THE SYNTHESIS OF A HETEROGENEOUS CATALYST FROM CALCINED AGROWASTES (CHICKEN EGG SHELLS DOPED WITH RIPE PLANTAIN PEELS) FOR BIODIESEL PRODUCTION

BY

UWAYO GODWIN OBHOSE
PG-ENG0701791

PRESENTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING IN
PARTIAL FULFILMENT FOR THE AWARD OF MASTER OF ENGINEERING, CHEMICAL ENGINEERING (M.ENG (CHE)).
DEPARTMENT OF CHEMICAL ENGINEERING
FACULTY OF ENGINEERING
UNIVERSITY OF BENIN,
BENIN CITY
EDO STATE, NIGERIA.

MAY, 2021.

CERTIFICATION

This is to certify that this project was carried out by **UWAYO GODWIN OBHOSE**

In the Department of Chemical Engineering, University of Benin, Benin City, Edo State, Nigeria.

PROF. EMERITUS T. O. K. AUDU **(Project Supervisor)**	**Date**
ENGR. (DR. (MRS)) E.A. OYEDOH **(Programme Co-ordinator)**	**Date**
DR. N. A. AMENAGHAMWON **(Head of Department)**	**Date**
EXTERNAL EXAMINER	**Date**

DEDICATION

Firstly, this research is dedicated to THE ALMIGHTY HIMSELF, JESUS CHRIST my guide and my family members who have been of immense support.

ACKNOWLEDGEMENT

I wish to express my profound gratitude to all who contributed immensely to the completion of this research.

My foremost gratitude goes to my dad and his beloved wife, Mr and Mrs Okosun Uwayo Y.S for his financial and moral support throughout the course of this research.

I am also grateful to my supervisor, Professor Emeritus T. O. K. Audu whose fatherly role as supervisor provided me the ground for embarking on this research.

I am not forgetting senior lecturers of the Department of Chemical Engineering, University of Benin who made contributions and corrections to the work to make it better and friends too numerous to mention who gave me their unrelenting support all through my stay in the University of Benin.

TABLE OF CONTENT

TITLE **PAGES**

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The potential of calcined agrowastes particularly chicken eggshells (CES) impregnated with ripe plantain peels (RPP) as a suitable catalyst for the conversion of waste cooking oil to biodiesel (FAME) by trans-esterification was investigated. The catalyst derived from these agro-wastes was synthesized by dry impregnation using physical mixing. The free fatty acid (FFA) content of waste cooking oil used for transesterification was measured to be 0.131%. The reaction conditions with methanol to oil molar ratio of 6:1, reaction time of 90 minutes, catalyst loading of 2% oil weight and a temperature of 60°C was kept constant while the catalyst's design mixing ratios of 'RPP: CES' was varied. The FT-IR, XRD and elemental analysis by XRF revealed the catalytic action of these materials (RPP and CES) is a result of their metallic content (K^+ and Ca^{2+}) and their microstructural formation change is noticeable when calcined at above 700°C. The experiment was carried out by the trans-esterification of the oil using each of the different designed catalyst samples to investigate the influence of their different mixing ratios on biodiesel yield. The results of the chart plots using Microsoft Excel 2010 showed that the optimum biodiesel yield consistent with ASTM D-6751 and EN 14214 standards was 75.04 % and the catalyst mixing ratio of 1:3 by mass was the optimal design ratio.

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND OF STUDY

Over the last century, the world's economy relied heavily on the use of fossil fuels as its main primary energy source amongst others. This is due to their efficiency, ready availability and easy accessibility. Fossil fuels which include; coal, petroleum (crude oil) and natural gas are sources of thermal energy usually processed in the form of gaseous, liquid or solid fuel with applications found in transportation, electricity generation and agricultural production. In the past few decades, the consumption of fossil fuel has increased at an expeditious pace leaving behind a challenging target when the high energy demand to be met is considered (International Energy Agency, 2012). Fossil energy has been a fundamental driver of the technological, social, economic advancement and development made towards ensuring a thriving global economy such that maintaining the healthiness of the present global economy hinges on increasing the production rates of these fossil fuels so as to meet the ever increasing demands leading to its extensive use.

However, fossil energy sources are non-renewable as they typically require extraction normally carried out using the 'low-hanging fruit principle' which means, large concentrations of high quality and easily accessed fuels tend to be depleted before extraction efforts are directed towards low-quality or hard to produce fuels, which in the end leads to the depletion of their natural reserves due to rising energy demands. Besides depletion, the extensive use of fossil fuel is ramped up with other challenges which includes;

- ✓ The increased upstream production costs due to the need for new technologies when it entails drilling in hostile or fragile environments as well as the associated accidents during production operations leading to fluctuating or rather rising fuel prices.
- ✓ The increased environmental burden culminating into challenges like global warming and climate change or the risks they portend and the costs required to manage them.
- ✓ The arising international conflict over scarce and depleting resources, a trend already noticeable in South China Sea and Central Asia.

Thus, in order to tackle these challenges, the need to reduce the use of fossil fuels as much as possible and as well find alternative energy sources which are sustainable and environmentally-benign, to supplement the use of fossil fuels became paramount. For example in 2015 at the Paris Climatic Summit, where about 195 countries came together to a pledge with the single ambition to limit global temperature increase, well below 2 degrees Celsius in order to combat climate change. Consequently, exploring renewable sources such as wind, geothermal, solar, and hydro and biomass resources became a new crave, as they are not only sustainable or readily available but are also environment-friendly. Many renewable energy sources are already extensively in use for heating operations and electricity production, but their application in the transportation industry has been limited due to the high energy demand required by transport fuels most especially when compatibility with the internal combustion engine of a vehicle or machine is considered.

The transport sector world-wide has considerably increased its fuel consumption reaching 61.5% of the total fuel produced especially within the last decade. Globally, 93% of the current transport sector energy use is still fossil fuel based, due to their high energy content and easy handling properties (International Energy Agency, 2017). Unlike other renewable sources, the only natural renewable resource of biological origin, large in quantity and enough to offset or substitute the use of fossil fuel in the internal combustion engines of these

machines is biomass. The incentives for exploring biomass comes from its abundance and the *carbon-neutrality* in its carbon cycle when utilized, as this enables the recycle of carbon trapped from the atmosphere to be transformed through the different energy production and consumption processes including chemosynthesis and photosynthesis into the different energy products and useful by-products. These bio-energy products includes; thermal energy (heat), electricity, fluid fuels referred to as 'biofuels' with other by-products which includes organic and inorganic bio-chemicals like bio-based foams, plastics, fertilizers, lubricants amongst many others meant for both domestic and industrial use. Biofuels which includes; bioethanol, biogas and biodiesel are normally sourced from renewable biomass sources like agricultural crops, residues and other biological materials. Conversion processes for transformation into biofuels includes; anaerobic digestion for biogas, fermentation for bioethanol, pyrolysis for bio-oil, trans-esterification for biodiesel, etc.

Biodiesel also known as fatty acid methyl esters (FAME) is a liquid biofuel which has been considered the most favourable substitute or alternative for petroleum diesel when applied to the internal combustion engines of vehicles or machines. Reasons for this includes; reduced exhaust emissions, improved biodegradability, reduced toxicity, improved lubricity, higher flash point and lower vapour pressure (Margaroni,1998; Knothe and Steidley, 2005). Conceicao *et al.* (2005) reported that among the possible biofuels produced with potential enough to run a compression ignition (i.e. a diesel engine); the most feasible alternative is biodiesel. Lifecycle analysis of biodiesel demonstrates that the overall CO_2 emissions are reduced by 78% when utilized instead as opposed to emissions when petroleum-based diesel fuel is used (Gerpen, 2005). According to Scarisbrick and Ferguson (1995), the most exceptional advantage of biodiesel is the fact that it holds a positive energy balance in that the energy used in the production of the fuel is less than the energy value of the fuel produced together with that of many of its associated useful by-products.

The American Society for testing and materials (ASTM) defines "*biodiesel"* as mono-alkyl esters of long chain fatty acids derived from different lipid-rich feedstock particularly vegetable oils and animal fats.

1.2 STATEMENT OF THE PROBLEM

Petroleum diesel contributes largely to environmental pollution as it releases greenhouse gases into the atmosphere and combating the consequent effect of climate change involves turning to more environmentally benign and sustainable fuels. Biodiesel is considered a very suitable alternative to petroleum diesel due to some properties which include; low toxicity, biodegradability, ready availability and sustainability as it is easy to access from renewable biomass sources. The benefits of biodiesel over petro-diesel include; the significant reduction in greenhouse gas emissions, non-sulphur emissions and non-particulate matter pollutants. However, the commercialization of its production in developing countries suffers a major setback, due to the high production costs involved which is a function of the high cost of feedstock oils used, be it edible or nonedible; the cost of catalysts particularly homogeneous catalysts, and the labour costs amongst others. Thus, the use of low cost materials in terms of catalysts and feedstock oil in overcoming this setback becomes a necessity if the economic feasibility of production on a large scale as well as the long term viability is to be considered. The benefit here is that these materials are cheap or almost wasting away as they are readily available and can be locally sourced such that the cost of producing biodiesel will be reduced while their burden of disposal on the environment is mitigated.

1.3 AIMS AND OBJECTIVES

The aim of this investigation is to synthesize a catalyst from a blend of calcined agrowastes; ripe plantain peels (RPP) and chicken egg shells (CES) for the transesterification of waste cooking oil (WCO) into biodiesel.

The set out objectives to be met include:

1. Synthesis of the catalyst through impregnation (doping) by physical mixing in different selected 'RPP: CES' mixing ratios by mass.
2. Characterization of the prepared catalyst samples.
3. Activation of the synthesized catalyst samples i.e. calcined (RPP+CES) using methanol (CH_3OH) 99.8% pure.
4. Analysis and Characterization of the waste cooking oil (WCO).
5. Pre-treatment of the oil (WCO) by filtration and decantation.
6. Trans-esterification of the waste cooking oil (WCO) into biodiesel (FAME) using the various synthesized catalyst samples.
7. Characterization of the biodiesel produced.
8. Optimization of the catalyst design ratios as a function of their biodiesel yield.

1.4 SCOPE OF STUDY

In the course of doing this work; locally available agro wastes would be sourced as the low-cost feed stock or raw material for use in the preparation of biodiesel.

- ✓ The feed stock materials to be sourced includes; egg shells ,ripe plantain peels and waste cooking oil obtained from domestic/kitchen wastes, pastry shops and bakeries.
- ✓ The catalyst would be prepared from chicken eggshells and ripe plantain peels after pre-treatment by calcination and impregnation byphysical mixing in selected trial mixing ratios by mass.
- ✓ The waste cooking oil would be pre-treated before trans-esterification into biodiesel (Fatty Acid Methyl Esters) is carried out.
- ✓ Optimization of the catalyst for the trans-esterification process would be done with the aid of a computer software particularly Microsoft Excel 2010.

1.5 SIGNIFICANCE OF STUDY

Biodiesel production incurs costs higher than that of conventional petrol-diesel, a consequence of the combined costs of raw materials and labour employed during production which is also due to the cost of high priced catalysts and feedstock oils used. Locally sourced and readily available feedstocks obtained from bio/agrowastes when feasible and appropriate offsets production costs as the economic feasibility and long term commercial viability of biodiesel production depends on the availability of these low-cost feed stocks be it the feedstock oil or the catalyst used. Particularly, the offset in production costs resulting from the use of low cost feed stock oils can also be supplemented by using catalysts that can possibly be derived from these agrowastes. The merits to using these catalysts can be summarised as follows; natural availability, environmental friendliness, the renewable nature and low costs (Kumar et al, 2015). Moreover such use of agricultural or biological wastes helps to reduce the environmental burden arising from the indiscriminate disposal of such wastes and as such solves the problem of energy and environmental conservation simultaneously.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

Biodiesel refers to any diesel fuel substitute derived from renewable biomass; it can be described as a sulphur-free, biodegradable, non-toxic, oxygenated and eco-friendly alternative to petroleum diesel. Chemically, it is defined as a bio-fuel composed of mono-alkyl esters of long-chain fatty acids derived from renewable sources like agricultural plants, animals, bio-wastes or materials containing triglycerides. Biodiesel fuels can be generally classified into first generation, second generation and third generation depending on the type of feed stocks used in their production. Some of these renewable feed stocks harnessed fom energy crops whether as whole biomass, wastes or residues includes; vegetable oils, animal fats, greases, waste cooking oils, algal oils, oleaginous microorganisms, etc. (Audu, 2011;Duarte *et al.,* 2013; Eloka-Eboka *et al.,*2017; Gaurav *et al.,* 2019). First generation biodiesel fuels are those produced using edible vegetable oils such as soybean, rapeseed, and palm oil as their main feedstock. Second generation biodiesel fuels derives from feed stocks such as non-edible vegetable oils, wastes of edible oils like frying oil, halophytes and animal fats. For third generation biodiesel which is more advanced, these fuels are produced using microbial oils derived from oleaginous microbes as feedstock like fungi, bacteria and microalgae.

Biodiesel is a clear amber-yellow liquid with energy content, physical and chemical properties similar to petro-diesel fuel and as such it serves as an alternative diesel fuel either directly or in a mixture with petro-diesel for internal combustion engines without requiring any modifications either to the ignition system or the fuel injector. It is non-flammable, non-explosive with a flash point of 423k, as compared to 337k for petro-diesel. It possesses better

lubricant properties which enhances engine yield and extends engine life (Vasudevan and Briggs, 2008). It is virtually nontoxic, almost completely free of sulphur and aromatics with oxygen content of about 11-15% in its molecular structure which helps to speed up its combustion processes in compression ignition engines as well as decrease pollutants such as; unburned hydrocarbons by 45.2%, particulate matter emission by 66.7%, carbon dioxide (CO_2) by 78% on a life cycle basis and carbon monoxide (CO) emissions by 46.7% (Murrillo *et al.,* 2007; Lapuerta *et al.,* 2008).

Biodiesel as a liquid biofuel is usually obtained through various chemical processes involving different mechanisms which includes; direct use (blending), thermal cracking (pyrolysis), micro-emulsion and esterification or majorly trans-esterification (Colin *et al.,* 2014). Based on the quality of feedstock, the trans-esterification of vegetable oils with alcohols or the direct esterification of fatty acids obtained from oil and soap industrial wastes (mucilage) using alcohols are the very commonly used methods of production. Trans-esterification is the most conventional method with a chemical approach by well-developed technologies commercialized worldwide. It is a stepwise chemical process carried out with or without the use of catalysts but requires the use of alcohol and the appropriate reaction conditions to drive its reaction forward.

From an environmental point of view, biodiesel as an alternative diesel fuel shows clear advantages over conventional petroleum or mineral diesel fuel as it is renewable, biodegradable with combustion products having reduced level of pollutants like greenhouse gases (Al-Zuhair, 2007; Salis *et al.,* 2005). Comparable to petroleum diesel in the conversion of primary energy to fuel product energy as their life cycle energy efficiency is close (80.55% versus 83.28%) where 1 MJ of biodiesel requires an input of 1.2414 MJ of primary energy, resulting in a life cycle energy efficiency of 80.55% whereas same quantity of mineral diesel energy requires a primary energy input of 1.20 MJ. Although biodiesel as compared to

petroleum diesel has so many advantages, there are obviously disadvantages which includes; cold weather starting problems, lower energy content, corrosion when exposed to brass and copper, deposits in injector or on the piston head, fuel pumping difficulty due to high viscosity, excessive engine wear and a higher production cost preventing its widespread use (Putrasari *et al.,* 2019). The properties of biodiesel are summarised in Table 2.1

Table 2.1 Properties of Biodiesel Fuel

Common name	Biodiesel (bio-diesel)
Common chemical name	Biodiesel (bio-diesel)
Chemical formula range	Fatty acid (m)ethyl ester
Chemical formula range	C14–C24 methyl esters or C 15-25 H 28-48 O2
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density range (kg/m^3, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	470–600
Solubility in water	Insoluble
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Biodiesel is usually produced to meet high quality standards, with specifications such as ASTM D6751 (USA), EN 14213 (European Union), IS 15607 (India), etc. These standard specifications have been established by various fuel standard-setting organizations, e.g. American Society for Testing and Materials (ASTM in the U.S.) and the European Committee for Standardization (CEN). These specifications are used for pure biodiesel (B100) also known as '*neat fuel'* to maintain the quality of the produced biodiesel for marketing. For biodiesel blends, they are referred to as "BXX", where the XX indicates the amount of biodiesel in the blend (i.e., a B80 blend is 80% biodiesel and 20% petro-diesel). Potential markets for biodiesel covers a wide range of applications, including most transport vehicles

like trucks and buses, stationary generation, mining equipment, marine diesel engines, etc. Table 2.2 shows the ASTM standards of biodiesel and petroleum diesel fuels.

Table 2.2 ASTM standards of biodiesel and petroleum diesel (http://www.astm.org/Standards/D6751)

Property	Test method	ASTM D975 (petrodiesel)	ASTM D6751 (biodiesel, B100)
Flash point	D 93	325 K min	403 K
Water and sediment	D 2709	0.05 max %vol	0.05 max %vol
Kinematic viscosity (at 313 K)	D 445	1.3 – 4.1 mm^2/s	1.9 – 6.0 mm^2/s
Sulphated ash	D 874	-	-
Ash	D 482	0.01 max %wt	-
Sulfur	D 5453	0.05 max %wt	-
Cetane number	D 613	40 min	47 min
Aromaticity	D 1319	35 max %vol	-
Carbon residue	D 4530	-	0.05 max %mass

2.2 HISTORY OF BIODIESEL PRODUCTION

Dr. Rudolf Diesel invented the diesel engine to run on a host of fuels including coal-dust suspended in water, heavy mineral oil and vegetable oils. His first engine experiments were although catastrophic failures, his perseverance paid off when in 1900 at the world fair exhibition in Paris he demonstrated with an engine running on 100% peanut oil which he presented and won the grandprix prize. He developed his engine from 1911 to 1912 into using vegetable oil so that in 1913, his engine had been modified to run on petroleum diesel. By the 1930's and 1940's, vegetable oils were already being used as diesel substitutes from time to time, although only in emergency situations. The merits to the consideration of vegetable oil as diesel fuel include factors like; portability for transit, ready availability, renewability, high heat content (about 88% the heat content of petroleum diesel), lower sulphur content, lower aromatics and biodegradability. Vegetable oils when used as an alternative engine fuel have extreme viscosities ranging from 9 to 17 times that of petroleum-derived diesels and considering the fact that modern diesel engines have fuel-injection

systems that are very sensitive to viscosity change, their injection and atomization characteristics significantly differ from those of petroleum derived diesel fuel mainly due to their high viscosities. Therefore, the drawback to using vegetable oils as an alternative diesel engine fuel had more to do with its higher viscosity in addition to the lower volatility and reactivity of their unsaturated hydrocarbon chains. Thus, tackling these problems became a priority which entails reducing the fuel viscosity of the vegetable oil in order to improve compatibility and performance with the diesel engine. One method to achieving this involved blending the oil with petro-diesel in the presence of some additives such as metal oxides, polymeric materials, ferrous materials and nano-additives like carbon nanotubes (CNT). These additives are capable of improving fuel properties like; increasing engine oxygen level, reducing exhaust emissions, improving the fluid flow, reducing ignition delay due to better combustion as well as improving the viscosity index (Ribeiro *et al.,*2007). Other methods of tackling these viscosity problems includes; pyrolysis, micro-emulsion and trans-esterification. Heating and blending of vegetable oils may reduce their viscosities as well as improve their volatilities; however they still remain poly-unsaturated as their molecular structures are still unchanged. The most convenient of these methods for tackling the high viscosity problem of using vegetable oils with fuel-injection system is the chemical process of trans-esterification. This process converts the triglycerides contained in the vegetable oil into *fatty acid methyl esters* (FAME) also called biodiesel as one of its end products. Biodiesel is the only alternative fuel till date that can be used directly in existing diesel engines due to better properties such as its high cetane number, low viscosity and improved heating rate when compared to those of pure vegetable oil. Some advantages it has over vegetable oils include; shorter ignition delay, longer combustion duration and low particulate emissions resulting in the minimization of carbon deposits on injector nozzles.

Today, as a consequence of the increase in the demand for energy, increase in crude oil prices, limited fossil fuel resources and environmental concerns, there is a renewed focus on the use of vegetable oils and animal fats as feedstock for conversion into biodiesel to serve as an alternative fuel for diesel engines. The use of petroleum diesel as fuel intensifies local air pollution and magnifies the global warming problems caused by the carbon dioxide produced. A particular case where the emission of pollutants creates environmental problems is in the closed environment of underground mines where the use of biodiesel rather than petro-diesel has the potential to reduce the level of pollutants and the potential level for probable carcinogens when utilized.

