia (Glycine max). The United States leads all other producers with nearly 32% of global soybean production, with Brazil following in second with 28%. (John, 2009).

In addition to glycerin, soybean biodiesel manufacturing provides additional valuable byproducts such as soybean meal and pellets (used as livestock feed) and flour (which have a high content of lecithin, a protein). Grain yields range from 2,000 to 4,000 kg/hectare. Because the seeds are high in protein, the oil content is roughly 18%.

2.2.5.3. Oil Palm

The oil palm is a tropical plant that reaches a height of 20 to 25 meters and has a lifespan of approximately 25 years. Eight years after sowing, the crop reaches maturity.

The fruit yields two types of oil: palm kernel oil, which is extracted from the fruit's kernel, and palm oil, which is extracted from the pulp (after oil extraction, palm kernel cake is used as livestock food). Numerous oil-rich cultivars have been created. Malaysia and Indonesia are the top-producing nations.

Palm oil is used for frying, as a raw component in the production of margarine, and as an additive in butter and baked goods, which has led to a rapid increase in international demand in recent years. It should be noted that at room temperature (20-22oC) , pure palm oil is semisolid.

It is frequently mixed with other vegetable oils and partially hydrogenated for different applications.

2.2.5.4 Sunflower

Sunflower "seeds" are fruits with inedible walls known as husk that enclose the seed, which is located within the kernel. The significance of sunflower stems from the high quality of edible oil extracted from its seeds. It has high nutritional qualities, taste, and flavor. Furthermore, after oil extraction, the remaining cake is fed to livestock. It should be noted that sunflower oil contains very little linoleic acid and can thus be stored for long periods of time. Sunflower adapts well to adverse weather conditions, requires no specialized agricultural equipment, and can be grown in crop rotation with soybeans and maize. Current hybridcan s produce 48-52% oil.

2.2.5.5 Peanut

The weather during harvest has a big effect on the quality of peanuts. Peanuts are mostly used to make peanut butter and other foods that people eat. They are also used in candy and other processed foods. Peanut oil, which is in high demand around the world, is made from peanuts that aren't as good, like those that can't be used to make candy. Peanut oil is used in cooking and as a flavoring ingredient in the candy industry. The flour that is left over after the oil is taken out is high in protein and of good quality. It is made into pellets and fed to animals.

2.2.5.6 Castor Seed

The castor oil plant grows best in tropical areas with temperatures between 20 and 30 degrees Celsius. It can't survive in temperatures below 20 degrees Celsius. It's important to keep in mind that once the seeds start to grow, the temperature can't drop below 120 degrees Celsius. During its growing phase, the plant needs a warm, humid environment. When it's ready to be picked, it needs a dry season. It needs a lot of sunlight and can grow in many different kinds of soil. The total amount of rain that falls during the growth cycle must be between 700 and 1,400 mm. Even though the castor oil plant can survive drought, it needs at least 5 months of rain a year. Castor oil is a type of triglyceride, and about 90% of it is made up of ricinolenic acid.

It is poisonous because it has between 1% and 5% ricin, which is a poisonous protein that can be removed by cold pressing and filtering. Because it has hydroxyl groups in its molecules, it is much more polar than most other vegetable oils.

2.2.5.7 Cotton

Cotton is the most traded non-food commodity. It is produced in more than 80 countries and sold all over the world. After it is picked, it can be sold as raw cotton, fiber, or seeds. Cotton mills take the fibers and seeds out of raw cotton. In the textile business, cotton fiber is turned into fabric and thread. Cotton seeds also make cotton oil and cotton flour. Cotton flour is high in protein and is used to feed animals and, after more processing, to make food for people.

2.2.5.8 Jojoba

Even though jojoba can survive long periods of drought, it needs to be watered to produce a crop that can be sold. Jojoba grows best when it is warm, but the flowers can't open until it gets cold. During harvest time, there must not be much rain (summer). Ten years after it was planted, the plant is doing its best. Because jojoba oil is mostly used in cosmetics, its market is already very full.

2.2.5.9 Jatropha caucas

Jatropha caucas is a perennial shrub to small evergreen tree up to 6 m tall, adaptable to all soil types, and does not require any specific nutritional regime. It was introduced in Africa and Asia and is currently grown all over the world. It was thought that Portuguese settlers introduced it to India during the 16th century. It is a multipurpose, deciduous, tiny tree that is said to be cultivated in the drier regions of central and western India. It has recently been introduced in the northern and southern regions of India. The plant is widely dispersed and easily integrates into agricultural systems as hedges, windbreaks, and erosion barriers, or as a source of fuel.

2.2.6.0 Almond

Tropical almond (Terminalia catappa) is a big, spreading tree that is now found in coastal areas across the tropics. Strong winds, salt spray, and relatively high salinity in the root zone do not harm the tree. It grows best on sandy soils that are properly drained and aerated. Historically, the species has been particularly important to coastal communities, offering a wide range of non-wood products and services. It has a fibrous root structure that spreads and plays an important role in coastal stability. It is commonly planted across the tropics for shade, decorative benefits, and edible nuts, particularly along sandy seashores. The wood is a valuable and attractive general-purpose hardwood that may be used into furniture and interior building timbers. Fruits begin to appear at the age of three, and the nutritious, flavorful seed kernels can be consumed immediately after extraction. Tropical almond is easily propagated from seed, grows quickly, and thrives with little care in proper settings. Selected varieties of the species attract wider commercial planting for joint wood and nut production.

2.3 Methods of Biodiesel Production

Transformation of vegetable oils into biodiesel can be realized using four technologies:

1. Heating/pyrolysis
2. Dilution/blending
3. Micro-emulsion
4. Transesterification.

2.3.1. Pyrolysis

Pyrolysis is a chemical change that happens when heat is applied to a substance without air or nitrogen being present. When vegetable oils are broken down by heat, the liquid parts should be similar to diesel fuels. The viscosity, flash point, and pour point of the pyrolyzate are all lower than those of diesel fuel, but it has the same number of calorific values. The cetane number of the pyrolyzate is lower. The pyrolyzed vegetable oils have acceptable levels of sulfur, water, sediment, and copper corrosion, but they don't have acceptable levels of ash, carbon residual, and pour point (Location et al., 2002).

2.3.2. Dilution

Diesel fuels, solvents, or ethanol can be used to dilute vegetable oils. The viscosity and density of vegetable oils go down when they are diluted. When 4% ethanol is added to diesel fuel, the thermal efficiency, torque, and power of the brakes go up, while the amount of fuel used by the brakes goes down. Because ethanol has a lower boiling point than diesel fuel, an unburned blend spray may help start the combustion process.

2.3.3. Micro-Emulsion

Micro emulsion could be a way to deal with the problem of the thicckness of vegetable oil. Colloidal dispersions that are clear and stable in terms of temperature are called micro-emulsions. The sizes of the droplets in a microemulsion range from 100 to 1000. Micro-emulsions can be made by mixing vegetable oils with an ester and a dispersant (co-solvent), or by mixing vegetable oils, alcohol, a surfactant, and a cetane improver, with or without diesel fuels. All of the microemulsions made from butanol, hexanol, and octanol met the highest viscosity requirement for diesel fuel. 2-octanol was found to be a good amphiphile when it came to dissolving methanol in triolein and soybean oil with micelles.

2.3.4. Transesterification

The reaction of a triglyceride (from an oil or fat) with an alcohol (ethanol or methanol) to produce a fatty acid methyl ester is known as transesterification reaction (FAME). The reaction can take place in the presence of a catalyst.

Among these techniques, transesterification is the most extensive, convenient, and promising method for reducing the viscosity, density, and other properties of straight vegetable oils.

2.3.5.TRANSESTERIFICATION

The majority of biodiesel is produced through a chemical reaction known as transesterification. In the presence of a catalyst, it is the chemical conversion of oil to its corresponding fatty ester. Long chain fatty acid esters are converted into mono alkyl esters in this reaction. Biodiesel is a fatty acid methyl ester chemically.

Transesterification is the reaction of a lipid with an alcohol to produce esters and glycerol as a byproduct (Gashaw & Lakachew, 2014). In essence, it is the process of exchanging the organic group R" of an ester for the organic group R' of an alcohol. The addition of an acid or base catalyst frequently catalyzes these reactions.

Alcohol + ester $\longrightarrow$ different alcohol + different ester

Methanol and ethanol are the most commonly used alcohols, but methanol is preferred due to its low cost and physical and chemical advantages (polar and shortest chain alcohol).

2.3.5.1 Transesterification Reaction Mechanism

The overall reaction between a triglyceride and an alcohol is given by,

Triglyceride + 3 ROH ↔ Glycerol + 3 alkyl ester

(i)Reaction (I) is supposed to occur in three consecutive and reversible steps: triglycerides are converted to diglycerides, diglycerides are converted to monoglycerides, and monoglycerides are converted to glycerol. Each step produces an ester, resulting in three ester molecules from one molecule of triglycerides (Singh et al., 2020).

Triglyceride + ROH ↔ Diglyceride + alkyl ester (ii)

Diglyceride + ROH ↔ Monoglyceride + alkyl ester (iii)

Monoglyceride + ROH ↔ Glycerol + alkyl ester (iv)

In the aforementioned calculations, ROH acts as an alcohol. Stoichiometry states that 3 moles of alcohol are required to produce 3 moles of alkyl ester for every mole of triglyceride (biodiesel). Because the reaction is reversible, an excessive amount of alcohol is always used to accelerate the reaction. A 6:1 alcohol to oil ratio is commonly used in industrial procedures to produce high alkyl ester yields. According to (Meher et al., 2006), molar ratios less than 6:1 resulted in incomplete reactions, whereas molar ratios of 15:1 and above made glycerin separation difficult and reduced the apparent yield of esters because some glycerol remained in the biodiesel phase.

Akhihiero et al. (2013) used a molar ratio of 8:1 in the transesterification of jatropha seed oil.

The carbonyl carbon of the starting ester (RCOOR1) is nucleophilically attacked by the incoming alkoxide (R2O) in the transesterification mechanism, yielding a tetrahedral intermediate that either reverts to the starting material or proceeds to the transesterified product (RCOOR2).

The various species are in equilibrium, and the distribution of the product is determined by the relative energies of the reactant and product.

2.4. Factors Affecting Transesterification Reaction

Once the reaction has been identified, the conditions under which it occurs must be determined. The parameters that will have the greatest influence on the reaction are:

1. Reaction Temperature
2. Reaction time
3. Molar Ratio (Alcohol to Oil ratio)
4. Catalyst Concentration
5. Mixing Intensity
6. Type of catalyst
7. Properties and Composition of the Feedstock

2.4.1. Reaction Temperature

Depending on the source of the literature, different temperatures are used for the transesterification reaction. It is common knowledge that higher temperatures shorten reaction times and speed up reactions. In addition, greater temperatures typically result in higher ester yields. (Rashid et al., 2008). It should be noted, however, that if the reaction temperature exceeds the boiling point of the alcohol, it will evaporate, resulting in a lower yield (Sharma & Singh, 2008). It is also widely accepted that the optimum temperatures for transesterification typically range between 50 and 60oC, depending on the type of oil to be processed (Leung et al., 2010).

2.4.2. Reaction Time

Since the conversion rate increases with reaction time, the reaction time clearly influences the outcome of the reaction (Ma & Hanna, 1999). If the reaction time is not long enough, the ester yield will be low, and thus some of the oil will be unreacted.

2.4.3. Methanol/Oil Molar Ratio

One of the most significant variables that can impact ester production is this. The best value for the process can be found based on the kind of catalyst that is being employed. Higher molar ratios result in a faster increase in ester yield. Higher molar ratios are typically required when utilizing acid catalysts, possibly because the use of acid catalysts is associated with oils with a high FFA content. (Ma & Hanna, 1999)

2.4.4 Catalyst Concentration

The type of catalyst being employed has a significant impact on this parameter; different catalysts call for varied concentrations. Different concentrations will be required to get the same yields, even if they are members of the same group (like potassium and sodium hydroxides). Therefore, titration will be required to establish the ideal value for each catalyst. The creation of soap in the presence of a large amount of catalysts causes the yield of methyl esters to decrease if the amount of catalyst is more than the optimum, which also causes the reactants' viscosity to increase. (Rashid et al., 2008).

2.4.5. Mixing

It has been discovered that the reactants first form a two-phase liquid solution during the transesterification reaction. The reagent and oil are combined together to provide complete contact between the reagent and the oil during transesterification. The mixing effect was discovered to play an important influence in the slow rate of reaction. Mixing is required for the reaction to occur. Without mixing, the reaction occurs solely at the interface of the methanol and the oil, and it is far too slow to be feasible. As a result, a mixing device is required in the process reactor (Rashid et al., 2008).

2.4.6. Type of Catalyst

The type of catalyst used for a transesterification reaction affects the reaction. There are different classes of catalyst and they include homogeneous and heterogeneous catalysts, acid and base catalysts, organic and inorganic catalysts.

2.5. Catalysis in transesterification

To activate the transesterification process, either chemical or biological catalysts are used. Homogeneous agents (alkali or acid), heterogeneous agents (solid acid or solid alkali catalysts), heterogeneous nano catalysts, and supercritical fluids make up the chemical catalyst (SCFs). Although the reaction requires significant energy and a time-consuming purification process to obtain the refined end product, these catalysts are successful in completing the process (Rashid & Anwar, 2008). Immobilized lipases are the most popular biological catalysts. Enzymatic transesterification is more environmentally friendly than other processes. Its main downside is its prohibitively high cost.

2.5.1. Chemical catalysts

2.5.1. Homogeneous catalysts

Homogeneous chemical catalysts have several advantages, including good selectivity, rapid turnover frequency, fast reaction rate, and easy activity modification. Historically, in research, acid or alkali were utilized as homogeneous catalysts. The most common alkali catalysts are sodium hydroxide (NaOH), sodium methoxide (CH3ONa), and potassium hydroxide (KOH). NaOH is used over KOH because it dissolves quickly in methanol. Because of its excellent purity and low cost, NaOH is also utilized in transesterification; also, a minimal amount is required compared to KOH. Strong alkali catalysts such as NaOH, KOH, CH3ONa, and CH3OK (potassium methoxide) are used in the production of biodiesel.

In contrast, alkali metal alkoxides are said to be more active than hydroxides. Even when water-free vegetable oils and alcohol are used in alkali-catalyzed transesterification, the CH3Ona solution produces a little amount of water due to the interaction of NaOH and methanol.

The addition of water and FFA promotes soap formation by triglyceride hydrolysis, lowering biodiesel yield and decreasing product quality. If the oil contains more than 1% FFA, product recovery becomes difficult in an alkali-catalyzed transesterification reaction; in this scenario, a portion of the process may pursue the saponification route, resulting in soap formation. The resultant soap avoids biodiesel and glycerine separation. As a result, two-step transesterification is proposed (acid first, alkali second). The initial acid-based esterification efficiently reduces the FFA content of the oil and prepares it for alkali catalysis. Sulfuric acid and acetonitrile were used as catalysts and co-solvents in the first stage of candlenut oil esterification. The FFA level was reduced to 0.8 wt%, and the esterification was performed as an alkaline transesterification using acetone as a co-solvent and KOH as an alkali catalyst. The two-step methods produced 99.3% biodiesel under optimal conditions.

