MODIFIED KAOLINITE CLAY AS CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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DECLARATION

I declare that the work in this dissertation titled "MODIFIED KAOLINITE CLAY AS CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL" was carried out by me in the Department of Chemical Engineering, Ahmadu Bello University, Zaria, under the supervision of Dr. Olusegun A. Ajayi and Dr. Bello Mukhtar of the Department of Chemical Engineering, Ahmadu Bello University, Zaria. The information derived from the literature has been duly acknowledged in the text and a list of reference provided. No part of this dissertation was previously presented for another degree in this University or any other Institution.

_____ _____

Signature Date

CERTIFICATION

This dissertation entitled "MODIFIED KAOLINITE CLAY AS CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL" by Victor Dominic TEKU, meets the regulations governing the award of the degree of Master of Science (M.Sc) of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This M.Sc dissertation work is dedicated to my beloved parents, siblings, my wife and children.

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First and foremost, all praise, thanks and adorations to the Almighty God, the creator of the universe for sustaining me to accomplish this degree programme. Without His limitless grace and mercies, this work would not have been realized. For the success of this work and His countless blessings upon my life, I will forever praise Him.

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ABSTRACT

The challenges of continual depletion, economic crisis and environmental issues of the petroleum fuels have attracted the scientists' interest to seek for alternatives to fossil fuels.Biodiesel is the alternative to petrol diesel because; it has similar physicochemical properties to petrol diesel. However, biodiesel has not been competing favourably well economically with petrol diesel due to high cost of production.In this work, biodiesel was produced from waste cooking oil (WCO) using modified kaolinite clay as a heterogeneous acid catalyst. Kaolinite clay sourced from Kankara town in Katsina State was beneficiated, calcined and acidified to produce the catalyst. The catalyst was characterised using X-ray Fluorescence(XRF), X-ray Diffraction(XRD) and Scanning Electron Microscopy(SEM).The effect of the following variables namely: Silica to alumina mass ratio, reaction temperature, methanol to oil ratio, reaction time and catalyst dosage were studied. Important fuel properties such as viscosity, acid value, density and flash point were determined and compared with ASTMD6571 standard for biodiesel. The catalyst was found to retain its catalytic properties even after reuse for four runs. The optimum conditions for biodiesel production were; reaction temperature of60°C, amount of catalyst of 4wt %, methanol to oil molar ratio of 15: 1 and reaction time of 120 min. The optimum yield of biodiesel was 92.7%. The results showed that the important fuel properties of the biodiesel produced at optimum conditions;viscosity (2.5cP), acid value (0.35), cetane number (53.7), flash point (154^0C) and density ($0.86 g/cm^3$)met the biodiesel ASTM D6571 standard.

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LIST OF SYMBOLSANDABBREVIATIONS

θ	Diffraction angle (^{o})
λ	Wave length (Á)
AIPEA	Association Internationale Pour I' Etude des Argiles
AV	Acid Values (mgKOH/g)
BSE	Backscattered Electrons
CEC	Cation Exchange Capacity
CP	Cloud Point (℃)
CSTRs	Continuous Stirred Tank Reactors
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectrophotometer
ICRISAT	International Crops Research Institute for the Semi-Arid-Tropics
JNCs	Joint Nomenclature Committees
MeOH	Methanol
MIN	Minute
MW	Megawatt
NGRL	National Geological Research Laboratory
NM	Nanometer
NR50	Nafion®
PFR	Plug-Flow Reactor
PP	Pour Point (℃)
RGFR	Renewable global futures report
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
SiO_2	Silica

SV	Saponification Values	(mgKOH/g)
SZ	Sulphated Zirconia	
THF	Tetrahydrofuran	
WCO	Waste Cooking Oil	
WZ	Tungstated Zirconia	
XRD	X-Ray Diffraction	
XRD	X-ray Diffraction	
XRF	X-ray Fluorescence	

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

The production of sustainable alternative fuels is attracting increasing academic and industrial interest. Biodiesel, a non-petroleum-based, is one of these sustainable fuels and has many advantages such as low emissions, biodegradability and better lubricity (Jacobson *et al.,* 2008). Biodiesel consists of alkyl esters derived from either the transesterification of triglycerides (TG) in oils and fats or the esterification of free fatty acids (FFA) with short-chained alcohols (Boz*et al.,* 2009). The production of biodiesel by transesterification has a drawback because the utilization of high FFA feeds in traditional biodiesel production processes leads to depletion of the catalysts, as well as increased purification costs, because the FFA is saponified by the homogeneous alkaline catalyst, producing excess soap (Zheng*et al.,* 2006). Esterification of FFA to alkyl esters in the presence of an acidic catalyst is a route to improve the use of high FFA oils in biodiesel production (Carmo*et al.*, 2009).

Waste cooking oil (WCO) has nowadays been reckoned among the liquid wastes which are generated daily from various sources comprising households, restaurants, catering establishments, and industrial kitchens (Castellanelli*et al*., 2008).Due to the heat that is usually applied in frying processes, the physical and chemical features of the cooking oil change from their original form (Cvengroš*et al*., 2004, Azman*et al*., 2012). Waste cooking oil which is expected to be treated and managed in a manner that could not be detrimental to the human health and/or the environment, is being disposed of by consumers via sinks, waste bins, drainage systems, toilets, or directly to the immediate water bodies and lands.

According to Chhetri*et al*., (2008) a greater quantity of WCO generated all over the world is being released into theenvironment. This act in the long run contributes to water and soil contamination, causes aquatic life distraction, sewer system blockages and overflow, increases water treatment and waste management cost, and consequently generates undesirableimpacts to the entire environmental system(Chen*et al*., 2009).

Esterification is normally carried out in a homogeneous phase in the presence of acid catalysts such as H_2SO_4, HF, H_3PO_4, HCl and p-toluene sulfonic acid (Carmo*et al*., 2009; Srilatha*et al.*,2009). This pretreatment step has been successfully demonstrated using sulfuric acid (Marchetti and Errazu, 2008). Unfortunately, the use of the homogeneous sulfuric acid catalyst adds neutralization and separation steps, as well as the esterification reaction, to the synthetic process (Mbaraka*et al.*, 2003). Moreover, these catalysts are hazardous and corrosive liquid acids (Srilatha*et al.,* 2009). Therefore, heterogeneous catalysts can be considered as an alternative to minimize environmental damage and reduce biodiesel cost.

There has been tremendous upsurge of interest in the use of different heterogeneous and environment friendly catalysts for various organic transformations (Sartori *et al.,* 2004). In recent years, such catalysts can help to minimise waste production, render the synthetic process more attractive from both the environment and process economic point of view. The solid catalysts can be easily separated from the reaction products by simple filtration and quantitatively recovered in the active form. As they can be recycled, the process becomes less expensive and at the same time the contamination of the products by trace amount of metals is avoided, as in the case of Lewis acid catalyst.

There are several works that deal with the production of catalysts using sulfonated carbons (Liu *et al.,* 2008; Mo *et al.,* 2008), modified zirconias (López*et al.,* 2008), mesoporous sulfonic acid (Mbaraka and Shanks, 2006) and heteropoly acid-based catalysts (Xu*et al.,* 2009). However, there are few studies on the use of clay-based catalysts in the esterification of fatty acids. One such study is a report by Kantam*et al.,* (2002) where Fe^{3+}-montmorillonite was used for the esterification of stearic acid with methanol. Clay catalysts are interesting materials not only because of the low cost of their raw materials (Vaccari, 1999), but also because they are less harmful to the environment (Rezende, 2006). In addition, acid activation is one of the modifications that can be made in clays (Araújo*et al.,* 2000; Flessner *et al.,* 2001). This causes the disaggregation of clay particles, elimination of impurities and dissolution of external layers, altering the chemical composition and the structure of clays (Belver*et al.,* 2002).

The main consequences of acid activation are increases in surface area, porosity and number of acidic sites compared to the parent clays (Lenarda*et al.,* 2007). Acid treated montmorillonites are offered from various companies as catalysts for hydrocarbon cracking, such as the well-known commercial montmorillonite clay K-10, whose surface acidity and catalytic activity can be enhanced considerably through exchange with transition metal ions (Centi and Perathoner, 2008). However, the catalytic activity of another major group of clay minerals, kaolinite, remains poorly studied. Considering the facts stated above, this work focuses on the preparation, characterization and catalytic tests of acid-activated metakaolins prepared from Kankara kaolinite clay to carry out bothesterification andtransesterification of waste cooking oil with methanol in a single step.

1.2 Problem Statements

Homogeneous catalysts used in the production of biodiesel makes the cost of production high due to extra cost of product purification. These catalysts are not eco-friendly and are also corrosive.

Globally, conventionally grown edible oils are the major feedstocks used for biodiesel production. This causes an imbalance between their utilisation as energy sources and food consumption and contributes to the higher cost of biodiesel feedstocks.

1.3 Aim and Objectives

This work is aimed at developing a solid acid catalyst using Kankara kaolinite clay for biodiesel production.The objectives were to:

1. beneficiate, calcine and acidify Kankara kaolinite clay to produce the catalyst for biodiesel production.
2. characterisethe acid catalyst produced using SEM, XRF and XRD techniques.
3. characterization of waste cooking oil
4. study the effect of operating conditions on the yield of biodiesel produced.
5. conduct catalyst reusability test.
6. characterization of biodiesel produced.

1.4 Justifications

The cost of catalyst production influences the overall cost of biodiesel production, therefore there is need to used cheap and readily available locally sourced materials for their

production. Nigeria is richly blessed with abundant locally sourced kaolinite clay; this can be utilized for catalyst production to boost the economic value of the natural resources.

Solid acid catalysts are environmental friendly compared to homogeneous acid catalysts and are also easy to produce. The use of solid catalyst helps in cutting down the cost of purifying the biodiesel produced.

Utilization of waste cooking oil for biodiesel production will add value to it and reduce environmental pollution caused by improper disposal of the oil and the health challenges associated with its consumption.

1.5 Scope

The scope of this research work was limited to, synthesis and characterization of solid acid catalyst using kaolinite clay from Kankara, Kankara local government area, Katsina State. The performance of the catalysts produced wereevaluatedby producing biodiesel using waste cooking oil sourced from a food vendor in Romi, Chikun local government area, Kaduna State. Study of the effect of Si/Al ratio, contact time, reaction temperature, catalyst dose and oil to methanol ratio on the production of biodiesel as well as characterization of the biodiesel produced.

CHAPTER TWO

2.0 LITERATURE REVIEW

This section reviews theexisting methods of producing biodiesel, beginning with information on renewable energy, biodiesel, feedstock for production and current catalysed and non-catalysed production processes, heterogenous acid catalysts used in biodiesel production, clay mineral, kaolin clay, characterisation of solid catalyst and fuel properties of biodiesel were discussed.

2.1 Renewable Energy

Renewable energy is generally defined as energy that comes from resources which are naturally replenished on a human timescale such as sunlight, wind, rain, tides, waves and geothermal heat (Gerpen*et al.,* 2004). Renewable energy can replace conventional fuels in four distinct areas: electricity generation, hot water/space heating, motor fuels, and rural (off-grid) energy services.

About 16% of global final energy consumption presently comes from renewable resources, with 10% of all the energy from traditional biomass, mainly used for heating, and 3.4% from hydroelectricity. New renewable (small hydro, modern biomass, wind, solar, geothermal, and biofuels) account for another 3% and are growing rapidly (Edwin, 2011). At the international level, at least 30 nations around the world already have renewable energy contributing more than 20% of energy supply. National renewable energy markets are projected to continue to grow strongly in the coming decade and beyond (Renewable global futures report 2013).Wind power, for example, is growing at the rate of 30% annually, with a worldwide installed capacity of 282.5gigawatts (GW) at the end of 2012. Biofuels include a wide range of fuels which are derived from biomass. The term covers solid biofuels, liquid biofuels, and gaseous biofuels (Demirbas, 2009). Liquid biofuels include bioalcohols, such as bioethanol, and oils, such as biodiesel. Gaseous biofuels include biogas, landfill gas and synthetic gas.

Bioethanol is an alcohol made by fermenting the sugar components of plant materials and it is made mostly from sugar and starch crops. These include maize, sugar cane and, more recently, sweet sorghum. The latter crop is particularly suitable for growing in dry land conditions, and is being investigated by the International Crops Research Institute for the Semi-Arid-Tropics (ICRISAT) for its potential to provide fuel, along with food and animal feed, in arid parts of Asia and Africa (New Agriculturist Report, January, 2008).

With advanced technology being developed, cellulosic biomass, such as trees and grasses, are also used as feedstocks for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil (Pinto *et al*., 2005).

2.2 Biodiesel

Biodiesel is made from vegetable oils, animal fats or recycled greases. Biodiesel can be used as a fuel for vehicles in its pure form, but it is usually used as a petro-diesel additive to reduce levels of particulates, carbon monoxide, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using transesterification and is a common biofuel in Europe.

It is safe, biodegradable, and produces less air pollutants than petroleum-based diesel. Biodiesel can be used in its pure form (B100) or blended with petroleum diesel. Common blends include B2 (2% biodiesel), B5, and B20. Most vehicle manufacturers approve blends up to B5, and some biodiesel approve blends up to B20 (Haq*et al*., 2008).

2.3 Feedstocks for Biodiesel Production

Biodiesel can be produced from a variety of bio-lipids. The choice of feedstock for biodiesel production depends greatly on climate, local soil conditions and availability; consequently different regions are focusing their efforts on different types of oil. Mostly, the raw materials of

biodiesel are soybean oil, sunflower oil, Cottonseed oil, palm oil, palm kernel oil, coconut oil (copra), groundnut oil, rapeseed oil and canola oil (Pinto *et al.*,2005). Beef and sheep tallow and poultry oil from animal sources as well as waste cooking oil are also sources of raw materials (Montefri, Tai and Obbard, 2010). Other biodiesel feedstock sources include: neem seed, Jatropha, almond, barley, camelina (Camelina sativa), fish oil, karanja (Pongamiaglabra), laurel, oat, poppy seed, okra seed, rice bran, sesame, sorghum and wheat (Anwar *et al.*, 2010 and Altun, 2011). The fatty acid composition of the triglyceride used for the production of biodiesel determines the physical and chemical properties of the fatty acid methyl or ethyl esters produced. Most biodiesels are produced from food- grade oils and are referred to as first generation biodiesel. With vegetable oil price soaring high in recent years, the cost of producing biodiesel will keep rising since the feedstock acquisition currently accounts for over 80% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry (Meng*et al.*, 2009). Biodiesel will lose its competitive advantage due to high price coupled with problems associated with the impacts on food security and land change. To mitigate these challenges, scientists are developing a new generation of biodiesel feedstocks of varying type, quality, and cost to help avoid such problems. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. Also, genetic modification is employed to obtain favourable traits of biodiesel crops, such as higher yields or the ability to grow on non-arable land (Zhang *et al.*, 2010 and Boakye, 2013).

2.3.1 Waste cooking oil (WCO)

Waste cooking oil and the non-edible seeds oil are potential feedstocks for biodiesel production. Waste cooking oil (WCO) refers to vegetable oil which has been used in food production and

which is no longer viable for its intended use. Thus, the waste output of a process is often someone else's raw input material. WCO arises from many different sources, including domestic (home), commercial (restaurants, eateries) and industrial (hotels). WCO is a potentially problematic waste stream which requires to be properly managed. The disposal of WCO can be problematic when disposed incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conducive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways (Szmigielski*et al.,* 2008).

The origin of WCO determines its fatty acid compositions while history or duration that oil exposed to heat, food, and oxygen during cooking determines the oil's physical and chemical properties such as viscosity, water content, and FFA content. Oil degradation during cooking occurs through three main reactions: thermolytic, oxidative, and hydrolytic reactions (Issariyakul and Dalai, 2014). As a result of combination of these reactions during food preparation, various reaction derivatives are formed leading to an increase in polar content of the oil. It is advisable that used cooking oil should no longer be utilized for edible purpose when its polar content exceeds 25% (Kulkarni and Dalai, 2006). This concern has raised interests in utilizing used cooking oil as feedstock for biodiesel production.

Estimated amount of waste cooking oil (WCO) being generated in some countries has been reported (Carter *et al.,* 2005; Kulkarni and Dalai, 2006; Chhetri*et al.,* 2008).Unfortunately, published data from Sub-Sahara Africa is not available. However, given Nigeria's current population size of over 170 million people and as such, there is an increase in the rate at which fast food companies, restaurants and hotels are being set up. The large amount of WCO

generated from these establishments on a daily basis can now be sold at a cheap price to biodiesel manufacturers. The use of waste vegetable oil will eradicate the environmental problems posed by the improper disposal of such waste and in turn reduce the overall cost of biodiesel production. Ibifubara*et al*., 2014 reported that the use of WCO as feedstock reduces biodiesel production cost by about 60 – 70% because the feedstock cost constitutes 70-95% of the total cost of biodiesel production. Therefore, to promote the global commercialization of biodiesel, low-cost non-edible oils and waste vegetable oils should be employed as feedstocks.