2.3 METHODS OF BIODIESEL PRODUCTION

Biodiesel can be chemically processed using the following different mechanisms which includes; direct use (blending), thermal cracking (pyrolysis), micro-emulsion and trans-esterification/esterification (Colin *et al.,* 2014) as shown in figure 2.1

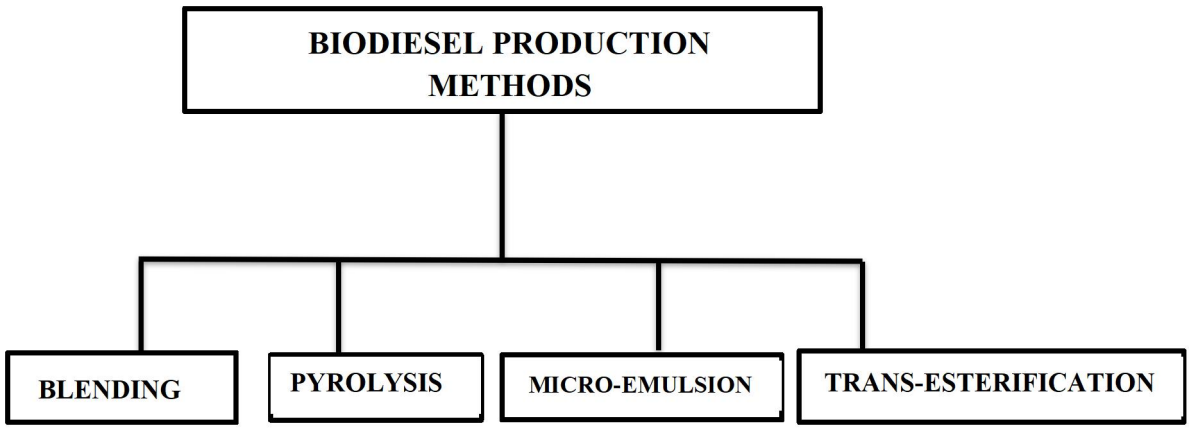


Figure 2.1 Methods of Biodiesel Production

2.3.1 Transesterification

Trans-esterification is the most convenient and commonly used method particularly in the industry for producing biodiesel from oil and fat feedstock types, due to the following; high

conversion rate, relatively low production costs, mild reaction conditions and the compatibility the obtained product which chemically resembles petroleum diesel have for existing petroleum diesel engines without modifications (Zhan *et al.,* 2019). This chemical process converts oils and fats (triglycerides) into their alkyl esters with reduced viscosity to meet the quality of petroleum diesel fuel. The trans-esterification reaction can be either catalysed or non-catalysed; Catalysed trans-esterification can be done either chemically by the use of base (alkali) and acid catalysts, or biologically through enzymatic catalysts specifically lipases. There are also less investigated though efficient ways to produce biodiesel with nano-engineered and ionic liquid catalysts. Meanwhile, Non-catalysed trans-esterification is carried out in the absence of a catalyst, by using an alcohol at supercritical conditions where the alcohol, usually methanol and sometimes ethanol, is at a temperature and pressure above its critical point, where distinct liquid and gaseous phases do not exist (Demirbas, 2007). In the supercritical state, the dielectric constant of alcohol is decreased so that a two-phase formation of vegetable oil and alcohol mixture is not encountered with only a single phase found favouring the reaction. Trans-esterification is a reversible reaction that proceeds essentially by mixing the reactants usually under heat, pressure, or both together. The simplest chemical reaction for trans-esterification of triglycerides is presented in figure 2.2.

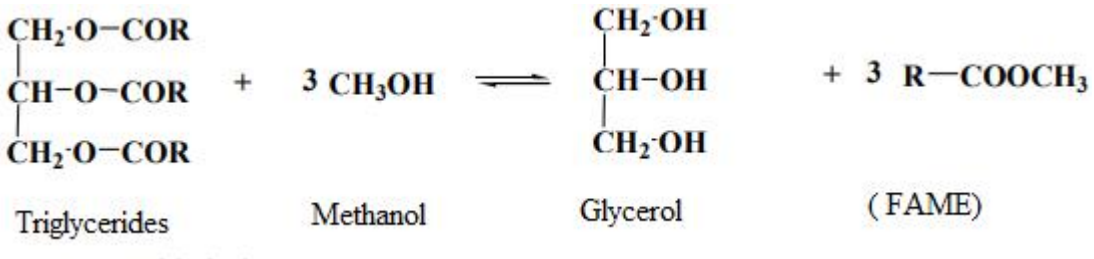


Figure 2.2 Trans-esterification of triglycerides

The trans-esterification process which involves a reaction between triglycerides in the vegetable oil and alcohol produces the biodiesel (mono alkyl ester) and glycerol as shown in the process flow diagram below (Raghuvanshi and Singh, 2014) in figure 2.3.

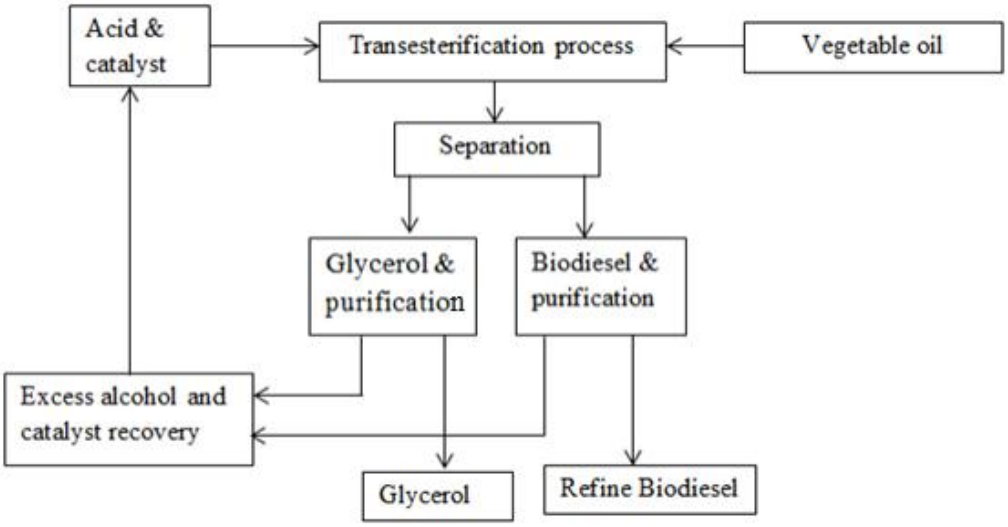


Figure 2.3 The Trans-esterification Process Flow Diagram (acid catalyst)

2.4 RAW MATERIALS FOR BIODIESEL PRODUCTION

Biodiesel production is majorly carried out with the following raw material which includes:

- Triglyceride sources such as vegetable oils (edible or nonedible), animal fats, halophytes, microalgae, wastes (waste or used cooking oil) amongst others. Most biodiesel production plants make use of vegetable oils as the feedstock oil.
- Short-chain alcohols commonly; methanol, ethanol, propanol and butanol.
- Catalysts although optional; biological materials such as enzymatic catalysts or chemical materials such as acidic or alkaline (basic) catalysts which can be either homogeneous or heterogeneous.
- Neutralizers(based on catalyst used); acidic neutralizers for basic catalyst and vice versa e.g. hydrochloric acid, phosphoric acid, sodium hydroxide, potassium hydroxide, etc.

2.4.1 Vegetable Oils

Vegetable oils are liquid fuels from renewable sources that do not over-burden the environment with emissions and they have the potential for making marginal land productive, by their property of nitrogen fixation in the soil. Lesser energy input is required for their production and they have higher energy content than other energy crops like those for alcohol. They produce 90% of the heat content of biodiesel and they have a favourable output/ input ratio of between 2:1and 4:1 for un-irrigated crop production. Vegetable oils are the most commonly used raw materials in biodiesel production due to the renewability of their sources, ready availability and the low free fatty acid content associated with their triglycerides as compared to those from other lipid-rich sources. They are mainly constituted by triglycerides, small amounts of diglycerides, monoglycerides, free fatty acids, water, sterols, phospholipids, odorants and other impurities. Triglycerides (TG), which make up about 95–98 wt. % of vegetable oil, are tri-esterified glycerols with three fatty acid molecules, i.e., a trimester (Hernandez *et al.,* 2009). Presently oils from soybean, safflower, corn, cotton seed, peanut together with 350 has been identified as potential feedstocks with fat content for producing biodiesel suitable for running diesel engines (Demirbas *et al.*2006; Goering *et al.* 1982; Balat *et al.* 2006).These feedstocks have turned out to be less effective and more time consuming (considering the lifecycle analysis) presenting a serious concern to the food versus fuel conflict. The use of food crops as energy crops has become controversial due to increasing global population which simultaneously increases the demand for energy to be consumed on utilities such as electricity and transportation, as well as the demand to satisfy nutritional needs. Thus, the use of edible vegetable oil is completely discouraged due to the problem of significant sustainability arising from the competition for arable land between food crops and biodiesel pre-reactants with the consequence of deforestation in a bid to increase arable land size for cultivation, as well as the possible increase in food crop prices due to competition for

arable land. To avoid these problems, it is suggested that other materials with lipid content which are non-edible or wastes from edible oils should be used as alternative triglyceride sources. Examples of such materials include; spent coffee, grounds, acorn, non-edible nuts and seeds, etc. In addition, waste vegetable oil, whether from edible sources or not, can also be considered as it has been proposed by many as the best source of oil to produce biodiesel although the available supply is less than the quantity required to replace the amount of petroleum-based diesel fuel burned for transportation and home heating; hence the need to sometimes consider other secondary sources like macro algae, microalgae, halophytes, etc.

Vegetable oils have to undergo the process of trans-esterification to become useable in internal combustion engines. Biodiesel which is the product of the trans-esterification process is biodegradable, non-toxic and essentially free from sulphur. It is a renewable fuel that can serve as an alternative fuel for mineral diesel such that it promotes the sustainable development, management, efficiency, energy conservation and environmental preservation goal. The objective of the trans-esterification process is to improve some properties of biofuel such as viscosity, flash point, cetane number, etc. The process of trans-esterification brings about drastic change in the viscosity of vegetable oil and the biodiesel produced is totally miscible with mineral diesel in any proportion as its viscosity comes very close to that of mineral diesel making adaptation possible with the existing fuel handling system. In this way, the flash point of the biodiesel gets lowered and the cetane number gets improved. Lower concentrations of biodiesel can even be used as a cetane number improver for a biodiesel blend. The calorific value of biodiesel is also found to be very close to mineral diesel. Some observations from engine tests using biodiesel indicates that the thermal efficiency of the engine generally improves with some cooling losses as some exhaust gas temperature increases, while smoke opacity generally gets lowered for biodiesel blends. The possible reason may be due to the lubricity of the biodiesel and hence the frictional losses. Different

physico-chemical properties of feed stock oils such as fatty acid composition, free fatty acid content, impurities, and moisture influences the production process of the biodiesel. The table 2.3, 2.4 and 2.5 shows the composition, fatty acid content and some physicochemical properties of feedstock oils used in biodiesel processes.

Table 2.3 **Fatty acid composition of various vegetable oil**

Fatty acid composition

Vegetable oil	Fatty acid composition % by weight									Acid value	Phos (ppm)	Peroxide value
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11	7	18.4
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07	8	64.8
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36	12	26.5
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20	9	82.7
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23	1.14	18	30.2
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20	32	44.5
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15	15	10.7

As shown in table 2.4, the main fatty acids in the structures of the main glycerides of vegetable oils are: palmitic acid $C_{16}H_{32}O_2$, oleic acid $C_{18}H_{34}O_2$, linoleic acid $C_{18}H_{32}O_2$.

Table 2.4 **Chemical composition of vegetable oils (main fatty acids)**

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

A list of the properties of vegetable oil feed stocks used in biodiesel production is provided in table 2.5

Table 2.5 **Properties of vegetable oils used in biodiesel preparation**

Vegetable oil	Kinematics viscosity (mm^2/s)	Cetane number	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (kg/l)	Lower heating value (MJ/kg)
Peanut	4.9	54	5	—	176	0.883	33.6
Soya bean	4.5	45	1	−7	178	0.885	33.5
Babassu	3.6	63	4	—	127	0.875	31.8
Palm	5.7	62	13	—	164	0.880	33.5
Sunflower	4.6	49	1	—	183	0.860	33.5
Tallow	—	—	12	9	96	—	—
Diesel	3.06	50	—	−16	76	0.855	43.8
20% biodiesel blend	3.2	51	—	−16	128	0.859	43.2

2.4.1.1 The Trans-esterification of Vegetable Oil

Trans-esterification is the process of separating the fatty acids from their glycerol backbone to form fatty acid esters (FAE) and free glycerol (Meher *et al,* 2006; Morrison and Boyd, 2005; Abdullah *et al,* 2007). Fatty acid alkyl esters commonly known as biodiesel can be produced in batches or continuously by trans-esterifying triglycerides such as animal fat or vegetable oils with lower molecular weight alcohols in the presence of a catalyst. Stoichiometrically, the trans-esterification reaction requires 3 moles of alcohol and 1 mole of triglycerides i.e. a triglyceride is allowed to react with a threefold excess of an alcohol such as ethanol or methanol, and this alcohol takes the place of the ester linkage to glycerol, yielding three fatty acid esters of the new alcohol and glycerol. This reaction is reversible and excess alcohol is needed to shift the equilibrium towards the products (Ma *et al.,* 1999). The forward reaction is pseudo-first order and the reverse reaction is second order (Meher *et al.,* 2006). Therefore with a second order kinetic behaviour, the elementary reactions in its mechanisms can be modelled by second-order rate equations such

$$r_{n,i} = k_{n,i} C_{x_1} C_{x_2}, \quad . \quad . \quad . \quad . \quad (2.1)$$

that:

where $r_{n,i}$ represents the rate of the *n*-th elementary reaction which occurs in the trans-esterification process, and C_{xi} represents the concentration of component x_i which is involved

in the trans-esterification reaction. Furthermore, the term $k_{n,i}$ denotes the rate constant for an elementary reaction, which is defined by the Arrhenius equation

$$k_{n,i} = \alpha_{n,i} \exp\left(\frac{-Ea_{n,i}}{RT}\right). \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2.2)$$

This reaction occurs stepwise with diglycerides and monoglycerides as intermediate products depicted in figure 2.4.

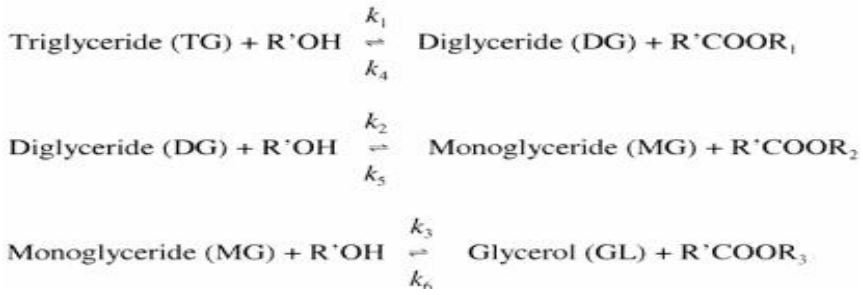


Figure 2.4 Step-wise trans-esterification of vegetable oil

The "R" groups are the fatty acids, which are usually between 12 to 22 carbons in length. The large vegetable oil molecule is reduced to about 1/3 its original size, lowering the viscosity to make it similar to diesel fuel. The resulting biofuel operates similar to diesel fuel when used in an engine. Parameters considered influential on the trans-esterification process were being the reaction time, the mass or molar ratio of alcohol to oil and concentration of the catalyst. Although the type of catalyst and alcohol, the agitation rate in the reactor and the reaction temperature though fixed for a trans-esterification process still has effect on the process.

2.4.2 Waste Cooking (Vegetable) Oil

Waste cooking oil refers to used vegetable oil obtained from edible oil sources such as palm oil, coconut oil, soybean oil and other food oils. Waste cooking oil is used edible oil obtained from the culinary, hospitality, restaurant and household industries. Preparation of food through repeated frying makes the edible vegetable oil unsuitable for consumption due to the presence of high free fatty acid (FFA) content. Most of the waste cooking oil (WCO)

generated from fried food involves using large amounts of oil because of the need for full immersion of food at temperatures between 150°C to 200°C during the deep frying process. As a result of these high temperatures, changes are generated in its chemical and physical composition, as well as in its organoleptic properties that affects both the food and oil quality. The oil which is burnt repeatedly together with the transport of matter and heat between the frying food and vegetable oil in association with the exposure to air, moisture and unhealthy environment leads to different chemical reactions which includes hydrolysis, oxidation and polymerization during the frying process; these reactions produce peroxides, reduces the unsaturation of fatty acids, increases foaming, viscosity, density and the concentration of free fatty acids as well as polar materials present (Choe & Min, 2007). In addition the water content of the oil increases and the colour of the frying or cooking oil is changed. Used cooking oil is normally black, with a strong odour and does not have large amount of solids because its collection is passed through a fine mesh. The re-use of domestic oil which contains carcinogenic compounds produced during the frying process poses a high risk to the health of consumers and based on the type of food subjected to frying, it absorbs between 5% and 20% of the used oil, as such it can significantly increase the amount of hazardous compounds infused into food, (EREN. 2003). The methods used for biodiesel production from used cooking oil are similar to most conventional trans-esterification processes but because used cooking oil contains various other compounds or contaminants and generally has high free fatty acid content, the use of waste cooking oil as a feedstock oil in biodiesel production needs pre-treatment before processing into the fuel.

2.4.2.1 Pre-treatment of Waste Cooking Oil

- Waste cooking oils as feed stock oils contain wastes which are products of decomposition that impair the oil quality causing reduction in productivity in the trans-esterification reaction which may also generate undesirable by-products to hurt the final biodiesel product. For the treatment of waste cooking oil to make it adequate for use, refining operations that can be applied are filtration, de-acidification or neutralization and whitening. Refinement has a right effect on the biodiesel yield of the reaction increasing it from about 67% to 87% after bleaching as it reduces the amount of free fatty acids (i.e. acid number) as well as the saponification reactions (EREN, 2003). The acid number or acid value of edible oils or their corresponding esters indicates the quantity of free fatty acids (FFA) and mineral acids (negligible) present in the feedstock sample. According to ASTM D 664 and EN 14104, the acid number is expressed in milligrams (mg) potassium hydroxide (KOH) required to neutralize 1 g of sample. For these reasons, it is important to refine the waste cooking oil for the biodiesel production. The processes of degumming and deodorization are not necessary because these oils have already been treated prior to use and although during use degradation odour occur, the removal is not essential to biodiesel production.
- ***Filtration:*** This operation is for removing solids, inorganic materials, and other contaminants in the oil. It can be carried out using a wire mesh filter at temperatures higher than 60°C or at low temperatures depending on the physical condition of the oil with carbonaceous substances produced from burnt organic material, pieces of paper, waste food and other solid particles removed.
- ***De-acidification:*** It is the process by which the high free fatty acids are reduced or removed, various methods can be used as:

a. Neutralization with alkaline solution, a process where the acids are removed in the form of soaps.
b. Esterification with glycerine, a process that seeks to regenerate the triglyceride.
c. Extraction by solvents, a process which uses ethanol in proportion 1.3 times the amount of oil.
d. The distillation of fatty acids, a method that requires a high energy cost.
e. Removal of fatty acids with ion-exchange, a resin of strongly basic character for the removal of fatty acids and the colour of the oil is used.

A method that provides greater account of productivity in the removal of free fatty acids is the neutralization by either of caustic soda or potash as they do not only remove or reduce free fatty acids, but also helps in the bleaching of the oil. There are basically two procedures;

- Neutralization with dilute alkali with concentrations used between 0.75 to 2N
- Neutralization with concentrated alkali where the concentration of caustic soda or potash vary between 2 and 5 N.

In each of these procedures mentioned above, neutralization is carried out hot, with oil at a temperature between 50-60℃ and the addition of caustic soda or potash (lye) between 70-80℃.

2.4.2.2 Trans-esterification of Used/Waste Cooking Oil

The production of methyl esters is processed in two stages, initially esterification followed by trans-esterification. In general used oil possesses high viscosity i.e. the presence of high free fatty acids. In order to break down the high free fatty acids, a two stage acid and base treatment process is widely used. The first step is to esterify the free fatty acids (FFA) with methanol by acid catalyst like sulphuric acid (H_2SO_4) reducing the amount of free fatty acids. The second step is trans-esterification of the pre-treatment product by using basic catalyst

like potassium hydroxide and sodium hydroxide (NaOH) among others. Although the esterification reaction in the pre-treatment step reduces the amount of free fatty acids (FFA's) in the used oil into corresponding fatty acid methyl ester also known as biodiesel yet the unconverted FFA's and triglycerides still remains in the pre-treated oil. As such, a trans-esterification reaction process also known as the alcoholysis process as discussed previously is performed to complete the reaction.

2.4.3 Alcohol

The selection of alcohol for use is usually based on cost and performance considerations (Encinar *et al,* 2007). Short chain alcohol such as methanol, ethanol, and butanol are majorly used in biodiesel production. Methanol and ethanol are not miscible with triglycerides at room temperature and the reaction mixture is usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions are usually formed. In the case of methanolysis, these emulsions breakdown quickly and easily to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are too stable which severely complicates the separation and purification of esters (Zhou and Boocock, 2006; Encinar *et al*, 2007).