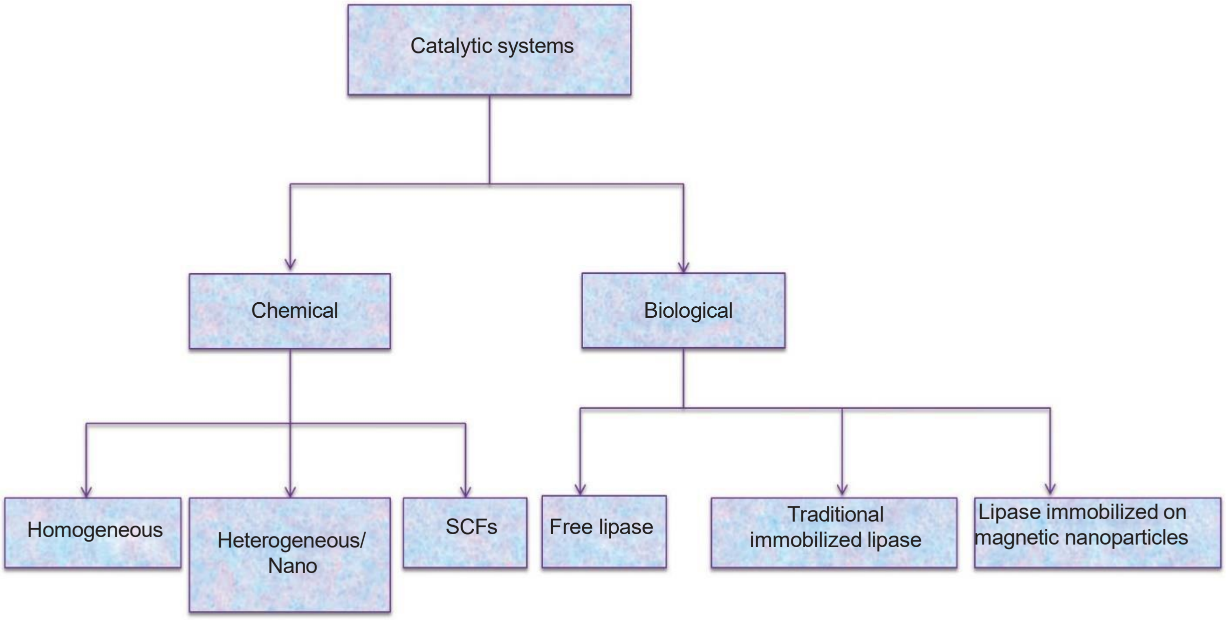


Figure 2.1: Types of catalyst in transesterification reactions

2.5.1. Heterogeneous catalysts

It is known that heterogeneous catalysts improve the trancesterification process by getting rid of the extra processing costs that come with homogeneous catalysis and by reducing the amount of pollution that is made. Yang and Xie (2007) found that heterogeneous catalysts make it easy to recover, reuse, and make a green process that costs less (Niju et al., 2014). These catalysts can handle high amounts of FFA and water. Heterogeneous catalysts that are both effective and cheap help bring down the overall cost of making biodiesel (Niju et al., 2014). In hard situations, like high temperature and pressure, heterogeneous catalysts are thought to be essential. These catalysts can handle different stages of water treatment, are easy to get back from reaction mixtures, and can be changed to make them more active, more selective, and last longer. You can make heterogeneous catalysts to help active molecules stick to and get stuck on the surface or in the pores of a solid support like silica, alumina, or ceria. Transition metal oxides and alkali earth metal oxides, mixed metal oxides, ion exchange resins, and alkali metal compounds supported on alumina or zeolite are used in chemical reactions like isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation, and transesterification (Niju et al., 2014). As catalysts, alkaline earth metal oxides like BeO, MgO, CaO, SrO, BaO, and RaO have been used successfully. MgO and SrO (Atabani et al., 2012). Strontium oxide, or SrO, is very basic and doesn't dissolve in methanol. It works the same way for up to ten times. Heterogeneous transesterification catalysts that work well are made of modified zeolites, anionic clays (hydrotalcite), calcium carbonate rock, EST-4 (Eni Slurry Technology), Li/CaO, MgO/KOH, and Na/NaOH/-Al2O3. When biodiesel is made from oils high in FFA, solid acid catalysts help with both esterification and transesterification (Boey et al., 2011). For the transesterification of castor oil, NaY zeolite-supported La2O3 catalysts made with a physical mixing method gave 84.6% biodiesel under the best reaction conditions. Zirconocene perfluoro octane sulphonate stays the same in both air and water. Lewis' acid catalyst was used in the direct esterification of FFAs and the transesterification of triglycerides. This catalyst also acts as a reaction-induced self-separating agent because it changes from being homogeneous to being heterogeneous during the reaction. Finally, the catalyst turns into a white solid that can be reused (Al-Widyan & Al-Shyoukh, 2002). Solid acid catalysts work less well than solid base catalysts [46]. Transesterification uses solid-base catalysts like CaO, MgO, SrO, KNO3/Al2O3, K2CO3/Al2O3, and others.

Basic hydrotalcites, such as KF/Al2O3, Li/CaO, KF/ZnO, as well as anion exchange resins, base zeolites, and Mg/Al and Li/Al, are all examples. Calcined Li/Al hydrotalcites, which have a high Lewis basicity, are more active in fatty acid glycerolysis than Mg/Al material, which has a lower level of Lewis basicity. Several different molar ratios of magnesium to aluminum catalysts, ranging from 1.5 to 5, have been employed in the generation of biodiesel. High Mg/Al catalyst ratios have showed outstanding performance, despite the fact that their surface areas are very tiny. The catalyst that was just described contains crystals that are flakes and are highly defined. These crystals have strong basic sites and have H values that are higher than 11. These catalysts are capable of producing a biodiesel yield of greater than 92% under optimal reaction conditions (Atadashi et al., 2013). Impregnating mixed metal oxides has as its primary objective the enhancement of base or acid strength, surface area, and stability beyond that which is possible with single metal oxides (Atadashi et al., 2013). At a temperature of 60 degrees Celsius with a methanol-to-oil molar ratio of 12 to 1, a 9% Li-doped MgO catalyst produces 93.9% fatty acid methyl ester (FAME). The incorporation of Li into this catalyst generates a robust base site, which ultimately results in a higher biodiesel production rate. When compared to Na/BaO and K/BaO, the activity of Li-doped BaO was significantly higher during a transesterification reaction. Li/ZnO catalysts have good catalytic activity, however their performance is greatly reliant on the amount of lithium loading as well as the temperature (Gondra, 2010a). The KF/-Al2O3 catalyst possesses a strong base site that is responsible for promoting transesterification at lower temperatures, but the medium base strength necessitates higher temperatures (Robles-Medina et al., 2009).

Solid base catalysts with a long catalyst life, high activity, and mild reaction conditions are favoured because of their low impact on the environment. One example of this type of solid base catalyst is calcium oxide (CaO). Calcium oxide is commonly crafted by combining calcium hydroxide and calcium nitrate as its foundational components. Furthermore, a wide variety of naturally occurring waste products that are rich in calcium, such as bone, mollusk shells, and chicken eggshells, can be used as the starting point for the synthesis of catalysts. This eliminates the need to dispose of waste while simultaneously resulting in the production of catalysts that are extremely affordable. A solid base catalyst composed of CaO nanocatalyst was able to convert 93% of jatropha oil into biodiesel. When CaO is loaded onto KF, a solid-base catalyst with a high catalytic activity known as CaO/KF (or KF/CaU) is produced [85]. CaO leached out the calcium (Ca2+) ions that impair product quality, despite the fact that it had a high catalytic activity in the transesterification process. Because water is present, the calcium diglyceride begins to hydrolyze, which in turn triggers the release of Ca2+ ions into the environment (derived by the instability of CaO with the by-product glycerol). CaO is directly dissociated when it forms during the reaction with methanol, which results in the creation of soluble Ca2+. The calcium ions that have been leached react with the FFA that are present in the oil, which results in saponification and deactivates the effective function of the catalyst. As a consequence of this, the utilization of suitable sustaining materials may be of assistance in preventing the leaching of Ca-active species (Palniandy et al., 2019). One of the most major drawbacks of utilizing CaO is the requirement for the use of heat activation in order to eliminate the adsorbed

CO2 and moisture. In order to prevent carbonization, the procedure must be carried out in an environment consisting of either nitrogen or a vacuum (Arifin et al., 2011). During the process of transesterification, the mixed metal oxide catalysts displayed an excellent tolerance to the FFA and water content of the crude oil. CaTiO3, CaMnO3, Ca2Fe2O5, CaZrO3, and CaO-CeO2 are some examples of the mixed metal oxide catalysts that are utilized throughout the biodiesel synthesis process. Catalysts made of CaZrO3 and CaO-CeO2 are notable for their stability and productivity (Agarwal et al., 2012). When evaluated by transesterifying jatropha oil under ideal reaction conditions, the CaO-MgO catalyst produced between 75 and 90% FAME. Mn0.5Ce0.5OX acid-base bifunctional mixed-metal oxide catalysts were shown to be extremely effective for the manufacture of biodiesel, with the ability to achieve a conversion rate of 100% under optimal reaction conditions. Acidic sites were present in this catalytic system, whereas basic sites were present in Mn. It is possible that the catalytic performance of MnCeOX could be improved by including K into the structure of the catalyst during the production phase.

Several mixed metal oxide catalysts, such as CaO-MgO, CaO-ZnO, CaO-La2O3, and MgO-ZnO, are utilized in the transesterification reaction with a catalyst amount of 3 wt%, an oil/methanol molar ratio of 1:25, a temperature of 120°C, and a working time of 3 h. CaO-ZnO possesses the most catalytic activity among them all (Hsu et al., 2011). In the transesterification of cottonseed oil, CaO-MgO mixed metal oxides loaded on Al2O3 catalysts produced 97.62% yield. (Viriya-empikul et al., 2010). In canola oil transesterification, a Li-impregnated CaO-La2O3 mixed metal oxide was utilized. Strong interactions exist between lithium, calcium, and lanthanum in the structure of this catalyst. Even after Li impregnation, the presence of La2O3 in the support structure maintained the BET (Brunauer-Emmett-Teller) surface area as well as the stability of the catalyst, as indicated by the preceding material. In 2.5 hours at 65 degrees Celsius, the catalyst converted 96.3% of the biodiesel (Liu et al., 2008). Recently, waste products have been utilized as catalysts in chemical reactions. Low-cost solid waste products have showed potential for the generation of biodiesel in a sustainable manner. Cement waste from concrete and mortar containing quartz, calcite, sodium/calcium aluminosilicates, albite, and portlandite are the most prevalent mineral wastes. As a result of its mineral matrix, cement has an alkaline character (Boey et al., 2011).

A high concentration of calcium carbonate can be found in eggshell, and this calcium carbonate can be calcined at a temperature of 900 degrees Celsius to produce CaO. During the transesterification process, it had a high level of catalytic activity and produced biodiesel at a concentration of up to 93.5%. The manufacture of catalysts with waste materials can assist solve problems related to waste disposal, and the value-added materials can be useful in a wide variety of industrial processes. Solid organic waste-based catalysts have been produced and employed well; examples include plantain peels (Liu et al., 2008), wood, coconut shells, palm trunks, and sugarcane bagasse. Banana peels include potassium and sodium oxides, which have been transformed to their equivalent oxides. A banana peel catalyst was produced by first drying the peel in an oven at 80 degrees Celsius for forty-eight hours and then calcining it at 700 degrees Celsius for four hours. It played a role in both stages of the transesterification process that were required for neem oil. The calcined peels of the tucum palm, which contain a high concentration of K, P, Ca, and Mg ions, displayed good catalytic activity. The temperature of the calcination was 800 degrees Celsius. The waste shells of the Cyrtopleura costata (angelwing clam), when subjected to the optimal reaction conditions, produced 84.11% biodiesel and had the potential to be recycled three times with a yield of over 65% biodiesel each time (Liu et al., 2008). In order to create biodiesel from jatropha oil in a single step with a yield of 96.1% at 70 degrees Celsius, calcined animal bone was utilized as a catalyst. CaO that was supported on waste fly ash was able to convert palm oil into 94.5% biodiesel when the reaction conditions were optimal. The production of a solid base catalyst for the transesterification of soybean oil required the use of cinder, a solid waste product that is a byproduct of the coal-burning industry. Cinder was utilized as a support for CaO/KF. A catalyst generated from rice husks was able to create a high yield of biodiesel (more than 90%) thanks to the strong acid sites and vast surface area that it possessed. The creation of a sulphonated carbon-based catalyst for the esterification of caprylic acid using coffee residue resulted in a conversion rate of 71.5% in four hours. This was accomplished using coffee residue (Martyanov & Sayari, 2008). At a temperature of 800 degrees Fahrenheit, birch bark wood ash and fly ash from a power plant that runs on biomass were calcined to produce heterogeneous catalysts. A yield of 88.03 percent was achieved by using sulphonated coconut shells as a solid-acid catalyst in the reaction. In order to manufacture biodiesel, oil palm trunks and heterogeneous acid catalysts produced from sugarcane bagasse were both utilized; the resulting yields were 88.8 and 96%, respectively. Homogeneous systems typically do not allow access to the active molecules that are present in heterogeneous catalysts, which can result in decreased catalytic activity. In addition, the external-surface active sites of a porous solid support play an active role in lowering the overall activity of the catalysts. This is because the external-surface active sites are exposed to the environment. In circumstances like these, researchers need to develop a catalyst system that not only demonstrates excellent catalytic activity and selectivity, but also keeps catalyst separation and regeneration intact. In order to attain this goal, grafting, which involves the formation of covalent bonds, adsorption, and the application of nanostructured catalysts are all viable options. A nanocatalyst is a type of catalyst that combines the desired qualities of homogeneous and heterogeneous catalysts into a single entity for use in chemical reactions.