2.4 Biodiesel Production Processes

2.4.1 Batch processing

The simplest method for producing alcohol esters is to use a batch, stirred tank reactor. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole: mole) have been reported in several work done, with a 6:1 ratio most common (Sharma *etal*., 2008). The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65°C, although temperatures from 25 to 85°C have been reported (Gerpen,2005). The most commonly used catalyst is sodium hydroxide, with potassium hydroxide also used. Typical catalyst loadings range from 0.3 to 1.5% (Clement *et al.,*2004). Thorough mixing is necessary at the beginning of the reaction to bring the oil, catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester –oil phase. A conversion of 85 to 94 % can be obtained (Gerpen, 2005). Some research groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to 95% and above (Sharma *et al*., 2008). Higher temperatures and higher alcohol: oil ratios also can enhance the percent completion. Typical reaction time ranges from 20 min to more than1 h (Sharma *et al*., 2008).

Figure 2.1 shows a process flow diagram for a typical batch system. The oil is first charged to the system, followed by the catalyst and methanol. The system is agitated during the reaction time. Then agitation is stopped. In some processes, the reaction mixture is allowed to settle in the reactor to give an initial separation of the esters and glycerol. In other processes the reaction mixture is pumped into a settling vessel, or is separated using a centrifuge.

The alcohol is removed from both the glycerol and ester stream using an evaporator or a flash unit. The esters are neutralized, washed gently using warm, slightly acid water to remove residual methanol and salts, and then dried. The biodiesel producedis then transferred to storage. The glycerol stream is neutralized and washed with soft water. The glycerol is then sent to the glycerol refining section.

For yellow grease and animal fats, the system is slightly modified with the addition of an acid esterification vessel and storage for the acid catalyst. The feedstock is sometimes dried (down to 0.4% water) and filtered before loading the acid esterification tank. The sulfuric acid and methanol mixture is added and the system is agitated. Similar temperatures to transesterification are used and sometimes the system is pressurized or a co-solvent is added. Glycerol is not produced. If a two-step acid treatment is used, the stirring is suspended until the methanol phase separates and is removed. Fresh methanol and sulfuric acid is added and the stirring resumes (Sharma *et al*., 2008).

Once the conversion of the fatty acids to methyl esters has reached equilibrium, the methanol/water/acid mixture is removed by settling or with a centrifuge. The remaining mixture is neutralized or sent straight into transesterification where it will be neutralized using excess

base catalysts. Any remaining free fatty acids will be converted into soaps in the transesterification stage (Lateef, 2010).

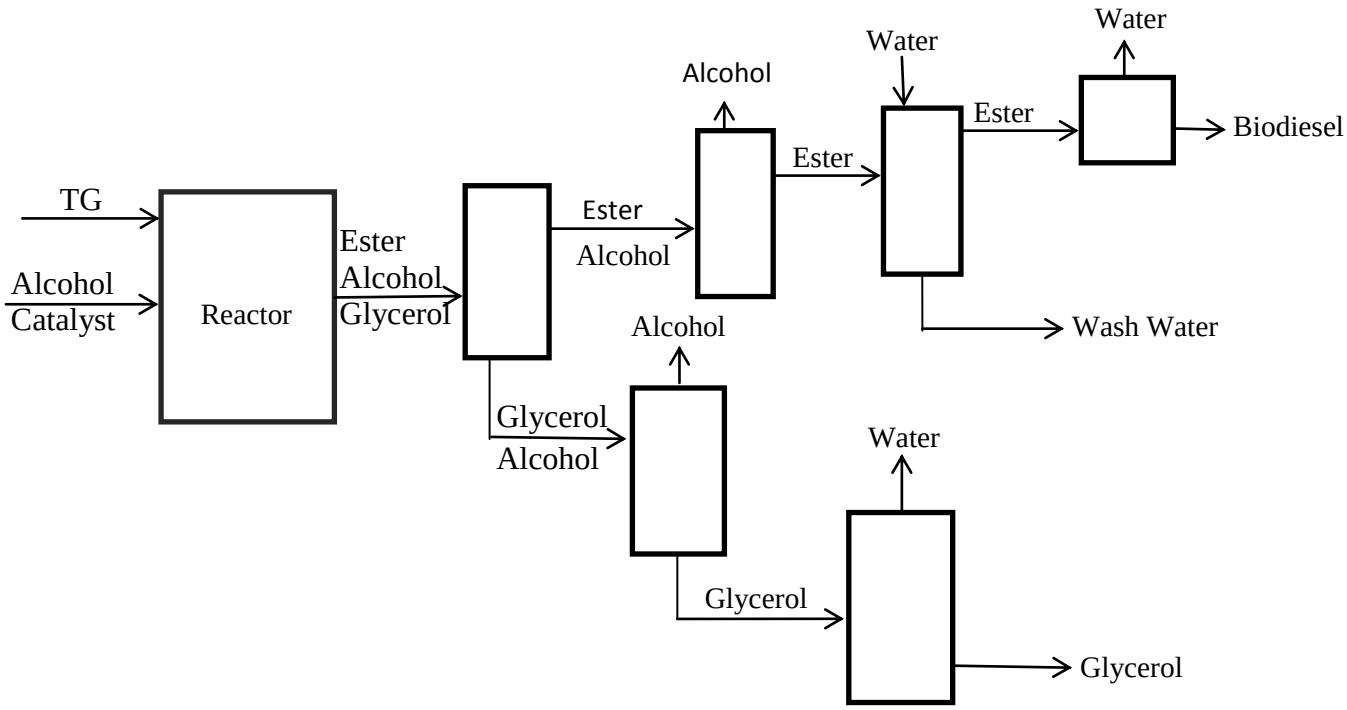


Figure 2.1 Batch Reaction Process (Lateef, 2010)

2.4.2 Continuous process systems

A popular variation of the batch process is the use of continuous stirred tank reactors (CSTRs) in series. The CSTRs can be varied in volume to allow for a longer residence time in CSTR 1 to achieve a greater extent of reaction. After the initial product glycerol is decanted, the reaction in CSTR 2 is rather rapid, with 98% and above conversion common (Clement *et al*., 2004).

An essential element in the design of a CSTR is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of the glycerol product in the ester phase. The result is that the time required for phase separation is extended (Gerpen*et al.*, 2004).

There are several processes that use intense mixing, either from pumps or motionless mixers, to initiate the esterification reaction. The reaction mixture moves through this type of reactor in a continuous plug, with little mixing in the axial direction. This type of reactor, called a plug-flow reactor (PFR), behaves as if it were a series of small CSTRs chained together (Gerpen*et al.*, 2004).

The result is a continuous system that requires rather short residence times, as low as 6 to 10 min, for near completion of the reaction. The PFRs can be staged, as shown in Figure 2.2, to allow decanting of glycerol. Often this type of reactor is operated at an elevated temperature and pressure to increase reaction rate. A PFR system is shown in Figure 2.2

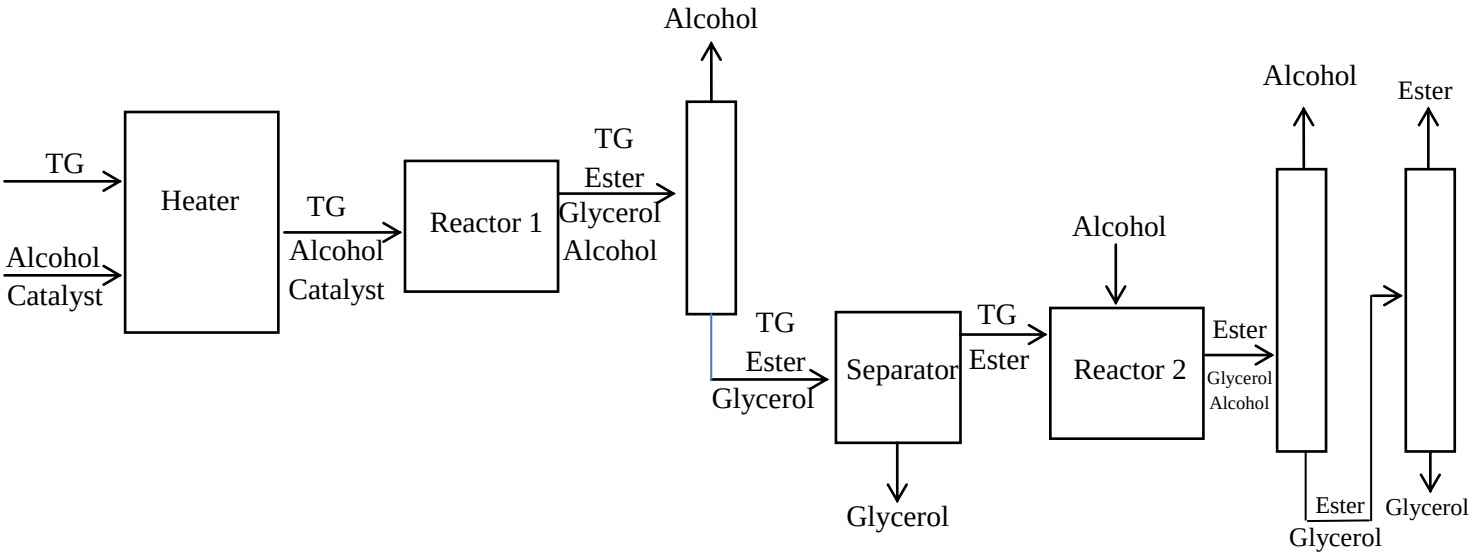


Figure 2.2 Plug Flow Reaction System (Lateef, 2010)

2.4.3 Esterification process

Esterification is a reversible reaction, which occurs by the reaction of carboxylic acids (fatty acids) and alcohols in the presence of catalyst, resulting in the formation of water and an ester product as shown in Equation 2.1. Dias *et al.,* 2008 reported that the study of esterification reaction is necessary to enable biodiesel production from acid raw materials be more cost effective.

$$\underset{FFA}{RCOOH} + \underset{Methanol}{CH_3OH} \overset{Catalyst}{\rightleftharpoons} \underset{Methylester}{RCOOCH_3R} + \underset{Water}{H_2O} \quad (2.1)$$

This reaction is of great importance not only to the possible increase on the biodiesel production, but also because it will affect the properties of future biodiesel (Marchetti*et al.,* 2007). In addition to transesterification of triglyceride, biodiesel can be produced from free fatty acids through esterification. Triglyceride is a type of ester and the reaction that converts triglyceride into biodiesel is known as transesterification (transforming ester). In contrast, free fatty acid is not an ester and therefore the reaction to produce biodiesel from FFA is called esterification which can be termed as making esters (Issariyakul and Dalai, 2014).

2.4.4 Transesterification process

Transesterification, also known as alcoholysis, is the conventional methodology for biodiesel production. It involves the displacement of alcohol from an ester by another alcohol in a process akin to hydrolysis, except that an alcohol is used instead of water as shown in Equation 2.1. The product of the reaction is a mixture of alky esters which are known as biodiesel and glycerol. This process has been extensively used to nosedive the viscosity of triglycerides. Meanwhile, it is a reversible reaction which proceeds essentially via the mixing of triglycerides and alcohols in

the presence of a catalyst. Stoichiometrically, one mole of triglyceride requires one mole of alcohol in transesterification but in order to preclude reversible reaction to occur, excess alcohol is usually used to shift the equilibrium towards the formation of the esters, according to Le Chateliers principle (Veljkovic, 2012).

$$\begin{array}{l} H_2C-OCOR' \\ | \\ HC-OCOR'' \\ | \\ H_2C-OCOR''' \end{array} + 3\ ROH \xrightleftharpoons{\text{Catalyst}} \begin{array}{l} ROCOR' \\ + \\ ROCOR'' \\ + \\ ROCOR''' \end{array} + \begin{array}{l} H_2C-OH \\ | \\ HC-OH \\ | \\ H_2C-OH \end{array} \qquad (2.2)$$

Triglyceride Alcohol Alky esters Glycerol

Several primary alcohols have been used for biodiesel production. These include methanol, ethanol, Isopropanol and butanol (Gerpen*et al.,* 2004). The choice of which alcohol to use is determined by its cost, water content, case of recovery for recycle and the quantity required. High water content can lead to poor esterification reaction resulting in high yield of free fatty acids and soap. Methanol is most commonly used in transesterification mainly due to its economic benefits (Ma and Hanna, 1999). The choice of methanol can also be attributed to its short carbon chain length and less propensity to saponify thereby, increase the ester yield as well as reduce consumption of the catalyst, when compared to other alcohols (Issariyakul*et al.,* 2006; Mendow*et al.,* 2011).

2.4.4.1 *Base catalysis/transesterification*

Biodiesel production requires a feed stock (fat or oil) and an alcohol. In most cases, a catalyst also is present. Depending on the quality of the feedstock, either esterification or transesterification reactions are used for biodiesel production. Most of the current biodiesel

production operations use base catalysis (transesterification). This method works well if the free fatty acid, moisture and phosphorous contents of oil/fat are less than 0.1% and less than 10 ppm, respectively. Typical feedstocks for biodiesel production are soybean, canola/rapeseed, sunflower, cottonseed, palm seed and palm kernel, corn and mustard seed oil. Pork, beef and poultry fat and grease also can be converted to biodiesel. Palm oil and animal fat may have a high free fatty acid content, which causes soap formation that has adverse effects on downstream processing and leads to yield reduction.

Sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH_3ONa) are the most common catalysts for transesterification. Sodium methylate (sodium methoxide) is more effective than NaOH and KOH as a catalyst, but it is more expensive. Sodium methoxide is sold as a 30% solution in methanol for easier handling. Base catalysts are very sensitive to the presence of water and free fatty acids. The amount of sodium methoxide required is 0.3 to 0.5% of the weight of the oil. A higher amount of catalyst (0.5 to 1.5% of the weight of the oil) is required when NaOH or KOH is used. NaOH and KOH also lead to water formation, which slows the reaction rate and causes soap formation (Nurhan, 2012).

Saponification is one of the side reactions affecting the yield of biodiesel from vegetable oil. The production of soap, sometimes called alkaline hydrolysis, converts tri-alkylglycerols to glycerol and form a mixture of salts of long chain carboxylic acids. The saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water is shown in Equation 2.3

$$\underset{FFA}{RCOOH} + \underset{Catalyst}{NaOH} \quad \underset{Soap}{RCOONa} + \underset{Water}{H_2O} \qquad (2.3)$$

Methanol is the most common alcohol used for conversion of fats and oils to biodiesel. Methanol is flammable, so proper handling is required for safety. Transesterification is a reversible reaction, thus excess methanol is required to shift the equilibrium favourably.

Table 2.1 shows approximate amounts of oil, alcohol and catalyst required and the amount of biodiesel and glycerine produced through transesterification. Theoretical biodiesel yields for biodiesel produced from soybean and tallow are 1004.2 kg/1000 kg soybean and 998.1 kg/1000 kg tallow respectively. The amount of methanol in Table 2.1 is based on 100% excess, and the data are for transesterification using sodium methoxide as a catalyst (Nurhan, 2012).

Methanol and oil do not mix well, and the poor contact between the oil and methanol reactants means the reaction rate is slow. Vigorous mixing at the beginning of the reaction improves reaction rates. Near the end of the reaction, reduced mixing helps the separation of glycerine and the reaction would proceed faster in the top layer, which is oil and methanol. At ambient temperature (21 ℃ or 70 °F), the reaction takes four to eight hours to complete (Lotero*et al*., 2005). The reaction is usually conducted below the boiling point of methanol (60 ℃ or 140 °F). At this temperature, the reaction time may vary between 20 – 90 min. A higher temperature will decrease reaction times, but this requires use of a pressure vessel to prevent the evaporation of methanol which has boiling point of 65℃ or 148°F. The reactor is either sealed or equipped with a condenser to minimize alcohol evaporation during the conversion process. Higher oil conversion rates can be achieved if the production system is set up as a two-step process with two reactors. In such cases, glycerine formed in the first reactor is removed, and the reaction is completed in the second reactor.

Table 2.1 Approximate reactant and product amounts for transesterification reaction. Chemicals/Feedstock/Product Amount (lbs)

Chemicals / Feedstock / Product	Amount (lbs)
Oil / fat	100
Methanol	22
Catalyst	0.3 – 0.5
Biodiesel	100
Glycerine	11
Excess methanol	11

Nurhan, 2012.

2.4.4.2 *Acid catalysis*

If the free fatty acid content of the feedstock is greater than 1%, base catalysis is not suitable. There are two approaches for handling high free fatty acid content feedstock. One way would be to refine the feedstock before base catalysis. Free fatty acids can be removed by chemical neutralization or physical deacidification. Chemical neutralization involves treatment with caustic (NaOH or KOH). Soap formed during this process is removed, and the remaining oil is ready for base catalysis. Physical deacidification, or steam stripping, also removes free fatty acids. This process is performed under vacuum and requires steam.

Fats and oils with high free fatty acid content can be converted to biodiesel using acid catalysis, which is the second approach for handling high free fatty acid content feedstock. This technique uses a strong acid (Aranda*et al*., 2008).