Most of the literature reviewed shows that the use of methanol dominates (Alcantara *et al.,* 2000; Encinar *et al.,* 2005; Felizardo *et al.,* 2006; Refaat *et al.,* 2008; Yuan *et al.,* 2008) and methyl esters are the predominant commercial products, which is because methanol is considerably cheaper and more available than ethanol (Pinto *et al*., 2005) as well as the downstream recovery of unreacted methanol is much easier to process (Zhou and Boocock, 2006). In addition, considering the reaction performance, it is more feasible to reach higher conversions with methanol than with ethanol as the process becomes more complex, expensive and requires a higher consumption of energy and time when ethanol is used

(EREN, 2003). Giron *et al.* (2009) found out that it requires less reaction time when using methanol rather than ethanol, either in acid or alkaline catalysis reaching high yields.

On the other hand, the advantage of using ethanol is its renewability as it can be produced from agricultural renewable resources, attaining total independence from petroleum-based alcohols (Saifuddin and Chua, 2004; Encinar *et al.,* 2007). Also, the extra carbon atom brought by the molecule slightly increases the heat content as well as the cetane number and as an extraction solvent, it is preferable to methanol because of its much higher dissolving power for oils. In addition, another important advantage is that the ethyl esters have cloud and pour points lower than the methyl esters (Encinar *et al.,* 2007).

However, the disadvantages to its use starts with complicating the recovery of pure alcohol in the process as it form an azeotrope with water (Cheng *et al.,* 2008). In addition, the performance of ethyl esters is less compared to the methyl esters due to the lower molecular weight of methanol (32.04g/mole) when compared to that of ethanol (46.07 g/mole) as using methanol with low viscosity (0.59 mPas at 20℃) produces biodiesel of low viscosity whereas ethanol with a higher viscosity (1.074 mPas at 20℃) produces biodiesel with increased viscosity and as a result such fuel of high viscosity will not be properly pulverized by the injection systems that have diesel engines. Moreover, the opacity of fumes is increased limiting their application in automotive engines (Benjumea *et al.,* 2007). Furthermore, the base-catalysed formation of ethyl ester is difficult when compared to the formation of methyl esters; a reaction which is attributed to the more difficult formation of the ethoxide anion (OmTapanes et al., 2008).

2.4.4 Catalysts

Catalysts are used to accelerate a chemical reaction by reducing the activation energy which is energy needed to initiate the reaction. These catalysts are employed to activate the trans-esterification process as they are also effective in bringing the process to completion after which purification is done to obtain the end product. The activity of catalysts specifically in application to solid acid/base catalyst in the trans-esterification reaction depends on their structure, strength of basicity/ acidity, surface area and stability.

2.4.4.1 Selection Of Catalysts

The selection of a catalyst is based majorly on the following factors;

- ✓ The suitability and activity of the catalyst.
- ✓ The nature and type of feedstock oil used.
- ✓ The availability and accessibility to the source of the catalyst materials.
- ✓ The cost of the raw catalyst, its constituents and the renewability.

2.4.4.2 Types of Catalyst

There are basically two types of catalysts which are used for the process of trans-esterification;

- ➢ Chemical catalysts
- ➢ Biological catalysts

2.4.4.3 Chemical Catalysts

The chemical catalysts are majorly of two types; homogeneous and heterogeneous catalysts which are further classified into two classes: acidic and alkaline each for both types.

Homogeneous Catalysts

Homogeneous catalysts are usually in a single phase either as liquid or gaseous. The advantages of homogeneous catalysts includes; high selectivity, good turn over frequency, high speed of reaction and the moderate temperature as well as pressure conditions required for the optimization of their catalytic activity (Ma *et al,* 1999; Vivek *et al,* 2011; EREN, 2003). These catalysts can be either acids or alkalis; acid catalysts offers a high yield but requires an extended reaction duration as its reaction rate is too slow, a higher oil/alcohol molar ratio and temperatures exceeding 100℃ for its action such that getting conversions of 99% with a concentration of 1% sulphuric acid in relation to the amount of oil takes about 50 hours (Marchetti *et al,* 2007; Zheng *et al,* 2006; EREN, 2003). Sulphuric acid, (H_2SO_4), phosphoric acid (H_3PO_4), hydrochloric acid, among others can be used. For example sulphuric acid catalysed the trans-esterification reaction of Zanthoxylum bungeanum seed oil with methanol in the ratio 8:1 and recovered biodiesel greater than 94 percent in about 12 hours; Tin tetrachloride catalysed the esterification of same with an output recovered greater than 96 percent within optimum reaction conditions (Zhang *et al.,* 2012; 2015). These catalysts are usually used with excess alcohol needed, such that the recovery of glycerine becomes more difficult as the quantities of alcohol required is quite larger compared to other type of catalyst (Arbelaez and Rivera, 2007). In addition, these acid catalysts are more corrosive to production equipment than alkali catalysts (Errazu *et al,* 2005).

Basic (Alkali) catalysts on the other hand, accelerates the reaction rate with the disadvantage that they produce soaps in the presence of the high amounts of free fatty acids and water to which we must add an appropriate amount of base to neutralize these free fatty acids. The most commonly used basic catalysts includes; potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium methoxide ($KOCH_3$) and sodium methoxide (CH_3ONa) which seems inappropriate for industrial application, as this is more expensive and requires

the total absence of water (EREN, 2003). Methoxide has been described as the preferred catalyst for trans-methylation rather than hydroxides as they prevent soap formation in the trans- esterification process of biodiesel production and can be obtained via several different methods (Jackson, 2006). Sodium hydroxide (NaOH) is preferred over KOH (potassium hydroxide) because it dissolves quickly in methanol. In recent years, the use of sodium methoxide is fast-growing as it has become the catalyst of choice for modern large-scale biodiesel production accounting for more than 70 percent of the biodiesel produced in North America. The traditional method entails preparation of the catalyst solution within the biodiesel plant by mixing either sodium hydroxide or potassium hydroxide with methanol as shown below.

$$NaOH + H_3C\text{-}OH \longleftrightarrow H_3CO^- + Na^+ + H_2O. \quad . \quad . \quad . \quad (2.3)$$

$$KOH + H_3C\text{-}OH \longleftrightarrow H_3CO^- + K^+ + H_2O. \quad . \quad . \quad . \quad (2.4)$$

In another method, sodium methoxide is placed in a methanol solution as shown below.

$$H_3C\text{-}O\text{-}Na \longleftrightarrow H_3C\text{-}O^- + Na^+ . . \quad . \quad . \quad . \quad (2.5)$$

In this way, the sodium methoxide produced is known by many names, names such as alcoholate, methoxide and methylate. The catalyst produced this way is made in a water-free process and when used during the trans-esterification does not contribute to soap formation process as it reduces the amount of methanol needed for the reaction, the loss in the yield of the biodiesel produced and the waste in feedstock oil used which would have gone into soap formation. Major technology providers of biodiesel process technologies and plant designs that utilize sodium methylate as catalyst includes; Lurgi PSI, Desmet Ballestra and Crown Iron Works.

An alkali catalysed process reaches high purity and yields in short periods of time ranging from between 30-60 minutes (Liu *et al,* 2006). Although different kinds of base and acid catalysts are available for trans-esterification processes, virtually almost all commercial biodiesel producers use basic catalysts. When KOH is used as a catalyst, by-products for potassium fertilizers such as potassium chloride, potassium sulphate and potassium nitrate can be produced if the product is neutralized with phosphoric acid (Arbelaez and Rivera, 2007).

Heterogeneous Catalysts

For heterogeneous catalysts, they are found in two phases with a contact area. The use of these catalysts makes for a simpler and more economic purification process which is due to the easy separation of products and reactants. The easy separation of products makes for a simplification of the manufacturing process since these catalysts can be separated from their products of reaction with a simple filtration process and then reused (Lles *et al,* 2008). In addition, they are not corrosive to the reactor (Guan *et al,* 2009). Among the most common heterogeneous catalysts are the metal oxides such as: magnesium oxide (MgO), calcium oxide(CaO), zinc oxide (ZnO), aluminium oxide (Al_2O_3); Ion exchange resins: anion-exchange resins and cationic resins; Boron-based catalyst like silica supported boron trifluoride (BF_3); Carbon-based catalysts like D-glucose, sucrose, starch, vegetable-oil asphalt, delignified waste paper, cellulose; sulphated oxides; bio-wastes like calcined eggshell waste, oil palm ash and calcined plantain peel ash (K_2O major component); Nano-catalysts; Lewis acids (Phosphoric, sulphuric, hydrochloric-acids) / Bronsted catalysts (BF_3, $TiCl_4$ (Arbelaez and Rivera, 2007). To achieve high yields with these catalysts, reaction must be carried out at a higher temperature which increases the energy costs (Bournay *et al,* 2005). High reaction time, due to the slow speed of trans-esterification reaction with these catalysts as compared to homogeneous catalysts, a consequence of the mass transfer resistance (Guan *et al*, 2009).

Heterogeneous catalysts are currently not very popular due to the high cost or the inability to complete the degree of reaction as required by ASTM specification standard (Gerpen *et al,* 2004).

2.4.4.4 Biological Catalysts

Biological catalysts are large complex molecules called enzymes, which contain specific pockets for reactants to fit into. Once they are trapped inside, the enzyme aids the reaction either by forming temporary bonds with the reactants to help them fit together or by simply holding them close enough to each other to actually react and form the products.

Enzymes

The use of enzymes for catalysis is due to their high selectivity and incredible specificity. For enzyme catalysis, lipases come foremost as they constitute a diverse and ubiquitous family of enzymes produced by animals, plants and microorganisms. It is the breed from microorganisms (bacterial and fungal) that are mostly used as biocatalysts in biotechnological applications and organic chemistry. They have been successfully used in novel applications for the synthesis of bio-products including biodiesel (Jaeger and Eggert, 2002). Lipases are effective for trans-esterification reaction with the advantage that they allow the use of alcohol with a high content of water (at more than 3%), even at low temperature. Considered hydrolases, they naturally hydrolyse triacylglycerols (Salis *et al.,* 2005) and are capable of converting triglycerides, diglycerides, monoglycerides and free fatty acids into Fatty Acid Alkyl Esters in addition to fat hydrolysis (Akoh *et al.,* 2007). It is their stability that enables them to catalyze the unnatural reaction of trans-esterification (Jegannathan *et al.,* 2008).

2.4.5 Catalyst Synthesis and Composition

The preparation of a catalyst or a catalyst's system as a complex is not limited only to the constituting materials, or their compositions and structures but also entails the consideration of activities within them like the occurrence of mass transfer, heat transfer, chemical reaction and so on. Catalytic activity is a function of its specific surface area, base strength and base site concentration. Heterogeneous catalysts are widely used and influential in both industrial and environmental applications. A heterogeneous catalyst is one composed of several constituents which includes; the catalytic active ingredient (species), promoter and support (carrier) (Knozinger and Weitkamp, 1997).

The Catalytic Agent (Active Species)

These chemical species are the catalytically active component in the catalyst which generate the active sites that participate in the chemical reaction such that the activity of any catalyst is proportional to the concentration of these active sites although not always directly. The availability of active sites mainly depends on the dispersion of the catalytic agent. Dispersion is defined as the ratio of the total number of exposed atoms (molecules) of catalytic agent available for reaction to the total number of atoms/molecules of catalytic agent present in the catalyst sample (Carberry, 2001). These agents or active species are constituted of one or more compounds which either contribute each one with its own different functional property or interact between themselves creating synergistic effects at their interfaces. Catalytic agents may be broadly divided in the following categories: Metallic conductors (e.g Fe, Pt, Ag, etc.), Semiconductors (e.g. NiO, ZnO,etc.) and Insulators (e.g. CaO, Al_2O_3, SiO_2,MgO etc.).

Promoters

These are substances added during preparation of catalysts to improve the physical and chemical properties of catalyst like the activity, selectivity or stability of the catalytic agents. Promoters can be physical or chemical; Physical promoters enhance or maintain the physical integrity of the support alone or together with the deposited catalytic agents as such they improve the thermal stability and mechanical resistance of catalysts e.g. Alumina (Al_2O_3), Silica (SiO_2), Titania (TiO_2) and Magnesia (MgO). Chemical promoters modify the activity, selectivity and lifetime of the catalyst such as Lithium oxide (Li_2O) and Potassium oxides (K_2O). The promoter is present in a small amount and by itself has little or no activity and can be added during catalyst preparation or during reaction.

Support

The support or carrier forms the largest amount of the catalytic component and provides a large surface area for the dispersion of a small amount of the catalytically active agent. Supports give the catalysts its physical form, texture, mechanical resistance and certain activity particularly for bifunctional catalysts. Common supports are alumina, silica, silica-alumina, active carbon, zirconia, magnesia, silica, titania, zeolite, molecular sieves etc. The area of a support can range from 1 - 1000 m^2 /gm and the activity of the support varies according to the nature of the catalytic reaction in which the catalyst is present.

The Calcination Process

This process involves the heating of the solid catalyst material to a high temperature for the purpose of removing volatile substances, oxidizing a portion of mass, or rendering them friable. Calcination, therefore, is sometimes considered a process of purification. The importance of

calcination in catalysis is to decompose the impregnated metal salts of nitrates, chlorides, carbonates and organic chelates, leaving a metal or metallic oxide on the support surface.

The Activation Process

In the activation process, the deposited metal precursor is converted into the active phase usually by a calcination step, resulting in the metal oxides, followed by a reduction if metallic particles are required, common active phases include metal oxides or metal sulphides.

2.4.6 Preparation of Heterogeneous Catalysts

The preparation of catalysts begins with the selection of required ingredients which includes; the supports, precursors of active components, promoters and solvent. Catalyst preparation methods (processes) can be broadly categorized as follows:

Bulk preparation process: Bulk catalysts and supports are prepared by this method. Bulk preparation is mainly done by the following methods; Precipitation process, Co-precipitation and Sol-Gel process done using binders, lubricants or forming agents.

Impregnation process: This process involves preparing catalysts by first preparing their supports through bulk preparation methods and then dispersing the catalytically active material onto the support. The active materials can be dispersed on the supports by various methods which includes deposition (active material from gas phase onto solid support involving gas-solid interface), doping, wet impregnation (mixing of aqueous solutions of active material with solid support forming a liquid-solid interface) and dry impregnation.

Physical Mixing process: This process involves physically mixing the active substances with a powdered support, precursors of support in a ball mill or a co-catalyst and this sometimes involves mechano-chemistry which gives neat grinding. The final mixture is then agglomerated and activated (Farruto and Bartholomew, 1997; Richardson, 1989).

2.4.7 Characterization of Heterogeneous Catalyst

Characterization of heterogeneous catalyst refers to the determination of its physical and chemical characteristics, which are responsible for its performance in a reaction. The characteristics of catalysts include: chemical composition of the bulk and surface of the solids, surface area and porosity (micro, meso and macro), bulk solid structure, phase composition, crystallite size; surface morphology; surface chemical properties such as: location and oxidation state of active metals, acid-base property, reducible – oxidizable property; aggregate properties such as aggregate or particle size, density, mechanical strength and attrition resistance; Catalytic properties like the activity, selectivity, and stability.etc. The primary objective of catalyst characterization is to understand the relationship among physical, chemical and catalytic properties. For this purpose, the physical and chemical properties are determined by various characterization techniques and related to its activity and selectivity. This is essential for design and process optimization. The characterization is also done to monitor the changes in physical and chemical properties of the catalyst during preparation, activation and reaction stages for better understanding and quality control. Determination of the extent of deactivation of catalysts during the reaction process is also important. Characterization of used catalysts can help to determine the causes of deactivation and minimize it. It also helps to design procedures for catalysts regeneration.

2.4.7.1 Characterization Techniques

Structural analysis

a. Surface area using the widely accepted BET (Brunauer Emmet and Teller) method for analysing multilayer physisorption isotherms of inert gases to determine surface area.
b. Pore analysis by BJH method and mercury intrusion method.

c. X-Ray Diffraction (XRD) used to detect crystalline materials having crystal domains greater than 3-5 nm and for characterization of bulk crystal structure and chemical phase composition.

Thermal analysis

a. Temperature programmed reduction (TPR) which measures the rate of reduction of active metals as a function of temperature and can be correlated with activity of catalysts (b)Temperature programmed desorption (TPD) takes measurement of the rate of desorption of adsorbed molecules as a function of temperature and is mainly used to study acid –base property of catalysts.
b. Thermo Gravimetric Analysis (TGA) for the measurement of weight loss (or gain) as a function of temperature in a controlled gaseous atmosphere and with its use a process associated with mass change can be detected and analysed.
c. Differential Thermal Analysis (DTA) monitoring the temperature difference between sample and reference such that a process associated with latent heat of transition can be detected and analysed.

Chemisorption technique

It is used to determine the dispersion of metal in catalysts and the surface metal area.

Spectroscopic techniques

(a) Infra-red spectroscopy for identifying compounds and investigating sample composition, the studying of structure and bonds (e.g. FTIR)
(b) Raman spectroscopy for studying oxidation state and interaction of metal oxides
(c) Gas Chromatograph Mass Spectrometry (GC-MS)

Microscopic technique

(a) Transmission electron microscopy (TEM) to determine the micro –texture and micro structure with resolution better than 0.2 nm.

(b) Scanning electron microscopy (SEM) to image the topography of solid surface with resolution better than 5 nm (Sowell et al., 2006; Zhang et al., 2009).

2.4.8 Reaction Mechanisms and Catalyst Kinetic Model

Reaction mechanisms and kinetic models are important to designing a suitable and effective catalyst under the given biodiesel reaction conditions. Solid acid catalysed mechanism of esterification and trans-esterification of FFA with methanol is normally represented by two models, a single site *Eley-Rideal (ER)* and by dual-site mechanisms *Langmuir Hinshelwood (LH)* (Abebe *et al.,* 2011).

The Eley-Rideal (ER) model depicts the reaction mechanism in which one reactant species (say A) is adsorbed while the second reactant species (say B) is not adsorbed on the catalyst surface. ER is preferred when a low carbon alcohol such as methanol is used. In the single site mechanism model, the alcohol is adsorbed on the catalyst site in ER mechanism. Alkoxides ion on the surface attacks the positively polarized carbon of triglyceride which is present in the liquid phase. The mechanism includes three main steps: Physisorption and chemisorption of triglyceride (TG) in to the catalyst site, surface reaction where an intermediate tetrahedral is formed as the alcohol attacks the electrophilic carbon and the final step which involves the cleavage of the fatty acid ester and diglyceride from the catalyst and the desorption from the site.

On the other hand, LH model for a heterogeneous catalyst can be used in the trans-esterification of vegetable oil with methanol using a metal catalyst (Dossin et al., 2006). The

adsorption step comes first which takes place on the active sites of the catalyst surface. The next step is the surface reaction step where the two reactants (triglyceride and alcohol) are absorbed on the catalyst active site with the reaction taking place among the adsorbed species. The final step is the desorption step, where a fatty acid alkyl ester and diglyceride are produced. This dual-site model is preferred when trans-esterification reaction takes place in the presence of a higher carbon alcohol. It is a simple kinetic model that assumes isothermal condition about and within the catalyst with temperature gradient equal zeros (Smith, 1981).

The heterogeneous catalyst in a transesterification reaction is as shown in the Figure below;.

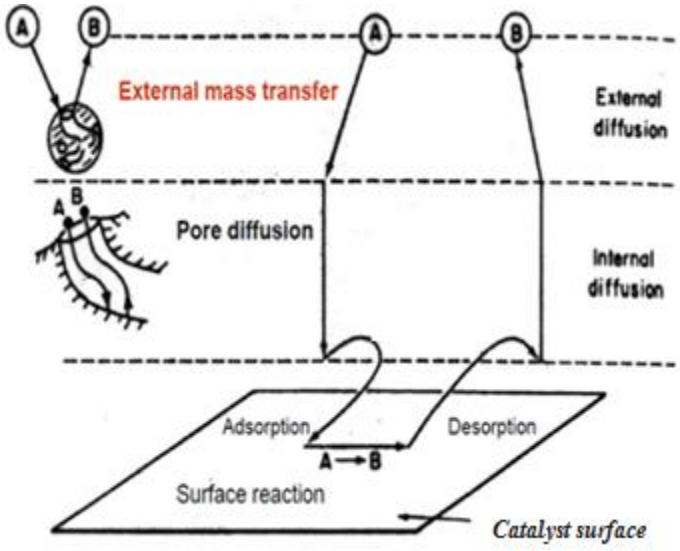


Figure 2.5 Transesterification reaction with a heterogeneous catalyst (Fogler,2006)

The reaction entails the external diffusion (mass transfer) of the reactants as the alcohol and triglycerides diffuse from their *bulk fluid* mixture into the catalyst through a boundary layer (which poses with a bulk mass transfer resistance) around the catalyst particles. As the velocity of the moving fluid varies, the concentration changes from C_{A0} (bulk concentration) to C_{AS} (concentration on the catalyst surface). The diffusion when reactant in the moving fluid transfers through the catalyst surface into the catalyst pores (pore diffusion) is represented by an internal mass transfer resistance at the interface (Fogler, 2006). The

adsorption process then occurs with reactants adsorbed to the surface of the catalyst where the trans-esterification reaction takes place at the interface of contact.