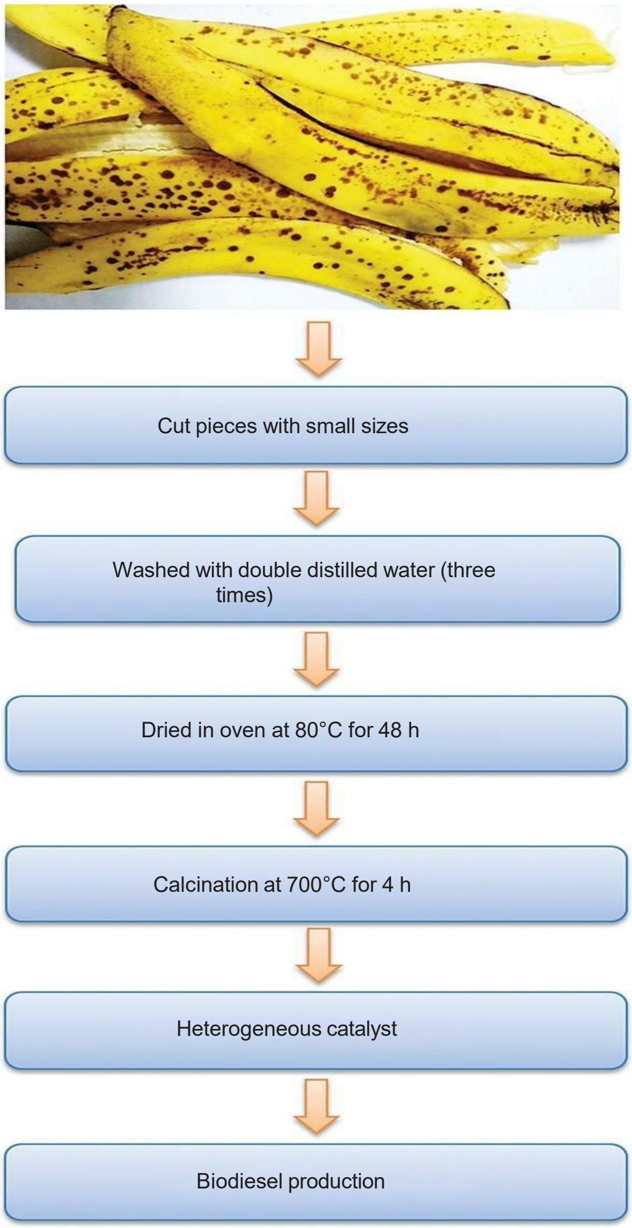


Figure 2.2: Banana peel used as heterogenous catalyst for biodiesel production

2.5.2 Basic Solid Catalysts

Because bases are more effective in the transesterification process than acids are, bases are perfect for producing high-quality oils that have low FFA concentrations. In the process of producing biodiesel with a solid base catalyst, continuous flow and a packed bed arrangement are frequently used. This, in turn, encourages the joint productiion of high-purity glycerol and catalyst separation, which ultimately reduces the costs of generation and encourages the reuse of the catalyst. Clays such as hydrotalcites and supported alkali metals are examples of solid base catalysts. Alkali or alkaline earth oxides, basic zeolites, immobilized organic bases, and supported alkali metals are all included in this category.

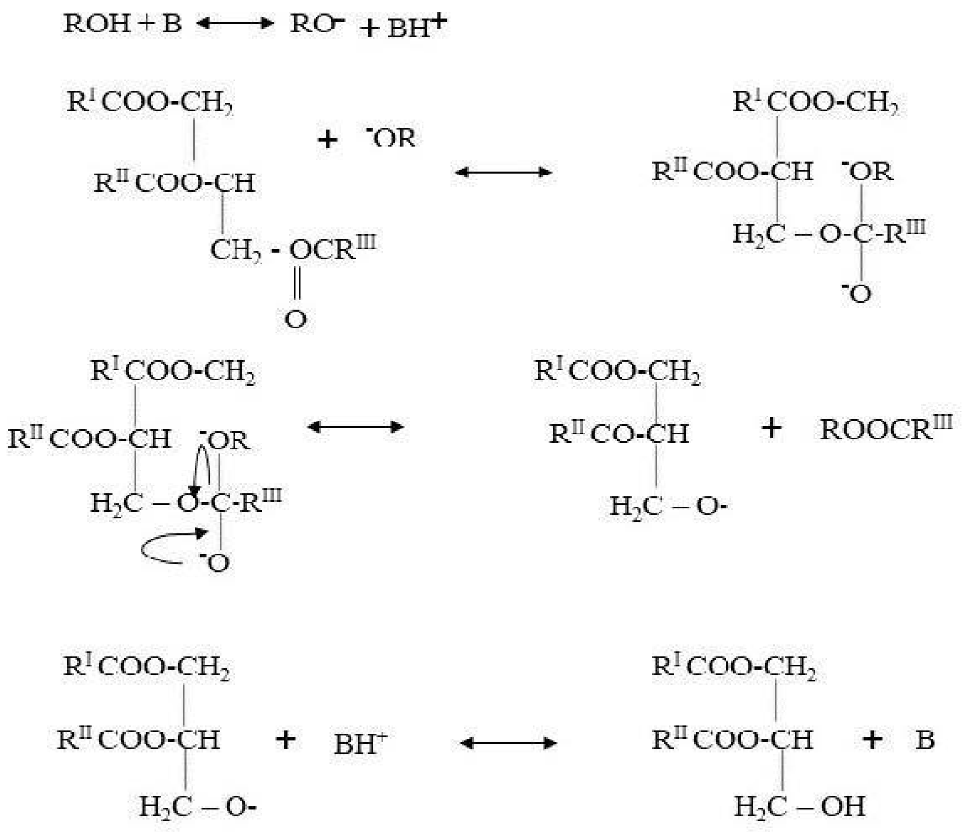
Solid bases do have capacity to improve electrons to reactants, as well as to take protons from those reactants. The Brnsted basic and the Lewis basic activity centers both make up the majority of solids in these bases. In the past ten years, there has been a lot of work done to synthesize biodiesel by the use of heterogeneous base-catalyzed transesterification, low-qualified oils or fats that include FFAs, and water. The conventional heterogeneous catalysts catalysts have a poor catalytic efficacy, which has to be improved. Using a variety of catalytic materials, it was investigated to see if it was possible to improve glyceride transesterification.

Hydrotalcites, metal oxides, metallic salts, supported base catalysts, and zeolites are among the solid material-based catalysts that are researched and developed the most frequently. As was mentioned earlier, the Lewis or Brnsted basic sites of the catalyst are responsible for carrying out reactions involving heterogeneous bases. These basic sites react with a monohydric alcohol (often methanol) to produce the desired product. In the subsequent processes, the combination of alkoxide that was formed reacts with the triglyceride ester that was present in the oil to produce biodiesel and glycerol. The mechanism behind base-catalyzed transesterification is illustrated in

Figure 6. As potential heterogeneous transesterification catalysts, solid basic catalysts such as ZnO, CuO, zeolites, CaO, SrO, MgO, and BaO, as well as basic polymers and carbonates such as MgCO3, CaCO3, BaCO3, and SrCO3, have garnered significant interest.

2.5.2.1 MgO as a Base Heterogeneous Catalyst

Derivatives of alkaline earth metals and oxides are employed by a variety of researchers. These include Ba, Be, Ca, Mg, Ra, and Sr. SrO and MgO, along with other alkaline earth metals with good heterogeneous characteristics, are frequently used as a catalyst for the synthesis of biodiesel. When MgO was utilized as a catalyst, Lopez and colleagues found that there was a 18% conversion of triacetin feedstock during a 8-hour reaction time at a calcination temperature of 600 degrees Celsius (Ma & Hanna, 1999). This lower conversion rate is attributable to the fact that the catalyst has a very limited surface area. (Martino Di Serio, Riccardo Tesser, Lu Pengmei, and Dipartimento, 2019) used MgO catalyst and recorded a 92% biodiesel production utilizing 5.0 wt% of the catalyst in 1 h, using a 12:1 methanol to oil molar ratio. They did this by using a 12:1 methanol to oil molar ratio. Through a transesterification reaction, it was discovered by Dossin et al. (2006) that MgO has the ability to produce 500 tons of biodiesel in batch reactors while maintaining the temperature of the surrounding environment. The production of biodiesel in batch reactors is more cost-effective when temperatures are kept at room temperature. Under supercritical circumstances (300 degrees Celsius) and with a high methanol to oil molar ratio, a MgO catalyst has the potential to produce 91% fatty acid methyl ester (FAME), as indicated by the findings of various studies (39.6:1) (Dossin et al., 2006).



Figu

2.5.3.1. CaO as a Base Heterogeneous Catalyst

CaO was employed by Liu et al. (Liu et al., 2008) in their production of biodiesel from soya bean oil in the capacity of a solid base catalyst. He emphasized some of the advantages of using CaO as a solid base catalyst, including its increased catalytic life, high activity, and moderate reaction conditions. Researchers have recently become interested in using calcium oxide (CaO) as a heterogeneous catalyst due to the low cost of its manufacturing (Olutoye & Hameed, 2011). Additionally, calcium oxide has a high basic character. According to Liu et al(2008) .'s research, 95% of the oil was converted to the ester by the process of transesterification. The researchers used 8% CaO relative to the mass of the oil, a three-hour reaction time, and a 12:1 methanol to oil molar ratio. Viola et al. were able to achieve a conversion rate of 93% using the same method by utilizing CaO as the catalyst, maintaining a reaction duration of 80 minutes, maintaining a reaction temperature of 65 degrees Celsius, and using a 5% catalyst while maintaining a 6:1 oil-to-methanol molar ratio. According to Shu et alresearch .'s from 2007, employing a CaO in ammonium carbonate solution resulted in a conversion of 93% of Jatropha curcas oil.

(Morshed et al., 2011) utilized recycling reactors to improve biodiesel synthesis from vegetable oil by employing CaO as a heterogeneous catalyst. This was accomplished by using CaO as a recycling catalyst. They claimed that the reaction conditions were acceptable after 75 minutes, with a methanol to oil molar ratio of 6:1, and catalyst weight of 3% relative to the oil mass for the synthesis of 100% biodiesel.

Using CaO as a heterogeneous catalyst at a calcination temperature of 550 degrees Celsius, Ivkovi et al. (2017) found that methanolysis of sunflower oil could be accomplished. During the transesterification reaction, they utilized a catalyst that was 1% based on the weight of the oil, and they kept the reaction going for two hours at a temperature of 60 degrees Celsius. This resulted in a yield of 98% with a 6:1 M ratio of sunflower oil to methanol.

CaO was utilized as a heterogeneous catalyst in the transesterification reaction (Sakai et al., 2009) to create biodiesel from rapeseed oil. This reaction produced biodiesel. They took a different approach to handling the CaO. They began by making the CaO active by pretreating it with methanol at 25 degrees Celsius for one and a half hours. CaO that has not been activated can therefore be transformed into Ca(OCH3)2, which possesses a higher catalytic activity than CaO that has not been activated. Ca(OCH3)2 was ultimately put to use in the process of transforming rapeseed oil into FAME and glycerin. In order to produce biodiesel, Puna et al. conducted research on CaO and changed CaO with Li. They were able to improve the catalytic activity of both catalysts as well as their stability. In point of fact, by utilizing two sequential batch procedures, it was possible to boost the amount of biodiesel produced by more than 92%. As a consequence of this, the catalysts are appropriate for use in the generation of biodiesel.

2.5.4 Biocatalysts

To avoid the saponification issues connected with transesterifying oils with high FFA utilizing a basic catalyst, great efforts have been made to explore enzyme catalysts during the transesterification of oils. Since enzymatic transesterification only produces a little amount of soap and operates at a neutral pH and moderate reaction temperature, it can be cost-effective. Enzymes can be utilized again as catalysts if they are immobilized on stable supports and given a fresh set of circumstances. Enzymatic immobilization often uses a variety of methods, including cross-linking, covalent bonding, and microencapsulation. Because they are inexpensive, lipases are used as a key enzyme during transesterification. In mild circumstances, lipases can catalyze both hydrolysis and the transesterification of triglycerides (TG). (Chakraborty et al., 2011).

Lipases are known to be useful in a variety of synthetic reactions such as transesterification, aminolysis, and esterification. Lipases' unique properties, such as enantioselectivity, regioselectivity, and specificity, allow them to catalyze reactions at low temperatures.

Pressure and temperature are used, with negligible by-product production. Special care has been taken in recent decades to produce biodiesel employing lipases as biocatalysts.

Morshed et al. (2011) used commercially available Thermomyces lanuginosus (TL) lipase immobilized on Fe3O4/Au in a solvent-free method to produce biodiesel from wasted coffee grounds. The biodiesel yield was 51.7% after three hours. Within a twenty-four-hour reaction period, a 100% biodiesel yield was obtained. The reported reaction kinetics were thought to be relatively quick. Furthermore, the biocatalyst from the study was applied repeatedly throughout the transesterification procedure and shown no significant decrease in catalytic activity after three cycles. Saranya et al. (2020) isolated a low-cost biocatalyst from the fungus strain Cladosporium tenuissimum CS4. Following purification, the resulting biocatalyst was used to produce biodiesel from diatomic microalgal oils. Surprisingly, the biocatalysts performed better (87%) than the typical acid catalyst (83%). Pseudomonas mendocina cells were immobilized in a magnetically fluidized bed reactor (MFBR) producing biodiesel from biowaste products (Xie et al., 2006). It demonstrated good reusability in MFBR for ten cycles while sustaining biodiesel yields of 87.5%.

Nano-biocatalysts have attracted a lot of interest in recent years for the enzymatic generation of biodiesel to lower the large cost of lipase. Nanomaterials have been widely used for enzyme immobilization in this regard. Because of their enormous surface area, particle size, and high enzyme loading capacity, nanomaterials are a particularly effective technique of advancing immobilized enzymes. Miao et al. (2018) synthesized lipase-immobilized surface amino-functionalized magnetic nanoparticles (APTES-Fe3O4) and employed glutaraldehyde as a coupling agent to form a covalent link between lipase and APTES-Fe3O4 magnetic nanoparticles. Under ideal conditions, they produced 89.4% biodiesel production during the transesterification step. Nematian et al. (2020) used a modified nano-biocatalyst to produce biodiesel from 35% lipid-containing Chlorella vulgaris microalgae oil. They created the enhanced nano-biocatalyst by covalently attaching and electrostatically attracting Rhizopus oryzae lipase (ROL) to Fe3O4 superparamagnetic nanoparticles (MNPs). Using their modified catalyst during the nanocatalyzed transesterification process, they achieved a 75% conversion of fatty acid methyl ester (FAME). In an enhanced reverse fluidized bed bioreactor, Narayanan and Pandey (2018) used nanosilicon immobilized lipase to produce biodiesel. They stated that under optimal conditions, the bioreactor can reach a conversion rate of more than 80%.

2.6. Composition of Waste Shell

Several invertebrates have evolved hard shells formed of crystalline biogenic minerals to protect and sustain their sensitive bodies. The major ingredient of the shells is calcium carbonate (also known as calcite), which accounts for 95-99 percent of their makeup. Gashaw and Teshita (2014) Mollusk shells include organic matrix proteins as secondary components in addition to calcium carbonate, which are known to be vital for the nacreous layer and critical in calcification. Mollusk shells are classified into three layers: periostracum, prismatic, and nacreous. The periostracum layer is the outermost layer, which is mostly made up of conchiolins. The prismatic layer is the middle layer, which is mostly made up of aligned calcite crystals. The oriented aragonite crystals dominate the inner pearlite layer.