Soap formation is not a problem because there are no alkali metals in the reaction medium. Acid catalysts can be used for transesterification of the triglycerides, but the reaction might take several days to complete. Acid catalysis also is used for direct esterification of oils with high free fatty acid content or for making esters from soap stock, which is a byproduct of edible oil refining. The esterification of free fatty acids to alcohol esters is relatively fast; it would take about one hour at 60 ℃ to complete the reaction. Water is formed during this reaction. To improve reaction rates, water needs to be removed from the reaction medium by phase separation(Lam *et al*., 2010).

Acid catalysis requires a high alcohol to free fatty acid ratio (20:1 or 40:1 mole ratio) and large amount of catalyst (5 – 25%). Sulphuric acid and phosphoric acid are the most common acid catalysts. The feedstock is sometimes dried to 0.4 % water and filtered before the reaction. Then,

an acid and methanol mixture is added to the feedstock. Once the conversion of the fatty acids to methyl esters has reached equilibrium, the methanol, water and acid mixture is removed by settling or centrifugation. Fresh methanol and base catalyst are added into the remaining oil for transesterification. The rest of the process is the same as base catalysis. Reaction times of 10 to 120 min have been reported (Winardi*et al*., 2012).

Both transesterification and esterification reactions can be operated either as a batch or continuous process. A batch process is better suited to smaller plants that produce less than 1 million gallons per year and provide operation flexibility. Continuous processing allows use of high-volume separation systems, and therefore increases throughput.

2.4.4.3 *Enzymatic conversion*

There is interest in using lipases for enzymatic catalysis of oils for biodiesel production. The enzymes can be used in solution or immobilized onto a support material, which allows the use of fixed-bed reactors. The reaction can be performed at 35 to 45 ℃.

However, the reaction is very slow, requiring from 4 to 40 h. The major problems of enzyme-catalysed biodiesel production process are high cost of enzymes, low conversion efficiency, rapid deactivation of enzymes and thermal instability of enzymes (Christopher*et al*., 2014).

2.4.4.4 *Solid catalyst*

The processes discussed above, is referred to as homogeneous catalysis. It involves utilization of a catalyst that is soluble in alcohol. In these systems the catalyst ends up in the by-products, and it is not recovered for re-use. There are also solid catalysts that can be used for biodiesel production. This process, which is referred to as heterogeneous catalysis, utilizes fixed-bed reactors, and the catalyst stays in the reactor and is used for an extended time. Sulphuric resins

such as Nafion® NR50, sulphated zirconia (SZ) and tungstated zirconia (WZ) have sufficient acid site strength to catalyze biodiesel forming transesterification reactions as efficiently as sulphuric acid (Su *et al*., 2014). Alkaline earth metal oxides, various alkaline metal compounds supported on alumina or zeolite can catalyse transesterification reactions. In general, heterogeneous catalysis systems are designed for continuous operation and produce high-purity glycerine (greater than 98%). The product, fatty acid esters, does not require water washing, and yields are generally high. It also has been reported that catalyst requirements per ton of biodiesel for heterogeneous catalysis are much lower than for other processes (Sheikh *et al*., 2013). However, these systems operate under high temperature and pressure.

2.4.5 Non-catalyzed systems

2.4.5.1 *Biox process*

Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in thetriglycerine (TG) phase. One approach that is nearing commercialization is the Biox process. This process uses a co-solvent, tetrahydrofuran (THF), to solubilise the methanol. The result is a fast reaction, on the order of 5 to 10 min, and no catalyst residues in either the ester or the glycerol phase. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. After the reaction is complete, the excess methanol and the tetrahydrofuran co-solvent are recovered in a single step. This system requires a rather low operating temperature, 30°C. Other co-solvents, such as MTBE, have been investigated(Gerpen, *et al*., 2004). The ester-glycerol phase separation is clean and the final products are catalyst and water free. The Biox process is depicted by Figure 2.3.

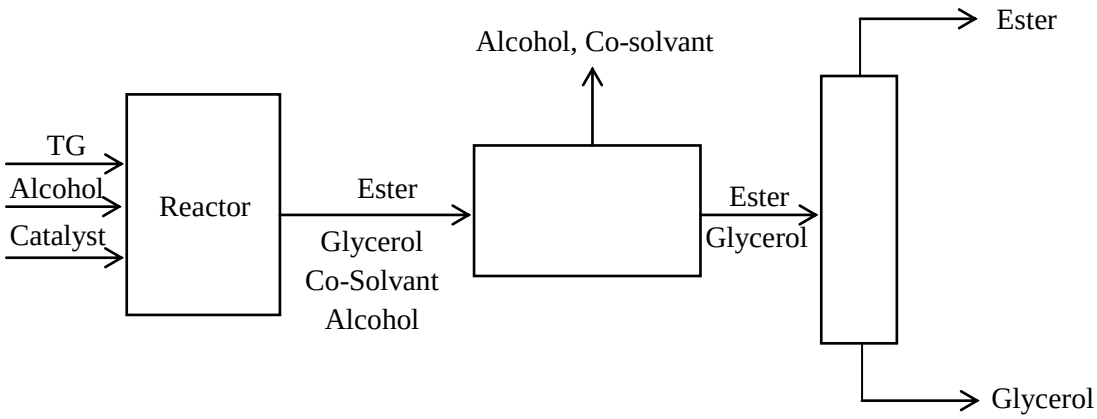


Figure 2.3 Biox co-solvent process (Gerpen*et al*., 2004)

2.4.5.2*Supercritical process*

When a fluid or gas is subjected to temperatures and pressures in excess of its critical point, there are a number of unusual properties exhibited. There no longer is a distinct liquid and vapour phase, but a single, fluid phase present. Solvents containing a hydroxyl (OH) group, such as water or primary alcohols, take on the properties of super-acids (Saifuddin*et al*., 2015).

A non-catalytic approach is the use of a high (42:1) alcohol to oil ratio. Under supercritical conditions (350 to 400°C and > 80 atm or 1200 psi) the reaction is complete in about 4 min. Capital and operating costs can be more expensive, and energy consumption higher (Marchetti*et al.*, 2013).

An intriguing example of this process has been demonstrated in Japan, where oils in a very large excess of methanol have been subjected to very high temperatures and pressures for a short period of time. The result is a very fast (3 to 5 min) reaction to form esters and glycerol. The reaction must be quenched very rapidly so that the products do not decompose. The reactor used in the work to date is a 5 ml cylinder that is dropped into a bath of molten metal, and then quenched in water.

Clearly, while the results are very interesting, the scale-up to a useful process may be quite difficult(Saka and Minimi., 2006). Figure 2.4 depicts one conception of a configuration for a supercritical esterification process.

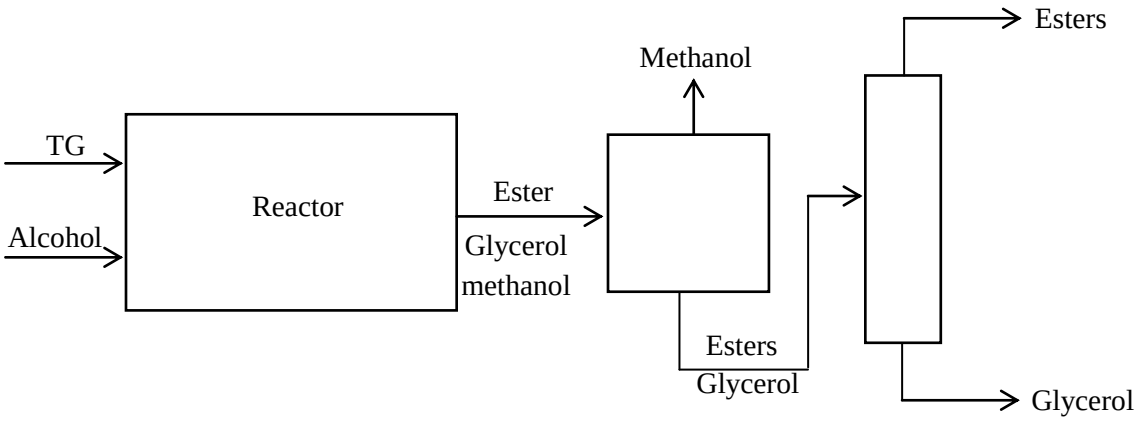


Figure 2.4 Supercritical Estherification Process (Saka and Minimi., 2006)

2.5 Heterogenous Acid Catalysts used in Biodiesel Production

In general, a catalyst that is to be used for synthesis of biodiesel should be selective, specific, and result in esterification / transesterification with high conversion and yield of biodiesel. A solid acid catalyst should possess high stability, numerous strong acid sites, large pores, a hydrophobic surface providing a favourable condition for reaction, and should also be economically viable.

2.5.1 Reaction mechanism of solid acid catalyst

Solid acid catalysts are point of interests in producing biodiesel from different feedstocks as they can catalyze esterification and transesterification reactions in producing biodiesel (Kulkarni*et al*., 2006). The overall reaction mechanism of heterogeneous (solid) acid catalyzed esterification and transesterification reaction are depicted in Figure 2.5.

The free fatty acids (RCOOH) and methanol (CH_3OH) take part in esterification reaction, whereas glycerides (RCOOR') and methanol take part in the transesterification reaction. The carbonyl oxygen of free fatty acid or glyceride interacts with the acidic site of the catalyst to form carbocation. Then a tetrahedral intermediate is produced by the nucleophilic attack of alcohol to the carbocation. In the esterification reaction, this tetrahedral intermediate formation generates one mole of water during rearrangement and formation of one mole of ester ($RCOOCH_3$), and in case of transesterification the tetrahedral intermediate only rearranges and forms one mole of similar ester to that of the esterification reaction (Kulkarni*et al*., 2006). It is found that esterification reactions are faster than transesterification reaction (Atay*et al*., 2007). Water is one of the products of the esterification reaction.

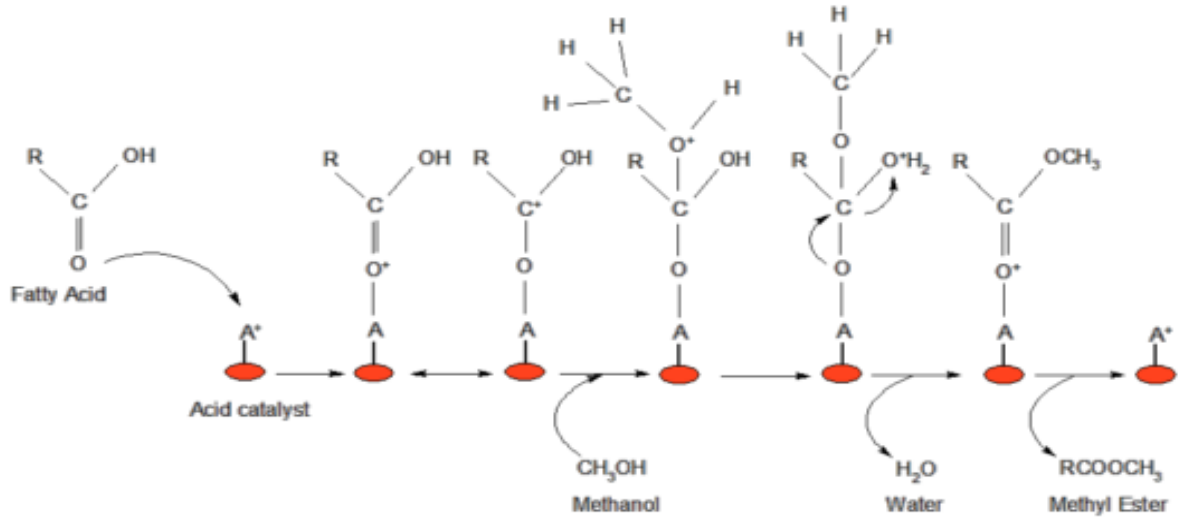
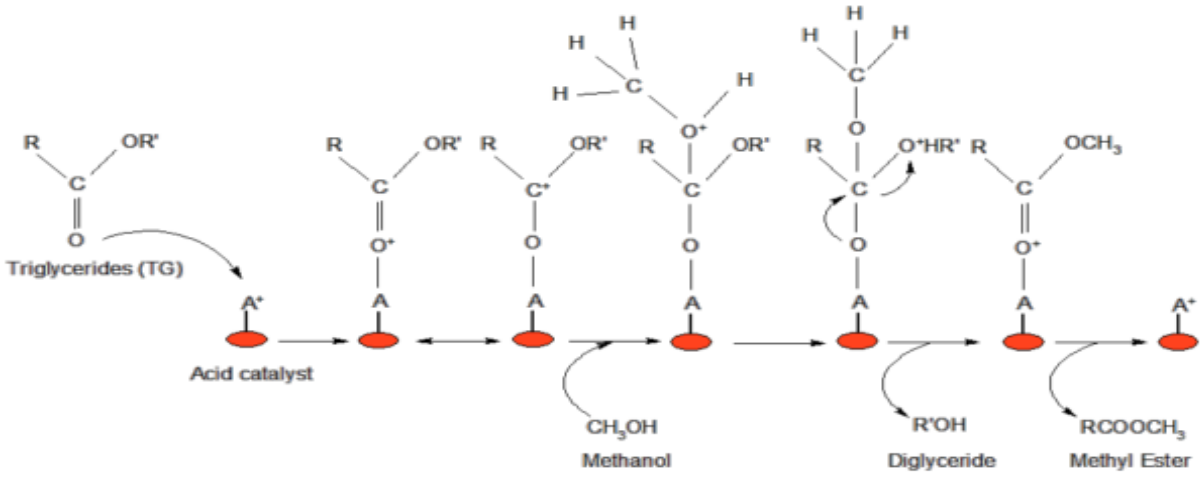


Plate I: (a) Reaction mechanism of acid catalyzed esterification reaction



(b) Reaction mechanism of acid catalyzedtransesterification reaction (Baroi, 2014)

2.6 Clay Minerals

Clay minerals are hydrous alumino silicates and are abundant in soils and sedimentary rocks (Moore and Reynold, 1997). They are very important minerals as a result of their surface properties and the fact that they are reactive hence making them very important in industrial applications and environmental control (Hall, 1987;Bergaya*et al.,* 2006). For example, the properties of clay minerals such as acidity, high surface area and cation exchange capacity (CEC) make them play important roles such as catalysts, supports and adsorbents for toxic substances (Hall, 1987; Bergaya*et al.,* 2006). They are mainly composed of layers (sheet-like structures) and are therefore referred to as phyllosilicate minerals(Salahudeen*et al*., 2014).

The Joint Nomenclature Committees (JNCs) of the Association Internationale Pour I' Etude des Argiles (AIPEA) and Clay Minerals Society have defined clay as a naturally occurring material composed primarily of fine-grained minerals which is generally plastic at appropriate water contents and will harden when dried or fired. Clay minerals have also been defined by JNC as phyllosilicate minerals and minerals which impart plasticity to clay and which harden upon drying or firing (Guggenheim and Martin, 1995). Examples of phyllosilicate minerals are kaolin, smectites, vermiculites, chlorites etc. According to these definitions therefore, clay mineral is a constituent of clay.

Clay mineral layers are held together mainly by van der Waals bonding and some contribution from electrostatic interaction (owing to the ionic interaction with interlayer cations-for clay minerals with interlayer cations) or hydrogen bonding (for 1:1 clay minerals such as kaolinites). Consequently, clay minerals are soft with excellent cleavage ability and also exhibit several degrees of disorder (Moore andReynold, 1997; Meunier, 2005).

2.7 Kaolinite Clay

Rocks that are rich in kaolinite are known as kaolin or china clay. The name is derived from *Kao-ling* a village near Jingdezhen, Jiangxi province, China. The name entered English in 1727 from the French version of the word: "kaolin", following Francois Xavier d'Entrecolles's reports from Jingdezhen. Kaolinite has a low shrink-swell capacity and a low cation exchange capacity(1-15 meq/100g). It is a soft, earthy, usually white mineral (dioctahedralphyllosilicateclay), produced by the chemical weathering of aluminiumsilicateminerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors.



Plate II: Kaolin image

The kaolin group are dioctahedral 1:1 phyllosilicates and comprises kaolinites, halloysites, nacrite and dickite as polytypes. It is difficult to differentiate them based on basal XRD reflections of their oriented aggregates. The general molecular formula of kaolin is $Al_2O_3.2SiO_2.2H_2O$. The structural formula of kaolinite is as shown in Figure 2.7.

The dioctahedral 1:1 phyllosilicates such as kaolinites are ideally electrically neutral and requires no interlayer cation. Consequently, water spheres or shells cannot be held in the interlayer and as a result, 1:1 phyllosilicates such as kaolinites are non swelling clay minerals (Bawa, 2012).

The layers of this clay mineral are held together by hydrogen bond. The ideal layer charge of kaolinite like other 1:1 phyllosilicates is zero. The point of zero charge for kaolinite is about 4.7. The implication of this is that at pH more than 4.7, kaolinite will be negatively charged and may exhibit adsorption towards cationic species.