2.5 BIOMASS DERIVED CATALYSTS FROM AGROWASTES

The issue of energy and environmental conservation can be tackled using low cost derived heterogeneous catalysts generated from bio or agrowastes. The utilization of these materials as catalysts provides a greener synthesis route for biodiesel production. These catalysts offers several advantages, including renewability, non-toxicity, high catalytic activity, stability in both acidic and basic conditions with high water tolerance properties depending on the amount and strengths of active acid or basic sites. Examples of such wastes include; egg shells, fish scales, dolomites, animal bones or other agro-waste derived catalysts from plants like banana peels, cassava peels, plantain peels, palm kernel shells, coconut husks, cocoa pods, etc. These catalysts are easily accessible due to availability, the ease in handling and preparation, biodegradability, non-toxicity, cost-effectiveness and their environmental friendliness. Various studies have shown that the heterogeneous catalysts of calcium and potassium oxides offer faster reaction rates and the biomass catalytic preparation of calcium and potassium oxide catalysts derived from waste resources is a function of their feasibility in terms of local availability of their biomass sources, the suitability for their industrial application and sustainability in the commercial sector. Common sources of calcium oxide and potassium oxide respectively are natural waste-based shells (eggshells) and plant-based ash (plantain or banana peels) amongst many others which are littered over the country side. These materials are usually incinerated to high temperatures to convert into useable forms for catalyst preparation.

2.5.1 Chicken Egg-Shell as Catalyst

One way to produce calcium oxide (CaO) is from the available renewable resources like bones, shells, ashes, limestone (marble) etc. Particularly, the use of egg shell wastes which is of keen interest is a natural material well-known to contain a good amount of calcium oxide (Tangboriboon *et al.,* 2012). Egg shell wastes from the food industries are abundant in the environment although fish bones, coral reefs, and limestone ores are commonly other sources of calcium oxide (Lesbani *et al,* 2016). Each year a large amount of untreated eggshell wastes is dumped on open landfills despite the fact that eggshell consists of a large amount of calcium carbonate that can be useful in the manufacture of many valuable products. This dumping of eggshells creates disposal problems since eggshells have a slower decomposing rate as well as releases harmful odour upon biodegradation. The sourcing for calcium oxide for the formation of catalyst applies to eggshells of different species (IMA-NA, 2016).

Chicken eggshells due to its greater abundance compared to any other species of eggshells can be readily used as a heterogeneous catalyst. Studies undertaken by (Nakano et al, 2003) shows that the composition of the chicken eggshell involves approximately 94% of calcium carbonate, 1% each of magnesium carbonate and calcium phosphate and 4% of organic matter. Hincke *et. al.,* (2012) and Chang *et. al.,* (2007) investigated the composition of different types of eggshell and found that at an average the organic matter of the eggshell involves the highest percentage of sialic and uronic acid. Both the inner and outer wall of the eggshell showed less presence of nitrogen. When the eggshell was subjected to amino acid analysis, it showed the presence of hydroxy-proline and proline in lower quantity as well as alanine and glycine in higher quantity. It was also pointed out that in several studies; the incineration temperature affects the extent of conversion of the calcium carbonate in the egg shell into calcium oxide (CaO) obtained from the eggshell source through the process of calcination and compared to most of those from other sources, it is less expensive. For the

process of calcination, Mićić *et al,.* (2015) performed calcination of CaO at different temperatures to activate basic sites on its surface and showed that the activity of CaO catalyst for biodiesel synthesis is a complex function of the nature of its active sites and textural properties, both induced by the activation temperature. Thermal treatment at 800 °C, resulted in the best CaO crystallinity and preferable pore structure beneficial to its catalytic activity. Li et al. (2014) studied the effects of incineration temperatures on calcium oxide catalyst (between 200 and 1000 C) using soybean-oil transesterification processes. It was concluded that the catalyst performance is optimized by incinerating the eggshell at 800 C. This is in order to maximize the number of basic sites on the surface of calcium oxide (CaO) catalyst, giving a catalyst with the best catalytic activity. Ali *et. al.,* (2016) pointed out that with a thermogravimetric analysis (TG)/ Differential thermal analysis (DTA),complete conversion of calcium carbonate to calcium oxide can be attained by incinerating egg shell at a temperature between 800 and 1000 C. If incineration occurs at an ambient temperature of less than 700 C, the conversion of calcium carbonate into calcium oxide will be incomplete (Ali *et al,* 2016; Geuens *et. al.,* 2008; Mahesh *et al,* 2015). Thus, calcium oxide (CaO) produced from eggshells as an eco-friendly material interestingly serves as an alkali catalyst in the trans-esterification process of biodiesel synthesis and it has shown suitability in catalytic characteristics; in terms of purification of the product, reusability, ease of use and its vast availability within natural resources. In addition calcium oxides (CaO) are structure building as they influence the structure, specific surface area and thermal resistance of catalyst systems under reaction conditions as such serve as support materials to a catalyst system. However, the issue of cost-efficiency arises as well as on practical application directly as a catalyst in the trans-esterification process, ions in the calcium oxide (CaO), surface could form a hydrogen bond with methanol and glycerin, resulting in an increase in the glycerin viscosity and formation of the suspension of calcium oxide (CaO) which leads to a difficulty

in the separation of products (Liu et al., 2010),and slower reaction rates. To overcome this problem, impregnation, doping or physical mixing through agglomeration or mechano-chemistry are some of the profound techniques used to synthesize as well as upgrade the catalytic properties of the calcium oxide (CaO) supported catalysts. These can be done with any catalyst supports or other metal oxides (Liu *et al.,* 2010; Kesica *et al.,* 2012). Active components can be loaded on a porous support to obtain the desired physical properties together with a high catalytic activity of any solid catalyst. Published articles which concern the modification of calcium oxide (CaO) catalyst, includes; Kumar *et al.* (2012) who prepared potassium ion impregnated calcium oxide support in nano-particle form as a solid base catalyst for the production of biodiesel where the synthesis is done using the wet impregnation method. Li/CaO catalyst was prepared using the same technique, followed by calcinations at 575 and 800 ^{o}C and used for the trans-esterification of soybean oil. Al_2O_3-supported calcium oxide prepared conventional incipient wetness impregnation of aqueous solution of the $Ca(NO_3)_2 \cdot 4H_2O$ precursor on an aluminium oxide support and it was calcined at 450^{o}C for 2 h before being used in order to promote the basicity of calcium oxide. Kawashima *et al.* (2008) prepared different kinds of mixed metal oxide catalysts using a simple physical mixing method, followed by calcination at high temperatures.

2.5.2 Plantain Peels as Catalyst

Irvine (1965) stated that agricultural waste materials contain a good percentage of potash. These materials include palm bunch wastes, cocoa pods, plantain leaves, plantain peels, banana leaves, banana peels, maize cob, wood, sugar beet waste and many others. When these materials are burnt in air, the ashes contain oxides of potassium and sodium which when dissolved in water yield, the corresponding hydroxides (Onyegbado *et al,* 2002) according to the equations;

$$Na_2O + H_2O \longleftrightarrow 2NaOH. \quad . \quad . \quad . \quad . \quad . \quad .(2.6)$$

$$K_2O + H_2O \longleftrightarrow 2KOH. \quad . \quad . \quad . \quad . \quad . \quad .(2.7)$$

Plantain (Musa *paradisiacal*) is a common staple food in West Africa, which is consumed, either as boiled, fried, roasted, or baked. Although people do eat unripe plantain in some countries, it is noteworthy that people generally prefer ripe ones. About half of the world's plantain production comes from Western and Central Africa, where Nigeria is one of the leading producers (FAO, 2006). In 2014, the world production was 30.7 million metric tons of which Nigeria produced 3.04 million metric tons (FACSTAT, 2014) and despite this large production, she does not export plantain because its production is largely consumed locally. The rise in cottage industries that made use of plantain for snacks (plantain chips) in the farming urban population coupled with the demand for easy and convenient foods made from plantain locally, also makes for an increased consumption (Akinyemi *et al.,* 2010). The high consumption of plantain in Nigeria and by extension West Africa produces solid wastes in the form of peels which are typically discarded with only a small fraction of them fed to goats locally, an indication of the large kitchen wastes that would be generated the world over in plantain wastes. It could be argued that catalyst development from plantain itself would have negative impact on food security as it is one of our staple food or snack and as such, the use of its peel is preferable for catalyst development. Besides, most consumers of plantain prefer it when ripe than unripe such that harvesting the green (unripe) peel could become a threat to food security. Hence, the use of ripe plantain peels for catalyst development is preferred as it is economical, considering eco-friendliness and the conservation of food resources.

Potassium is the most abundant mineral in plantain peels with an estimated value of 37g kg-1 in the green peel. This value is increased by a small amount during the ripening process (Emaga *et al.,* 2007; IITA, 2009; Addison, 2011). Combustion is the main process for using

biomass energy directly with the resultant production of ash by-products (Blauvelt, 2007 and Gerpen, 2010). The combustion of biomass produces ash from where potassium oxide may be extracted. The plantain peel or biomass is burned in a very hot-fire to make very white ash (Etiegni and Campbell, 1991; Khemani, 2008). In this way, all of the potassium salts is converted to potassium oxide which is a lot cheaper than the commercial KOH. It has been observed that the ash-derived potash gives a promising future as a sustainable source of raw material for potash-based industries. Potash alkali and metal contents of ashes obtained from plantain peels have been investigated by a number of researchers and showed that the alkali content of the ash ranges from 61 to 81.9% and the analysed potassium concentration in the peels gave as high as 750 mg/kg (Izonfuo and Omuaru, 1988). Potassium oxide can be used as catalyst promoters in order to improve stability, surface area and reactivity. It helps in chemisorption and in the equalization of activities of various lattice planes while increasing activity at the same time as well as eases the decomposition of the catalyst surface creating more active sites as well as resists sulphur poisoning.

2.6 BIODIESEL SYNTHESIS AND PRODUCTION

Biodiesel synthesis involves a combination of processes leading to the production of biodiesel with the most relevant variables being; reaction temperature, molar ratio of alcohol to oil, amount of catalyst, mixing intensity (rpm), raw oils used and catalyst type. It involves the pre-treatment of raw materials, the transformation by trans esterification into biodiesel and by-products as well as the post-treatment of these products. A biodiesel production plant on an industrial or commercial scale comprises several sections that carry out the pre-treatment of raw materials, the trans-esterification reaction, and the post-treatment of products. Taking case-study with a biodiesel production line in a plant equipped with the American Society of Agricultural Engineering technology which comprises the following:

- Two pre-treatment sections processing the crude vegetable oil (a degumming section and a refining section);
- A central section carrying out the trans-esterification process;
- Three post-treatment sections (an ester washing section, a glycerol separation section, and a methanol recovery section).

In the pre-treatment section, the degumming and refining (esterification) section where crude vegetable oil is pre-treated with the minimum cleaning methods of degumming, bleaching and neutralization carried out to prevent high processing losses due to their emulsifying properties, remove the rot and darkening of their oils as a result of thermal instability and the presence of high free fatty acids (FFA's), reducing the amount of FFA's and removing impurities.

The trans-esterification section mainly comprising chemical reactors plays the most important role in the biodiesel production process, with reactor operating conditions having a crucial impact on both the process variables and the quality specifications. The main parameters affecting trans-esterification reaction are the catalyst loading, the methanol to oil molar ratio, the mixing (agitation rotation) speed, the reaction temperature, the residence time and the feedstock rate. To raise the miscibility of reactants and consequently, the possibility of their contact for improving the final product yield, higher alcohol-to-oil molar ratio greater than or equal to 6:1 is needed. Agitation is another vital parameter due to its important influence on the mixing of reactants that are not miscible, on the reaction rate and on the mass transfer in the biodiesel production process. Higher temperatures improve the trans-esterification process by reduction of the mass transfer effect and the higher energy state of the molecules. The required residence time is directly dependent on other parameters such as mixing intensity, residence time distribution (RTD) and temperature that enhances the rate of trans-esterification reaction.

2.6.1 The Production Process in a Biodiesel Plant

Biodiesel production can be processed in either of a batch or continuous form in terms of a reactor. In biodiesel processing, Zahan *et al.* (2019) presented that in comparison with batch reactors, the continuous reactor offers better performance in improving heat and mass transfer, as well as reducing production costs, to obtain a final product of superior quality.

Batch Production Process: In batch production, processing is carried out in a batch reactor where the reactor may be sealed or equipped with a reflux condenser. The oil is first charged to the system, followed by the catalyst and methanol. The alcohol to triglyceride ratios applied varies from 4:1 to 20:1 (mole: mole) with a 6:1 ratio most common. Alkali catalysts such as sodium hydroxide or potassium hydroxide are mostly used. Thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. The system is agitated during the reaction time before agitation is stopped towards the end of the reaction, where less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester – oil phase. Completions of 85% to 94 % are possible with these processes. In some cases, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol while for others the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge. Figure 2.6 shows a process flow diagram for batch processing.

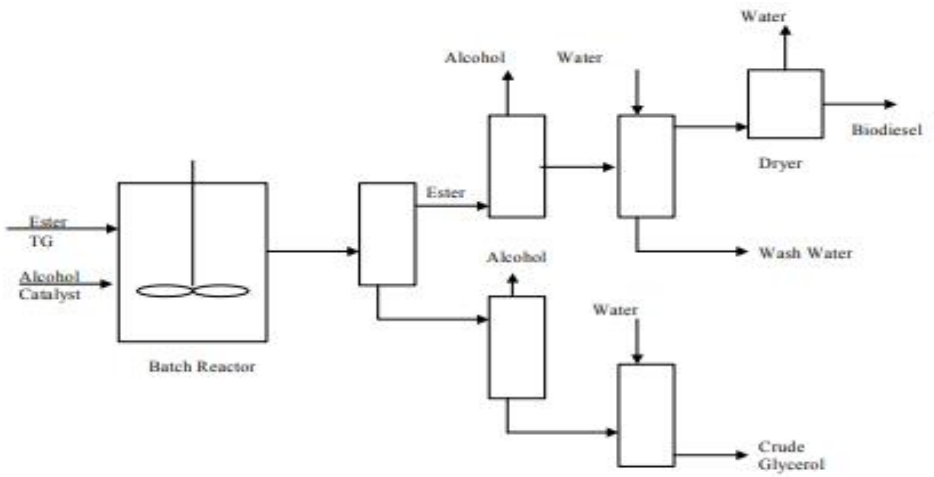


Figure 2.6 Batch-reaction processes (Zahan, 2019)

Batch processes are inexpensive requiring much less initial capital and infrastructural investment. It is flexible as it allows for variation in feedstock composition, type and quantity. The major drawback to this process includes; less productivity, large variation in product quality, more intensive labour and energy requirements. It is generally used in small biodiesel production plants.

Continuous Production Process:

Continuous production processes are preferred over batch processes in large-capacity commercial production because these processes result in consistent product quality and low capital and operating costs per unit of product. Continuous reactors can be either a continuous stirred tank reactor (CSTRs) or plug flow reactor (PFRs) (Noureddini et al. 1998, Peterson *et al*., 2002, Harvey *et al.,* 2003; Gerpen, 2005; Knothe *et al.,* 2005). Modern commercial plants generally use continuous reactors instead of batch systems, with the continuous stirred-tank reactor one of the most commonly used. In using the continuous stirred tank reactors (CSTRs), they are arranged in series and they can be varied in volume to allow for a longer residence time so as to achieve a greater extent of reaction. An essential element in the design of a CSTR is sufficient mixing input to ensure that adequate agitation required to ensure

uniform chemical composition and temperature is maintained. The effect of which increases the dispersion of the glycerol product in the ester phase and consequently, the time required for phase separation is extended. The reactants are continuously added and the product continuously withdrawn.

For the plug-flow reactor (PFR), it is good for processes that require intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. Instead of spending time in an agitated tank, a tubular reactor is used which behaves as if it were a series of small CSTRs chained together. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. The result is a continuous system that requires rather short residence times, as low as 6 to 10 minutes, for near completion of the reaction. This type of reactor is operated at an elevated temperature and pressure to increase reaction rate. The continuous flow processes typically requires intricate process controls and online monitoring. Figure 2.7 below shows a plug flow reaction system.

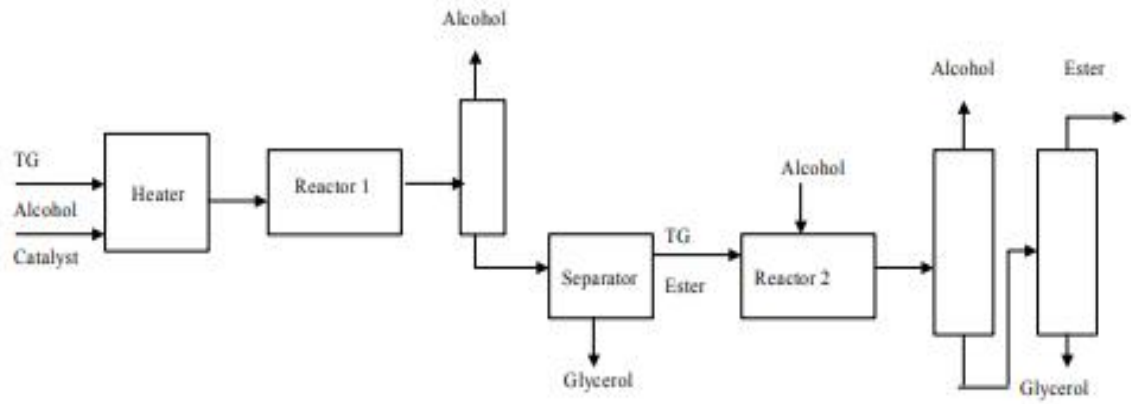


Figure 2.7 Continuous-flow processes (Plug-flow reaction system)

2.6.2 Operating Conditions for Biodiesel Production

Biodiesel synthesis on an industrial scale springs up several challenges creating drawbacks for the chemical production process. Some of these challenges includes; the complex removal of

catalyst, excessive energy requirements, recovery of glycerol, undesirable side reactions and the cost of the refined feedstock. Phase equilibria consideration is therefore very important in the treating production problems as the trans-esterification of triglycerides with methanol may encounter such challenges. Particularly, the reactant and alcohol are generally immiscible, whereas the FAME product is miscible, hampering mass transport or retarding the reaction. Separation and purification of the product phase which is a mixture of solid catalyst, unreacted oil, glycerol and biodiesel, adds further complexity and cost to production. These problems may be alleviated or best avoided by the implementation of standard procedures and safety design factors in the conceptual design stage of the plant.

Rojas and Torres (2009) established ranges of operating conditions or parameters from which design factors can be selected considering the trans-esterification reaction in the biodiesel production process as shown in table 2.

Table 2.6 ***Ranges of Selection Parameters for Trans-esterification Operating Condition***

SELECTION PARAMETERS	RANGES		
	Low	Middle	High
Catalyst concentration (% w/w)	0.2% - 1%	>1% - 3%	>3% - 15%
Molar ratio alcohol/oil	3:1 - 6:1	>6:1 - 12:1	>12:1 - 80:1
Temperature (°C)	50 - 60	>60 - 100	>100 – 200
Yield (%)	20 – 70	>70 - 90	> 90 – 100
Reaction time (hours)	0.16 – 1	>1 - 2	> 2 – 40

In establishing conditions appropriate for the production process, design factors for optimum operating conditions given by these middle range factors as well as book values from other scientific articles are considered. Commonly selected factors includes; molar ratio of alcohol to oil, catalyst loading, temperature and washing agent as shown in table 2.

Table 2.7 ***Ranges for Design Factors (Rojas and Torres, 2009)***

DESIGN FACTORS	RANGE
Molar ratio alcohol/oil	6:1 -12:1
Catalyst Percentage (% wt.)	1% -3%
Temperature (°C)	60-100
Washing agent	Water(40°C) or Acetic acid

Modern biodiesel production plants use technology capable of adapting to the challenging and changing operating conditions of the biodiesel industry to keep process variables at optimum and meet requisite standards during operation. The choice of technology for processing of raw materials into biodiesel consider factors like; raw material types, product recovery, material handling, material and heat balances management, general equipment arrangement, pump, instrumentation and control management in order to guarantee the efficiency and sustainability of process. Although these processing technologies are expensive, the target objective is achieving low costs and high production capacities while maintaining the standard quality of target products. Some solid catalyst-based process technologies applied to different plants for the production of biodiesel on a commercial or pilot stage includes;

- ✓ Esterifip-H process by Axens (France)
- ✓ ENSEL process by Benefuel incorporated.(USA)
- ✓ Catilin's process by Catilin.(USA)
- ✓ Nippon's process by Nippon Shokubai Co.Ltd.(Japan)
- ✓ Endicott process by Endicot biofuels.(USA)

Plant technology providers well-known for their experience in the planning, design and development of biodiesel production plants includes; Agrar-technik (AT), Axens, BDI, CD-Technology, CMB, DeSmet Ballestra, Energea, Lurgi, etc. Many of these technologies can be combined under various conditions and feedstock in an infinite number of ways. The process flow diagram of biodiesel process technologies such as Esterifip-H process developed by

Institut Francais du Petrole (IFP) and designed by Axens, RepCat process by Biodiesel International (BDI) and Lurgi are as shown as Figures 2.8 (a), (b) and (C).