Eggshells are classified as membranous for snakes and lizards, flexible for most turtles, rigid for some turtles and geckos, and rigid for all crocodiles, birds, and dinosaurs. Bird species have the highest quality amniotic eggs among oviparous vertebrates. An eggshell is a complex bio-ceramic that may be finely adjusted to meet the environmental conditions of a certain species. It enables for the control of metabolic gas and water exchange. Calcium carbonate (calcite), which is also the major component of eggshell, is the most abundant inorganic substance in an egg, accounting for approximately 98 percent of its chemical composition. Mg (0.9%) and P are also present in trace concentrations in eggshell (0.9 percent).

Calcite (b-CaCO3), vaterite (m-CaCO3), aragonite (l-CaCO3), and amorphous calcium carbonate are the four primary polymorphs of calcium carbonate. Calcite, aragonite, and vaterite are polymorphs in nature that can co-exist in a variety of marine creatures. Notably, the most stable polymorph of calcium carbonate is calcite with rhombohedral structures, followed by orthorhombic Aragonite. It produces long structures known as columns, palisades, or crystallites. Aragonite is more soluble because the presence of magnesium (Mg) causes weaker connections in the crystal structure. At room temperature, the most unstable polymorph, Vaterite with a hexagonal structure, easily changes into aragonite or calcite. As a result, only trace amounts of vaterite can be found in nature. Some shells include chitin in addition to calcium carbonate. Oyster shells, for example, are mostly calcium carbonate with a chitin outer layer and an interior layer of calcite (90%) and aragonite (10%). Chitin, along with cellulose, is one of the most abundant biopolymers in the waste shell. Chitin is made up of (1-4)-linked polysaccharides. Oligomer is 2-acetamido-2-deoxy-D-glucose with linkage. The majority of commercial chitin is derived from crab shells. Around 40% of waste shells are made up of chitin, fat, meat offcuts, calcium carbonate, and colors (Chakraborty et al., 2011). The proportion of chitin in shells varies from 15-40% depending on the species and aquaculture conditions. Despite this, the chitin with the greatest composition is closely bonded with calcium (20-50%) and proteins (20-40%), which provide structural stiffness to the shell. As a result, additional pretreatment processes are necessary to extract each component.

2.6.1. Waste Shells-Derived Catalyst for Biodiesel Production

After calcination at temperatures ranging from 800-1000 °C, the majority of waste shells can be converted into active CaO. The majority of the pure CaO produced from waste shells converted the low FFA feedstock (palm oil, Camelina Sativa oil, soybean oil, and some low FFA waste cooking oil) into biodiesel. Transesterification of Camelina sativa oil FFA: 1.6%) over waste eggshell and lobster shell-derived catalysts resulted in high biodiesel output (90%-97%). Calcination at 900 °C was used to prepare both waste shells. At 65 °C for 3 hours, a 1% (w/w) catalyst loading with a 12:1 MeOH:oil molar ratio catalyzed the transesterification. The scientists compared the biodiesel yields from commercial CaO, discarded eggshell, and lobster shell catalysis. The highest levels of biodiesel produced were 99%, 97%, and 90%, respectively.

(Demirbas, 2009) used discarded mussel, cockle, and scallop shell as a catalyst for transesterification of palm oil (FFA: 0.1%) in a glass reactor at 65oC with MeOH:oil molar ratio of 9:1 within 3 h and 10 wt.% catalyst loading. The waste mussel shell-derived catalyst produced 97.23% biodiesel with a huge surface area of 89.91 m2/g and pore volume of 0.130 cm3/g. Shell-derived catalysts from scallop (74.96 m2/g, 0.097 cm3/g) and cockle (59.87 m2/g, 0.087 cm3/g) yielded 96.68% and 94.47%, respectively. The most important aspect of heterogeneous catalysts in industrial applications is their reusability. According to previous research, the bulk of waste shell-derived CaO catalysts can be reused up to five times without further regeneration treatment (Lotero et al., 2005). Notably, Laskar et al. successfully recovered CaO from snail shell. The spent catalyst was rinsed and dried before being revived at 900 oC for 4 hours.

The experimental results showed that 91% of biodiesel yields were consistently obtained within the eighth run, but reduced to 77% in the ninth cycle over the regenerated catalyst, indicating that the active sites of pure CaO catalyst could be regained after regeneration.

It is worth noting that, according to Table 1, the bulk of pure CaO produced from shell had reduced catalyst stability. When the standard reflux system was compared to microwave-assisted transesterification, it was discovered that the microwave system successfully transforms the biodiesel in a quicker reaction time. This finding was consistent with Khemthong et al., who demonstrated an effective transesterification activity on palm oil (FFA: 0.55%) utilizing CaO produced from waste eggshells in 4 minutes using a microwave at 900W. When compared to the usual heating process for biodiesel production, this method increased the transesterification rate. Several conditions were examined in order to find the best one for carrying out the transesterification reaction. Overall, the authors achieved a maximum biodiesel output of 96.7% at 122^{o}C utilizing 15% catalyst loading and an 18:1 MeOH:oil molar ratio. Microwave technology's success is due to the presence of electromagnetic radiation, which delivers energy directly to the molecules of reactants, resulting in strong local heating capable of accelerating molecular reformation. Some investigations on microwave-assisted biodiesel manufacturing found that high microwave power could speed up the reaction and increase product output in a short period of time (4 – 5 min).

Trash cooking oil (WCO) is primarily defined as high-temperature frying oil, edible fat mixed in kitchen waste, and oily wastewater, and has been demonstrated to contain a high concentration of acidic chemicals (FFA: >3%). The level of FFA in the feedstock is a crucial criteria for selecting a catalyst. With an alkaline catalyst, WCO with a high FFA concentration will result in increased soap formation, hence it must be prepared with an acid catalyst to minimize FFA concentration (Rezaei et al., 2013). As a result, it is possible that WCO with low FFA value will easily trans-esterify to biodiesel. Clearly, (Arifin et al., 2011) successfully transesterified the WCO with FFA values ranging from 0.30 to 0.61%. The biodiesel yield was discovered to be between 86 and 94%. Because the FFA for these WCO is less than 3%, an unwanted saponification reaction during the transesterification step would not occur. Although waste shell-derived CaO is an excellent catalyst for transesterification of low FFA feedstock with high biodiesel yield (90-99%) and reusability (3-6 cycles), it performs poorly in the presence of high FFA and moisture feedstock. The presence of moisture promotes the hydrolysis of triglycerides to diglycerides and additional FFAs, whereas the presence of acidic FFA promotes the reaction with the basic CaO catalyst.

In general, the CaO-catalyzed transesterification process yields two plausible pathways: the first preferable step is a partial heterogeneous reaction attributed to basic sites of the Ca-O surface; the second unfavorable step is a homogeneous reaction that contributes to Ca2+ liquid species that leach into methanol, resulting in the loss of active sites. The leached Ca2+ then interacts with FFA in oil to generate soap as a byproduct of the saponification process. The production of soap during reactions caused the catalyst surface to be poisoned, reducing both transesterification reactivity and reusability. Furthermore, the presence of a catalyst-soap suspension in the reaction media makes separation of glycerol and biodiesel product problematic, reducing biodiesel production. As a result, further modification of CaO obtained from waste shell is required in order to improve the hydrophobicity of the catalyst and generate new acid sites (Lewis or Bronsted acid sites) in the CaO system. The existence of both acid-based features of the catalyst is critical for the biodiesel synthesis process, which is especially well suited to a wide range of low-cost and high acid oil feedstock. Lewis/Bronsted bases sites (attributed to lattice oxide and OH phases) encourage transesterification of triglyceride oil to ester, whereas Lewis/Bronsted acid sites (attributed to metal and H+ phases) favor esterification of FFA in oil. As a result, the presence of acid sites from modified CaO appeared to be insensitive to FFAs and moisture, stifling the saponification reaction and increasing yield. In general, the basic nature and acid active sites of catalysts can be determined using various types of analysis, such as Hammett's indicators (references), CO2/NH3 desorption from thermal programmed desorption (TPD), or a microcalorimetry instrument that provides the basic/acid density as well as the adsorption profile strength (weak, medium, and strong). Other techniques, such as Fourier-transform infrared spectroscopy (FTIR), Electron Spin Resonance Spectroscopy (ESR), Nuclear magnetic resonance (NMR), photoluminescence, Raman, UV-Visible Spectroscopy (UV-Vis), and X-Ray Photoelectron Spectroscopy (X-Ray Photoelectron Spectroscopy), can provide detailed information about Lewis and Bronsted sites for acid-based profiles (XPS).

2.6.2. Modified Waste Shells-Derived Catalyst for Biodiesel Production

As previously stated, waste shells are a natural and renewable resource that can be used to produce CaO-based catalyst. Calcination can convert the calcium carbonate in discarded shells to calcium oxide (CaO), which can be used as a bio-based material in the production of biodiesel. Although CaO has a high transesterification activity, it is unstable, sensitive to FFA, and frequently dissolves and leaches Ca2+ ions. This event reduced catalytic performance during a reusability trial in which the leached Ca2+ contaminated the final biodiesel product. Additional chemical components have been added to CaO catalysts in order to improve system stability and catalytic activity. Considering the better basicity of these AMOs, mixing them with CaO generated from waste shell has been prioritized. Boro et al. examined WCO biodiesel synthesis using a variety of Ba (0.5%, 1.0%, 1.5%) doped waste Turbonilla striatula shell-derived CaO catalyst concentrations. The basicity qualities rose as the Ba content grew from 0.5% to 1.0%, and decreased as the Ba concentration increased to 1.5%. This author proposed that the decrease in basicity is related to a decrease in the CaO species. The study found that Ba1.0/CaO had a greater biodiesel output (98%) and could be reused four times. Similarly, Boro's research on converting Nahor oil (FFA: 8%) and WCO (FFA: 11%) into biodiesel rich fuel using a Ba modified waste shell-derived CaO catalyst and a Ba/CaO catalyst generated 98% biodiesel. Mg/CaO derived from waste eggshell was also discovered to be useful in the transesterification of edible waste oil. EDX analysis revealed that the MgO/CaO catalyst included 26.03% calcium, 41.93% oxygen, and 32.04% magnesium. At the ideal conditions of 4.5 wt% catalyst loading amount, 16.7:1 MeOH:oil molar ratio at 69 oC for 7 h with reusability up to six times, the greatest biodiesel yield of 98.37% was achieved with reusability up to six times. Tomano et al. studied the characteristics of Sr substituted cuttlebone-derived CaO for the conversion of palm olein to biodiesel. The Sr species were loaded in a 1-10 wt.% range. The mapping study revealed a variation in the concentration of Sr dispersion on the CaO surface. However, the presence of abundant Sr species on the CaO surface may reduce the BET surface area of the Sr/CaO catalyst. Overall, the highest BET surface area is found in Sr/CaO with a Sr loading of 1%. For 3 hours, the transesterification was carried out at 60 oC with a 9:1 methanol/oil ratio and a 5% catalyst loading. The maximum biodiesel conversion was 95% at 1% Sr/CaO. The biodiesel yield obtained by AMO doped CaO was generally greater than 95%, and the catalyst can be reused up to 5 times after regeneration.

Transition metals (TM) such as Zn, Fe, Mn, Al, Mo, Cu, and others are key materials employed in many catalytic reactions. TMOs are commonly utilized in oxidation, dehydrogenation, selective oxidation/reduction, ammoxidation, metathesis, water-gas shift, and other processes. TMOs' distinct physicochemical features, such as surface acidity and basicity, cationic and anionic vacancies, high mobility of lattice oxygen, and so on, favor specific reaction paths. TMO addition could be used to adjust the chemical properties of CaO due to their good chemical properties. As a result, TMO modified CaO will have both acidic and basic sites that actively convert high FFA feedstock to biodiesel via esterification and transesterification processes. Joshi et al. [109] evidently succeeded in converting high FFA feedstocks (Jatropha (6.25% and Karanja oils (8.75%)) to biodiesel via Zn, Fe, Mn, and Al-doped CaO produced from eggshell. Surprisingly, TMO doped CaO catalyst has a higher specific surface area and basicity character than pure CaO. The elevated basicity of TMO modified CaO could be attributed to the presence of a synergistic interaction between the multi-metal ions. The scientists also noted that the oxygen anion's electron-donating characteristic in the TMO makes the coupled metal ions more electropositive, which may result in the production of more Lewis base sites on the surface of CaO. The TMO doped CaO effectively transesterified and esterified the high FFA feedstocks with yields ranging from 76-98% and the capacity to be reused for four cycles with a biodiesel yield ranging from 92-95%, as expected. Similarly, Rahman et al. reported on the transesterification of eucalyptus oil using Cu and Zn doped eggshell CaO. Zn doped CaO had better basic sites, a greater surface area, and a larger pore volume than Cu doped CaO and CaO alone. The transesterification of eucalyptus oil was carried out under optimal conditions: 5% catalyst loading, a 6:1 MeOH:oil molar ratio, and a temperature of 65 oC for 2.5 hours. The biodiesel output was Zn/CaO > Cu/CaO > CaO for catalytic transesterification of eucalyptus oil. The scientists reported that the Zn/CaO could be reused up to seven times, with the biodiesel output remaining above 85% until the sixth run. Kaur and Ali's investigation, in which the transesterification of jatropha oil occurred over Mo doped CaO at reaction parameters: 12:1 ethanol to oil molar ratio, 65 oC employing 5 wt.% catalyst loading within 4.5 h of reaction time, agreed on the effectiveness of TMO modified CaO. The results revealed that 99% of the biodiesel was produced and that the catalyst could be reused up to five times. Das et al. used a cobalt-doped waste eggshell generated CaO catalyst to convert lipid isolated from the algal Scenedesmus quadricauda to biodiesel. In this study, 98% of the algal oil was effectively turned into biodiesel using a Co/CaO catalyst. It should be noted that the Co/CaO displayed stable activity for at least three reaction runs. In general, the TMO doped catalyst yielded high biodiesel yields in the 90-97% range and can be reused in up to five consecutive runs. According to the findings, the TMO modified CaO catalyst is the most promising approach for overcoming active Ca2+ dissolution and boosting catalyst stability. The yield of AMO doped CaO was generally greater than 95%, and the catalyst can be reused up to 5 times after regeneration.