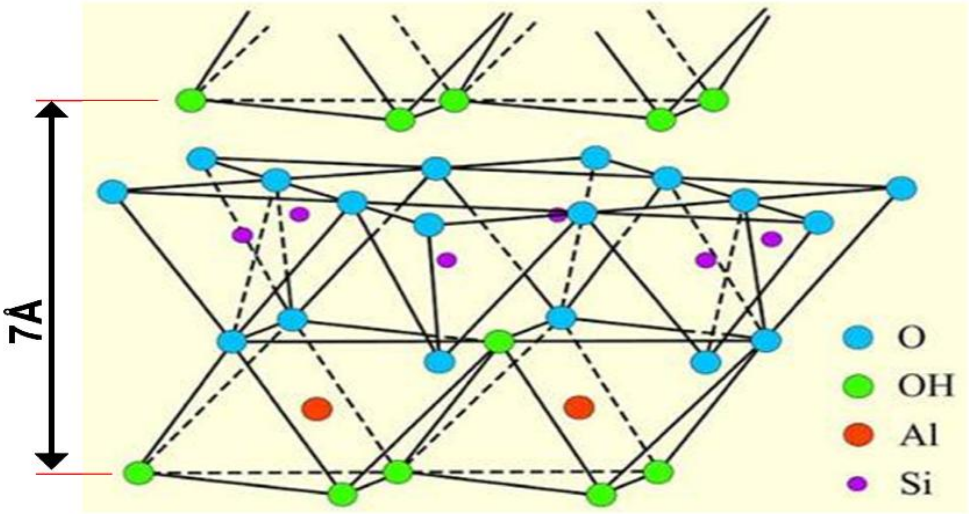


Figure 2.5 Structure of tetrahedral and octahedral sheet forming (1:1) structure of kaolinite with a d-spacing of 7Å (Bergaya*et al*., 2006)

Kaolin is resistant to acid leaching due to its high octahedral aluminum content, and the transformation of kaolin into metakaolin would increase the susceptibility of the former to the aluminum and iron cations leaching from the octahedral layer (Lenarda*et al*., 2007). The phase transformations that occur when kaolin is calcined at high temperatures are demonstrated by the chemical reactions illustrated as follows (Carneiro, 2003):

$$\underset{\text{Kaolinite}}{2SiO_2 \cdot Al_2O_3 \cdot 2H_2O} \xrightarrow[\sim 537^{\circ}C]{} \underset{\text{metakaolinite}}{2SiO_2 \cdot Al_2O_3} + 2H_2O(g) \qquad (2.4)$$

$$\underset{\text{Metakaolinite}}{2SiO_2 \cdot Al_2O_3} \xrightarrow[\sim 983^{\circ}C]{} \underset{\substack{\text{Primary 1 : 1 mullite} \\ \text{(Al-Si spinel)}}}{Al_2O_3 \cdot SiO_2} + \underset{\text{(amorphous)}}{SiO_2} \qquad (2.5)$$

2.7.1 Source of Kaolinite Clay in Nigeria

The bulk of the Kaolinite clay deposits in the country are either sedimentary or residual in origin and are usually associated with granitic rocks. Occurrences of kaolin have been recorded in different parts of the country and specific abundant deposits have been identified in parts of Enugu, Anambra, Kaduna, Katsina, Plateau, Ondo, Ogun, Oyo, Bauchi, Sokoto, and Borno States. Of these reserves, about 800 million tons of probable/proven deposits have been quantified (RMPDC, 2014). For this work the kaolinite clay used was obtained from Kankara in Katsina State.

2.7.2 Application of kaolinite clay

Kaolin is one of the most valuable of the industrial clays which is used in most manufactured products. Prominent uses include paper filling and coating; paint, plastic, adhesive and ink pigment; rubber reinforcing agent; ceramic raw materials for porcelain, dinnerware, tiles and

enamels; catalyst for petroleum cracking and auto exhaust emission catalytic control devices; cosmetics base; and digestive coating remedy. Kaolin is used in ceramics, medicine, coated paper, as a food additive in toothpaste, as a light diffusing material in white incandescent light bulbs, and in cosmetics (Jorge *et al*., 2011). It is also used in paint to extend titanium dioxide (TiO_2) and modify gloss levels; and in adhesives to modify rheology. Kaolin was long used in the production of common smoking pipes in Europe and Asia. The largest use is in paper production, including ensuring the gloss on some grades of paper (Bawa, 2012). Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or as liquid slurry.

2.8 Characterization of Solid Catalyst

Characterization is as important as developing the material; it is a judgmental analysis that verifies the type of material that is developed or synthesized. Some conventional characterization techniques are discussed in the next sub-sections.

2.8.1 Scanning electron microscopy (SEM)

SEM is an instrument that scans a sample surface with a high-energy electron beam in a vacuum chamber. The electron beam comes typically from a tungsten filament and has energy from 0.5 to 40 keV. When the electron beam strikes the samples, the electrons interact with the atoms and emit signals that contain information about the sample. The most commonly used signals are the secondary electrons (SE), the backscattered electrons (BSE) and x-rays. The SE signal comprises vital information on the morphology and topography of the samples. The BSE signal is most valuable for illustrating the contrasts in composition in multiphase samples. The characteristic x-rays are mainly used for elemental analysis. Almost all solid surfaces can be analyzed by SEM. It has a large depth of field, which allows more of a sample to be focus at one time. The SEM also can produce images with high spatial resolution, which means that closely spaced features can be

examined at high magnification. All these advantages have made SEM one of the most useful instruments in different research areas today.

2.8.2 X-ray diffraction (XRD)

Crystalline phases diffract x-rays according to the Bragg law;

$$n\lambda = 2\mathrm{d}\sin\theta \qquad (2.6)$$

Where θ is diffraction angle for a lattice spacing d, λ is the wavelength of the x-rays, and n is an integer. Powder or polished polycrystalline specimens are used, and diffraction 2θ angles are recorded. The identification of a phase is accomplished by comparing the d spacing and relative intensities of the sample material with reference data for known materials. Quantitative phase analysis to about 1% is possible when phases are randomly oriented and diffraction lines of different phases are clearly distinguished.

When x-ray radiation passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation. If the atoms are organized in planes (i.e., the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the x-rays, constructive and destructive interference will occur. These results in diffraction where x-rays are emitted at characteristic angles based on the spaces between the atoms organized in crystalline structures (http://www.rigaku.com/xrd/about_tech.html).

2.8.3 X-ray fluorescence (XRF) spectroscopy

XRF is a physical phenomenon involving the interaction of x-ray with matter, which has been used for numerous applications including art verification, biology, biomedicine, pharmaceuticals, electronics, environmental remediation, forensic science, geology and mineralogy, quality control processes and aerospace. The main purpose of using XRF for characterization of

materials is to verify the relationship between x-ray energy and atomic number and for quantitative analyses of major and minor elemental compositions. The fundamental principles behind XRF require the ionization of component atoms of material when they are exposed to short-wavelength x-rays or gamma rays with energy greater than ionization potential of the materials. X-rays and gamma rays can be energetic enough to expel tightly held electrons from the inner orbits of the atom. The removal of an electron in this way makes the electronic structure of the atom unstable, and electrons in higher orbital fall into the lower orbital to fill the hole left behind. In falling, energy is released in the form of a photon, the energy of which is equal to the energy difference of the two orbitals involved.

The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of different energy. Each of these transitions yields a fluorescence photon with a characteristic energy equals to the difference in energy of the initial and final orbital.

However, XRF is limited to analysis of relatively large samples usually greater than one gram, material that can be prepared in powder form and effectively homogenized, materials comprising high abundances of elements for which absorption and fluorescence effects are reasonably well understood (Rollinson, 1993).

2.9Fuel Properties of Biodiesel

Biodiesel quality depends on several factors that reflect its chemical and physical characteristics. The quality of biodiesel can be influenced by a number of factors: the quality of the feedstock; the fatty acid composition of the parent vegetable oil or animal fat; the production process and the other materials used in the process; the post-production parameters; and the handling and

storage. Given the fact that most current diesel engines are designed to be powered by diesel fuel, the physicochemical properties of biodiesel should be similar to those of diesel oil (Barabas and Todoruț, 2011).

The following properties of biodiesel affect the performance of diesel engine in the short term, hence standards are set to ensure that biodiesel produced for transportation is save for use.

2.9.1 Density

According to Barabas and Todoruț (2011) fuel density is the mass of unit volume, measured in a vacuum. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15°C. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. Biofuels generally have a higher density; this will affect the volume of oil delivered into the combustion chamber. The EN standard is 0.86 - 0.90 g/cm^3 (Moser, 2009).

2.9.2 Flash point

Flash Point measures the temperature at which enough vapour being given off cause an explosion when it comes into contact with a flame. It is used to classify fuels for transport, storage and distribution according to hazard level (Barabas and Todoruț, 2011). Generally biodiesel has a relatively high flash point compared to mineral oil. But sometimes methanol carries over from the production process and makes the biofuel hazardous. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. The EN and ASTM minimum standard are 120^0C and 93^0C respectively (Biodiesel standard, 2013; Moser, 2009; Barabas and Todoruț, 2011).

2.9.3 Acid value / number

This measures the amount of potassium hydroxide as mg KOH needed to neutralize 1 gram of fuel. It is expressed as mg KOH required to neutralize 1g of FAME. Acid number or neutralization number is a measure of free fatty acids contained in a fresh fuel sample and of free fatty acids and acids from degradation in aged samples. If mineral acids are used in the production process, their presence as acids in the finished fuels is also measured with the acid number. Cvengros (1998) revealed that free fatty acids as weak carboxylic acids pose far lower risks than strong mineral acids. It is influenced by the type of feedstock used for fuel production and its degree of refinement. Also, acidity can be generated during the production process. The parameter characterizes the degree of fuel ageing during storage, as it increases gradually due to degradation of biodiesel. High fuel acidity has been found to cause corrosion and the formation of deposits within the engine which is why it is limited in the biodiesel specifications. The EN and ASTM standard is maximum of 0.5 mgKOH/g (Hu *et al*.,2010, Biodiesel Standard, 2013).

2.9.4 Cloud point

The cloud point is defined as the temperature at which crystal growth is large enough (diameter≥0.5 μm) to be visible to the naked eye (Moser, 2009). It is the temperature at which small solid crystals are first visualized as the fuel cooled (Zhiyou*et al*., 2006). At temperatures below the CP, larger crystals fuse together and form agglomerations that eventually become extensive enough to prevent pouring of the fluid. Below the cloud point these crystals might plug filters or drop to the bottom of a storage tank (Barabas and Todoruț, 2011). The CP is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The lowest temperature at which the

fluid will pour is defined as the pour point (PP). According to ASTM D6571standard, the cloud point of biodiesel ranges between-3 to 15 ℃ (Hu *et al*., 2010).

2.9.5 Pour point

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. It is the temperature at which the fuel is no longer pumpable (Zhiyou*et al*., 2006). This occurs if the temperature of the biodiesel drops below cloud point (Moser, 2009), when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine's fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel was produced (Barabas and Todoruț, 2011). Biodiesel according to ASTM 6571 standard should have pour point between -5 to 10 ℃ (Diamantopoulos*et al*., 2014).

2.9.6 Cetane number

This is a measure of the ignition quality of the oil - fuels with low cetane numbers tend to give increased emissions due to incomplete combustion. Cetane number is related to the ignition delay time a fuel experiences once it has been injected into a diesel engine's combustion chamber (Moser, 2009). The higher the cetane number the better the ignition quality of the fuel. It is a very important property of a diesel fuel standard for biodiesel (Alnuami*et al*., 2014). On the basis of ignition quality, biodiesel can be said to be better than petroleum diesel because they have cetane numbers higher than that of petroleum diesel, this high cetane number is due to the higher oxygen contents. This means that they will burn smoothly and with less noise in a diesel engine than petroleum diesel. The EN and ASTM minimum standards are 51 and 47 respectively (Biodiesel standard, 2013; Moser, 2009; Barabas and Todoruț, 2011).

2.9.7 Viscosity

The viscosity of biodiesel is an important factor as it controls the characteristics of the injection from the diesel injector. Meher*et al*., 2006, revealed that it is important to control the viscosity within an acceptable limit to avoid problems with the fuel injector system performance since the viscosity of fatty acid methyl esters go to very high levels. The viscosity of biodiesel is higher than that of fossil diesel, and in some cases at low temperatures becomes very viscous or even solid. High viscosity affects the volume flow and injection spray characteristics in the engine, and at low temperatures may compromise the mechanical integrity of injection pump drive systems (when used as stand-alone B100 diesel fuel). According to ASTM D6571 standard the viscosity of biodiesel should range between 1.9 to 6 cP.

2.10 Previous Related Works

Jitputti*et al*., (2006) assessed the catalytic performance of zinc oxide and zirconium oxide as solid acid catalysts in transesterification reaction of palm kernel oil with methanol and found that after 1 h of reaction time, using 3 wt% catalyst and 6:1 molar ratio of alcohol/ oil, 86.1% methyl ester yields were obtained for zinc oxide while only 64.5 % for zirconium oxide. However, using sulfated zirconia, the yields considerably increased to 90.3% which might be due to high acidic strength of sulfateanions on the surface of zirconia.

Chen *et al*., (2007) found that by introducing 2 wt% catalyst and 12:1 alcohol/oil molar ratio, in the transesterification of cotton seed oil to methyl esters, after 8 h of reaction time the methyl ester yields in the presence of SO_4^{2-}/TiO_2 and SO_4^{2-}/ ZrO_2 were 90 % and 85 % respectively.

Park *et al*., (2010) stated that the optimum reaction conditions for tungsten oxide zirconiatransesterification with a FFA conversion of 96 % were 20 wt% WO_3/ZrO_2 at 150 ℃, 0.4 g/ml (oil), 9:1 (alcohol to oil, molar ratio) and 2 h reaction time.

Corro*et al*., (2010) transesterifiedJatrophacurcascrude oil (18.1wt% FFA) using HF-treated SiO_2 solid acid catalyst and found that after 2 h, using methanol to oil ratio of 12, reaction temperature of 70 ℃ and catalyst loading 10 wt% a conversion of 96% was attained.

do Nascimento*et al*., (2011) prepared a new eco-friendly catalyst for the esterification of oleic acid with methanol from a waste material, Amazon flint kaolin, that was thermally treated (at 850 and 950 ℃) and activated withsulfuricacidsolutions(1Mand4M).Theactivatedmetakaolinsampleswerecharacterizedby X-ray diffraction, scanning electron microscopy, N_2 adsorption–desorption and adsorption studies of pyridine usingTG/DTGandFTIRanalysis.Theleachedmetakaolintreatedat950 ℃andactivatedwith4Msulfuri cacidsolutionshowedthehighestnumberofacidsites(237.7mol/g) and offered the maximum esterification activity (98.9%) at 160 ℃, an acid : methanol molar ratio of 1:60 and 4h reaction time.

Rehab *et al*., (2015) prepared and characterized $CaSO_4$-SiO_2-CaO/SO_4^{2-} composite with various SiO_2 to CaO weight ratios. The experimental results showed that the composite with 1:1 SiO_2 to CaO weight ratio had the highest biodiesel production yield. The optimum conditions were; 3:1 methanol to oil molar ratio, 5 wt% (weight catalyst/ weight oil) catalyst loading at 55 ℃, 300 rpm stirring speed for 30 min reaction time.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The main materials used in this work were:

1. Kankara kaolin from Kankara, Katsina State
2. 98%w/w Sulfuric acid, General Purpose Reagent (Johnson Solomon Ltd)
3. 96%w/w Methanol (Analytical grade) from Haddis chemical store Samaru Zaria.
4. Waste cooking oil from a food vendor in Romi, Kaduna State.
5. Distilled water (PTDF Catalysis Laboratory at Chemical Engineering Department, ABU Zaria).

3.2 Apparatus

The apparatus used in the course of this work were listed in Table 3.1

Table 3.1 List of apparatus used this research work

Apparatus	Trade Name	Manufacturer
Conical flasks (500ml),	Pyrex	Scilabware Ltd, United Kingdom
Measuring cylinders (500 ml, 100 ml),	Pyrex	Scilabware Ltd, United Kingdom
Crucibles		ABU, Zaria
Tyler mesh Sieve (70µm)	Tyler	Endecotts, London
Buchner flask (1 liter)	Pyrex	Scilabware Ltd, United Kingdom
Sample containers		Plastic Company, Kano
Separating funnel	Pyrex	Scilabware Ltd, United Kingdom
Filter papers	Wattman	Wattman Ltd, England
Reflux condenser	Pyrex	Scilabware Ltd, United Kingdom
Beakers (1000 and 500 ml)	Pyrex	Scilabware Ltd,

Sinta glass filter funnel (Quickfit TM)	Quickfit	United Kingdom Scilabware Ltd, United Kingdom

3.3 Equipment

Table 3.1 Summaries the list of the equipment used for both synthesis and characterization.

Table 3.2: List of other equipment used in this work and their specifications

S/No.	Name	Model	Manufacturer
1	Weighing Scale (0-100kg Range)	1455T 18	WEDA,Holland
2	Scanning Electron Microscopy (SEM) machine	PhenomProx	Eindhoven, Netherlands
3	Analytical Balance	AB 204 (0 – 180g)	MettlerToledo, Switzer land
4	High Vacuum Pump	ES-100	Edwards, England
5	Exposed Element Furnace (0-1400°C)	TIKIR 11/12	Heraeus, Holland
6	Distilled water machine	A4000	Aquatron
7	X-ray Fluorescence Machine	Minipal 4	PANalytical, Netherlands
8	X-ray diffractometer	Empyreal	PANalytical, Netherlands
9	Fourier Transform Infrared Spectrophotometer	FTIR- 8400S	Shimadzu Japan
10	Magnetic stirrer hot plate	TMOV – 420	Stuart, England

3.4 Experimental Procedure

Three major steps are involved in this work; catalyst preparation, characterization and testing of the catalyst.