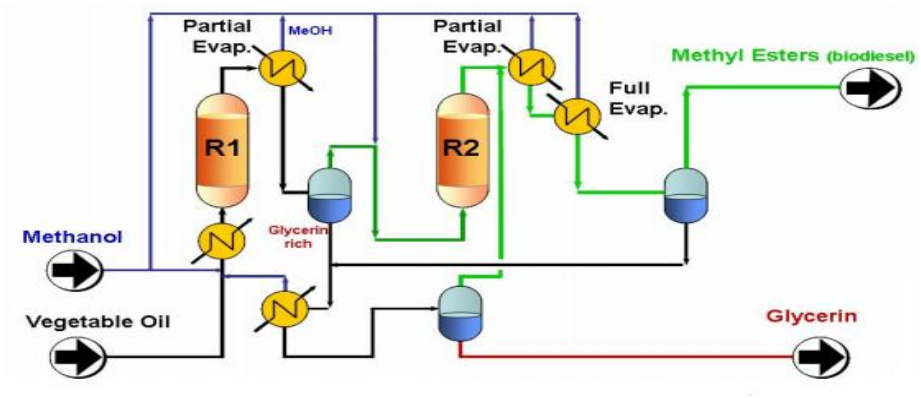


Figure 2.8 (a) Esterifip-H Process Flow Diagrams (Axens, France)

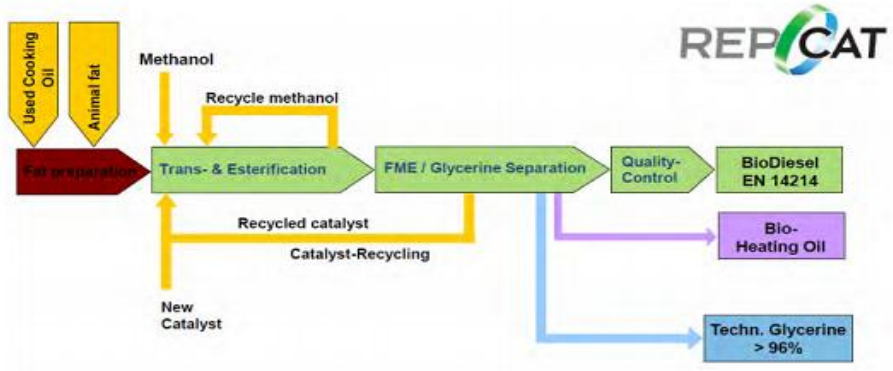


Figure 2.8(b) BDI RepCat Biodiesel Process Flow Diagram (Austria)

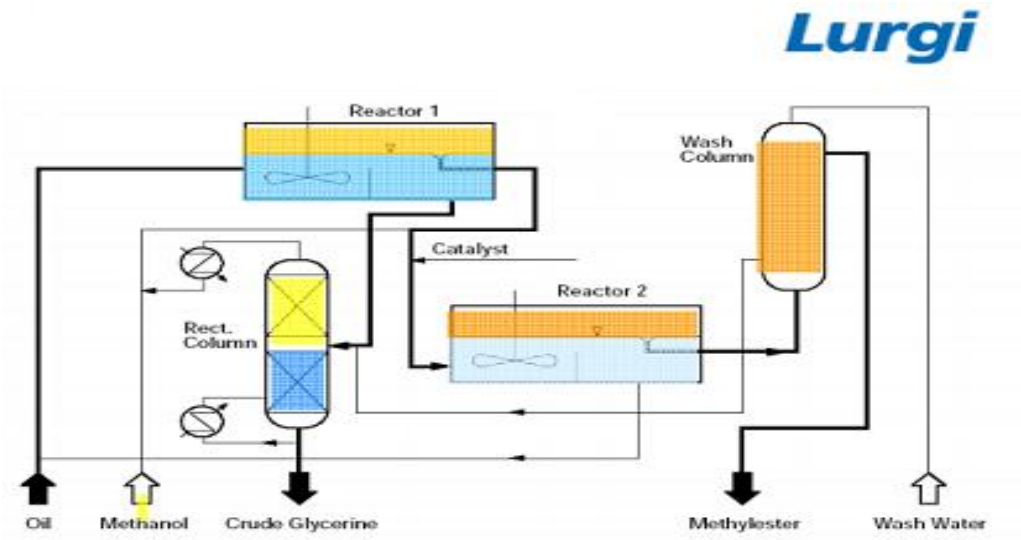


Figure 2.8 (c) Lurgi Biodiesel Process Flow Sheet (Germany)

Some advanced technologies used in biodiesel production to enhance the reaction (reactor) processes involved and their operating conditions includes; ultrasonic, microwave irradiation and plasma technologies. Although these are emerging technologies, at present they are not cost effective (Audu *et al.,* 2018).

2.7 SAFETY IN BIODIESEL PRODUCTION

In order to increase safety and loss prevention during the operation of a biodiesel plant;

- ✓ There should be the implementation of safety design factors in the conceptual design stage with regards to plant design, production capacity, raw material specification, production process technology and the types of utilities involved in its operation.
- ✓ Besides, some considerations have to be applied in the process design and operation as the following; identification and assessment of hazards, control of hazards, limitation of the risk/loss.
- ✓ Understanding properties and characteristics of raw material and chemicals involved in the biodiesel production process (by HAZOP study) is also necessary for the proper and safe use and handling of biodiesel and other chemicals (Anonim, 2009).
- ✓ Considering several technical aspects during operation to obtain sustainable biodiesel production (Anonim, 2011) like

i. Following the Standard Operating Procedure (SOP) for the operators to safely achieve the target of biodiesel production capacity/yield and quality.

ii. Minimization of wastes and emissions (methanol vapour, GHG, particulates, nuisance odours) to reduce the release of pollutants into the air.

iii. Use of minimum utilities (water, steam and electricity) for efficient consumption and lower biodiesel cost production.

iv. Awareness of biodiesel plant safety conditions to protect health and safety operators/workers and communities.

v. Regular maintenance of equipment to reduce idle capacity of biodiesel plant.

vi. Control of biodiesel quality for satisfaction and benefit of biodiesel users.

vii. Implementation of good material handling and distribution so that loss and risk can be minimized.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

3.1. 1 Feedstock

Waste Cooking (Vegetable) Oil

Waste cooking oil (WCO) as feedstock was obtained from a local pastry shop particularly Ede Bakery around Ekiadolor town, Benin City, Edo State, Nigeria.

Catalysts

For the heterogeneous catalyst, agro-wastes particularly ripe plantain peels and chicken egg shells were used as the raw materials. These raw materials for were obtained from the local surroundings around the University of Benin, Benin City, Edo state.

3.1. 2 Chemicals and Reagents

All the chemicals and reagents used in this work were of analytical grades manufactured by BDH chemicals Ltd., Poole England and GFS Chemicals, Inc. 867 McKinley Ave. Columbus, OH, USA. They are as itemised as shown in table 3.1

Table 3.1 **Chemicals Reagents used for Biodiesel Production**

Materials	**Remarks**
Methanol(CH_3OH)	Used for trans-esterification of Waste Cooking Oil and activation of catalyst
Sulphuric acid (H_2SO_4)	For pre-treatment of the Waste Cooking Oil
Distilled water	To remove ionic impurities and wash products.
Potassium Hydroxide (KOH)	For identifying the free fatty acid content using titration
Phenolphthalein	As indicator for titration
Ethanol (C_2H_5OH)	As solvent for dissolution of WCO
Hydrochloric acid (HCl)	For standardization of alkali (KOH) in titration.

3.2 EQUIPMENT/ APPARATUS

All equipment/apparatus used in this study and their uses are itemised as shown in table 3.2

Table 3.2 Equipment / Apparatus

Equipment/ Apparatus	**Remarks**
A hot plate muffle furnace (Model:STD-96-12)	For calcination of biomass
Electronic Magnetic stirrer (PCE-MSR-300)	For equal distribution of mixture
Electronic mass balance (JY502)	For weighing sample materials and reagents
Three-neck round bottom flask	For the trans-esterification process
Electric grinding blender	For grinding samples to required particle sizes
Oven	For drying samples
Beakers, Erlenmeyer flasks	For holding reagents used
Filter paper and surgical cotton wool	For filtration and removal of waste cooking oil residues

Water bath	For mild heating of samples
Buchner Funnel	For filtration of products
Separating Funnel	For separation of biodiesel from by-products

3.3 METHODS

3.3.1 Catalyst Preparation

The heterogeneous catalyst used was prepared from bio-waste materials collected from agro-wastes which includes; Egg Shells and Ripe Plantain Peels. It is worthy to note that the preparatory method is novel.

Calcination Treatment of Bio-waste Materials

A. *Ripe Plantain Peels* (RPP)

The samples (ripe plantain peels) were first sun dried until they became easily combustible after which they were washed with distilled water and cut to small pieces, and again were oven-dried at 80℃ for 6 hours. The dried pieces of peels were ground to powder using a porcelain pestle and mortar (a grinding blender can substitute where available) as shown in figure 3.1a.

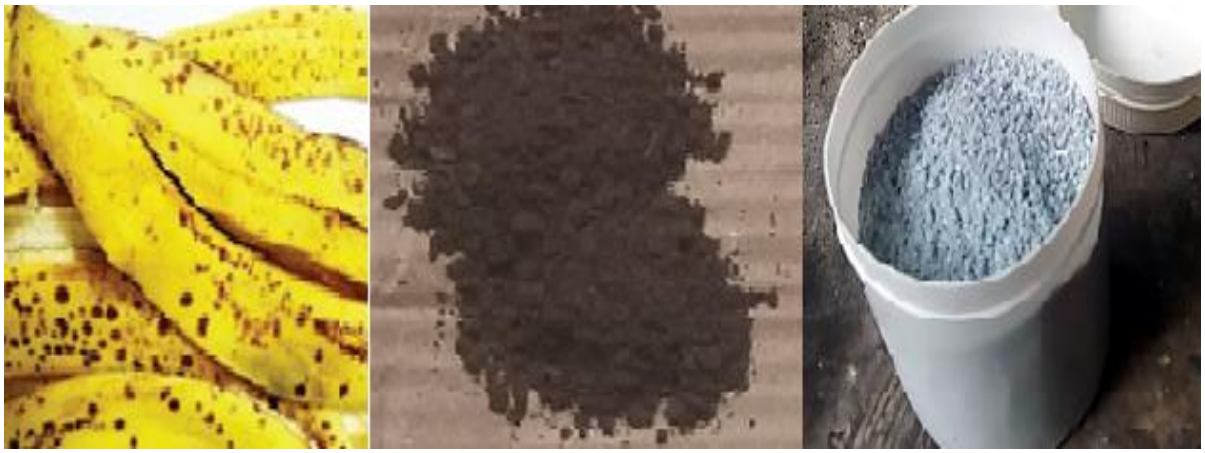


Figure 3.1(a) *Preparation of ripe plantain peel catalytic material*

A portion of the powder was calcined into granulated greyish blue powder from brown in a muffle furnace under static conditions at 750°C for a residence time of 4 hours. The coloured calcined ripe plantain peel (RPP) samples were stored for further analysis. All of the potassium salts in the peels are in this way converted to potassium oxides (K_2O) which is a lot cheaper than buying commercial KOH. The potassium oxide (K_2O) content was used as the chemical promoter in the catalytic system.

B. Chicken Egg Shell **(CES)**

The chicken eggshells (CES) were thoroughly washed with tap water in order to remove any particle of dirt or impurities remaining on its surface, followed by washing the samples with distilled water to prevent any ion from tap water remaining on the surface of the eggshells to avoid contaminating the process further. Washed eggshells were allowed to dry naturally in ambient environment after which the dried eggshells were reduced to small particle sizes using a domestic scale grinder as shown in figure 3.1(b)

Figure 3.1 (b) *Preparation of the egg shell catalytic material*

The dried and ground milkish-white CES were calcined in a muffle furnace under static conditions at 950°C for 4 hours to transform the calcium species in the shells into a calcined ashed-white material which contains calcium oxide (CaO) particles. The calcined CES was used as the catalyst support material to be impregnated with the chemical promoter in the catalytic system design.

C. Impregnation (Physical Mixing or Doping) Of Catalyst

Impregnation (doping) by physically mixing the calcined RPP and CES in the following trial mixing ratios by mass.

Tables 3.3 TRIAL 1: Catalyst-System ratios (Varying Calcined Chicken Egg Shells)

Calcined samples (RPP:CES)	**Trial ratios**			
	1:1	1:2	1:3	1:4
Mass of calcined RPP(g)	0.50	0.33	0.25	0.20
Mass of calcined CES(g)	0.50	0.67	0.75	0.80

Catalyst system with basis of mass = 1g

Table 3.4 TRIAL 2: Catalyst-System ratios (Varying Calcined Ripe Plantain Peels)

Calcined samples (RPP: CES)	**Trial ratios**			
	1:1	2:1	3:1	4:1
Mass of calcined RPP(g)	0.5	0.67	0.75	0.80
Mass of calcined CES(g)	0.5	0.33	0.25	0.20

Catalyst system with basis of mass = 1g

Figure 3.2 Catalyst mixing by different trial ratios

The mixing ratio of the catalyst design is informed from the fact that the surface areas of both materials when observed differs from each other with the surface area of ripe plantain peel per finger larger than that of chicken eggshell per egg. In addition, the RPP contains K_2O

which acts as the chemical promoter in the designed catalyst system while the CaO in the CES serves as its support material.

Analysis, Characterization, and Activation Of Catalyst

To characterize the chemically prepared catalyst sample, analytical techniques were utilized which includes; Brunauer-Emmett-Teller (BET) analysis, Hammet indicator (particularly phenolphthalein), Fourier Transform Infra-Red (FT-IR) spectroscopy, with X-ray methods specifically x-ray diffraction (XRD) and x-ray fluorescence (XRF).

Analysis using Hammett Indicators Method

0.25g of activated catalyst was added to a test tube and stirred with 5 mL of anhydrous methanol. Then, one drop of the Hammet indicator was added and left to equilibrate for 2 h, then change in colour was observed. The Hammet indicator used was phenolphthalein.

Analysis by Fourier Transform Infra-Red (FT-IR) Spectroscopy

The FTIR analyses of catalyst was carried out using an FTIR spectrometer (model 8500; Shimadzu), which was operated in the scan range of 4000–400 wavenumber/cm^{-1}. A standard KBr technique was used for preparing the samples.

Brunauer Emmet Teller Analysis

BET analysis using an ASAP 2020 surface area analyser (micrometrics) was performed to determine the specific surface area of catalyst sample.

X-ray diffraction (XRD) Analysis

The mineralogical identification (or crystallinity examination)of the samples was carried out using X-ray diffraction (XRD) on a Bruker D8 Advanced diffractometer, operating at 40 kV and 40 mA using Cu Kα radiation (λ = 1.5544 Å). Data were collected using a coupled θ–2θ configuration in the 2θ range of 2–80° with a step size of 0.02° and a scan time of 1s.

Activation of Catalyst

Chemical activation of the prepared catalyst was done using the following process:

The doped or mixed catalyst (calcined (CES + RPP)) samples were weighed out and mixed with methanol in a 1:4 ratio and the mixture was allowed to stand for a period of 4 hours in the presence of a magnetic stirrer at 650 rpm applied to maintain mixing of the reagents uniformly.

Figure 3.3 Activation of the designed catalyst

After 2 hours, the magnetic stirrer was removed from the reaction beaker and the activated catalyst particles were allowed to settle down. The supernatant methanol was decanted and the remaining slurry was kept open in ambient temperature for the next 2 hours to allow the volatile methanol to evaporate naturally leaving behind a dried activated catalyst sample.

Pre-Treatment of Feedstock Oil

The waste cooking oil (WCO) collected from the bakery was filtered with surgical cotton to remove every unwanted trace of food residues present in it. Then centrifugation was employed to discard any impurities or fat sediment. Next the oil was heated at 110°C to evaporate any trace amount of moisture content in a 2 litre beaker for 50 minutes using a hot plate with magnetic stirrer (Phan and Phan, 2008).

(a) Untreated waste cooking oil(WCO) ***(b)***Pre-treated WCO

Analysis and Characterization of the Feedstock Oil

Analysis was done for physicochemical properties of the waste cooking oil which includes the moisture content, acid value, saponification value, density, viscosity, iodine value and hydrogen peroxide value. Characterization of the oil was done using FTIR

Determination of Oil Density

Density measurement was carried out according to ASTM D-5.the density of the WCO was carried out at room temperature 25°C by gravimetric analysis, 25 ml of oil was measured in a

beaker and mass of the oil was determined using the electronic balance. Density was then calculated using the equation;

$\rho = \frac{m}{v}$ ------ (3.1)

Where m (g) is the mass of the oil sample in density bottle and v (cm^3) is the volume labelled on the density bottle.

m=45.96g, v= 50 ml (cm^3)

$\rho = \frac{45.69g}{50ml}$= 0.92g/ml=0.92$gcm^{-3}$.

Determination of Specific Gravity

Determination of the specific gravity of the waste cooking oil was carried out according to the procedure mentioned in ASTM D 1298.

ρ_{oil} = 0.92 gcm^{-3}, ρ_{water}=1 gcm^{-3}

$S.G = \frac{\rho_{oil}}{\rho_{water}} == \frac{0.92\ gcm-3}{1\ gcm-3}$=0.92

Determination of Moisture content

This was quantitatively determined by thermo-gravimetric analysis using a dry oven and a desiccator. 5.13g of the oil sample was weighed in a crucible using the electronic balance and the weight obtained was recorded. The crucible together with the oil obtained was placed in an oven at 110°C for about 1hour. The crucible together with the oil was removed from the oven and placed in a desiccator to cool off in the presence of a desiccant and weighed. The new mass of crucible + oil sample was recorded.

Change in mass (m)=0.03g, Initial mass = 5.13g

Moisture content percentage $= \frac{\text{Change in mass}}{\text{Initial mass}}$ x 100%= $\frac{m}{m_0} = \frac{0{,}03g}{5.13g}$ x 100% = 0.585%.

Determination of Viscosity

The viscosity measurement was carried out according to ASTM D-4212 by a Zahn flow-cup viscometer. The flow-cup viscometer was dipped into the oil sample and the efflux time taken for outflow of oil through the orifice at the bottom was recorded using a stop watch. The action was repeated for three times so that an average value can be taken. This was carried out at room temperature (30°C). The drain (efflux) times recorded were given as: t_1= 15.72s, t_2=15.31s and t_3= 15.56s.

The average time is given as; $\frac{t_1+t_2+t_3}{3} = 15.53s$

The viscosity was calculated using the Zahn cup general formula given as; v= k (t-c)

$\upsilon = 4.22(15.53-9.52) = 25.36mm^2/s$;

Dynamic viscosity (η) = kinematic viscosity (υ) x density(ρ); . . . .(3.2)

$\eta = 25.36mm^2/s \times 0.92\ g/cm^3 = 0.233\ cP$

Determination of Acid value (AV)

Acid value (AV)

The acid number or acid value of edible oils or their corresponding esters indicates the quantity of free fatty acids (FFA) present in the sample and is expressed as mg of

KOH/NaOH required to neutralize 1g of the sample. It was determined using the AOCS method and calculated with the formula:

$$\text{Acid value (AV)} = \frac{\text{M(g)x N}(\frac{\text{g}}{\text{L}})\text{ x V(mL)}}{m(g)} \quad . \quad . \quad . \quad .(3.3)$$

$$\%\text{ FFA content} = \frac{\text{V x N x 2.82 g}}{\text{Conversion factor(F)xSample mass (m)(g)}} x\ 100\%. \quad . \quad .(3.4)$$

Where, 'V' is the volume of KOH/NaOH solution used in mL, Conversion factor (F) =10, 'N' its exact normality of KOH/NaOH in g/L, 'M' is the molar mass in 'g' of KOH/NaOH and 'm' is the reacting mass in of the oil sample.

Using AOCS method of titration to neutralize free fatty acids in 1.05g of the oil sample with 0.05M (2.8N) KOH, given the average titre value V=1.8mL and Conversion factor (F) =10. The acid value is given as;

Acid value (AV) = 0.269 mgKOH/g of oil sample

% FFA content = 0.1353%

The FFA content is less than (<) 3%, as such there is no need to esterify. The process of biodiesel production becomes easier as conversion was done through the direct process of trans-esterification alone.

Determination of Saponification Value (SV)

The saponification value (SV) is defined as the weight of potassium hydroxide, in milligrams, needed to saponify one gram of oil. SV is an indicator of the average molecular weight and hence chain length of the fatty acids present in the sample as triglycerides. It is inversely proportional to the molecular weight of the lipid (Gohari et al., 2011). The saponification value of oil and biodiesel were estimated by the ASTM D1962 titration method.

The SV was calculated with the equation:

Saponification value (SV) = $\frac{M\,(g)xN(\frac{g}{L})x(V_0-V_1)(mL)}{m(g)}$ ..... (3.5)

where SV represents saponification value (mg KOH/ g oil); V_0 volume of hydrochloric acid solution required for the blank, (mL); V_1 volume of hydrochloric acid solution required for the test sample,(mL); N normality of HCL solution (0.5N); M= molar mass(equivalent gram) of KOH (56.1 g/mol); mass of the oil sample (g). Using ASTM 1962 method of titration given V_0= 91mL, V1=72.8mL and m= 7.012g.