CHAPTER THREE
MATERIALS AND METHODS

3.1 MATERIALS

Table 3.1: Materials and reagents used in study

Material	Source/Producer	Function
Palm kernel oil	Cafeteria, Uwasota, Benin City.	-
Palm kernel shell	Local traders from Uselu market, Benin City	-
Snail shell	Uselu Market, Benin City	-
Copper Sulphate	BDH Laboratory Supplies, Poole, England	For doping the palm kernel shell
Zinc oxide	Kermel Laboratory Supplies	Neutralization during carbonization of the catalyst
Methanol	Guangdong Guanghua Sci-Tech Co., Ltd China	For biodiesel production
Sulfuric acid (H2SO4)	Guangdong Guanghua Sci-Tech Co., Ltd China	Catalyst preparation/biodiesel production
Hdrochloric acid (HCl)	Guangdong Guanghua Sci-Tech Co., Ltd China	For Biodiesel production
Sodium hydroxide	TRUST Chemical Laboroatories	Neutralization during carbonization of the catalyst
Ethanol	Guangdong Guanghua Sci-Tech Co., Ltd China	Determination of acid value
Benzene	Central Drug House Ltd, New Delhi, India	Determination of free fatty acid content
Potassium hydroxide	LOBA CHEMIE PVT. LTD	Determination of acid value and saponification value

Phenolphthalein	Kermel Chemicals Reagent Company Ltd, Tianjin China	Indicator used in determination of acid value of the oil

Table 3.2: Equipment Used

Equipment	Model	Function
Magnetic stirrer	MS300 magnetic stirrer	Heat and stir oil mixture
Beaker	G-pyrex(250ml,500ml)	Reactor for biodiesel production
Conical flask	JINOTECH (250ml)	Reactor for biodiesel production
Thermometer		Determination of temperature
Weighing balance	M311L	Sample weight determination
Oven	DHG-0A JINOTECH	Drying to known temperature
Electric muffle furnace	SX-5-12 Electric muffle furnace	Calcination of the egg shell
Flash Point tester	SYD-261	Biodiesel flash point determination
Gas chromatography	GC MSD	Analysis of oil
Separating funnel	G-pyrex 500ml	Separation of biodiesel
Pour point tester	SYD-261	To determine the diesel pour point
Measuring cylinder	Ex 20^{0}C MC 250ml + 2ml	For measuring the specific volume of liquid samples
Density bottle	50ml	Used to measure the density of a liquid substance
Retort stand	-	For holding burette in place during titration
Burette	50ml Ex 27^{0}C (borosilicate glass)	For holding liquid used for titration
Funnel	-	Used for transferring liquids into burette, measuring cylinder or into reagent bottles.
Syringe	5ml plastic syringe	For taking small liquid samples
Droppers	3ml rubber dropper	For holding phenolphthalein indicator and releasing in droplets during titration.

Sieve	250µm sieve	Used fpr sieving crushed and calcined eggshell
Crucible	-	Used to hold crushed eggshell for calcination in furnace
Evaporating dish	-	Used for drying catalyst during preparation
Tongs	-	Used to remove crucibles from electric furnace

3.2. METHODS

3.2.1. Production of Palm kernel Ash

Palm kernel shells were extracted to be used as catalyst in the experiment. The shells were washed and dried in the oven to remove any form of impurities. The dried palm kernel shells were crushed into tiny mesh size of 0.6m. This was then filtered with a sieve of 0.6mm. The catalyst was carbonized and underwent pyrolysis reaction. The resulting biochar was then sulphonated. The following are the methods of its preparation.

3.2.1.1. Carbonization

The palm kernel shell biomass was carbonized using concentrated sulphuric acid (H2SO4), at ratio 1:1. The reaction was left for 24hrs to ensure contacting throughout the reactor. After 24hrs, the acidic mixture was neutralized by first diluting with water and adding sodium hydroxide solution until the carbonized biochar became neutral. A pH indicator was used to confirm its neutrality. The biomass was then washed thoroughly, filtered and placed in the oven to remove all traces of water.

3.2.1.2. Pyrolysis

The carbonated biochar was pyrolyzed by heating in the furnace in the absence of oxygen. Nitrogen gas was introduced to the setup during pyrolysis because the continuous flow of inert nitrogen gas into the pyrolysis reactor will remove the oxygen entering through the pipe and the oxygen gas in the reactor. The furnace was set at a temperature of 500^{o}C and left to pyrolyze for 1hr. At the end of the pyrolysis, the resulting biochar was cooled by adding water. A carbonaceous residue of high porous structure is gotten.

3.2.1.3. Sulphonation Process

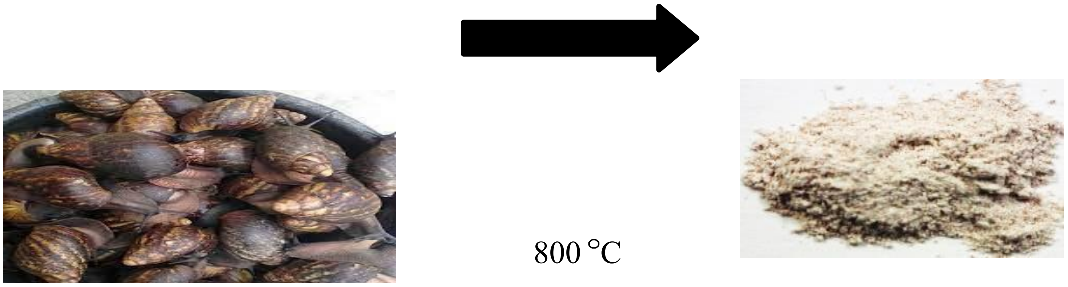
The resulting residue was put into 100 ml of sulphuric acid with a concentration of 98% and agitated for one hour. After that, the mixture was covered and cooked in a water bath at a temperature of 90 degrees Celsius for twenty-four hours.

After being filtered, the mixture was rinsed many times with hot deionized water until there were no traces of sulfate left in the sample. It was dried in an oven at 105°C.

3.2.2. Catalyst Preparation

3.2.2.1. Preparation of Calcium Oxide from Snail Shell

Snail shells were obtained from a vendor in Benin's Uselu market, Edo State, Nigeria. The snail shells were washed with hot water to remove impurities and pollutants from the shells. It was then dried in an oven at 105.3 °C for 2-4 hours. The dried snail shells were crushed in an agate mortar and processed to 75 m powder in a ball mill. The powder was calcined in a muffle furnace at 800°C for 24 hours to remove any trace of carbon and achieve a full conversion of $CaCO_3$ to CaO. The resulting ash was employed as a heterogeneous base catalyst in the manufacture of methyl ester.



Snail shell (CaCO3)

Catalyst (CaO)

Figure 3.1: Calcination of snail shell to convert CaCO3 to CaO

3.2.2.2. Characterization of Catalyst

The properties of the base catalyst were assessed by fourier transform infrared spectroscopy which gave the functional group, structure and bonds present in the catalyst.

3.2.2.3. Preparation of Palm kernel and Copper Sulphate Catalyst

Catalyst was prepared by doping palm kernel ash with CuSO4. Both of them were mixed in ratio 50:50. 20 grams of palm kernel ash and 20 grams of CuSO4 was prepared as an aqueous mixture using distilled water (10grams) as the medium. The aqueous mixture was oven dried for 4 hrs. The dried solid was crushed and calcined in a muffle furnace at a temperature of 800 °C for 6hrs after which it was removed, cooled and crushed for use.

On addition of water to the Palm Kernel and CuSO4 mixture, there was effervescence of gas and release of energy (beaker became increasingly very hot) during the stirring/mixing process, indicating that the reaction was exothermic. The aqueous mixture hardened within 4 minutes even before drying.

3.2.2.4. Doping of calcinated Snail shell with Palm Kernel ash + CUSO4

The heterogenous bifunctional catalyst was prepared by doping calcined snail shell with a 1:1 mixture of Palm kernel ash and $CUSO_4$. The palm kernel ash and $CUSO_4$ were mixed in 11 different loadings (100%, 90% , 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, & 0% wt% with respect to the palm kernel ash + $CUSO_4$ mixture).

3.3 Characterization of Catalyst

The prepared catalyst was analyzed with FTIR, EDXRF, XRD and SEM for particle structure and surface morphology respectively.

3.3.1 Test of the Catalytic Activity

In the presence of a sulphonated biochar catalyst doped with CUSO4 and snail shell, fatty acids were esterified with alcohol. The following procedures were used to complete it successfully:

50 grams of palm kernel oil, was transferred from the measuring cylinder into the beaker. After adding 1.50 grams of the doped biochar to 30.208 grams of methanol, the mixture was constantly swirled with a glass rod. The oil was heated in a flask with a flat bottom, and when it reached a temperature of 50°C, a mixture of methanol and catalyst was added to the reactor, which was then stirred magnetically at a speed of 600 revolutions per minute for two hours. The reaction was stopped by immersing the reactor in a bath of cold water to bring the temperature down. The centrifugation and decantation processes were used to phase separate the catalyst.

Following the removal of the catalyst, the reactor was put into an oven and preheated to 105°C for an hour in order to collect any remaining methanol. The titrimetric approach was utilized in the determination of the percentage conversion for the esterification process. In order to carry out the titration, 0.05 mol of KOH and phenolphthalein were used as the indicators, respectively.

From Equation 3.1, the percentage conversion of triglyceride, the formula FFA Conversion= (al-a2)100.

Equation 3.1 Where al represents the starting acid value of the used cooking oil and a2 represents the final acid value after the reaction is complete.

3.3.1.1 Catalyst Reusability test

Reusability study was performed by employing the optimum reaction condition of 3 wt% of catalyst loading and 15 : 1 MeOH : oil molar ratio at 60 °C for 1 h 30 mins. For this test, the spent catalyst used in the first cycle was centrifuged, recovered with methanol and hexane and dried in the oven at 105 °C for 4 h. The dried catalyst was re-calcined at 700 °C for 3 hours before it was used for the next reaction cycle.

3.3.1.2 Catalyst leaching test

Leachability study was performed by employing the optimum reaction condition of 3 wt% of catalyst loading and 15 : 1 MeOH : oil molar ratio at 60 °C for 1 h 30 mins. For this test, 3 wt% of the bio-functional catalyst produced is added to 26.70 grams of methanol and left for 1 hour. After one hour the catalyst is filtered and the filtrate is reacted with the PKO palm kernel oil. The reaction is left for 1 hour 30mmins at a constant temperature of 60 °C. The product from the reaction is tested for biodiesel properties, testing the acid value and FFA.

3.3.2 Biodiesel Production

3.3.2.2. Esterification and Transesterification Process (Biodiesel Production)

The modified calcium oxide prepared from calcined snail shell powder was used as the heterogeneous catalyst to catalyze the transesterification of methanol with PKO for biodiesel synthesis. Oil/methanol ratio was 12:1, with catalyst loading of 2%w/w, 4%w/w, 6%w/w and 8%w/w of the catalysts respectively. The reaction time was kept constant at 2 hours for all the reactions, at 60 ± 0.5°C and at a speed of 650rpm. After transesterification, separation of biodiesel was carried by washing with water and decantation and products were weighed to determine the percentage conversion.

3.3.3. Crude biodiesel purification

After obtaining the maximum separation, the crude biodiesel was purified by warm water washing with distilled water using a separation funnel. Since both glycerol and methanol are highly soluble in water, crude biodiesel is mixed with distilled water and agitated gently to avoid formation of emulsion, then slowly percolating droplets of water through the ester (Atadashi et al. 2011). The process was repeated until colourless wash water was obtained, indicating complete removal of impurities.

3.3.1 Determination of Free Fatty Acids

Palm kernel oil (PKO) was analyzed for acid value and subsequently, the free fatty acid was determined. The oil was first of all filtered to remove all the suspended particles, then 1g of the oil was weighed into 250ml conical flask. Approximately 50ml neutral solvent mixture containing ethanol and diethyl ether was added. The mixture was thoroughly mixed and titrated with 0.1N potassium hydroxide using phenolphthalein as indicator to a permanent peak colour. A blank titration of the same amount of the neutral solvent mixture without the oil sample was carried out.

Calculation:

$$AV = \frac{(A-B)\times N\times 56.1}{w} \text{ -------------------------- (iii)}$$

Where;

AV = Acid value

A = Volume of KOH to titrate sample

B = Volume of KOH to neutralise blank

N = Normality of KOH solution

w = weight of oil

Calculation of free fatty acid

$$\%FFA = \frac{1}{2}AV \text{ -------------------------------(iv)}$$

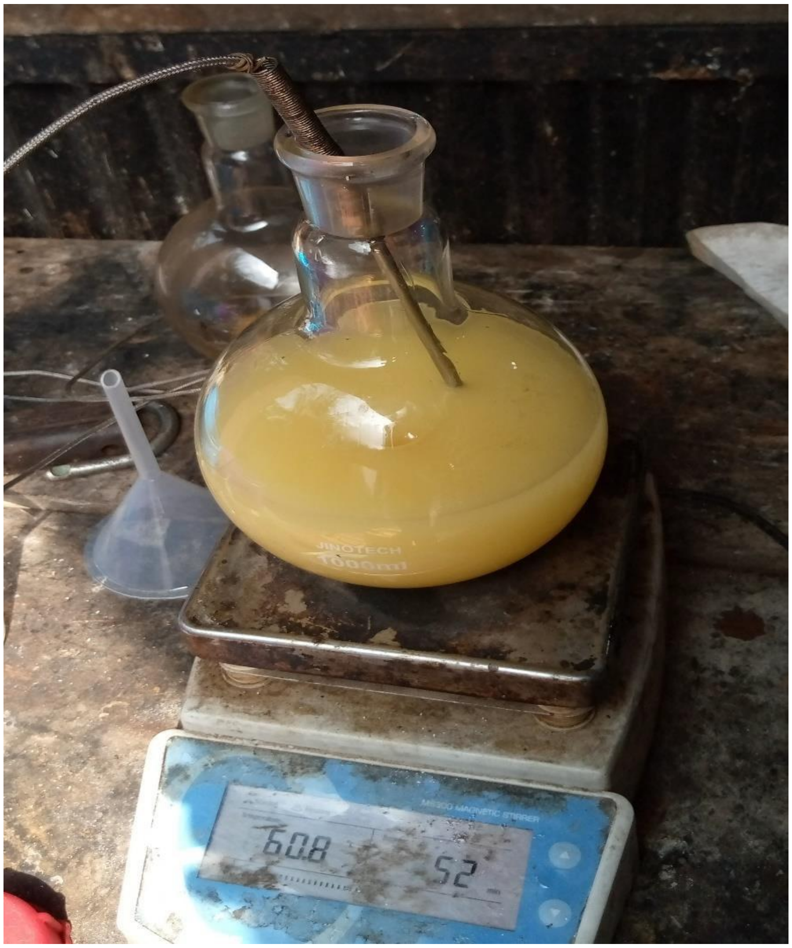


Figure 3.2: Transesterification of Oil to Biodiesel

3.3.2. Product Estimation

The weight of biodiesel produced from each run was determined using electronic weighing balance. The yield and conversion were calculated as follows:

$$\text{Yield (\%)} = \frac{\text{Weight}_{\text{Biodiesel}}}{\text{Weight}_{\text{Oil}}} \times 100 \text{ -------------------------------(v)}$$

3.3.3. Determination of Flash Point, ASTM D 93

The flash point of the bioidiesel produced was determined using Pensky Martens Closed Cup method (Figure 3.3). The cup was filled with the biodiesel up to the mark (75ml) and placed in the tester. The machine was then set to heat at about 5°c/min until a rise in temperature with simultaneous stirring was observed. Small open flame was maintained from an external supply of petroleum gas. Periodically, the flame was passed over the surface of the oil. When the flash temperature is reached the surface of the oil catch flame, the temperature at the point was noted and thus reported as flash point temperature.