3.4.1 Catalysts preparation

Three steps were used in preparing the catalysts; beneficiation, calcination and acidification.

3.4.1.1 *Beneficiation of Kankara kaolinite clay*

The beneficiation procedure followed was adapted from literature (Bawa, 2008; Edomwonyi-Otu, 2008). Raw kaolinite clay from Kankara village in Katsina State, Nigeria, was beneficiated by soaking it in water for three (3) days in a plastic container, with periodic stirring and the suspended impurities were decanted on a daily basis. The resulting mixture was sieved using 75 micron sieve and allowed to settle for 24 h. After settling, it was decanted and dried atmospherically for 2 d(days). The beneficiated clay was ground and sieved.

3.4.1.2*Calcination of Kankara kaolinite clay*

The dried kaolinite powder was then placed into larger (1000ml) crucibles and calcined in an electric furnace at 750 ℃ for 4 h to obtain the more reactive phase of kaolinite known asmetakaolin.

3.4.1.3 *Acidification ofmetakaolin using sulfuric acid*

In a typical run, 50g of the metakaolin was measured into a 1000ml conical flask and a calculated amount of distilled water that will bring the acid concentration to 60%was added and stirred. Calculated quantity of 98% sulfuric acid (5 folds stoichiometric requirement) was measured and then added to the metakaolin suspension in the conical flask and the reaction left

for 5, 10,15 and 20 min, after which additional distilled water was then added to quench the reaction (Aderemi*et al*., 2009; Ajayi*et al*., 2010). The reaction mixture was thenwashed with distilled water several timesfiltered through the sinta glass filter funnel and dried. Thereafter, it was ground and calcined at 400 ℃ for 2 h. Detailed calculations of the amount of acid used are given in Appendix A.

3.4.2 Characterization of the catalyst

Various instruments such as X- Ray Fluorescence (XRF), X-Ray Diffraction (XRD), and scanning electron microscopy (SEM) were used to characterise the catalyst to determine the silica to alumina ratio, change in structure and morphology of the catalyst.

3.4.2.1 *XRD analysis*

X-ray diffraction (XRD) patterns of the synthesized catalysts were recorded using a PANalytical England Philips diffractometer at the Universityof Johannesburg, South Africa, with a crystal monochromator at an accelerating voltage of 40 kV with 100 mA flux. The X-ray source was CuKα1 with a wavelength of 1.5406Á.

3.4.2.2*XRF analysis*

Chemical composition of the raw samples was obtained by XRF analysis using a PANalytical England Philips Fluorescence Machine at the National Geological Research Laboratory (NGRL), Barnawa Kaduna with a 15kV acceleration voltage and 10nA beam current.

3.4.2.3 *SEM analysis*

Scanning electron microscopy (SEM) for the morphologies of the synthesized acid catalysts was determined in University of Johannesburg, South Africa laboratory.

3.4.3 Pre – treatment of waste cooking oil (WCO)

The waste cooking oil (WCO) obtained from a food vendor was filtered using filter papers to remove food particles from the oil. Thereafter, the oil was heated to 100 ℃ to remove water present in the oil. The oil was then poured into a 4 litre gallon and covered tightly and stored at room temperature to prevent oxidation.

3.4.3.1*Determination of physico-chemical properties of the waste cooking oil (WCO)*

A simple method of titration outlined by Okpuzor*et al.,* (2009) was used to determine the acid value of WCO. Each oil sample (1g) was measured and dissolved with 50 ml of ethanol in a conical flask. Two drops of phenolphthalein indicator were added and titrated with 0.1M potassium hydroxide solution until the appearance of the first permanent pink colour which lasted for at least 30 seconds indicating completion of the reaction and the volume of the titre was recorded. The acid values of the WCO and that of the biodieselwere determined according to Equation 3.1

$$\text{A.V} = \frac{56.1 \times V \times C}{m} \quad (3.1)$$

Where V is the volume (ml) of standard volumetric potassium hydroxide (KOH) solution used, C is the concentration (mol/dm^3) of the standard volumetric KOH solution used, m is the mass (g) of the test portion and 56.1 is the molecular mass of KOH. The free fatty acid (FFA) were calculated using the Equation 3.2

$$\text{FFA} = \frac{28.2 * V * C}{m} \quad (3.2)$$

Where V, C and m are same as defined earlier.

Saponification value was determined according to titremetric method discussed by Pearson (1981). Two grams (2 g) of oil samples were weighed into a conical flask and 25 ml ethanol potassium hydroxide was added then the solution was refluxed for 30 min on a water bath. The mixture was titrated against 0.5 M HCl using phenolphthalein indicator. The same process was conducted for blank determination and the saponification value of WCO and the biodiesel were determined according to Equation 3.3

$$SV = \frac{(B-S)*28.05}{m} \quad (3.3)$$

where B is the titre value of blank (ml), S is titre value of the sample, and m is the mass of the test portion (2g).

The molecular weight (M) of the oil was determined from the SV and AV according to Equation 3.4 (Cheng *et al.*, 2008)

$$M = \frac{56.1*1000*3}{SV-AV} \quad (3.4)$$

where SV and AV are the saponification and acid values (mg KOH/g), respectively.

The Brookfield DV II + Pro viscometer was used to estimate the viscosity of samples at 40℃ according to ASTM D455. Exactly 16 ml of each sample was used. A spindle size of 16 was selected for the analysis because of the rheology of the oil samples.

3.4.4 Application of synthesised catalyst for biodiesel production

The acid activated clay samples (catalysts) were subjected to test by using each for reaction at 60 ℃ for 60 min, 1wt% catalyst and oil to methanol ratio of 1:6 to select the best Si/Al.

Each sample (24.3 cm^3) of methanol was measured and poured into a 1000ml flat bottom flask then 1g of the catalyst was added and the mixture stirred using a magnetic stirrer for 10 min while heating to a temperature of 30 ℃ and condensing the methanol into the mixture by a reflux condenser. For each run 100g (112 ml) of WCO was heated to 30 ℃ and poured into the mixture of methanol and catalyst then stirred. When the temperature of the mixture reached 60 ℃it was maintained for 60 min after which the reaction was stopped, allowed to cool and poured into a separating funnel. The mixture was left to stay for 12 h undisturbed to allow separation of glycerol from the biodiesel. Biodiesel obtained was filtered and heated to 100 ℃ to vapourise excess methanol and water from the product. The weight of the biodiesel was measured and used to calculate the percentage yield using the formula;

$$\% \text{ yield} = \frac{weight\ of\ biodiesel}{weight\ of\ oil} \times 100\% \qquad (3.5)$$

The catalyst with the highest yield was used for reaction at the same oil to methanol molar ratio and contact time used initially with temperatures of 50, 55, 60 and 65 ℃.

The best temperature and Si/Al ratio was then fixed while oil to methanol ratio and contact time was varied. Oil/ methanol ratio of 1:6, 1:9, 1:12, and 1:15 as well as contact time of 30, 60, 90, and 120 min were used.

The catalyst dosage is also varied at optimum value of other parameters. Dosage of 1wt%, 2wt%, 3wt% and 4wt% (relative to weight of oil) was used.

3.4.5 Reusability test

Biodiesel was produced using the best operating conditions obtained in section 3.4.4. The catalyst used was filtered, washed with methanol and dried at room temperature for 1 h then used

to catalyse the second transesterification reaction. The process was repeated for the third and fourth runs. Percentage yield of biodiesel was calculated for each biodiesel produced the four runs.

3.4.6 Characterization of Biodiesel

The methods employed in section 3.4.3.1 to determine the physico-chemical properties of waste cooking oil were used in determining the properties of the biodiesel produced.

3.4.7 FTIR analysis of biodiesel

FTIR analysis of the biodiesel produced was carried out using FTIR- 8400S Shimadzu fourier transform infrared spectrophotometer to ascertain the presence of ester functional group.

CHAPTER FOUR

4.0 RESULTS AND DISCUSION

The results of all the investigations carried out in this work are presented and discussed in this Chapter.

4.1 Characterisation of Catalyst

Three instruments namely X-Ray Florescence (XRF), X-Ray diffraction (XRD) and Scanning electron microscopy (SEM) were used to study the chemical composition, crystalline structure and the morphology of the catalyst prepared in this work.

4.1.1 Chemical composition

The chemical composition of the beneficiated, thermally activated and the four acid activated kaolin clay samples were determined using XRF and the results presented in Table 4.1.

From the results leached metakaolins showed an Al_2O_3 content smaller than that of the parent kaolin. This observation is in agreement with the findings ofAbdul, 2005 and Bawa, 2012. Ajayi*et al*., 2010 showed that the rate of aluminaleaching using sulfuric acid increases with time. K_2O and Fe_2O_3 were also found to decrease with increase in leaching time as observed from Table 4.1. The XRF result was used to determine the silica to alumina mass ratio. Detailed calculations of silica to alumina mass ratio are given in Appendix B.

Table 4.1: Chemical composition of the beneficiated, calcined and acid treated kaolin clay

	RAW	BENE	CALCINED	AD5	AD10	AD15	AD20
SiO_2	59.64	58.80	58.10	94.00	96.44	97.00	97.35
Al_2O_3	33.70	35.00	36.10	1.80	0.49	0.30	0.28
SO_3	-	-	-	0.89	0.78	0.45	0.34
Na_2O	0.256	0.081	0.40	1.10	0.20	0.68	0.650
K_2O	1.12	0.97	0.925	0.14	0.09	0.07	0.04
CaO	0.486	0.50	0.521	0.37	0.438	0.174	0.201
MgO	0.024	0.030	-	-	-	-	-
TiO_2	0.25	0.22	0.18	0.252	0.120	0.215	0.224
Fe_2O_3	1.62	1.60	1.50	0.247	0.188	0.131	0.128
MnO	0.018	0.02	0.022	0.014	0.013	0.017	-

ADt : Acidified for t minutes

BENE: Beneficiated clay

4.1.2 Scanning electron microscopy (SEM)

The SEM micrograph in Plate II(a) for beneficiated kaolin shows large plates and stacks indicating the order of silica and alumina layers in kaolinite(Abo-El-Enein*et al*., 2013). Some rod- like structures were observed in Plate II(a), which signified the presence of impurities in the kaolin. The calcined sample in Plate II(b) shows a similar pattern, though with a slight disorder in the plates. The particles were clustered together. The SEM study of the leached kaolin revealed that it was mainly formed by agglomerate of particles with rough surface. The SEM micrograph also showed porosity related to spaces between these agglomerate. This result is in agreement with the finding of do Nascimento*et al*., (2011).

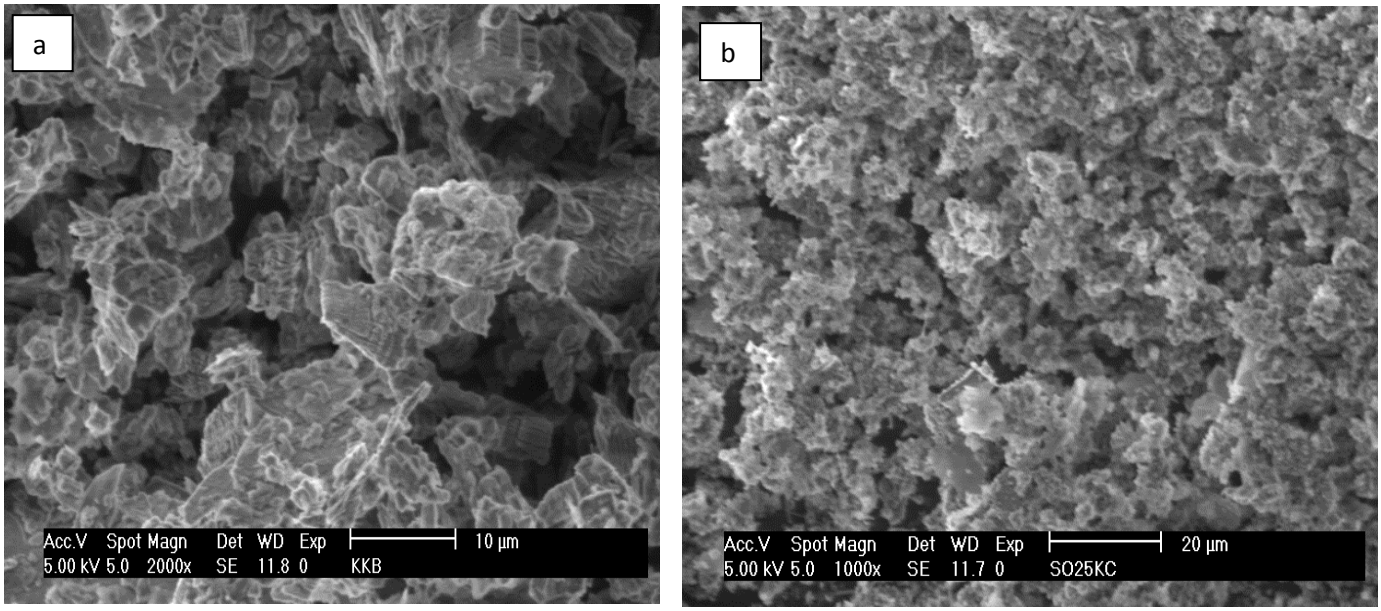


Plate II: Scanning electron micrographs for (a) Beneficiated kaolinite (b) Metakaolin

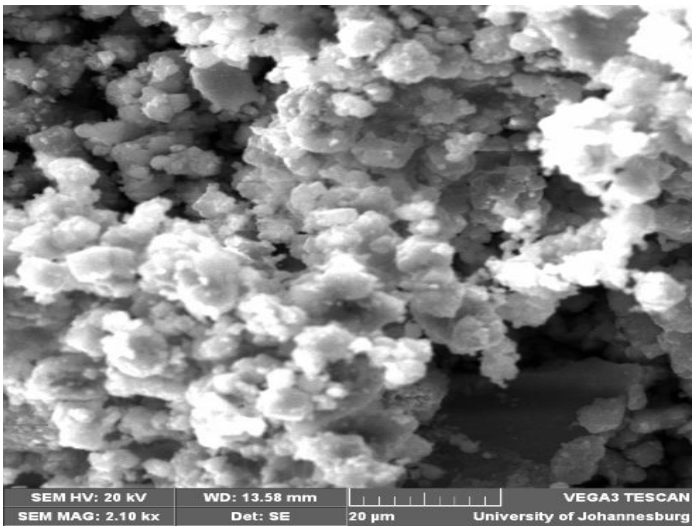


Plate III: Scanning electron micrographs for synthesized catalyst AD20

4.1.3 X-ray diffractograph (XRD)

The x-ray diffraction (XRD) result of beneficiated clay (shown in Figure 4.1), depicted sharp peaks typical of crystalline materials. The peaks of 2θ values at 14.5°, 23.8°, 24.9° and 29°, represent the crystalline structure of kaolinite as reported by Edomwonyi-Out *et al.*, (2013) with quartz as the major impurities having their main peaks at 10.3°, 21° and 31.5° as reported by Johnson *et al.*, (2014).

Thermal treatment of the Kankara kaolinite at 750℃ transformed the phase from the crystaline kaolinite to amorphous metakaolin (Ajayi *et al*.,2010). This is evident in the drastic drop in intensity in Figure 4.2. The transformation from the crystalline kaolinite to the amorphous metakaolin at 750℃ can be observed with quartz peaks in Figure. 4.1 still present, which obviously are impurities (Salahudeen*et al*.,2014).

In Figure.4.3, the data showed evidence of an amorphous SiO_2 phase that diffracts in the broad range 2θ = 15 - 35° as reported by Alex de Nazare de Oliveira *et al*.,(2013). This result coresponds to that of the XRF (Table 4.1) which indicates that the catalyst is majorly compose of SiO_2.