Saponification value (SV) = 0.0728mgKOH/g of oil.

Determination of Iodine Number (Value)

The iodine value is an indicator of the degree of unsaturation of fats and oils. The IV is the mass of iodine in milligrams that is consumed by 100 grams of oil (mgI_2/100g). The iodine number (value) was determined using (AOCS) method.

The iodine number (value) was calculated based on the following equation:

Iodine (number)value = $\frac{(V-V_0)\ x\ M\ x\ N_{Na_2S_2O_3}\ x\ 100\ x126.}{m}$ ……..(3.6)

Where V_{Na2SO3} is a volume of $Na_2S_2O_3$ needed for titration calculated by the difference in volume of $Na_2S_2O_3$ needed for titration between the blank solution and the test sample (V-V_0). Where V= volume of $Na_2S_2O_3$ needed for titration of blank and V_0= volume of $Na_2S_2O_3$ needed for titration of test sample. N= normality of $Na_2S_2O_3$, m =mass of the oil sample, M= molecular mass of iodine=126.9

Using AOCS method of titration together with wijjs's solution, given V_0=35.1mL, V=34.7mL, N=0.1N (g/1000mL), m=2g; the iodine value was calculated as;

Iodine (number)value = 25.38 mgI_2/100g of oil.

Determination of Peroxide Number Value (PV)

Peroxide value is a measure of peroxides contained in the oil. The PV of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. Peroxide value (PV) measures the milli-equivalents of oxygen (hydroperoxides) per 1000 gram of oil. The PV was determined according to the official method NF T60-220 of the Association Française de Normalisation (AFNOR, 1988). Peroxide number was calculated by the following equation:

$$PV(m.Eq\ O_2/kg) = \frac{(V - V_0)mL \times N(g/L) \times 1000}{\text{Sample mass}(m)(g)} \ldots\ldots\ldots (3.7)$$

Where V= sample titre value, V_0= blank titre value, N = normality of sodium thiosulphate, m= mass of oil sample (g) clear solution is obtained.

Using AFNOR 1988 method with wijjs's solution gives peroxide value as;

Peroxide value (PV) = 0.04m.EqO_2/kg of oil.

Trans-Esterification of Waste Cooking Oil

The trans-esterification of the pre-treated oil was done with methanol using the synthesized catalyst in a batch stirred reactor with a magnetic stirrer, stirred at 450 rpm. The reaction conditions of methanol to oil (molar) ratio of 6:1, catalyst loading of 2% weight of oil, residence time of 1.5 hours, and a temperature of 60°C was kept constant for the different designed catalyst samples used with 50 g of the oil sample, for each of the designed catalyst samples. The residual methanol was evaporated using a rotary evaporator at 100°C for 15 min.

Figure 3.5 Preparation of the biodiesel

The catalyst for each run was separated by filtration with the reaction mixture poured into a separating funnel and kept to settle for about 48 hours to separate the glycerol layer from the biodiesel. The Biodiesel yield for each catalyst sample was calculated using equation 3.8 and recorded.

$$\%\text{Yield} = \frac{\text{Mass of Biodiesel Produced}}{\text{Mass of oil sample used}} \text{X } 100\% \text{ - - - - - - - - - - (3.8)}$$

Analysis and Characterization of the Biodiesel

Analysis was done for the physicochemical properties of the biodiesel produced which includes the acid value, saponification value, density, viscosity, iodine value and hydrogen peroxide value. Characterization of the biodiesel was done using Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RESULTS

Ripe Plantain Peels (RPP)

***Figure 4.1*(a)** Uncalcined ripe plantain peel (brown) **(b)** Calcined ripe plantain peels (blue)

b) Chicken Egg Shells (CES)

***Figure 4.2*(a**) Uncalcined ground chicken eggshells (milk-white) **(b)** Calcined chicken egg shells (ashed)

4.1.1 Analysis and Characterization of the Catalytic Materials

Braunner Emmet Teller (Bet) Surface Area Analysis

Calcined Ripe Plantain Peel (RPP)

The adsorption average pore width was determined as 68.35 Å. The single point adsorption total pore volume was measured as 0.032122 cm^3/g. The BET surface area and t-plot external surface area of the calcined RPP were 18.80 and 26.54 m^2/g, respectively.

Calcined Chicken Egg Shell (CES)

The BET surface area (m^2 /g) was determined as 4.6 m^2/g, the total pore volume as 0.026708 cm^3/g, and the average pore radius was measured as 116.06Å.

Analysis Using Hammett Indicators

By adding phenolphthalein to the catalyst samples successfully changed the colour of (H^- = 9.2) from being colourless to pink.

Fourier Transform Infra-red Spectroscopy Analysis

Calcined Ripe Plantain Peel (RPP)

Observed peaks at 1600, 1396 and 1150 cm^{-1} in the samples are assigned to carbonate C–O stretching and bending vibrations, which is an indication of the presence of carbonate. The peak at 1396 cm^{-1} is very strong in and it is known for K_2CO_3 which breaks down into K_2O.

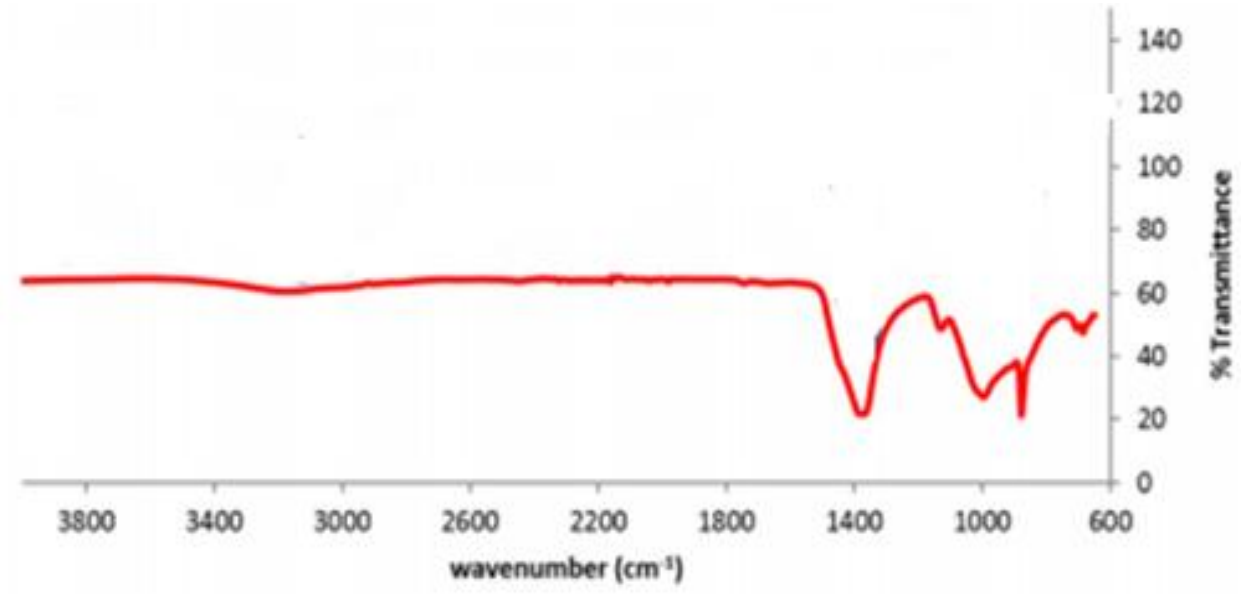


***Figure 4.3*(a)** FT-IR spectra of calcined RPP at 700°C

(b)Calcined Chicken Egg Shell (CES)

The carbonate is broken down to CaO as the absorption bands of CO_2^{3-} molecules can be seen to have migrated to higher energy as represented by 1403 cm^{-1}, 1065 cm^{-1}, 878 cm^{-1} and 529 cm^{-1} while the observed peaks showed a sharp stretching band at 3642 cm^{-1} which can be

attributed to the existence of the OH^{-1} group.

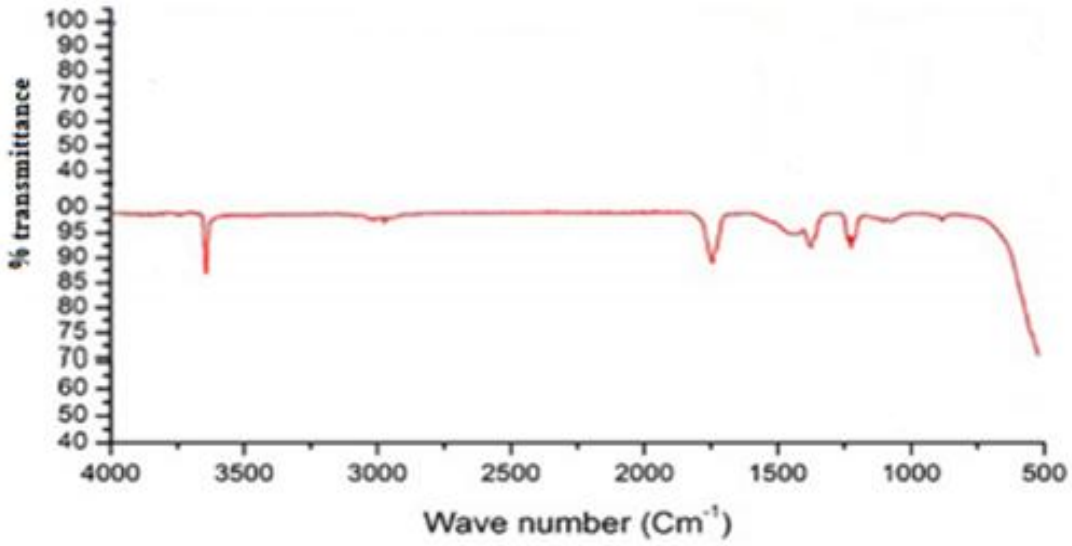


Figure 4.3(b) FT-IR spectra of calcined CES at 900°C

X-ray Methods

X-ray Diffusion (XRD) Analysis

(a) Calcined Ripe Plantain Peel (RPP)

The different diffraction angles marked at 15.9°, 20.3°, 37.2, 40°, 55.3° showed potassium compounds steadily increased.

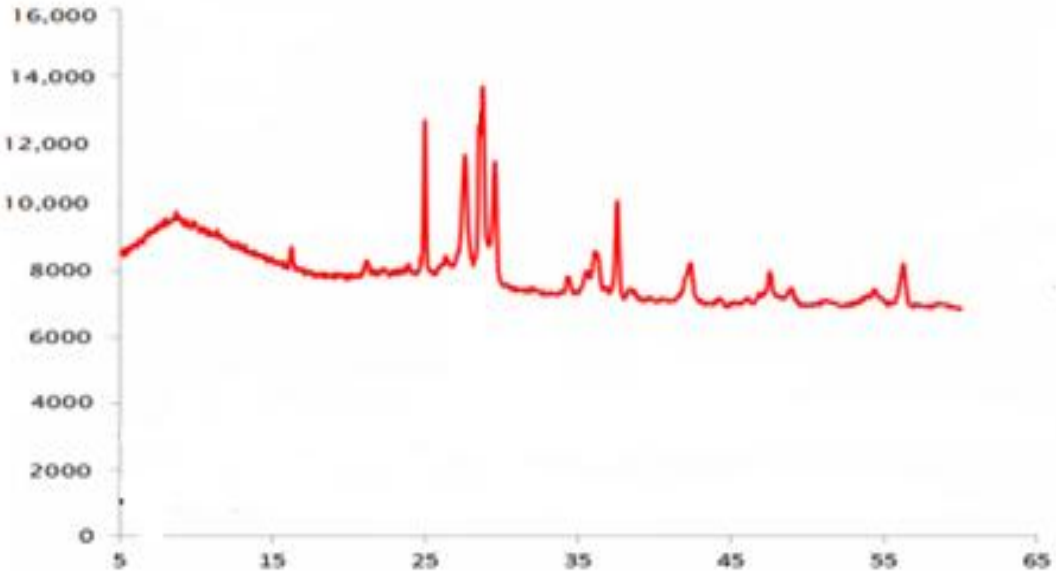


***Figure 4.4*(a)** XRD chromatograms of calcined RPP at 700°C samples

(b) ***Calcined Chicken Egg Shell (CES)***

The different diffraction angles marked at 20.8°, 40°, 39.7°, 55.3°, 59.8°, and 64.1° shows the decomposition of the calcium carbonate constituent into calcium oxide.

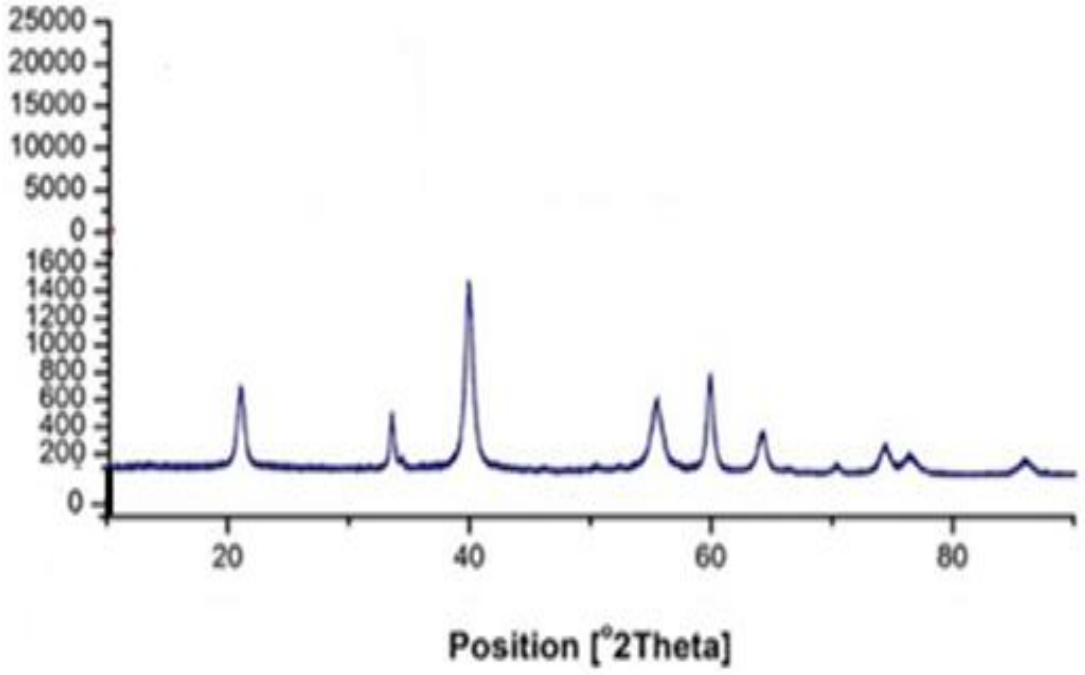


***Figure 4.4*(b)** XRD chromatograms of calcined CES, at 900 °C

X-ray Fluorescence (XRF) Analysis

Calcined Ripe Plantain Peels

The major elements present in the calcined samples were O, Mg, P, S, K, Si, Cl with K having the highest mass among the metallic elements.

Table 4.1 Elemental composition of the calcined RPP at 700°C

Elemental composition	Weight % of calcined RPP
O	**45.81**
Mg	**0.55**
K	**39.20**

Si	**5.56**
S	**0.66**
Ca	**3.36**

(b) ***Calcined Egg Shells***

The elemental chemical compositions present shows calcium (Ca) majorly with the others in trace amounts which includes; magnesium, sodium, sulphur, silicon, phosphorus, etc.

Table 4.2 Elemental composition of the calcined CES at 900°C

Elemental composition	**Weight % of calcined RPP**
S	**2.46**
Mg	**0.55**
K	**0.311**
Ca	**95.03**
Si	**0.363**
C	**3.07**

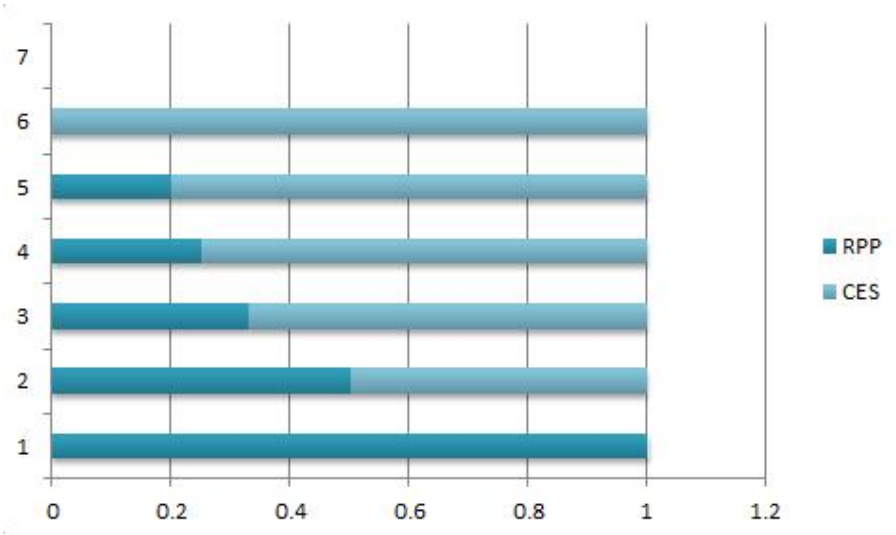
4.1. 5 Analysis of the Impregnation (DOPING) of the Designed Catalyst

TABLE 4.3 Mixing Ratios for Doping the Calcined Samples

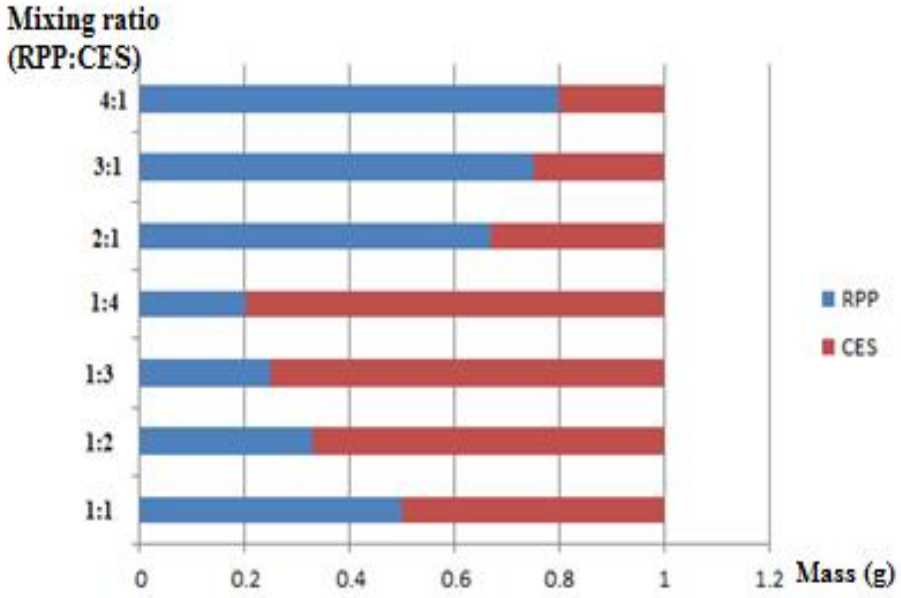
Trial ratios (RPP*: CES)*	1:1	1:2	1:3	1:4	2:1	3:1	4:1

Table 4.4 Mass fraction per gram of the calcined samples in the designed catalyst

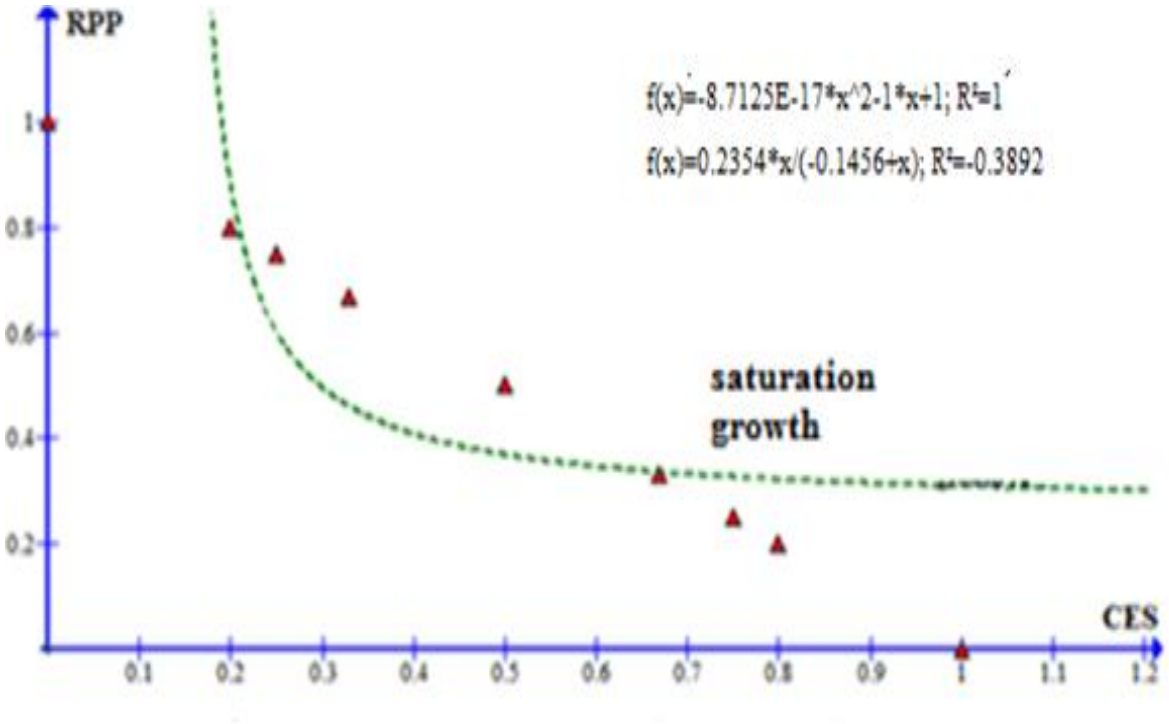
Mass Fraction (RPP*)*	1	0.8	0.75	0.67	0.5	0.33	0.25	0.20	0
Mass Fraction (*CES)*	0	0.2	0.25	0.33	0.5	0.67	0.75	0.80	1