Figure 3.3: SYD-261 Pensky Martens Closed cup Flash point Tester

3.2.2.1 Determination of Cloud Point

The Cloud point of the biodiesel was determined by filling 50ml beaker with the biodiesel sample up to the 28ml mark and immersing a thermometer in the biodiesel. The 50ml beaker was placed inside a 500ml beaker containing ice blocks. The thermometer was carefully observed to note when the biodiesel had started becoming cloudy. The temperature at which the cloudiness starts to form was noted as the cloud point of the biodiesel. The procedure was repeated 2 times and the average temperature was recorded.

3.2.2.2 Determination of Pour Point

The Pour point of the biodiesel was determined by filling 50ml beaker with the biodiesel sample up to the 28ml mark and immersing a thermometer in the biodiesel. The 50ml beaker was placed inside a 500ml beaker containing ice blocks. The temperature at which the cloudiness starts to form was noted as the cloud point of the biodiesel. The immersion of the beaker in the ice was continued until a point was reached where an immovable solid biodiesel was observed. At this point there was no more flow. The temperature at which this was observed was recorded as the pour point. This procedure was repeated 2 times and the average reading was taken as the pour point of the biodiesel.

3.2.2.3 Determination of Density

Empty 25ml cylinder was weighed as W_e. The cylinder was filled with biodiesel sample at 30^0c. The filled density bottle was reweighed as W_o. The biodiesel was poured out and the cylinder was washed, filled with water and reweighed as W_w. The density of the oil was determined using the formula;

Density = $(W_o - W_e)/V$------------------------------ (vi)

W_e = Weight of empty density

bottle W_o = Weight of bottle +

oil

W_w = Weight of bottle + water

The density of the biodiesel sample was determined as

3.2.2.4 Determination of Viscosity

The viscosity of the biodiesel was determined by filling 250ml beaker with the biodiesel sample. The sample is placed under the viscometer and the spindle of the viscosity is inserted in the oil/biodiesel sample. The viscometer is set to “run”. As the spindle rotates in the fluid readings are displayed on the viscometer. The viscosity of the oil/biodiesel is taken at a point where reading is almost consistent. This gives the viscosity of the oil/biodiesel

Figure3.4: Viscometer

3.2.2.5 Determination of the Biodiesel Composition

The percentage conversion to methyl ester and composition of the biodiesel was determined using the Gas Chromatography Mass Spectroscopy Detector (GC MSD)

Figure 3.5: Gas Chromatography Mass Spectroscopy Detector

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Physical and Chemical Properties of PKO

The results of analysis of the PKO are presented in Table 4.1. The amount of FFA in the oil was determined by titration and it was found to be 7.48% (Table 4.1). It has been shown in Studies that high FFA of oil reduces the effectiveness and leads to decrease in yield.

Table 4.1: Properties of PKO

Property	**Value**
Acid value (mg KOH/g)	14.98
FFA %	7.48
Saponification value (mg KOH/g)	235.8
Peroxide value (m_{eq}/kg)	24.7
Specific gravity @ 40°C	0.901

Koutroubas *et al.,* (1999) had reported that properties of oil can be affected by both locations and genotypes. The oil properties depend on the genotype but is also affected by environmental conditions such as cultural practices and time of harvesting (Salimon *et al.,* 2010). The obtained properties of the oil show quite a high peroxide value (PV), 24.7 m_{eq}/kg due to its high content of unsaturated fatty acids (Joshi *et al.,* 2011). The saponification value was 235.8 mgKOH/g and almost in the same range reported by Ogunniyi (2006) which was 232mgKOH/g. The high acid value of 14.98 mgKOH/g can be explained to be due to factors such as immature seeds and poor storage condition. The saponification value (SV) is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponify 1 g of sample.

4.2 Properties of Catalyst

The physical properties of the solid catalyst used in the transesterification reaction are presented above. It was observed that the properties resulted in a strong activity in the reactions. This assumption is supported by the SEM images of catalyst (Figure 4.1) (Buasri et al. 2013). Table 4.3 shows the properties of the biodiesel produced using heterogeneous catalyst at the standard conditions of the factors for transesterification.

4.2.1 Functional Groups of Catalyst

Oxygen containing surface functional groups plays important role in influencing the surface properties and adsorption behavior of activated carbons (Dawood and Sen 2014). These groups can be formed during activation process or can be introduced by oxidation after preparation of activated carbon. The FTIR spectra obtained for the prepared adsorbent is given in Figure 4.4. The sample showed three major absorption bands in the region 3900 – 1400 cm^{-1}.

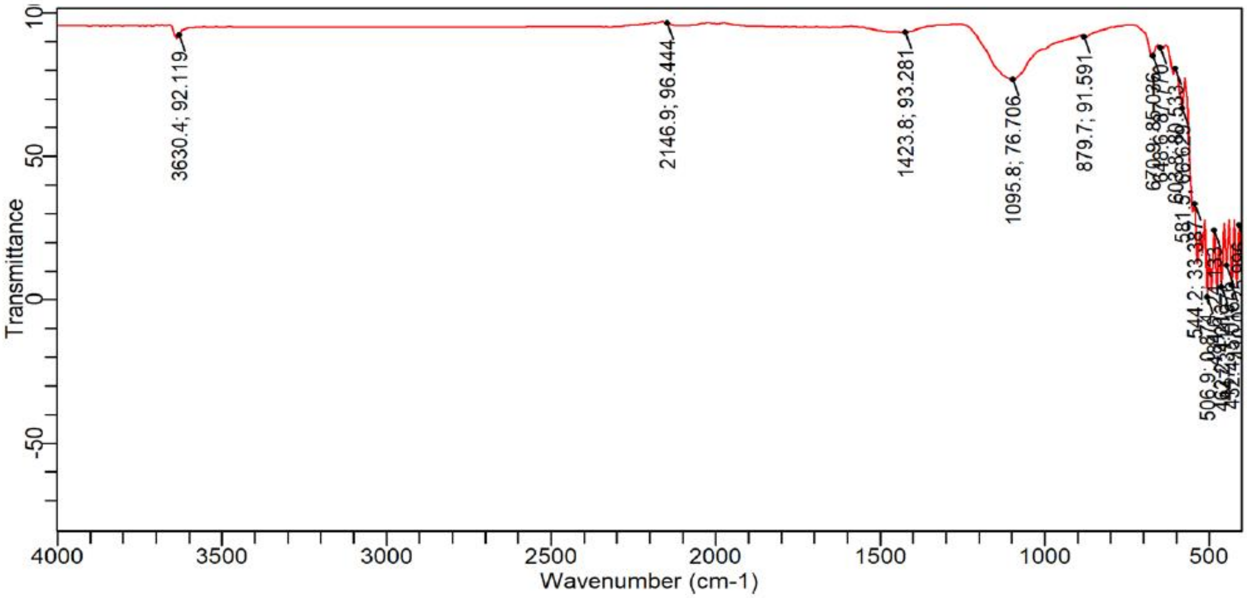


Figure 4.1: FTIR Spectrum of catalyst

From Table 4.2, the strong band around 1416 cm^{-1} indicates the stretching vibrations of Carbonate ion (CO_3^{-2}) bonds which is often found in calcined animal bones. Similarly, the weak peak seen at 3641 cm$^{−1}$ has been assigned to stretching vibrations of Heterocyclic amine (N – H) bonds. The summary of the results is as presented in Table 4.3.

Table 4.2: Summary of Spectrum peaks of Catalyst

Peak Number	**Wavenumber (cm^{-1})**	**Intensity**	**Functional group**	**Comment**
1	1476.0	97.792	Methyl (N – H)	Bend
2	3645.3	98.331	Carbonate ion (CO_3^{-2})	Strong stretch
3	3883.9	98.785	Heterocyclic amine (N – H)	Weak stretch

4.2.2 Surface Morphology of Catalyst

Micrograph of the catalyst obtained by the SEM images at 500x to 1500x magnifications are presented in Figure 4.1. Sample showed relatively uniform spherical particles in the size range of 20μm. It is worth mentioning that these particles' surface was rough and angular. Rough surfaces are known to posses more micropores and thus more efficient catalytic activities.