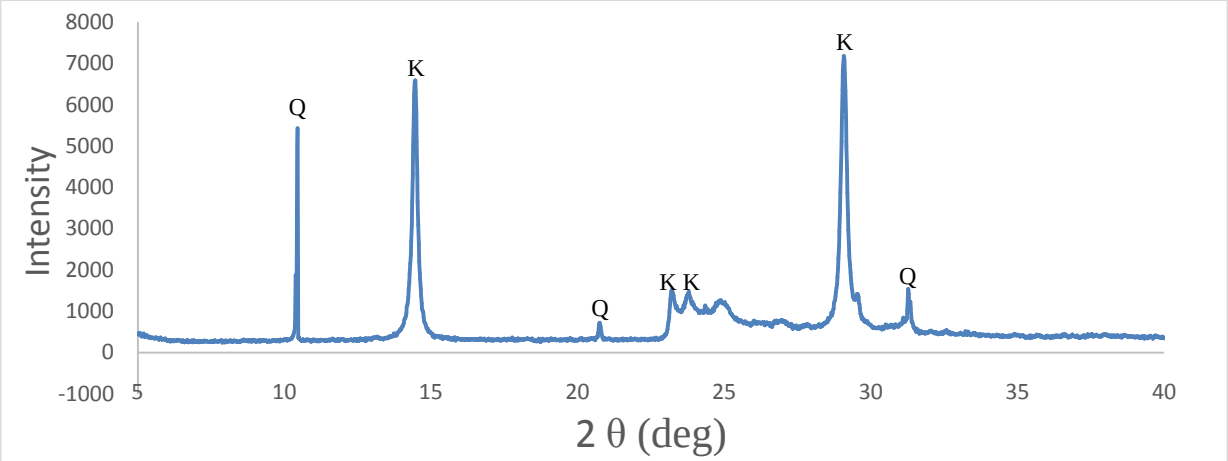


Figure 4.1: XRD pattern of the beneficiated kaolinite

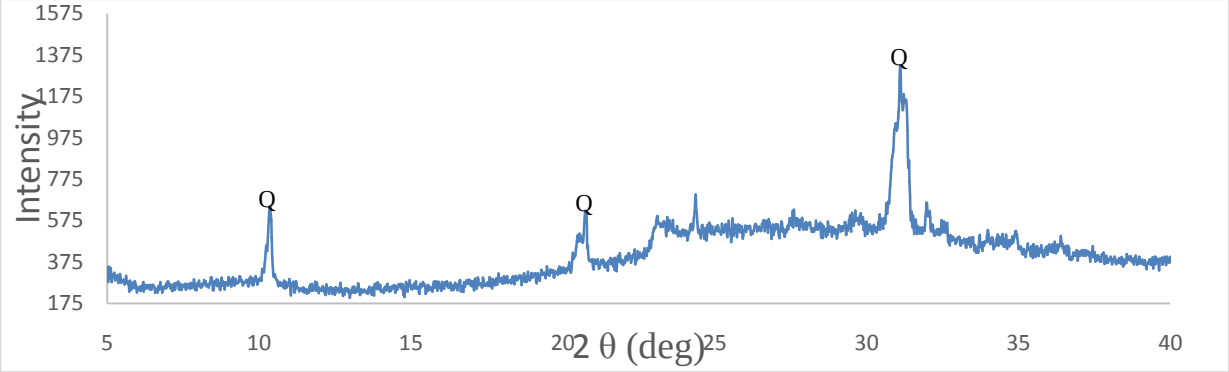


Figure 4.2: XRD pattern of the metakaolinite

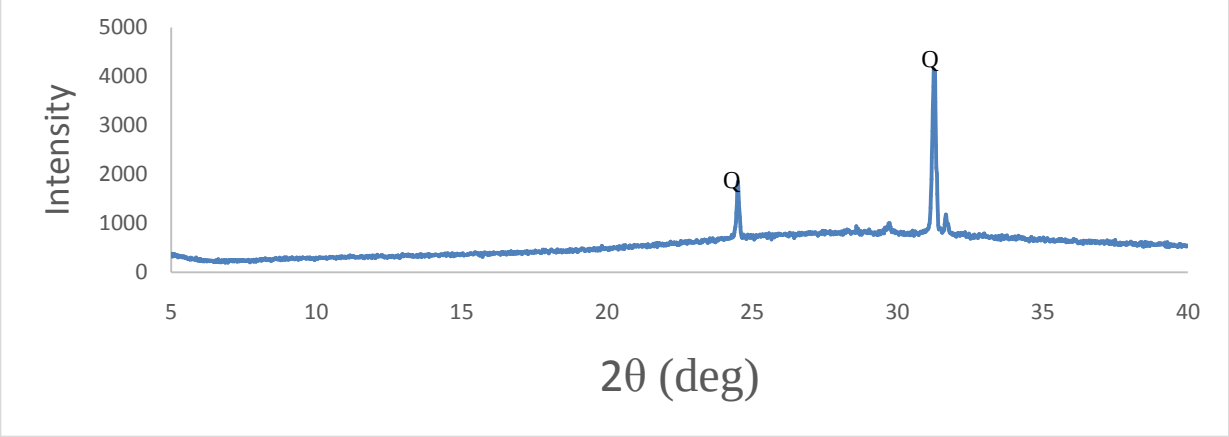


Figure 4.3: XRD pattern of the acidified metakaolinite

4.2 Properties of Waste Cooking Oil

The waste cooking oil used in the biodiesel production have some fuel related properties. Some of these properties are given in Table 4.2.

The viscosity of fresh oil (from source of WCO) was higher than that of WCO this may be as a result of the heat applied to the oil when frying. Both fresh oil and WCO has high viscosity and free fatty acid these properties hinders their direct use as fuel in diesel engines. Their high viscosity (Table 4.2) can have negative impact in the atomization of the fuel spray and function of the fuel injectors (Hussain*et al*., 2009). The acid value of WCO used in this study was found to be 3.6465 mgKOH/g, which corresponds to a free fatty acid value of 1.83%. The WCO has saponification value and molecular weight of 171.875 mgKOH/g oil and 1000.4 g/mol, respectively. The difference in the value when compared to what was reported by Aworanti*et al* (2013) might be due to variation in the duration the oil was exposed to heat, oxygen and food during cooking (Issariyakul and Dalai, 2014).

Table 4.2: Physical and chemical properties of oil feedstock.

Properties	WCO	Fresh oil
Acid value (A.V)mg KOH/g	3.6465	1.315
Free fatty acid (FFA)%	1.83	0.661
Saponification value mg KOH/g	171.875	182.3
Iodine value	169.795	118.35
Pour point℃	10	12.5
Cloud point℃	13.5℃	16
Densityg/cm^3	0.892	0.901
ViscositycP	11.5	20.5

4.3 Effect of Silica to Alumina Mass Ratio on Biodiesel Yield

The silica to alumina mass ratios obtained as a result of calcination and leaching of kaolin were 1.6, 52.2, 196.8, 323.3 and 347.2. The percentage yield of biodiesel produced using the five catalyst samples in transesterification reaction at 60 ℃, 1:6 oil to methanol ratio, 1 wt% catalyst dosage for 60 min were 77.3, 85.0, 86.4, 86.9 and 88.4 respectively as presented in Figure.4.4. This shows that the percentage yield increased with increasing silica to alumina ratio. As silica to alumina ratio increased, the surface areas also increase as reported by several researchers (Ajayi*et al*., 2010, Kumar *et al*., 2013). Though metal oxides commonly used in transesterification (CaO, Na_2O, TiO_2, $Al_2O_3$and SO_3) was small in the catalyst with highest yield, its specific surface area and interconnected system of large pore size was possibly responsible for the high yield as reported by Sani*et al.,* 2014. Corro*et al.,* 2011 studied the esterification of waste frying oil using acidified silica a yield of 86% was obtained, this result was similar to the yield (88%) in this work.

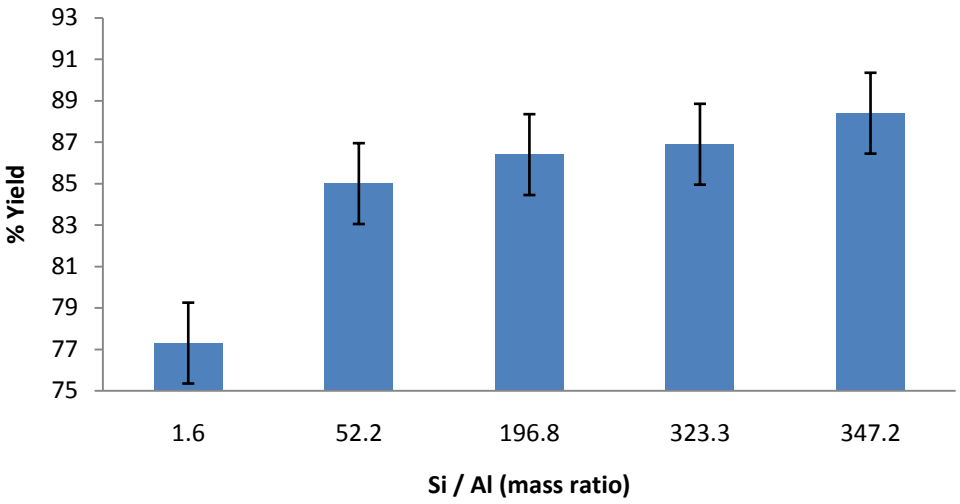


Figure 4.4: Effect of silica to alumina mass ratio on biodiesel yield

4.4 Effect of Reaction Temperature on Biodiesel Yield

Generally, transesterification can occur at reaction temperatures ranging from ambient to temperatures close to the boiling point of the alcohol used. A high reaction temperature usually speeds up the reaction and shortens the reaction period. In this work, the maximum temperature level was limited to 65 ℃ as temperatures higher than that might cause the methanol to evaporate excessively. Even though the methanol could be condensed back into the reactor, the extent of evaporation would affect the kinetics of the reaction and that could result in lower yield and affect the purity of the fatty acid methyl ester(FAME) produced. Moreover, the minimum temperature was selected as 50 ℃ because at lower reaction temperatures, the completion of the transesterification reaction tends to be too long and that might not be suitable or practical for mass production. Figure.4.5 shows the influence of reaction temperature on methyl esters yield. Oil to methanol molar ratio, catalyst amount and reaction time were fixed at 1:6, 1 wt% and 60 min respectively. The reaction was carried out at 50, 55, 60 and 65 ℃ to evaluate the influence of reaction temperature. The highest yield of WCO biodiesel was obtained at 60 ℃, which gave a maximum yield of 88.2%. The yield value decreased when the reaction temperature was 65 ℃ (80.1%). The decrease in the biodiesel yield at 65 ℃ may be due to the fact that methanol boils at that temperature. The increase in biodiesel yield with reaction temperature was due to the increased reaction rate and decreased mass transfer resistance. This observation is in agreement with the findings ofNuithitikul*et al*., 2011.

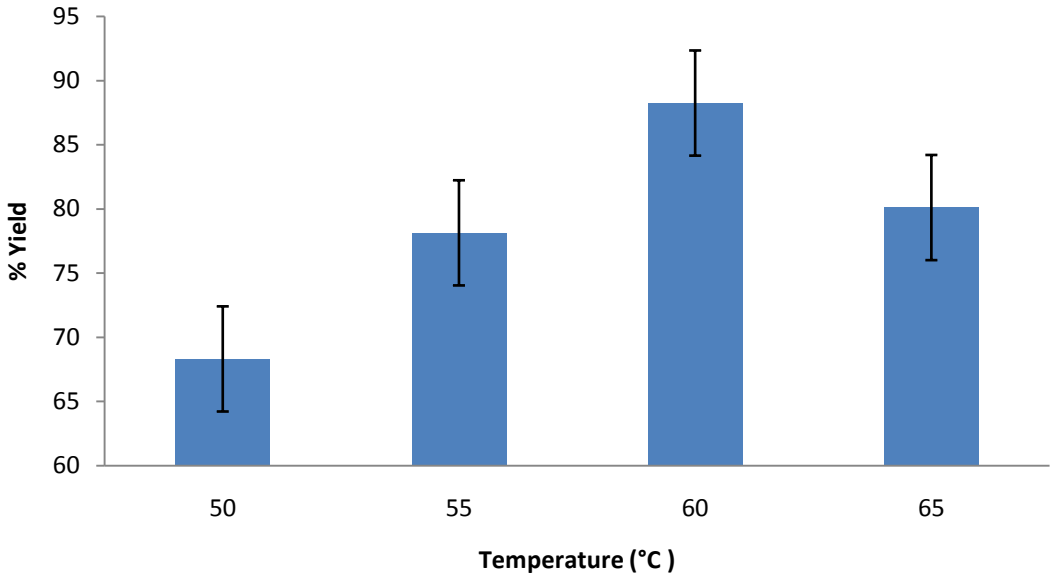


Figure 4.5: Effect of reaction temperature on percentage yield

4.5 Effect of Oil: Methanol Molar Ratio on Biodiesel Yield

From stoichiometry the transesterification reaction requires three moles of methanol and one mole of triglyceride in the presence of catalyst to yield three moles of biodiesel and one mole of glycerol. The transesterification reaction is reversible and higher amounts of methanol to oil molar ratio can shift the equilibrium to the product side according to Le chatellier's principle (Veljkovic, 2012). Figure.4.6 shows the influence of oil to methanol molar ratio on methyl esters yield. Catalyst amount, reaction temperature and time were fixed at 1wt%, 60°C and 60 min respectively. The reaction was carried out at 1:6, 1:9, 1:12, 1:15 (oil to methanol molar ratio). The percentage yield increased as the oil to methanol molar ratio increases and reached 90.3 % at 1:15 molar ratio. This is in agreement with previous studies of Li *et al.,* (2010) and Zhang *et al.,* (2010)that reported the optimum oil to methanol molar ratio of 1:15 for the production of biodiesel from soapstocks and acid oil respectively using different type of catalyst. Hayyan*et al.,* (2011) reported that in practice, the oil to methanol molar ratio should be much higher than 1:5 in order to shift the equilibrium to the product side.

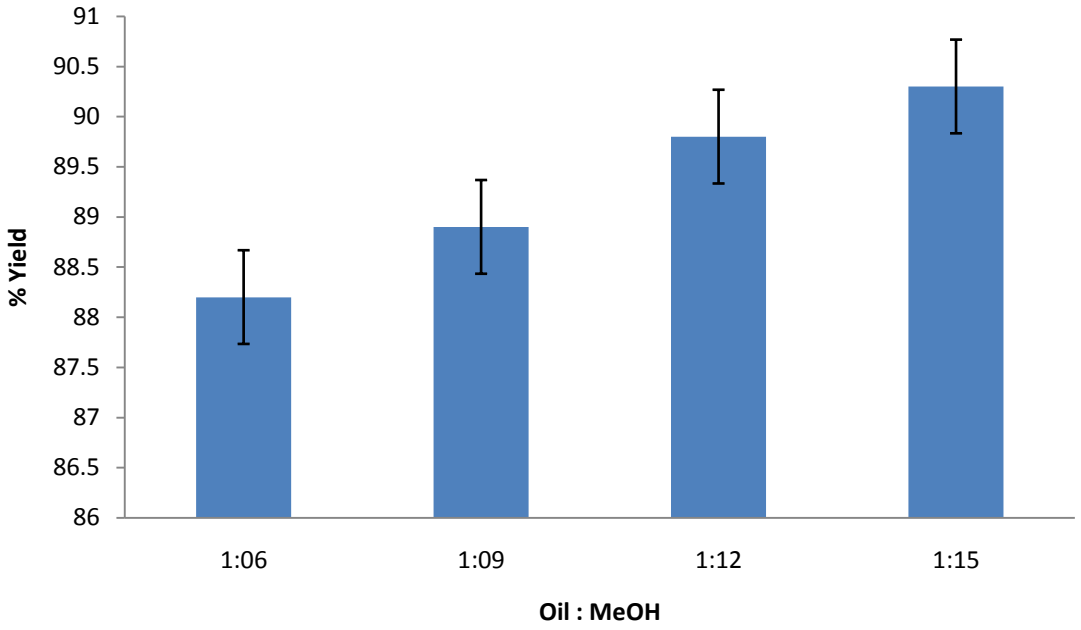


Figure 4.6: Effect of oil: methanol molar ratio on FAME yield

4.6 Effect of Reaction Time on Biodiesel Yield

Figure.4.7 shows the influence of reaction time on methyl esters yield, the Oil to methanol molar ratio, catalyst amount and reaction temperature were fixed at 1:15, 1wt% and 60 ℃ respectively. The optimal conversion for WCO biodiesel was obtained at 120 min reaction time which gave a maximum yield of 91.4% (Figure.4.7). It was observed that as the reaction time increases from 30 to 120 min, the percentage yield also increased from 84.2 to 91.4%. This result is in agreement with the literature(Hoque*et al.,* 2011).

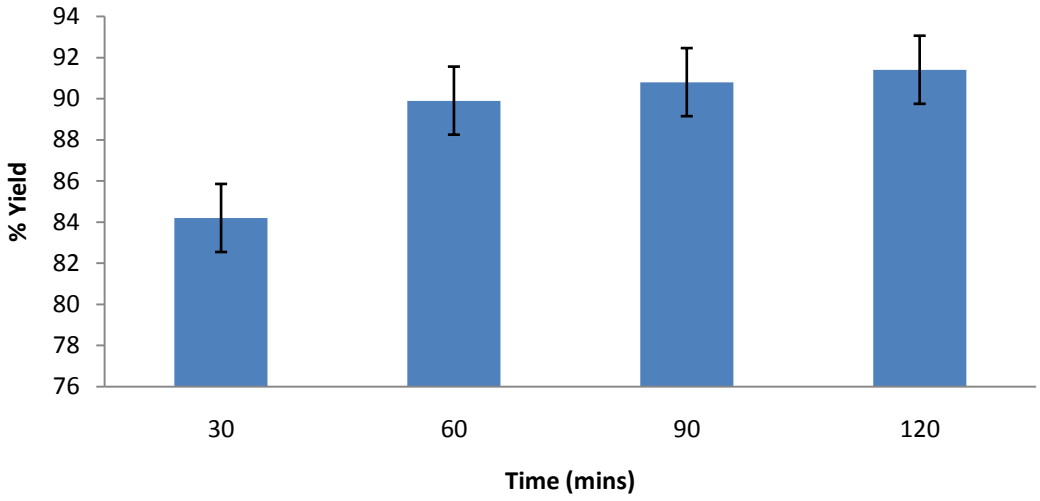


Figure 4.7: Effect of reaction time on biodiesel yield

4.7 Effect of Catalyst Dosage on Biodiesel Yield

Figure.4.8 shows the influence of catalyst amount on methyl esters yield. Oil to methanol molar ratio, reaction time and temperature were fixed at 1:15, 120 min and 60 ℃ respectively. As shown in Figure 4.8, as the catalyst amount was increased from 1 to 4wt% (weight of catalyst/ weight of oil), biodiesel yield increased from 91.1 to 92.7%. By increasing the amount of catalyst, the biodiesel production yield was increased. This is because with more catalyst addition, the total number of available active sites increased resulting in faster reaction rate to attain reaction equilibrium. From the economic point of view 1wt% catalyst can be considered as the optimum catalyst amount. These results agreed with the findings of Rehab *et al.,* (2015) and Saravanan*et al.,* (2015).