(a) Mixing of catalyst by mass fraction



(b) Mixing ratios by mass



(c) Saturation growth in mixing the catalytic materials

Figure 4.5 Analysis of the impregnation (doping) of the catalyst

4.1.6 Analysis and Characterization of Feedstock Oil

Table 4.5 Physicochemical Properties of Waste Cooking Oil

Physicochemical Properties	***Waste Cooking Oil***
Moisture Content	0.585%
Density	0.92gcm^{-3}
Kinematic viscosity	25.36 mm^2/s
Dynamic Viscosity	23.33
Specific Gravity	0.92

Acid Value	0.269
FFA content	0.135%
Saponification Value	0.0728mgKOH/g of oil
Iodine Value	25.38 mg I_2/100g of oil
Peroxide Value	1.04.EqO_2/ kg of oil

(a) Fourier Transform Infra-Red Spectroscopy Analysis Of Wco

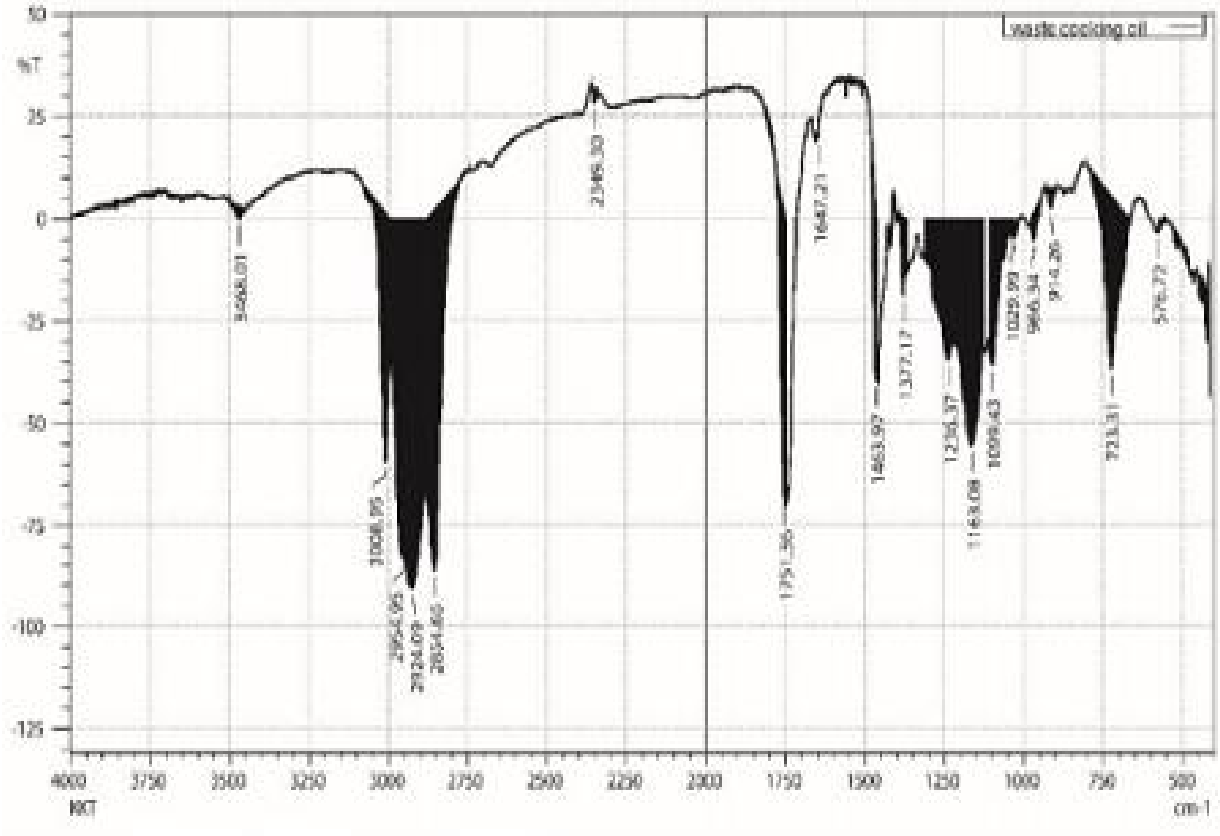


Figure 4.6(a) FTIR of the waste cooking oil used

The FTIR spectrum shows the absorption peaks of 'CH' at 2735.06cm^{-1} and 'OH' at 3466.08 cm^{-1} in the waste cooking oil sample.

4.1.7 Analysis and Characterization of the Biodiesel

(A) Fourier Transform Infra-Red Spectroscopy Analysis

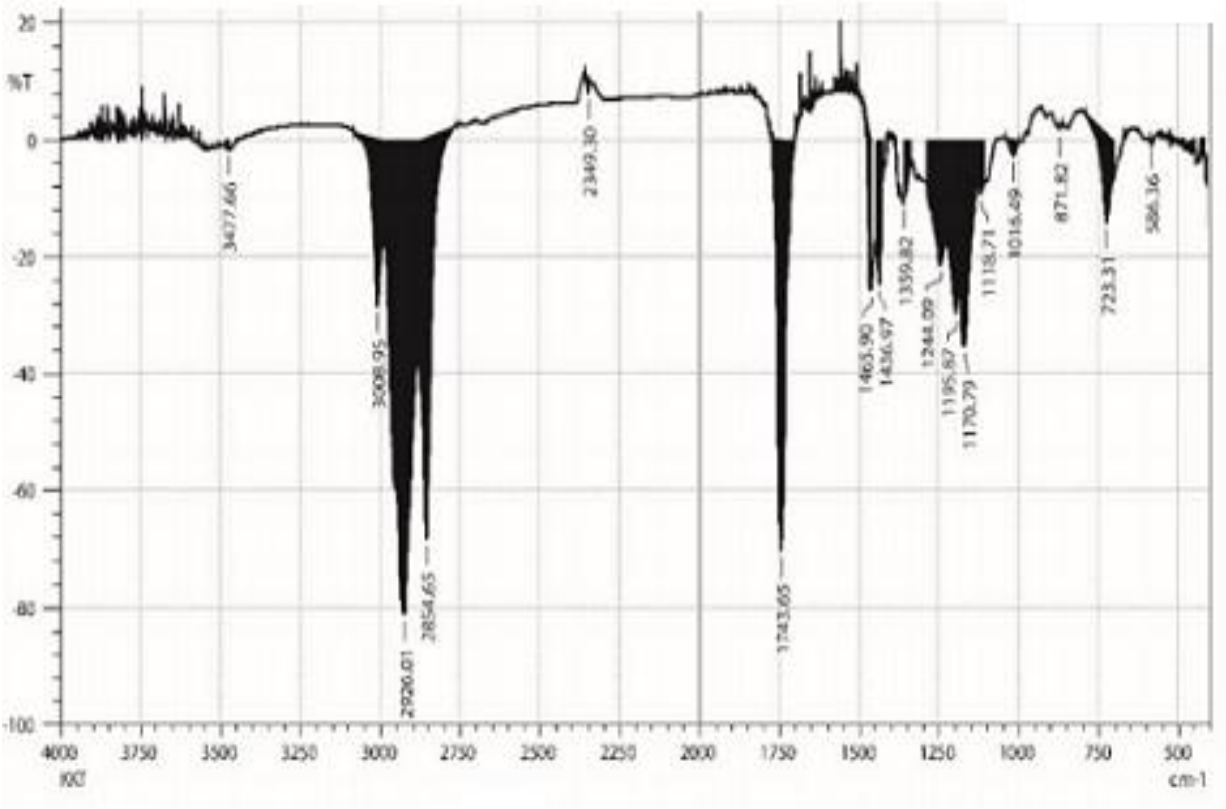


Figure 4.6(b) FTIR of Biodiesel produced from waste cooking oil

The change from ester groups to methyl ester has the strongest impact in the infrared spectrum. The most influencing result from trans-esterification is in the new signal at 1435 cm-1. The FTIR spectra of biodiesel fuel are as shown in table 4.6

Table 4.6 FTIR spectra of Biodiesel from waste cooking oil

SN	Frequency in cm^{-1}	Types of Vibration	Nature of functional group
1	3008.95	=C-H stretching	Olefin
2	2926.01	CH_2 stretching	Alkane
3	2854.65	CH_2 stretching	Alkane
4	1743.65	C=O stretching	Ester
5	1647.21	C=C stretching	Alkene
6	1436.97	O-CH_3 typical	Methyl ester group
7	1244.09	C-CO-O	Ester
8	1195.87	C-O/ O-CH_3	Ester
9	1016.49	C-O-C	Ester
10	723.31	$CH_2)_n$ rocking	Alkane

(B) Gas Chromatography Mass Spectroscopy Analysis

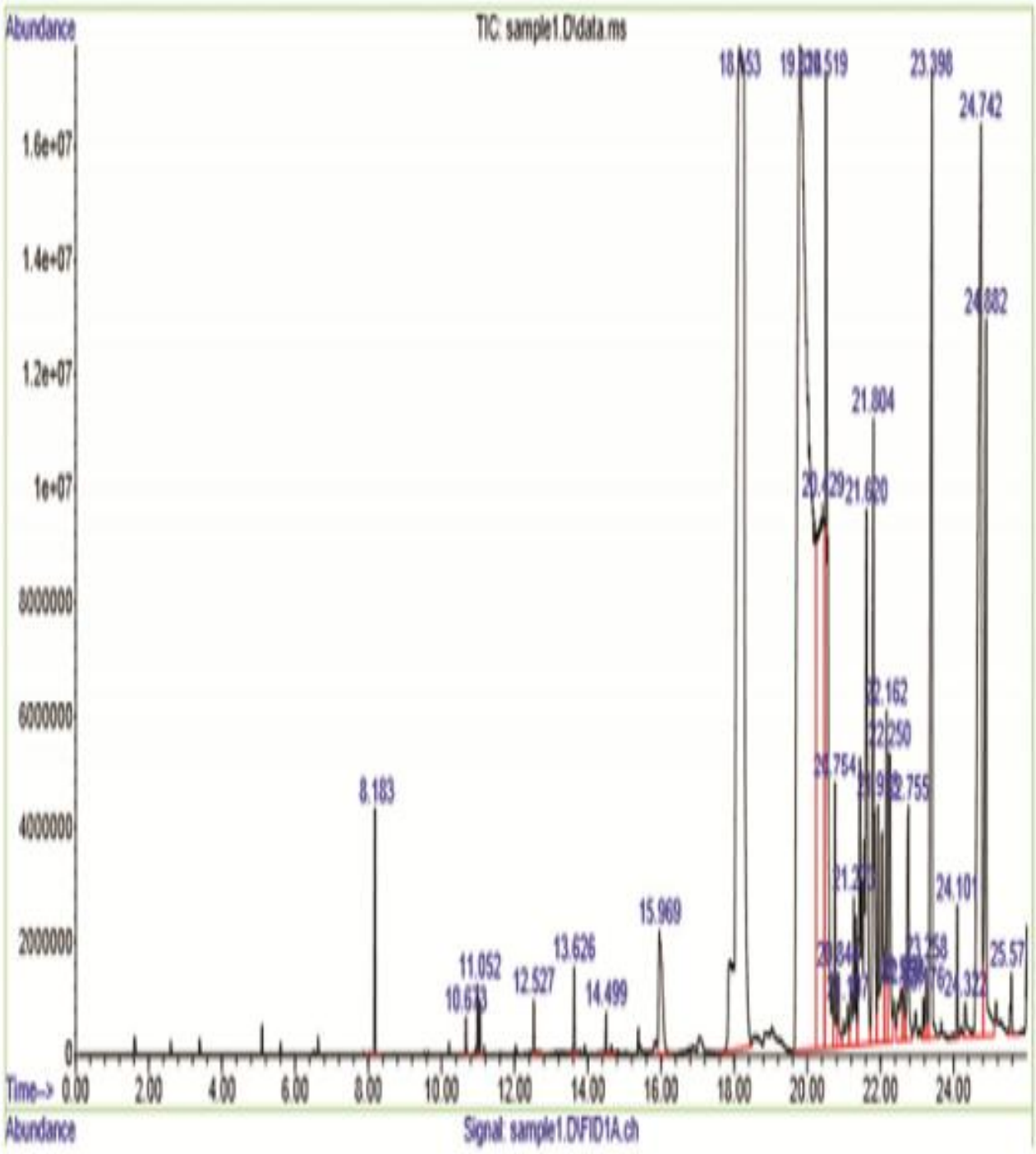


Figure 4.7 GC-MS Chromatogram obtained from the analysis of biodiesel from WCO

The biodiesel product analysed showed the presence of methyl esters such as decanoic acid methyl esters, tetra-decanoic methyl esters, octa-decanoic methyl esters amongst others, etc.

Analysis of the Biodiesel Yield

$$\%\text{Yield} = \frac{\text{Mass of Biodiesel Produced}}{\text{Mass of oil sample used}} \text{X } 100\%. \quad . \quad . \quad . \quad . (4.1)$$

Table 4.7 Amount of Biodiesel Yield% at 60°C given mass of oil sample = 50g

Number of runs	Catalyst mixing ratio used Calcined (RPP:CES)	Mass of beaker = 62.28g Mass of beaker + biodiesel product (g)	Mass of Biodiesel produced (g)	Percentage Yield of Biodiesel produced (%)
1	1:1	92.61	30.33	60.66%
2	1:2	96.84	34.56	69.12%
3	1:3	99.80	37.52	75.04%
4	1:4	84.58	22.30	44.60%
5	RPP only	78.63	16.35	32.7%
6	2:1	67.93	5.65	11.3%
7	3:1	63.53	1.25	2.5%
8	4:1	Complete saponification	-	-
9	CES only	75.88	13.60	27.20%

Table 4.8(a) Mass fraction of the catalytic materials versus Biodiesel Yield Percentage

Mass Fraction (RPP*)*	1	0.8	0.75	0.67	0.5	0.33	0.25	0.20	0
Mass Fraction (*CES)*	0	0.2	0.25	0.33	0.5	0.67	0.75	0.80	1
Mixing ratio (RPP:CES)	RPP only	4:1	3:1	2:1	1:1	1:2	1:3	1:4	CES only
Biodiesel Yield (%)	32.7	-	2.5	11.3	60.66	69.12	75.04	44.60	27.2

Table 4.8 (b) Biodiesel Yield% versus Catalyst mixing ratio

Biodiesel Yield (%)	60.66	69.12	75.04	44.60	11.3	2.5	-
Catalyst mixing ratio (Calcined RPP:CES)	1:1	1:2	1:3	1:4	2:1	3:1	4:1

Table 4.8 (c) The influence of mass fraction of catalyst mixture on biodiesel yield percentage

Biodiesel Yield (%)	32.70%	75.04%(optimum)	27.20%
Mass fraction ratio (RPP/CES)	1/0 (RPP only)	0.25/0.75 (mixed oxide i.e. RPP:CES)	0/1 (CES only)

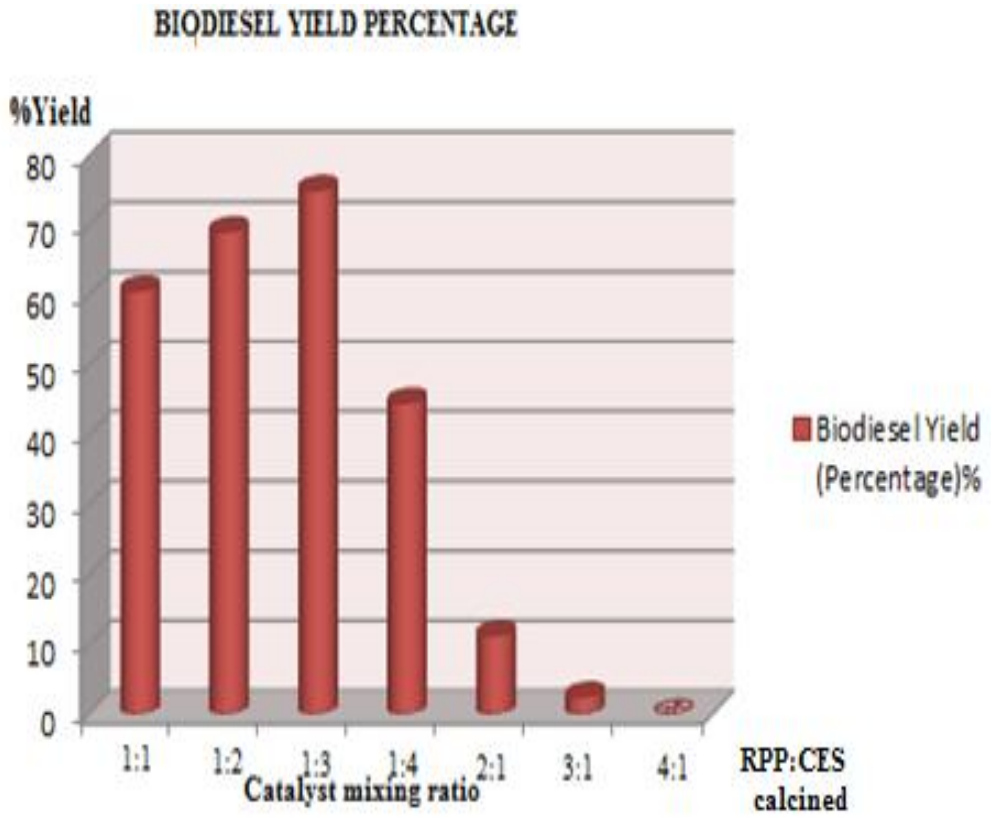


Figure 4.8 The influence of the catalyst mixing ratio on biodiesel yield

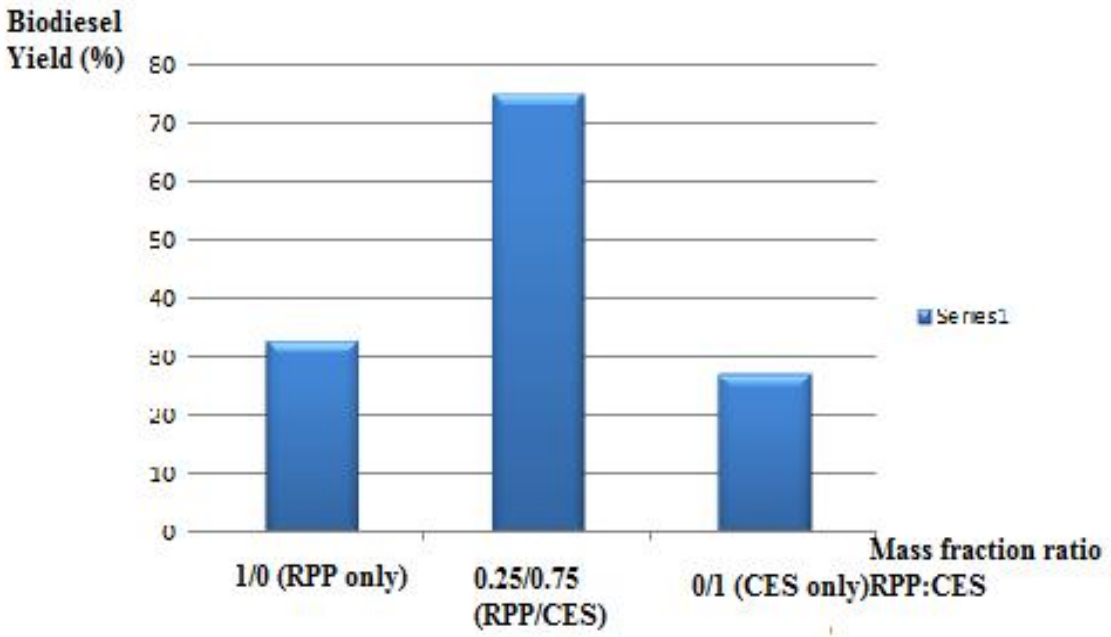


Figure 4.9 Comparing biodiesel yield from the different catalyst types using mass fraction.