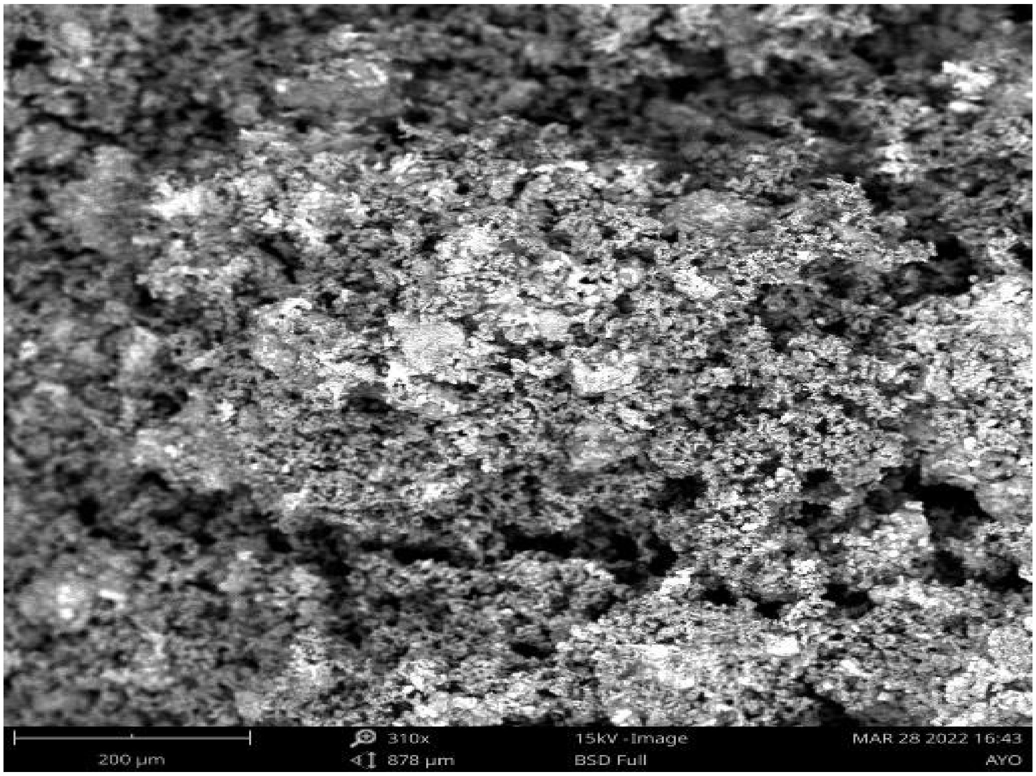


Figure 4.2: Micrograph of catalyst at 310x of magnification

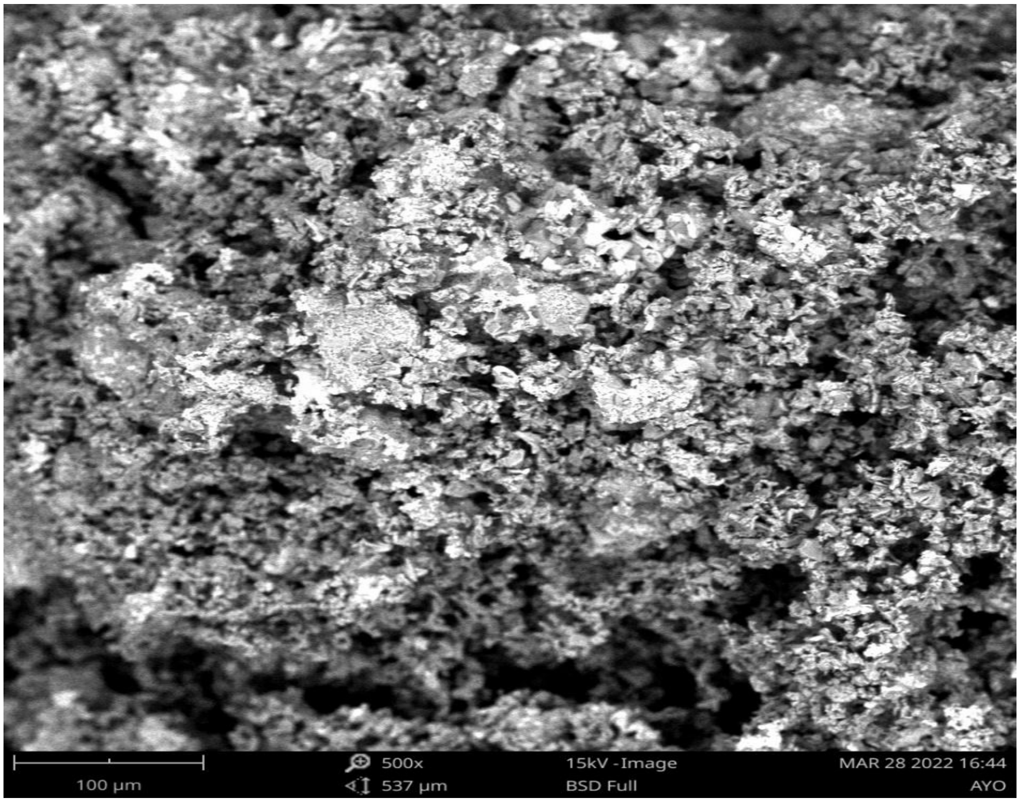


Figure4.3: Micrograph of catalyst at 500x of magnification

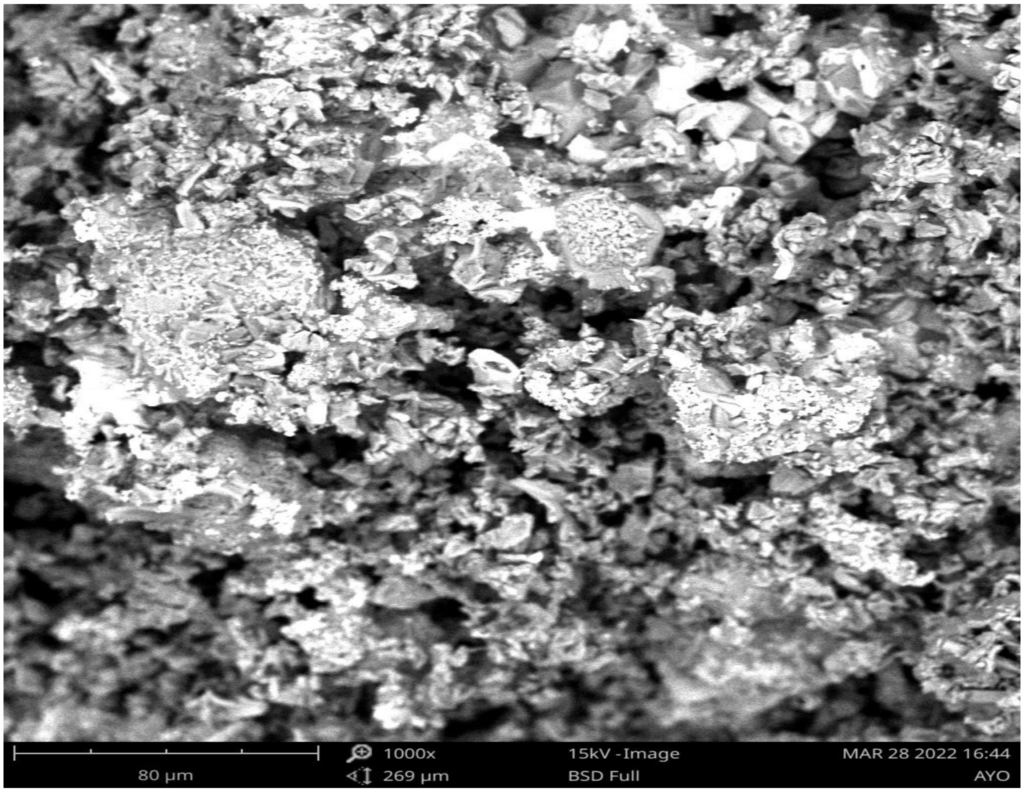


Figure 4.4: Micrograph of catalyst at 1000x of magnification

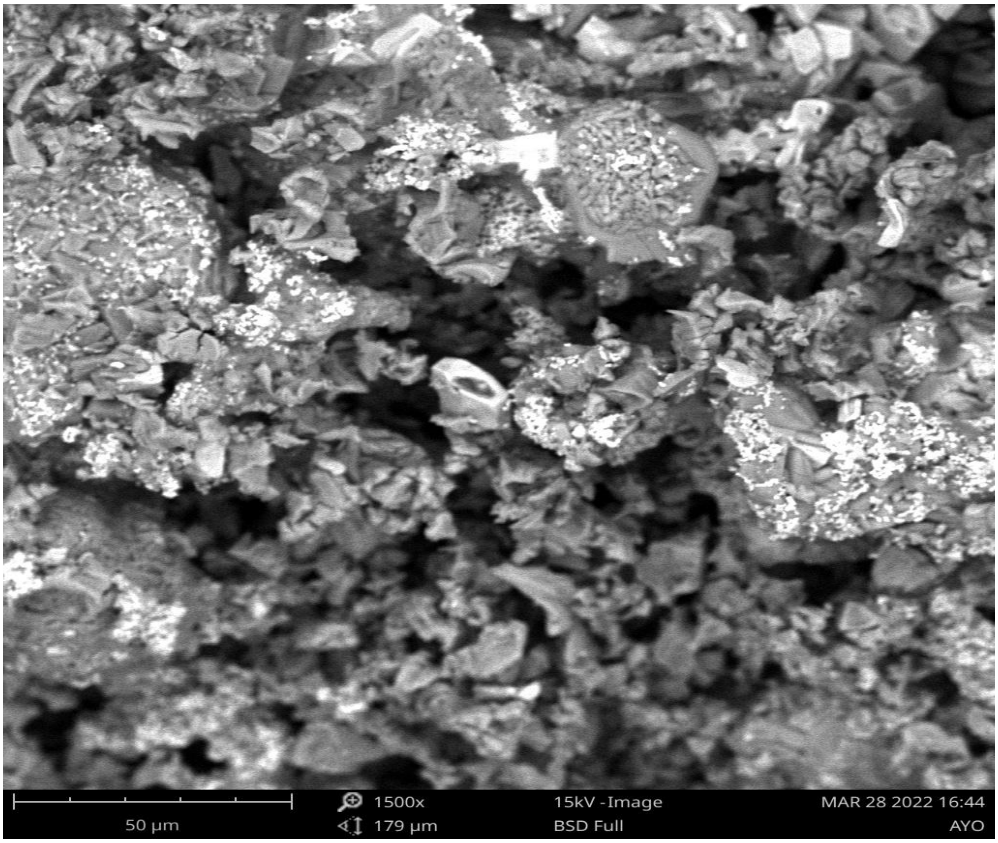


Figure 4.5: Micrograph of catalyst at 1500x of magnification

4.3.4 Elemental Composition of Catalyst

The results of elemental composition of catalyst were conducted using X-ray fluorescent (XRF) equipped with energy dispersive spectrometer (EDS). From Figure 4.3 the results obtained revealed the presence of calcium (Ca) at 70.485% in its oxide form at a peak of 109348 cps/mA making calcium the most predominant element followed by Copper (Cu) and Silicon (Si) both with same concentration of 2.4134% and 1.842% at peaks 2864 cps/mA and 142 cps/mA respectively. Other elements are presents in trace amounts.

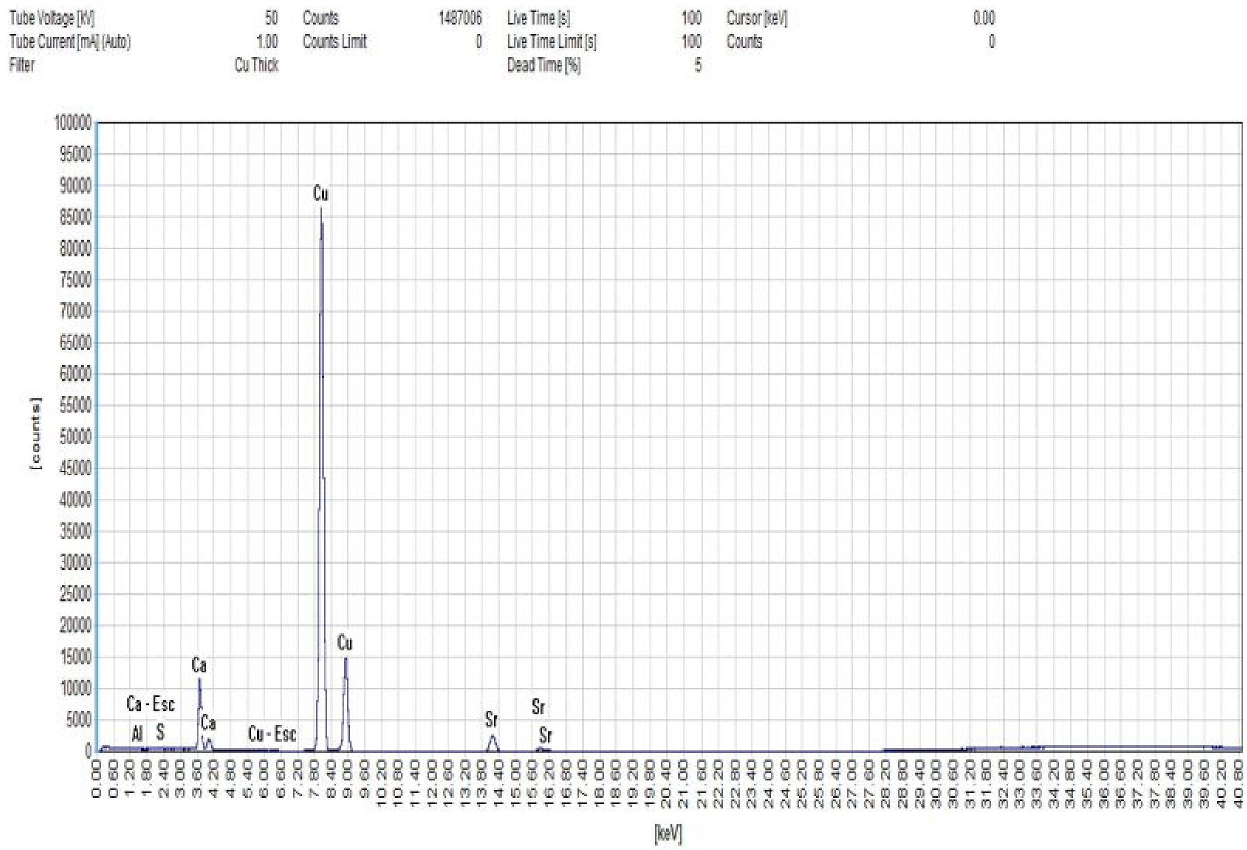
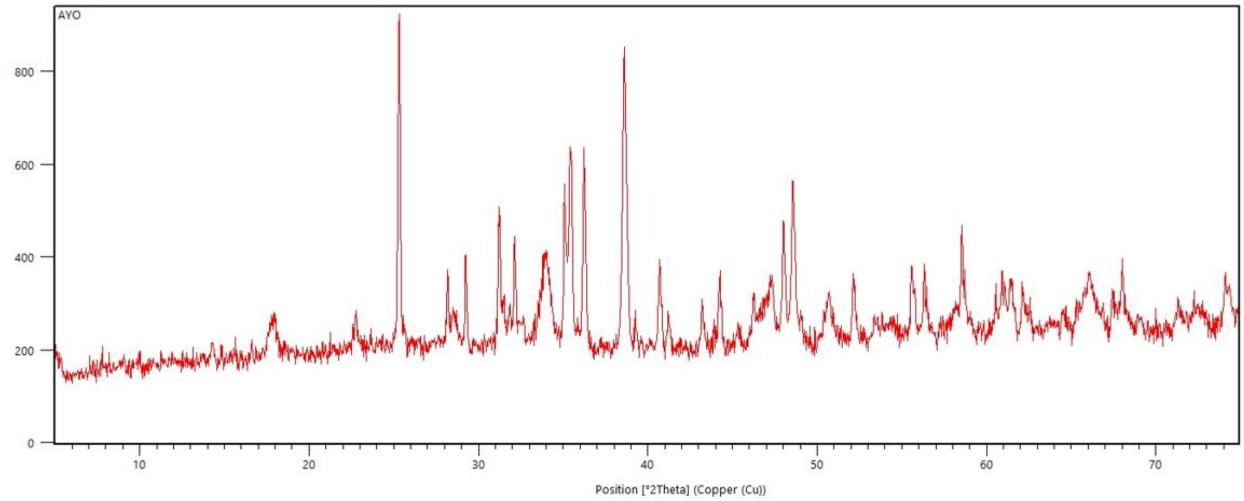


Figure 4.6: Spectrum of elemental composition of catalyst

4.3.4 Crystallinity of Calcined Snailshell

The crystallinity of the compounds present in the catalyst was determined with X-ray diffractometer. The results obtained (Figure 4.5) revealed an amorphous arrangement for the compound present in the catalyst.



4.4 Results of Catalyst Activity in Transesterification Reaction

The effectiveness of catalyst in the transesterification of palm kernel oil is shown in Figure 4.5. the results shown high catalyst performance in all formulations. However, the ash of palm kernel shells showed high alkalinity and in combination with copper sulphate enhances the overall performance as copper induces the acidic properties as most transition metals are either acidic or amphoteric. This situation may have introduced a double activity by the catalyst by simultaneous esterification and transesterification.

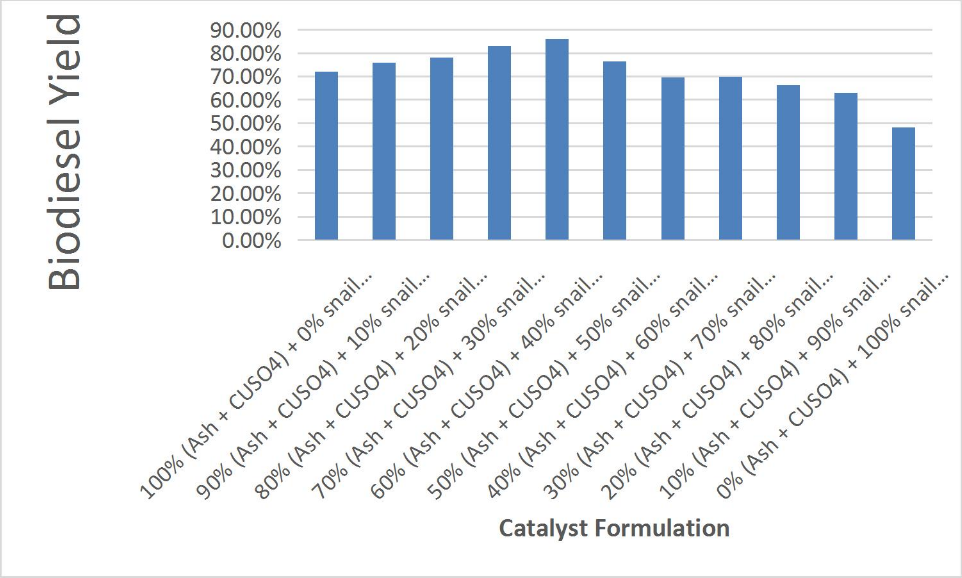


Figure 4.7: Performance of Catalyst in transesterification of palm kernel oil

Table 4.3: Properties of PKO Biodiesel

Property	Value	Test Method
Acid value (mgKOH/g)	0.902	
Free fatty acid (%)	0.451	
S. Gravity	0.8041	ASTM D941
K. Viscosity (mm^2/s)	4.131	ASTM D445
Flash point (^{o}C)	132	ASTM D93
Carbon residue (wt%)	0.73	ASTM D6751
Cloud point (^{o}C)	3.2	ASTM D6751
Pour point (^{o}C)	1.4	ASTM D6751

4.6 Reusability and leachability study

Reusability study is a significant characteristic of the introduction of heterogeneous Success in the regeneration of the catalyst has a substantial economic impact since it impacts the total cost of the process and the final product's price. Therefore, numerous reaction cycles were carried out under the ideal conditions of 3 wt% catalyst loading and 15:1 methanol to oil molar ratio at 60 °C for 1 hour 30 minutes using the best catalyst. Each reaction cycle was finished with the spent catalyst from the previous cycle being recovered through centrifugation and cleaned of polar and non-polar impurities on the catalyst surface using methanol and hexane. The catalytic activity of the used catalyst is restored through recalcination. The outcomes showed that after the second reaction cycle, the FAME yield dropped from 92.2% to 89.80%. The FAME yield further decreased in the third and fourth reaction cycles to 85.10% and 79.70, respectively, and to 72.60% after the fifth cycle. The reaction continued to run through another cycle, but sadly, it wasn't until the sixth cycle that the FAME yield fell to 58.9%. This work proved that the manufactured catalyst can be recycled for at least five further reaction cycles while still maintaining a respectable level of catalytic activity.