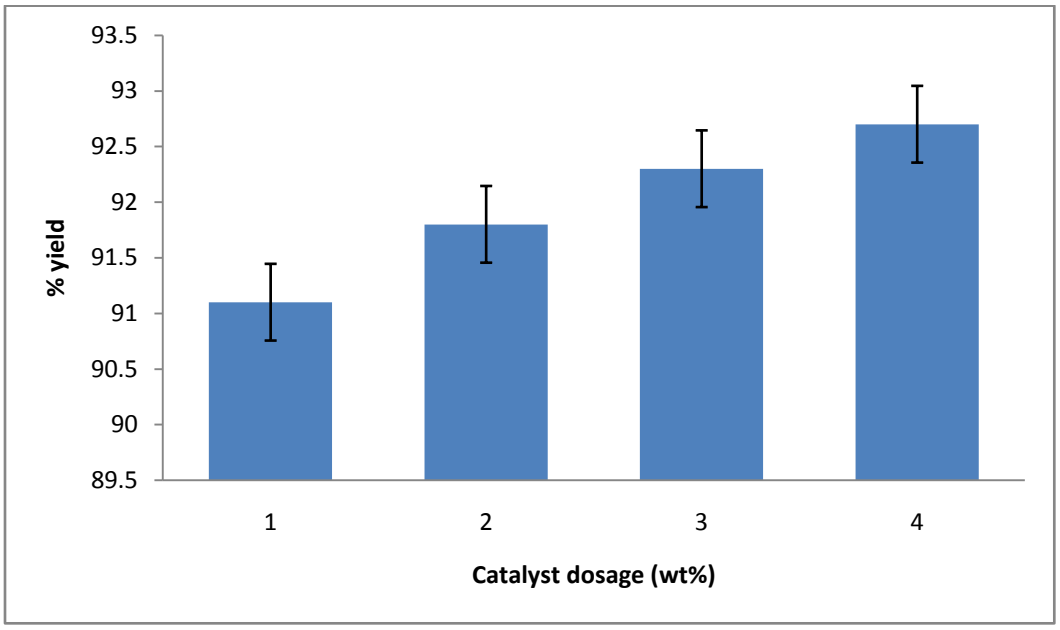


Figure 4.8: Effect of catalyst dosage on biodiesel yield

4.8 Catalyst Reusability Test

The yield data for reusability of four consecutive reaction cycles of catalyst are presented in Figure 4.9. The reactions performed under the same experimental conditions (60℃; oil/methanol molar ratio: 1:15, 120 min, and 4wt% catalyst). The percentage yield decreased as the number of cycles increased. It gave 92.8% yield upon the first trial; however, the percentage yield showed a slight decrease in the second trial (88.3%), which was likely due to the adsorption and accumulation of organic species on the catalyst surface leading to blocking of the active acid sites. As more and more organic species adsorbed and accumulated on the catalyst surface, the blockage of active sites was increasingly severe which led to a larger decrease in the third as well as the fourth trial compared with the second trail, but its activity was still above 71.8% in the fourth trial. Further transesterification reaction with the same catalyst after four cycles will give a percentage yield lower than71.8%, from the economic point of view the catalyst should not be used more than four times.

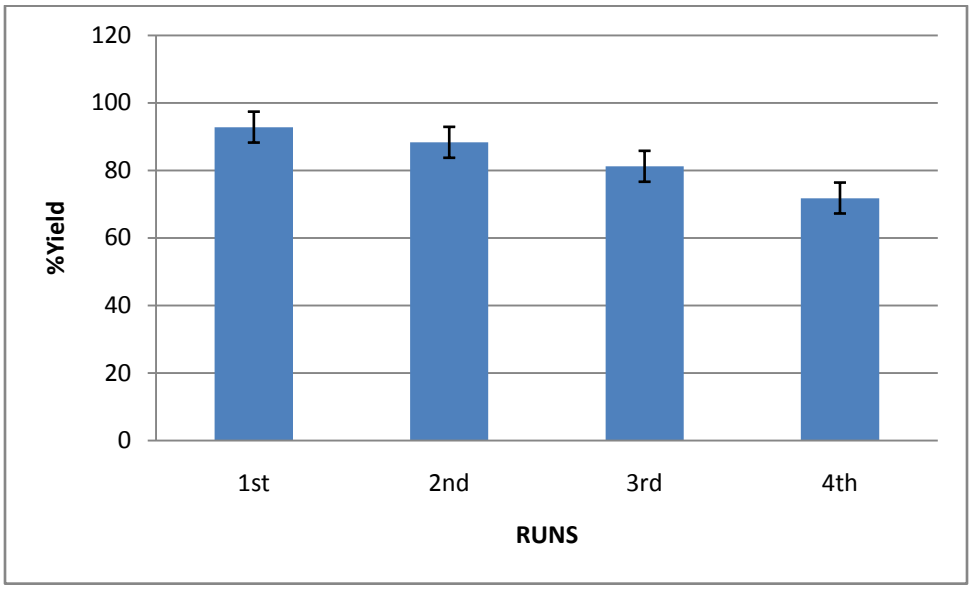


Figure 4.9: Reusability of the modified kaolin catalyst

4.9 Analysis of the Biodiesel Properties

Important fuel properties such as density, viscosity, pour point, cloud point, cetane number, and flash point of the biodiesel produced were determined and the results presented in Table 4.3

The results showed that the properties of biodiesel produced fell within the acceptable standard as observed in Table 4.3. The reduction in viscosity of WCO is very important for the efficiency of the engine. Many modern diesel engines use high technological injection pumps, which do not tolerates high viscous fluids, it clog fuel filters and become very risky to use at low surrounding temperature. Fuel atomization is also affected by viscosity. The 2.5 cP viscosity of the biodiesel obtained was within the ASTM D6571 standard of 1.9 to 6 cP. The acid value (AV) is a simple method for monitoring fuel quality. The AV of the WCO biodiesel was 0.35 mg KOH/g (Table 4.3), which satisfied the maximum AV of 0.50 mgKOH/g set in ASTM D6751 standard. Flash point is the lowest temperature at which fuel emits enough vapour to ignite. The flash point of the biodiesel produced was higher than that of Samuel *et al*., 2013 by 15℃. The high flash point of waste cooking biodiesel (154 ℃) compared to petroleum diesel (74 - 80 ℃) makes it safer to handle.

Table 4.3: Physico- chemical properties of the biodiesel and standard

Properties	ASTM D6571	Biodiesel produced	Waste cooking oil used
Density(g/cm^3)	0.86 – 0.89	0.86	0.892
Viscosity (cP)	1.9 - 6	2.5	11.5
Cloud point (℃)	-3 - 15	6	13.5
Pour point (℃)	-5 - 10	4	10
Cetane number	Min 47	53.7	39.85
Flash point (℃)	Min 130	154	196
Acid value(mg KOH/g)	$\leq$ 0.5	0.35	3.6465

The FTIR analysis of the biodiesel produced shows peaks at wave length of 1743 cm^{-1} which signified the presence of esters functional group in the biodiesel.

Based on the Beer- Lambert law, there is a direct relationship between absorbance and concentration of substances. At wave number of 1743 cm^{-1}, the absorbance associate to C=O stretch of esters increased in the biodiesel compared to the WCO as observed in Figure. 4.10. The absorbance of the biodiesel produced with 4wt%(4g) catalyst at same wave number was also higher than that of 1 wt% (1g). At wave number 3400 cm^{-1}, the absorbance associated to O-H stretch for carboxylic acid was high in WCO compared to that of the biodiesel; this showed that the acids in the oil were converted to esters as evident by the flattening of the peak from WCO to biodiesel produced with 4 wt% (4g) catalyst and the increase in absorbance associated to C=O stretch in the same order.

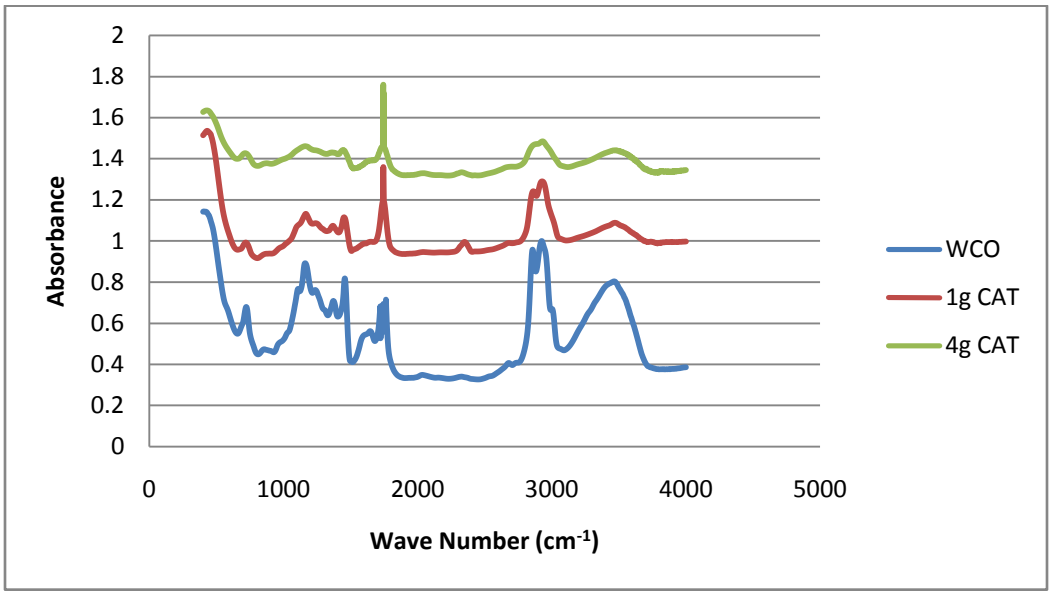


Figure 4.10FTIR analysis of WCO and biodiesel produced using1 wt% (1g) and4wt%(4g) catalyst dosage

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions were made from the results of the work carried out:

1. Solid acid catalysts were successfully synthesized via beneficiation, calcination and acidification ofKankara kaolinite clay for biodiesel production.
2. The synthesized catalysts were characterised using SEM, XRF and XRD techniques.
3. Physic-chemical properties of waste cooking oil were determined; viscosity (11.5 cP), acid value (3.6465 mgKOH/g) and free fatty acid (1.83) were obtained.
4. Highest biodiesel yield of 92.8% was obtained using 4 wt% catalyst amount, 120 min reaction time, 60°C reaction temperature and 1:15 oil to methanol molar ratio.
5. Reusability test carried out showed that after four runs with the same catalyst a biodiesel yield of 71.8% was obtained.
6. The properties of the biodiesel produced, viscosity (2.5cP), acid value (0.35), cetane number (53.7), flash point (154℃) and density (0.86g/cm^3) were within the ASTM D6571 standard.

5.2 Recommendation

1. Further research should be carried out for the process optimization using design of experiment (DOE).
2. The effect of having other oxides loaded to the catalyst should be investigated
3. Kinetic studies of the biodiesel production reaction using the synthesized catalyst should be carried out.

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APPENDIX A

DEALUMINATION SAMPLE CALCULATIONS

Calculations for stoichiometric quantity of acid and amount of water of dilution of filtrate prior to crystallization are presented in this appendix

The basic dealumination equation is:

$$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O \qquad \text{(A-l)}$$

102g 3 x 98g

Basis: 50g metakaolin

From XRF analysis metakaolin contains 36.1wt% Al_2O_3 (Table 4.1)

50g metakaolin contains 36.1% x 50g Al_2O_3 = 18.05g

From stoichiometry

102g Al_2O_3 requires 294g. H_2SO_4 (100wt%)

18.05g requires (18.05 x 294g)/102 = 52.03g H_2SO_4

Amount of 98% H_2SO_4 Required = (100 x 52.03g)/98 = 53.09g

ρ_{98} @ 30^oC = 1.8261gcm^{-3}

V_{98}= 53.09 / 1.8261 = 29.07cm^3

5 fold stoichiometric quantity = 5 x 29.07cm^3

V_{98} = 145.35cm^3

To dilute this to 60 wt% H_2SO_4

$60\rho_{60} V_{60} = 98\rho_{98}V_{98}$

$V_{60}= 292.76cm^3$

Amount of water to be added to dilute to 60%

$V_w= (\rho_{60}V_{60} - \rho_{98}V_{98})/\rho_w$

$V_w= 168.10cm^3$

Table A-1: Density values of sulfuric acid at different weight percent

Weight percent(%)	38	60	96	98
Density @ 30°C	1.2780	1.4808	1.8255	1.8261

APPENDIX B

SILICA TO ALUMINA MASS RATIO IN METAKAOLIN AND SYNTHESIZED CATALYST

From the XRF result CALCINED

	SiO_2	Al_2O_3
Percentage composition (%)	58.10	36.10
Mass ratio	1.6	1

$SiO_2/Al_2O_3 \approx 1.6$

From the XRF result (AD5)

	SiO_2	Al_2O_3
Percentage composition (%)	94.0	1.80
Mass ratio	52.2	1

$SiO_2/Al_2O_3 \approx 52.2$

From the XRF result (AD10)

	SiO_2	Al_2O_3
Percentage composition (%)	96.44	0.49
Mass ratio	196.8	1

$SiO_2/Al_2O_3 \approx 196.8$

From the XRF result (AD15)

	SiO_2	Al_2O_3
Percentage composition (%)	97.0	0.30
Mass ratio	323.3	1

$SiO_2/Al_2O_3 \approx 323.3$

From the XRF result (AD20)

	SiO_2	Al_2O_3
Percentage composition (%)	97.35	0.28
Mass ratio	347.6	1

$SiO_2/Al_2O_3 \approx 347.6$

APPENDIX C

DETREMINATION OF PHYSICO – CHEMICAL PROPERTIES OF THE WASTE COOKING OIL

Saponification Value

$$SV = \frac{56.1 * C_{HCl} * (B - S)}{w} = \frac{56.1 * 0.5 * (B - S)}{w} = \frac{28.05 * (B - S)}{w} \quad \text{C-1}$$

Where B = titre value of the blank, S = titre value of the sample, w = weight of the oil, 56.1 = molecular mass of KOH, and C = concentration of HCl (0.5 mol/dm^3)

Titre values: $B_1 = 44.6cm^3$, $S_1 = 32.35cm^3$

$$SV_1 = \frac{28.05 * (44.6 - 32.35)}{2} = 171.806 mgKOH/g$$

Titre values: $B_2 = 44.5cm^3$, $S_2 = 32.24cm^3$

$$SV_2 = \frac{28.05 * (44.5 - 32.24)}{2} = 171.946 mgKOH/g$$

$$SV_{average} = \frac{171.806 + 171.946}{2} = 171.876 mgKOH/g$$

Acid Value

$$AV = \frac{56.1 * V * C}{w} \quad \text{C-2}$$

Where 56.1 = molecular mass of KOH

V = titre value of KOH solution used (cm^3)

C = concentration of the standard volumetric (KOH) solution used ($0.1 mol/dm^3$)

w = mass of the test portion of the oil (g).

Titre values: $V_1 = 0.60cm^3$, $V_2 = 0.70cm^3$

$$V_{average} = \frac{0.60 + 0.70}{2} = 0.65cm^3$$

$$AV = \frac{56.1 * 0.65 * 0.1}{1} = 3.6465 mgKOH/g$$

$$\% FFA = AV * 1.99^{-1} = 3.6465 * 0.503 = 1.83\%$$

Molecular Weight

$$M = \frac{56.1 * 1000 * 3}{SV - AV}$$

Where SV = Saponification value of the raw WCO

AV = Acid value of the raw WCO

$$M = \frac{56.1 * 1000 * 3}{171.876 - 3.6465} = 1000.4 g/mol$$

APPENDIX D

DETERMINATION OF THE AMOUNT OF THE REACTANTS (WCO, METHANOL AND CATALYST) FOR THE REACTION

Basis: 100g of WCO

Mole of the WCO required = $\frac{mass\ of\ the\ WCO}{Molar\ mass\ of\ the\ WCO}$

n = $\frac{100}{1000.4}$ = 0.1mole

Volume of WCO required = mass of WCO / density of WCO

100 / 0.892 = 112.1cm^3

For Methanol to WCO ratio of (6:1),

Number of moles of methanol required

0.1*6 = 0.6moles.