Table 4.9 Physicochemical properties of the Biodiesel

Biodiesel Properties	**Waste cooking Oil**	**ASTM**
Acid value mgKOH/g	0.26	<0.8
Density at 40°C (kg/m^3)	863	865-900
Kinematic viscosity at 40°C (mm^2/s)	4.10	1.9-6.0
Iodine Value (mg I_2 / *l*100g of oil)	47.5	120
Peroxide value (m.Eq O2 per kg of oil)	1.45	1.25-3.96

4.2 DISCUSSIONS

The calcined catalytic materials used were analysed using FTIR, XRD and XRF with RPP (greyish blue) shown to contain majorly potassium oxide (K_2O) and CES (ashed milkish white) shown to contain calcium oxide (CaO) as recorded in Figures 4.1-4.4 (a-b)'s as well as the tables 4.1 and 4.2. The different design (mixing) ratios and mass fractions used in the preparation of the catalyst were recorded in tables 4.3 and 4.4, with the plots of mixing ratio

by mass, mixing ratio by mass fraction and the saturation growth rate (using ‘source forge’ an open source software and Microsoft Excel) shown in figure 4.5.

The waste cooking oil was pre-treated, characterized and the physicochemical properties analysed as shown in table 4.5 and figure 4.6(a). Different catalyst design (trial mixing) ratios of calcined 'RPP:CES' by mass were used in the trans-esterification of the pre-treated oil into biodiesel and the selected ratios of 1:1, 1:2 1:3 and 1:4 gave yields of 60.66%, 69.12%, 75.04%, and 44.60 % respectively with the catalyst design ratio of 1:3 giving the optimum yield at 75.04% as shown in tables 4.7 and 4.8 (a-c). It was noted that the presence of RPP due to the potassium ion (K^+) content in its composition increases the surface area per unit volume and as such improves the reactivity of the catalyst although increasing its concentration above a certain minimum decreases the biodiesel yield as this would lead to hydrolysis or end up in a saponification reaction as shown using the ratios 2:1, 3:1 and 4:1 with the ratio 4:1 particularly causing complete saponification as recorded in table 4.7. This is shown by the bar chart represented in figure 4.8 using Microsoft Excel. The biodiesel produced was characterised and analysed using FTIR and GCMS as shown in figures 4.6(b) and 4.7. Thus the impregnated catalyst with RPP/CES mass ratio 1:3 gave the optimum yield making it the optimal design ratio.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The catalyst was synthesized from a blend of calcined agro-wastes; chicken eggshells(CES) impregnated by physical mixing with ripe plantain peels (RPP) in different selected 'RPP: CES' mass ratios to check for their influence in the trans-esterification of waste cooking oil into biodiesel so as to obtain the optimum yield of biodiesel produced by the different ratios. Analysis carried out showed that the catalyst produced contains mixed oxides particularly CaO/K_2O together with other metallic oxides (ions) in minute or trace quantities as detected by FTIR, XRD and XRF analysis. The trans-esterification of the waste cooking oil was carried out at constant conditions of temperature 60°C, reaction time of 1.5 hour, methanol to oil (molar) ratio 6:1 and a catalyst loading of 2% weight of oil although with varying 'RPP: CES' catalyst design ratios used. The catalyst design with 'RPP: CES' mixing ratio of 1:3 by mass was found to give the highest FAME yield of 75.04 % and thus is the optimal design ratio.

5.2 RECOMMENDATION

The optimal catalyst design ratio given as 1:3 is recommended in the preparation of the impregnated catalyst to give optimal biodiesel yield for the trans-esterification process at the given operating conditions in a biodiesel plant.

REFERENCES

Abbaszaadeh A, Ghobadian B, Omidkhah MR, *et al.* (2012) Current biodiesel production technologies: A comparative review. Energ Convers Manage **63***:* 138–148.

Abdullah AZ, Razali N, Mootabadi H, Salmatinia B(2007). CriticalTechnical areas for Future Improvement in Biodiesel technologies IOP Publishing, Environ. Res. Lett., p.2.

Andrew C. Eloka-Eboka, Gillian Ogbene Igbum, F.L. Inambao, Biodiesel methyl ester production and testing from selected African tropical seed oil feedstocks, Energy Procedia,Volume142,2017,Pages755767,ISSN18766102,https://doi.org/10.1016/j.pro.2017.12.123 (https://www.sciencedirect.com/science/article/pii/S1876610217358514)

Antonio de la Hoz, Angel Diaz-Ortiz, Andres Moreno; Microwaves in Organic Synthesis, Thermal and Non-thermal microwave effects(2005).https:/doi.org/10.1039/B411438H

Anonim 2009.Biodiesel handling and Use Guide (4th Edition). National Renewable Energy Laboratory. U.S. departmeny of Energy. http://wwwosti.gov/bridge.

Atabani A.E, A.S. Silitonga, Irfan Anjum Badruddin, T.M.I. Mahlia, H.H. Masjuki, S. Mekhilef,A comprehensive review on biodiesel as an alternative energy resource and its characteristics,Renewable and Sustainable Energy Reviews,Volume 16, Issue 4,2012, Pages 2070-2093,ISSN 1364-0321,https://doi.org/10.1016/j.rser.2012.01.003.

Arbeláez, M., & Rivera, M. (2007). Diseño conceptual de un proceso para la obtención de biodiesel a partir de algunos aceites vegetales colombianos. Universidad Eafit. Medellín.

Audu, T.O.K. (2011). Current strides in bioenergy and biofuels technology development in Nigeria. 30th ISES Biennial Solar World Congress 2011, SWC 2011. 2. 1163-1168.

Audu, T.O.K., Matahula,W., Akinsola O.A.,(2018). Performance Evaluation of a Solar Photovoltaic Biodiesel Plant

Azcan N. and Danisman A., 2007. Alkali catalysed transesterification of rapeseed oil. Fuel 87, 1781-1788.

Blauvelt E. World Energy Discussion. Uses of Biomass (2007), http://worldenergydiscussion.Blogspot.com/2007/06/uses-of-biomass.html.

Behzadi S.,Farid M., (2007);Review: Examining the use of different feedstock for the production of biodiesel; Asia-Pacific Journal of Chemical Engineering.2. 10.1002/apj.85Bournay, L., Casanave, D., Chodorge, J., Delfort, D.Y., & Hillion, G. (2005). new heterogeneous process for biodiesel production: a way to improve the quality and the value of the crude glycerin produced by biodiesel plants, France.

Benjumea, P, Benavides, A.Y., & Pashova, V. (2007). El biodiesel de aceite de higuerilla como combustible alternativo para motores diesel, Universidad Nacional De Colombia Sede Medellín.

Buchori l.,Istadi I., Purwanto P; Effects of Weight hourly space velocity and catalyst diameter on performance of hybrid catalytic plasma reactor for biodiesel synthesis over sulphated zinc oxide acid catalyst; Bulletin of Chemical Reaction Engineering and Catalysis 12 (2), 227-234;2017..

Conceicao, M.M., Candeia, R.A., Dantas, H.J., Soledade, L.E.B., Fernandes, V.J. (Jr) and Souza, A.G. 2005. "Rheological Behaviour of Castor Oil Biodiesel". Energy & Fuels 2005. 19(5):2185 – 2188.

Collins A.M., Thomas A Dempster; Analysis and Modeling of Nannochloropsis growth in Lab green house, and raceway experiments; Journal of Applied Phycology 26(6), 2303-2314,2014.

Choe E,Min D.B.; Chemistry of Deep-Fat Frying Oils; July 2007. Journal of Food Science 72(5):R77-86; DOI:10.1111/j.1750-3841.2007.00352.x

Demirbas A (2007) Biodiesel from sunflower oil in supercritical methanol with calcium oxide. Energ Convers Manage 48: 937–941.

Demirbas A (2008) Biodiesel; A Realistic Fuel Alternative for Diesel Engines.

Duarte Carlos M., Wu Jiaping, Xiao Xi, Bruhn Annette, Krause-Jensen;Can Seaweed Farming Play a Role in Climate Change Mitigation and Adaptation; Frontiers in Marine Science(4)2017https://www.frontiersin.org/article/10.3389/fmars.2017.00100 DOI:10.3389/fmars.2017.00100 ISSN=2296-7745

D.W.Green, R.H. Perry, Perry´s chemical engineer´s handbook, 8th Edition, McGrawHill Company, 2007.

Encinar, J.M.; González, J.F.; Rodríguez-Reinares, A. Biodiesel from Used Frying Oil. Variables Affecting the Yields and Characteristics of the Biodiesel. Ind. Eng. Chem. Res. 2005, 44, 5491–5499.

Errazu, A., Marchetti, J.Y., Miguel V. (2005). Possible methods for biodiesel production, Planta Piloto De Ingeniería Química, Argentina.

Etiegni L. Campbell, A. G. (1991): Physical and Chemical Characteristics of wood ash. Bioresource Technology 37:173-178.

Felizardo, P., Correia, M.J.N., Paposo, I., Mendes, J.F. Berkemeier, R., & Bordado, J.M. (2006). Production of biodiesel from waste frying oils. Waste Manage., 26(5), 487-494.

G. Ertl, H. Knozinger & J. Weitkamp, Handbook of Heterogeneous Catalysis, Vol 1, Wiley – VCH, 1997.

Girón, E., Rojas, A. Y., & Torres, H. (2009).variables de operación en el proceso de transesterificaciónde aceites vegetales: una revisión. In: Catálisis Química, Vol 29 No 3.

Guan, G., Kusakabe, K. Y., & Yamasaki, S. (2009). Tri-potassium phosphate as a solid catalyst for biodiesel production from waste cooking oil, Department Of Living Environmental Science, Fukuoka Women's University.

Harvey,P.Adam, Mackley, R.Malcom, Seiliger Thomas, 2003; Process intensification of biodiesel production using a continuous oscillatory flow reactor . Journal of Chemical Technoloy nand Biotechnology, 78:338-341.Doi:10.1002/jctb.782.

Hoekman, S.K.; Broch, A.; Robbins, C.; Ceniceros, E.; Natarajan, M. Review of biodiesel composition, properties, and specifications. Renew. Sustain. Energy Rev. 2012.

H. Scott Fogler, "Elements of Chemical Reaction Engineering", 4th ed, Pearson International Edition, New Jersey, 2006.

H. S. Fogler, Elements of Chemical reaction engineering, Prentice Hall of India, 1999.
Izonfuo W.A. and Omuaru, V.O.T. J. Sci. Food Agric. 45, 333 (1988).

IEA (2012), *Energy Technology Perspectives 2012*, IEA, Paris https://www.iea.org/reports/energy-technology-perspectives-2012

IEA (2017), *World Energy Outlook 2017*, IEA, Paris https://www.iea.org/reports/world-energy-outlook-2017.

J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001.

Jerekias G.Khethiwe E. Clever k., Effects Of Fatty Acids Compositon on Fuel Properties of Jatropha Curcas Biodiesel; Smart Grid and Renewable Energy 11 (10), 165, 2020.

J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997.

J. M. Smith, Chemical Engineering Kinetics, McGrawHill Book Company, 1981.
J.T. Richardson, Principle of catalysts development, Plenum Press, 1989.

Khemani, H. sources of biomass materials (2008), http://www.brighthub.com /environment/renewable-energy/articles/6362.aspx.

Knothe, G. & Steidley, K.R. (2005). Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel, 84(9), 1059-1065.

Koh, M.Y. and Ghazi, T.I.M. (2011) A Review of Biodiesel Production fromJatropha curcas L. Oil, Renewable and Sustainable Energy Reviews, 15, 2240-2251.http://dx.doi.org/10.1016/j.rser.2011.02.01.

Knothe, G. and K.S. Steidly. 2005. “Kinematic Viscosity of Biodiesel Fuel Component and Related Compounds: Influence of Compound Structure and Comparison to Petrodiesel Fuel Components”. Fuel. Elsevier: New York, NY.

K.P. de Jong. , Synthesis of solid catalysts , Wiley –VCH, 2009 • J.T. Richardson, Principle of catalysts development, Plenum Press, 1989.

Kumar, R. R., Rao, P. H., and Arumugam, M. (2015). Lipid extraction methods from microalgae: a comprehensive review. *Front. Energy Res.* 2:291–296. doi: 10.1016/j.biortech.2014.10.030.Ayhan Demirbas (2007) Recent Developments in Biodiesel Fuels, International Journal of Green Energy, 4:1, 15-26, DOI: 10.1080/15435070601015395.

Lam, M.K.; Tan, K.T.; Lee, K. T. ; Mohammed, A.R.,(2009), Malaysian palm oil: Surviving the food versus Fuel Debate for a sustainable future. Renew.Sust. Energ. Rev.,(13) 6-7,1456-1464.

Lapuerta M.; Rodgriguez-Fernandez, J.; Agudelo, J.R., (2008). Diesel particulate emissions from used cooking oil biodiesel. Bioresour. Tech., 99 (4), 731-740.

Liu, P., Ou, S., Wang, Y., & Zhang, Z. (2006a). Preparation of biodiesel from waste cooking oil via two step catalyzed process, Department Of Food Science And Engineering.

Liu, P., Ou, S., Tang, S., Wang, Y. Y., & Xue, F.(2006b) comparison of two different processes to synthesize biodiesel by waste cooking oil, Department Of Food Science And Engineering, Jinan University.

Lidström, P., Tierney, J., Wathey, B., Westman, J. (2001). Microwave assisted organic synthesis - a review. Tetrahedron, 57(589): 9225-9283.

Lles, M., Pires, E., & Royo, C. (2008). Estudio de catalizadores heterogéneos en la síntesis de biodiesel a partir de aceite de girasol.

Mahamuni N.,Adewuyi Y.,(2010). Application of Tanguchi Method to Investigate the bEffects Of Process Parameters on the Transesterification of Soybean Oil Using High Frequency Ultrasound. Energy and Fuels-ENERG FUEL. 24. 10.1021/ef901488g.

Margaroni, D. 1998. “Fuel Lubricity”. Industrial Lubrication and Tribology. 50(3):108-118.

Metzer J.O., (2009),Fats and oils as renewable feedstock for chemistry. Eur.J. Lipid Sci. Tech., 111 (9), 865-876.

Micic RD, Tomić MD, Kiss FE, *et al.* (2014) Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification. Energ Convers Manage 86: 717–726.

Murillo, S.: Miguez, J.L; Porteiro,J.; Granada E.; Moran, J. C., (2007). Performance and exhaust emissions in the use of biodiesel in outboard diesel engines.Fuel. 86 (12-13), 1765-1771.

Niculescu, R.; Clenci, A.; Iorga-Siman, V.; Zaharia, C. Review on the Use of Bioethanol/Biomethanol—Gasoline Blends in Spark Ignition Engine; Sci. Bul. Automot. Ser. Year XXII, No. 26; University of Pites,ti: Pitesti, Romania, 2018.

Noureddini H, Dailey W., Hunt BA, Production of ethers of glycerol from crude glycerol: the byproduct of biodiesel production.

Onyegbado, C.O. Iyagba E.T. and Offor O.J., Journal of Applied Sciences and Environmental Management.

Om Tampanes, N. C., Gomes Aranda, D.A.; de Mosquita Carnneiro, J.W.; Ceva Antunes, O.A., (2008). Transesterification of Jatropha curcas oil glycerides: Theoritical and experimental studies of biodiesel reaction. Fuel, 87 (10-11), 2286-2295.

Parawira,W (2010) Biodiesel production from Jatropha curcas: a review. Sci Res Essays 5:1796-1808

Peterson C., Cook J., Taberski J., 2002; Continuous Flow Biodiesel Production (18), Applied Engineering in Agriculture (18)Doi:10.13031/2013.7702.

Phan A.N. and Phan T.M. 2008. Biodiesel production from waste cooking oils. Fuel. 87, 3490-3496.

Rakopoulos D.,Rakopoulos C.,Gikoumis E., Papagiannakis R., Kyristis D., 202014. Influence of Properties of various common biofuels on the combustion and emission characteristics of High speed DI(Direct Injection) diesel engine:Vegetable oil, biodiesel, ethanol, n-butanol, diethyl ether. Energy. 73. 354-366.10.1016/j.energy.2014.06.032.

Ranganathan, S.V., Narasimhan, S.L., Muthukumar, K. (2008). An overview of enzymatic production of biodiesel. Bioresour. Technol., 99(10): 3975-3981

Rashmi Chandra, M.V. Rohit, Y.V. Swamy, S. Venkata Mohan,Regulatory function of organic carbon supplementation on biodieselproduction during growth and nutrient stress phase of mixotrophic microalgae cultivation, Bioresource Technology, Volume 165, 2014, Pages, 279-287, ISSN09608524; https://doi.org/10.1016/j.biortech.2014.02.102.

Refaat, A.A., (2009). Correlation between the chemical structure of biodiesel and its physical properties. Int. J. Environ. Sci. Tech., 6(4), 677-694.

Ribeiro, N.M., Pinto A.C., Quintella, C.M., da Rocha, G.O. Teixeira, L.S.G., Guareiro, LLN., do Carmo Rangel, M.et al.,2007. The role of additives for diesel and diesel blended(ethanol or biodiesel) fuels: a review. Energy Fuels. 21 (4) 2433-2445.

Rojas, A .Y., & Torres, H. (2009). Variables de operación en el proceso de transesterificación de aceites vegetales: una revisión In: Catálisis Química.

Salamatinia, B., Mootabadi, H., Bhatia, S., Abdullah, A.Z. (2010). Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil : A response surface methodology approach. Fuel Process. Technol., 91(5): 441-448.

Salis A., Pinna M., Monduzzi M., SolinaV.,(2005) Biodiesel Production from triolein and short chain alcohols through biocatalysis. Journal of Biotechnology 1193 September, 2912990168-1656.

Sam Zhang, Lin Li, Ashok Kumar, Materials Characterization Techniques, CRC Press, 2009.

Schwab A, Bagby M, Freedman B (1987) Preparation and properties of diesel fuels from vegetable oils. Fuel 66: 1372–1378.

S. Lowell, Joan E. Shields, Martin A. Thomas ,Characterization Of Porous Solids And Powders: Surface Area, Pore Size And Density - Springer, 2006.

Singh, R. N., Singh, S.P. and Pathak, B.S. 2007. Performance of Renewable Fue lBased CI Engines; Agricultural Engineering International: the CIGR Journal of Scientific Research And Development. Manuscript. EE04 004 vol VI.

Singh, S.P.; Singh, D. Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. Renew. Sustain. Energy Rev. 2010.

Wei Z. Xu C., Xu, and B. Li, "Application of Waste Eggshell as Low-cost solid catalyst for Biodiesel production". Bioresour. Technol., vol 100,no.11, pp 2883-5, Jun. 2009.

Vasudevan, P.T. and Briggs, M. (2008) Biodiesel Production—Current State of the Art and Challenges. Journal of Industrial Microbiology & Biotechnology, 35, 421-430.http://dx.doi.org/10.1007/s10295-008-0312-2.

Vyas, A.P., Verma, J.L., Subrahmanyam, N. (2010). A review on FAME production processes. Fuel, 89(1): 1-9.

Yusuf, N.N.A.N Kamarudin, S.K. Yaakub, Z. Overview on the current trends in biodiesel production Energy Conversion and Management. Volume 52, Issue7, 2011, Pages 2741-2751, ISSN01968904, https://doi.org/10.1016/j.enconman.2010.12.004.

Zahan A.K., Kano M., (2019) Technological progress in biodiesel production: An overview on different types of reactors.Energy Procedia (2019) 156:452-457.

APPENDIX

Calculations for the trial mixing ratios in the catalyst design

Given a trial ratio; a: b; the mass of 'a' = $\frac{a}{a+b}x1g$ and mass of 'b'= $\frac{b}{a+b}x1g$=1-mass of 'a'

For 1:1; mass of calcined RPP = $\frac{1}{1+1}x1g = 0.5g$, mass of calcined CES = 1-0.5= 0.5g; it means a mass of 0.5g of RPP is mixed (doped) with 0.5g of CES.

For 1:2, mass of RPP = $\frac{1}{1+2}x1g$=0.33g, mass of calcined CES= 1-0.33=0.67g, it means 0.33g of RPP is mixed with 0.67g of CES.

For 1:3, mass of RPP = $\frac{1}{1+3}x1g$=0.25g, mass of calcined CES= 1-0.25=0.75g, it means 0.25g of RPP is mixed with 0.75g of CES.

For 1:4, mass of RPP = $\frac{1}{4+1}x1g$ =0.20g, mass of calcined CES= 1-0.20g=0.80g, it means 0.20g of RPP is mixed with 0.80g of CES.

For 2:1, mass of RPP = $\frac{2}{2+1}x1g$ =0.67g, mass of calcined CES= 1-0.67g=0.33g, it means 0.67g of RPP is mixed with 0.33g of CES.

For 3:1, mass of RPP = $\frac{3}{3+1}x1g$ =0.75g, mass of calcined CES= 1-0.75g=0.25g, it means 0.75g of RPP is mixed with 0.25g of CES.

For 4:1, mass of RPP = $\frac{4}{4+1}x1g$ =0.80g, mass of calcined CES= 1-0.80g=0.20g, it means 0.80g of RPP is mixed with 0.20g of CES.