Table 4.4: Reusability and leachability study

No of runs	Acid Value	Yield
1	0.8200	92.20
2	0.9802	89.80
3	1.034	85.10
4	1.194	79.70
5	1.790	72.60
6	2.341	58.90

Catalyst leaching is a common phenomenon for various catalytic reactions that hampers the development of heterogeneous catalytic systems. Leaching is the term used to describe the loss of active species from the solid that is transferred into the liquid phase, ultimately leading to the catalyst becoming inactive. Leaching is a particular phenomenon that occurs in the liquid phase. Interestingly, leaching has not been the subject of many published investigations.

To test for leaching of the catalyst produced using the filtration method. 3 grams of the bio-functional catalyst produced is added to 26.70 grams of methanol (15:1 methanol to oil molar ratio) and left for 1 hour. After one hour the catalyst is filtered and the filtrate is used to react with 50 grams of PKO palm kernel oil. The reaction is left for 1 hour 30mmins at a constant temperature of 60. The product from the reaction is tested for biodiesel properties, testing the acid value and FFA

Table 4.5: biodiesel properties, testing the acid value and FFA

Run	**Acid value**	**Biodiesel Yield**	**FFA**
1	2.312	0	1.156

After the test it was discovered that there was no leaching from the catalyst, this would be due to the carrier, biomass-derived activated carbon as a good support carrier.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

PKO is an excellent feedstock for biodiesel production due to its moderate FFA percent concentration. Catalyst from palm kernel shell showed high catalyst performance in the transesterification of PKO. Thus, the following conclusions can be drawn from the overall study;

- Palm kernel shell ash doped with copper and calcium oxide has an effective catalytic activity in transesterification reaction.
- Catalyst shows excellent catalytic activity and provides the maximum biodiesel yield of 93.2% at the optimized reaction conditions.
- The improved catalytic activity is attributed to the presence of the optimum strength of the active sites on the surface of the catalyst for the given biodiesel reaction.
- In addition, the bio-based catalyst shows substantial chemical stability and could be reused repeatedly for at least eight times for biodiesel production without major loss in its catalytic activity.
- The present study shows that the synthesized bifunctional heterogeneous catalyst has immense potential to produce low cost biodiesel from low cost feedstocks for sustainable energy production.

5.2 Recommendations

PKO has been demonstrated to be an excellent feedstock for biodiesel production. The following are therefore recommended for future study.

- Other species of oil palm seed oil should be investigated to check for their usability for producing value added products so as to further reduce disposals of agricultural wastes into the environment.
- Further investigation into the use of palm kernel shells for biodiesel production should be carried out to optimize other factors not studied in this work and to also improve on the yield of biodiesel obtained from the feedstock.
- Future studies should also analyze the effect of using a palm kernel shell catalyst on the production of biodiesel from low-cost feedstock in order to reduce separation costs.

REFERENCES

Adewale, P., Dumont, M. J., & Ngadi, M. (2015). Recent trends of biodiesel production from animal fat wastes and associated production techniques. In *Renewable and Sustainable Energy Reviews* (Vol. 45, pp. 574–588). Elsevier. https://doi.org/10.1016/j.rser.2015.02.039

Agarwal, M., Chauhan, G., Chaurasia, S. P., & Singh, K. (2012). Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. *Journal of the Taiwan Institute of Chemical Engineers*, *43*(1), 89–94. https://doi.org/10.1016/j.jtice.2011.06.003

Akhihiero, E. T., Oghenejoboh, K. M., & Umukoro, P. O. (2013). Effects of Process Variables on Transesterification Reaction of Jatropha Curcas Seed Oil for the Production of Biodiesel. *International Journal of Emerging Technology and Advanced Engineering*, *3*(6), 388–393.

Al-Widyan, M. I., & Al-Shyoukh, A. O. (2002). Experimental evaluation of the transesterification of waste palm oil into biodiesel. *Bioresource Technology*, *85*(3), 253–256. https://doi.org/10.1016/S0960-8524(02)00135-9

Alptekin, E., Canakci, M., & Sanli, H. (2014). Biodiesel production from vegetable oil and waste animal fats in a pilot plant. *Waste Management*, *34*(11), 2146–2154. https://doi.org/10.1016/j.wasman.2014.07.019

Arifin, S. F., Abdulla, R., Chan, E. S., Ravindra, P., Saribiyik, O. Y., Özcanli, M., Serin, H., Serin, S., Aydin, K., Raja, S. A., Robinson, D. S., Lindon, C., Lee, R., Jaichandar, S., Annamalai, K., Garlapati, V. K., Kant, R., Kumari, A., Mahapatra, P., … Jibrail B Kansedo. (2011). Factors Affecting Biodiesel Production. *Sustainability (Switzerland)*, *2*(2), 146–149. https://doi.org/10.1186/2043-7129-1-11

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, *16*(4), 2070–2093. https://doi.org/10.1016/j.rser.2012.01.003

Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., & Sulaiman, N. M. N. (2013). The effects of catalysts in biodiesel production: A review. *Journal of Industrial and Engineering Chemistry*, *19*(1), 14–26. https://doi.org/10.1016/j.jiec.2012.07.009

Boey, P. L., Maniam, G. P., & Hamid, S. A. (2011). Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: A review. *Chemical Engineering Journal*, *168*(1), 15–22. https://doi.org/10.1016/j.cej.2011.01.009

Chakraborty, R., Bepari, S., & Banerjee, A. (2011). Application of calcined waste fish (Labeo rohita) scale as low-cost heterogeneous catalyst for biodiesel synthesis. *Bioresource Technology*, *102*(3), 3610–3618. https://doi.org/10.1016/j.biortech.2010.10.123

Chitra, C. S. C. K. (2012). *Biodiesel Production From Rubber Seed Oil Using Activated.*

January.

Demirbas, A. (2009). Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*, *50*(1), 14–34. https://doi.org/10.1016/j.enconman.2008.09.001

Dossin, T. F., Reyniers, M. F., Berger, R. J., & Marin, G. B. (2006). Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B: Environmental*, *67*(1–2), 136–148. https://doi.org/10.1016/j.apcatb.2006.04.008

Gashaw, A., & Lakachew, A. (2014). Production of Biodiesel from Non Edible Oil and its Properties. *International Journal of Science, Environment and Technology*, *3*(4), 1544–1562.

Gashaw, A., & Teshita, A. (2014). *Production of biodiesel from waste cooking oil and factors affecting its formation : A review*. *3*(5), 92–98. https://doi.org/10.11648/j.ijrse.20140305.12

Gill, P., Soni, S. K., Kundu, K., & Srivastava, S. (n.d.). *Effect of blends of Rubber seed oil on engine performance and Emissions*. 1–16.

Gondra, Z. A. (2010a). *Study of factors influencing the quality and yield of biodiesel produced by transesterification of vegetable oils* (Issue June).

Gondra, Z. A. (2010b). *Study of factors influencing the quality and yield of biodiesel produced by transesterification of vegetable oils*. UNIVERSITY OF GAVLE.

Hsu, C., Chang, K., Lai, M., & Chang, T. (2011). Pretreatment and hydrolysis of cellulosic agricultural wastes with a cellulase-producing Streptomyces for bioethanol production.

Biomass and Bioenergy, *35*(5), 1878–1884. https://doi.org/10.1016/j.biombioe.2011.01.031

Igbokwe, J., & Nwafor, M. O. . (2014). *Synthesis And Characterization of Biodiesel From Nigerian Palm Kernel oil* . *03*, 264–266.

John, H. (2009). *Soybeans for Biodiesel Production – Farm Energy*. Farm Energy Publications. https://farm-energy.extension.org/soybeans-for-biodiesel-production/

Leung, D. Y. C., Wu, X., & Leung, M. K. H. (2010). A review on biodiesel production using catalyzed transesterification. *Applied Energy*, *87*(4), 1083–1095. https://doi.org/10.1016/j.apenergy.2009.10.006

Liu, X., He, H., Wang, Y., Zhu, S., & Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel*, *87*(2), 216–221. https://doi.org/10.1016/j.fuel.2007.04.013

Location, G., The, O. F., & Area, S. (2002). *Chapter 4. 1*, 139–149. https://doi.org/10.1227/01.NEU.0000028228.51706.2D

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., & Goodwin, J. G. (2005).

Synthesis of biodiesel via acid catalysis. *Industrial and Engineering Chemistry Research*, *44*(14), 5353–5363. https://doi.org/10.1021/ie049157g

Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review1Journal Series #12109, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska–Lincoln.1. *Bioresource Technology*, *70*(1), 1–15. https://doi.org/10.1016/s0960-8524(99)00025-5

Martino Di Serio, Riccardo Tesser, Lu Pengmei, and E. S., & Dipartimento. (2019). Biochar-derived heterogeneous catalysts for biodiesel production. *Environmental Chemistry Letters*, *17*(4), 1447–1469.

Martyanov, I. N., & Sayari, A. (2008). Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium, and calcium methoxides. *Applied Catalysis A: General*, *339*(1), 45–52. https://doi.org/10.1016/j.apcata.2008.01.007

Meher, L. C., Vidya Sagar, D., & Naik, S. N. (2006). Technical aspects of biodiesel production by transesterification - A review. *Renewable and Sustainable Energy Reviews*, *10*(3), 248–268. https://doi.org/10.1016/j.rser.2004.09.002

Morshed, M., Ferdous, K., Khan, M. R., Mazumder, M. S. I., Islam, M. A., & Uddin, M. T. (2011). Rubber seed oil as a potential source for biodiesel production in Bangladesh. *Fuel*, *90*(10), 2981–2986. https://doi.org/10.1016/j.fuel.2011.05.020

Niju, S., Begum, M. M. M. S., & Anantharaman, N. (2014). Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society*, *18*(5), 702–706. https://doi.org/10.1016/j.jscs.2014.02.010

Olutoye, M. A., & Hameed, B. H. (2011). Synthesis of fatty acid methyl ester from used vegetable cooking oil by solid reusable Mg1-x Zn1+xO2 catalyst. *Bioresource Technology*, *102*(4), 3819–3826. https://doi.org/10.1016/j.biortech.2010.11.100

Palniandy, L. K., Yoon, L. W., Wong, W. Y., Yong, S. T., & Pang, M. M. (2019). Application of Biochar derived from different types of biomass and treatment methods as a fuel source for direct carbon fuel cells. *Energies*, *12*(13), 1–15. https://doi.org/10.3390/en12132477

Prah, E. (2010). *Biodiesel Analytical Development and Characterisation* (Issue March). https://doi.org/10.1017/CBO9781107415324.004

Rashid, U., & Anwar, F. (2008). Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel*, *87*(3), 265–273. https://doi.org/10.1016/j.fuel.2007.05.003

Rashid, U., Anwar, F., Moser, B. R., & Knothe, G. (2008). Moringa oleifera oil: A possible source of biodiesel. *Bioresource Technology*, *99*(17), 8175–8179.

https://doi.org/10.1016/j.biortech.2008.03.066

Rezaei, R., Mohadesi, M., & Moradi, G. R. (2013). Optimization of biodiesel production using waste mussel shell catalyst. *Fuel*, *109*, 534–541. https://doi.org/10.1016/j.fuel.2013.03.004

Robles-Medina, A., González-Moreno, P. A., Esteban-Cerdán, L., & Molina-Grima, E. (2009). Biocatalysis: Towards ever greener biodiesel production. *Biotechnology Advances*, *27*(4), 398–408. https://doi.org/10.1016/j.biotechadv.2008.10.008

Romano, S. D., & Sorichetti, P. A. (2011). Dielectric spectroscopy in biodiesel production and characterization. *Green Energy and Technology*, *29*. https://doi.org/10.1007/978-1-84996- 519-4

Sakai, T., Kawashima, A., & Koshikawa, T. (2009). Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. *Bioresource Technology*, *100*(13), 3268–3276. https://doi.org/10.1016/j.biortech.2009.02.010

Sharma, Y. C., & Singh, B. (2008). Development of biodiesel from karanja, a tree found in rural India. *Fuel*, *87*(8–9), 1740–1742. https://doi.org/10.1016/j.fuel.2007.08.001

Shu, Q., Yang, B., Yuan, H., Qing, S., & Zhu, G. (2007). Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La3+. *Catalysis Communications*, *8*(12), 2159–2165. https://doi.org/10.1016/j.catcom.2007.04.028

Singh, D., Sharma, D., Soni, S. L., Sharma, S., Kumar Sharma, P., & Jhalani, A. (2020). A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel*, *262*(October), 116553. https://doi.org/10.1016/j.fuel.2019.116553

Van Gerpen, J. (2005). Biodiesel processing and production. *Fuel Processing Technology*, *86*(10), 1097–1107. https://doi.org/10.1016/j.fuproc.2004.11.005

Viriya-empikul, N., Krasae, P., Puttasawat, B., Yoosuk, B., Chollacoop, N., & Faungnawakij, K. (2010). Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresource Technology*, *101*(10), 3765–3767. https://doi.org/10.1016/j.biortech.2009.12.079

Xie, W., Peng, H., & Chen, L. (2006). Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis A: General*, *300*(1), 67–74. https://doi.org/10.1016/j.apcata.2005.10.048

Yang, Z., & Xie, W. (2007). Soybean oil transesterification over zinc oxide modified with alkali earth metals. *Fuel Processing Technology*, *88*(6), 631–638. https://doi.org/10.1016/j.fuproc.2007.02.006

Zhang, J., Chen, S., Yang, R., & Yan, Y. (2010). Biodiesel production from vegetable oil using heterogenous acid and alkali catalyst. *Fuel*, *89*(10), 2939–2944. https://doi.org/10.1016/j.fuel.2010.05.009

Zivković, S. B., Veljković, M. V., Banković-Ilić, I. B., Krstić, I. M., Konstantinović, S. S., Ilić,

S. B., Avramović, J. M., Stamenković, O. S., & Veljković, V. B. (2017). Technological, technical, economic, environmental, social, human health risk, toxicological and policy considerations of biodiesel production and use. *Renewable and Sustainable Energy Reviews*, *79*(May), 222–247. https://doi.org/10.1016/j.rser.2017.05.048

Element	Concentration	Peak(cps/mA)
Fe2O3	0.0117 %	44
CuO	17.260 %	102395
ZnO	0.0090 %	74
GeO2	0.000348 %	5
CeO2	1.265 %	2
Lu2O3	0.000375 %	30
Ta2O5	[0.0054] %	6
WO3	0.01105 %	15
MgO	0.81 %	1
Al2O3	0.940 %	15
SiO2	2.269 %	175
P2O5	0.0801 %	19
SO3	6.0208 %	7144
Cl	0.098 %	48
K2O	0.1216 %	126
CaO	49.097 %	76168
TiO2	0.0180 %	64
V2O5	[0.00073] %	5
Cr2O3	[0.00078] %	6
Rb2O	[0.000156] %	1
SnO2	1 %	0

U3O8	[0.008] %		1
Ag2O	0.000595 %	0	
Cs2O	0.00055 %		2