Therefore, amount of methanol required in gram is:

Mass (g) = number of moles * molar mass of methanol

0.6 *32.04 = **19.224g**

Volume of methanol required = mass of methanol/ density of methanol

1.224 / 0.7918 = 24.3cm^3

For Methanol to WCO ratio of (9:1),

Number of moles of methanol required

0.1*9 = 0.6moles.

Therefore, amount of methanol required in gram is:

Mass (g) = number of moles * molar mass of methanol

0.9 *32.04 = **28.836g**

Volume of methanol required = mass of methanol/ density of methanol

28.836 / 0.7918 = 36.42cm^3

For Methanol to WCO ratio of (12:1),

Number of moles of methanol required

0.1*12 = 1.2moles.

Therefore, amount of methanol required in gram is:

Mass (g) = number of moles * molar mass of methanol

1.2 *32.04 = **38.448g**

Volume of methanol required = mass of methanol/ density of methanol

38.448 / 0.7918 = 48.56cm^3

For Methanol to WCO ratio of (15:1),

Number of moles of methanol required

0.1*15 = 1.5moles.

Therefore, amount of methanol required in gram is:

Mass (g) = number of moles * molar mass of methanol

1.5 *32.04 = **48.06g**

Volume of methanol required = mass of methanol/ density of methanol

48.06 / 0.7918 = 60.70cm^3

Amount of catalyst used in the reactions

For 1wt% catalyst

Amount of the catalyst required in gram is:

= 1%wt of the WCO

i.e. $\frac{1}{100}$ * 100 = **1g**

For 2wt% catalyst

Amount of the catalyst required in gram is:

= 2%wt of the WCO

i.e. $\frac{2}{100}$ * 100 = **2g**

For 3wt% catalyst

Amount of the catalyst required in gram is:

= 3%wt of the WCO

i.e. $\frac{3}{100}$ * 100 = **3g**

For 4wt% catalyst

Amount of the catalyst required in gram is:

= 4%wt of the WCO

i.e. $\frac{4}{100}$ * 100 = **4g**

APPENDIX E

TRANSESTERIFICATION RESULTS

% Yield = $\frac{weight\ of\ biodiesel}{weight\ of\ oil} \times 100\%$

The mass of waste cooking oil used for each of the reactions was 100g.

Table E1: Effect of silica to alumina ratio.

Si /Al mass ratio	**Mass of sample bottle**	**Mass of sample bottle and biodiesel**	**Mass of biodiesel**	**% Yield**
1.6	9.3	86.6	77.3	77.3
52.2	9.2	94.2	85.0	85.0
196.8	9.4	95.8	86.4	86.4
323.3	9.3	96.2	86.9	86.9
347.2	9.3	97.7	88.4	88.4

Table E2: Effect of reaction temperature.

Temperature (^{0}C)	**Mass of sample bottle**	**Mass of sample bottle and biodiesel**	**Mass of biodiesel**	**% Yield**
50	9.4	77.7	68.3	68.3
55	9.5	87.6	78.1	78.1
60	9.4	97.6	88.2	88.2
65	9.3	89.4	80.1	80.1

Table E3: Effect of Oil to Methanol.

Oil to methanol ratio	Mass of sample bottle	Mass of sample bottle and biodiesel	Mass of biodiesel	% Yield
1:6	9.4	97.6	88.2	88.2
1:9	9.3	98.2	88.9	88.9
1:12	9.4	99.2	89.8	89.8
1:15	9.3	99.6	90.3	90.3

Table E4: Effect of reaction time.

Reaction time (mins)	Mass of sample bottle	Mass of sample bottle and biodiesel	Mass of biodiesel	% Yield
30	9.4	93.6	84.2	84.2
60	9.3	99.2	89.9	89.9
90	9.2	100	90.8	90.8
120	9.3	100.4	91.1	91.1

Table E5: Effect of catalyst dosage

Catalyst dosage (g)	Mass of sample bottle	Mass of sample bottle and biodiesel	Mass of biodiesel	% Yield
1	9.3	100.4	91.1	91.1
2	9.3	101.1	91.8	91.8
3	9.3	101.6	92.3	92.3
4	9.1	101.8	92.7	92.7

Table E6: Reusability Test

Run	Mass of sample bottle	Mass of sample bottle and biodiesel	Mass of biodiesel	% Yield
1	9.1	101.8	92.7	92.7
2	9.3	97.6	88.3	88.3
3	9.2	90.4	81.2	81.2
4	9.3	81.1	71.8	71.8

APPENDIX F

FTIR ANALYSIS OF BIODIESEL

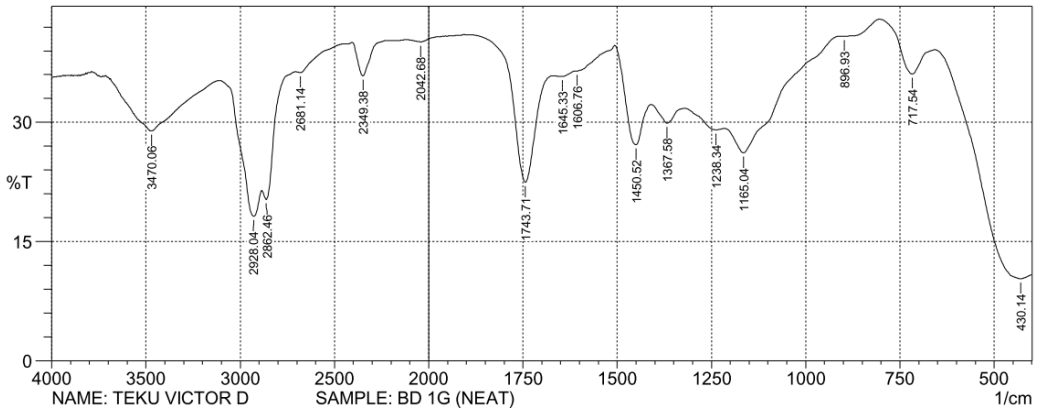


Figure F1: FTIR analysis of biodiesel produced using 1g

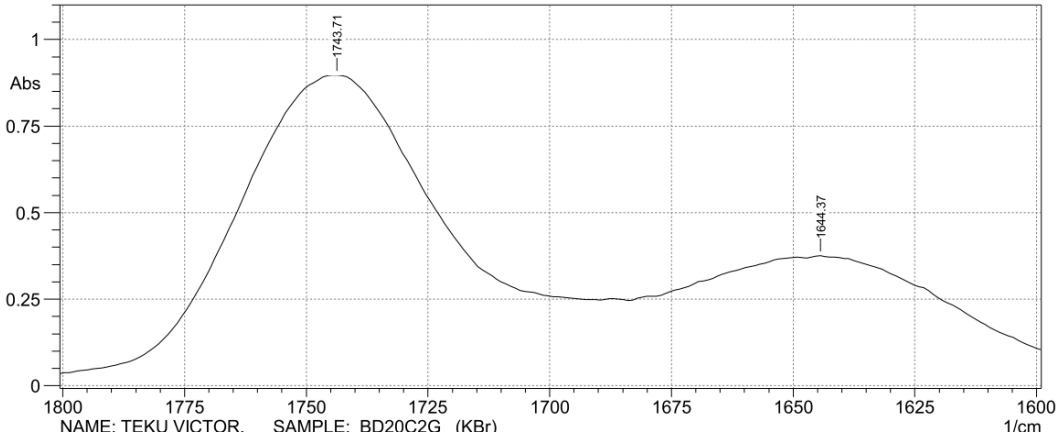


Figure F2: FTIR analysis of biodiesel produced using 2g catalyst

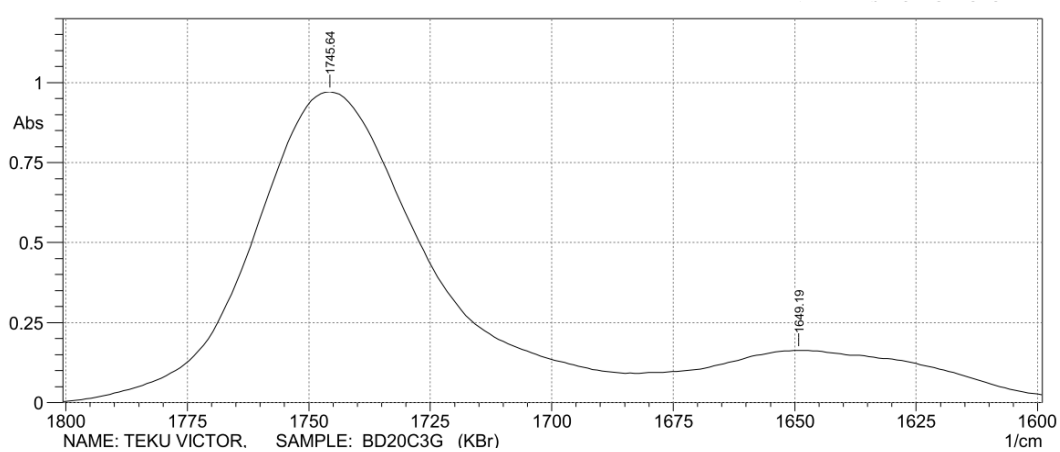


Figure F3: FTIR analysis of biodiesel produced using 3g catalyst

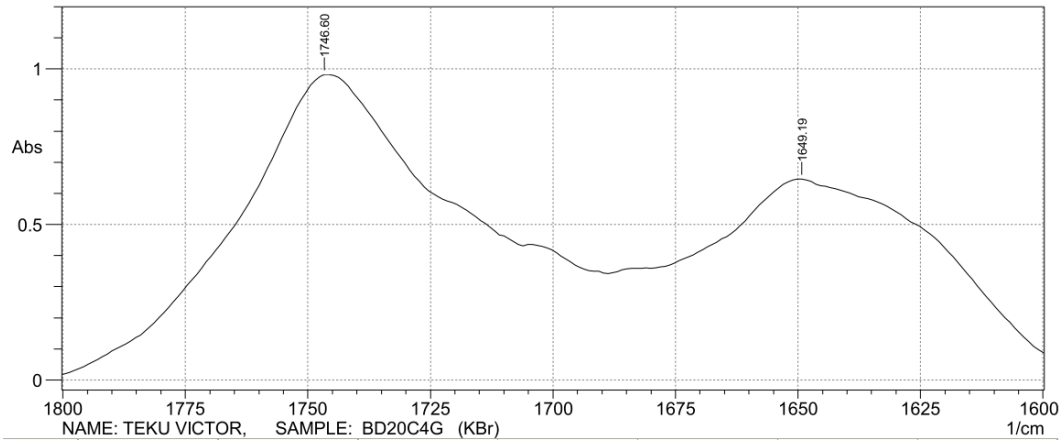


Figure F4: FTIR analysis of biodiesel produced using 4g catalyst

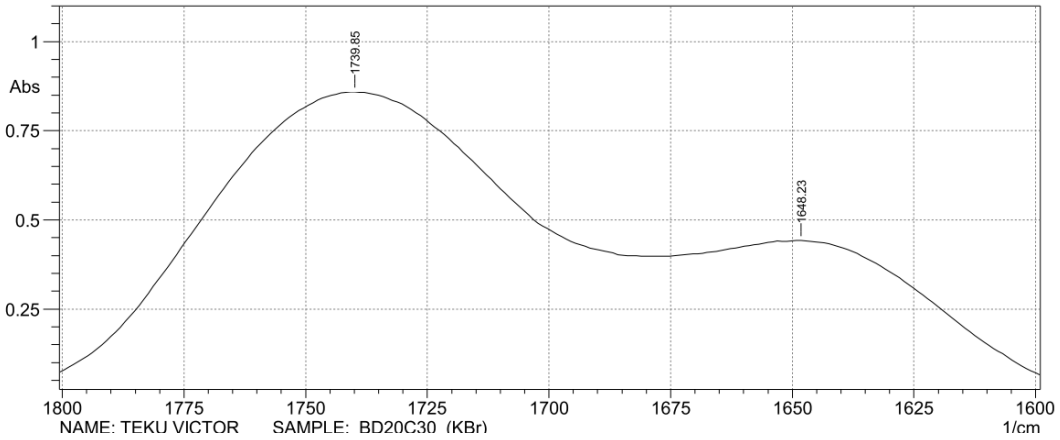


Figure F5: FTIR analysis of biodiesel produced using 30 mins reaction time

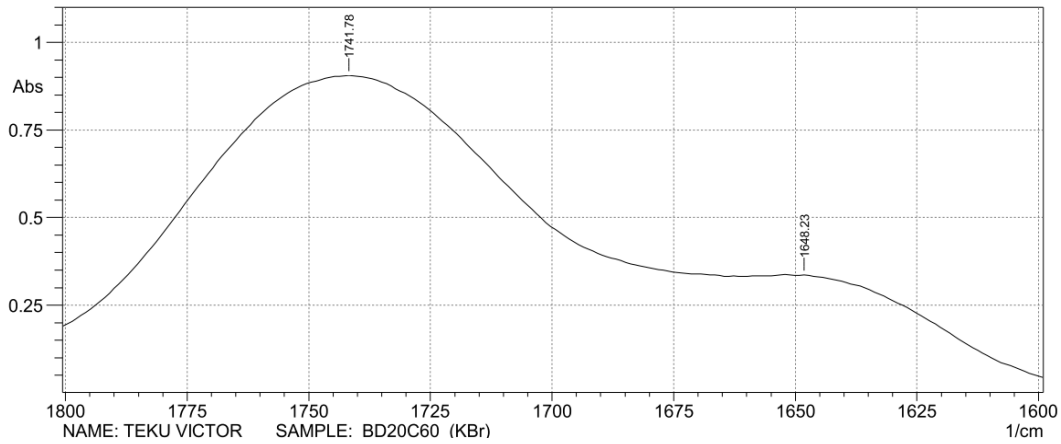


Figure F6: FTIR analysis of biodiesel produced using 60 mins reaction time

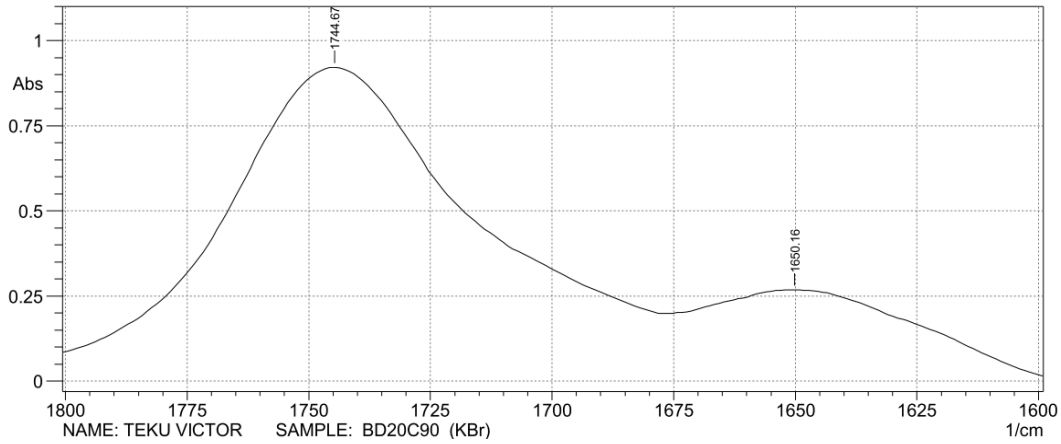


Figure F7: FTIR analysis of biodiesel produced using 90 mins reaction time

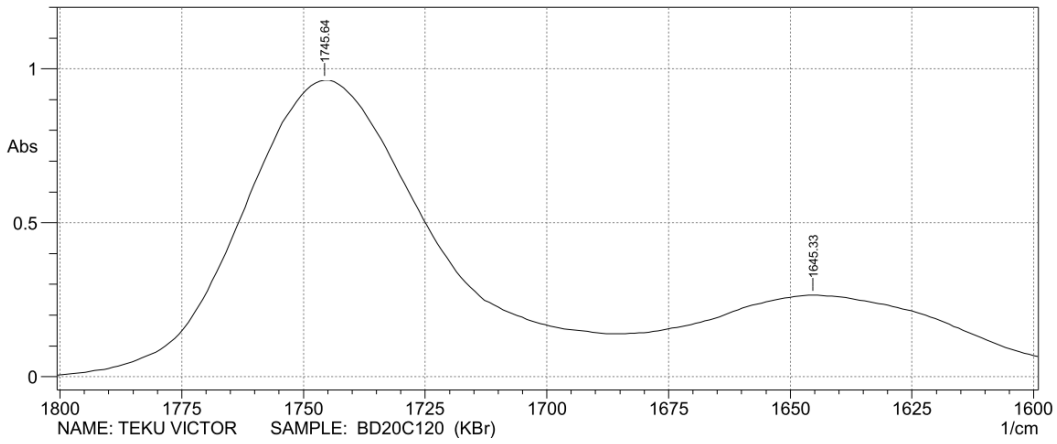


Figure F8: FTIR analysis of biodiesel produced using 120 mins reaction time