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**Biodiesel Production by Transesterification of Waste Cooking Oil Using
Modified Attapulgite**

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DECLARATION

I, Mabungela Ntandokazi, hereby declare that this dissertation entitled “**Biodiesel production by transesterification of waste cooking oil using modified attapulgate**”, handed in for the degree of Chemistry in the faculty of Applied and Computer Science at the Vaal University of Technology has not been submitted in any form to any other academic institution. This study presents original work by the author and all sources used or quoted have been duly acknowledged in the text. The research described in this thesis was carried out in the Department of Chemistry, Faculty of Applied and Computer Sciences, Vaal University of Technology, South Africa, under the supervision of Professor Fanyana Mtunzi and Doctor Elvera Viljoen.

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ABSTRACT

Biodiesel has an ability to solve the problem associated with the use of fossil fuels as a source of energy. The aim of this study was to produce biodiesel from waste cooking oil (WCO) by transesterification, catalysed with potassium hydroxide (KOH) supported on attapulgite (ATP) clay as the heterogeneous catalyst. WCO was used on the basis that it is one of the cheapest feedstocks for biodiesel production, is readily available and can minimise environmental impact.

ATP clay was first crushed and sieved to particle sizes of $\leq 90 \mu\text{m}$ and subsequently treated with hydrochloric acid (HCl) to remove impurities. The KOH supported ATP catalyst was prepared through ion exchange method by soaking ATP into KOH solution, dried in an oven and later calcined at $400 \text{ }^\circ\text{C}$ in a furnace. The prepared catalyst and ATP clay were characterised using Hammett indicator to determine the basic strength of the catalyst. XRF and EDX were used to determine the elemental composition of the catalyst whilst XRD was used to determine the crystallinity of the ATP after modification. The functional groups of ATP were determined by FTIR. BET was utilised to determine the changes on the surface area, pore volume and pore diameter of ATP and on the other hand, SEM was used to determine the morphological changes on the surface of ATP.

The XRD, FTIR, BET AND SEM-EDX showed that addition of potassium caused changes on the surface of the ATP. The optimal conditions for the transesterification reaction of waste cooking oil with methanol were found to be

oil-to-methanol molar ratio of 1:15, 3wt% catalyst amount, 65 °C, 3 h of a reaction time, at 200 rpm stirring rate and 94 % biodiesel yield was obtained.

After the catalyst was reuse three consecutive times, the decrease in biodiesel yield was observed (**Figure 17**) after each cycle. However, the 5MKOH/ATP catalyst is heterogeneous and can be used to transesterify WCO with good yield.

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List of Abbreviations

AC = Acid value

ASTM = American Society for Testing and Materials

ATP = Attapugite clay

BET = Brunauer–Emmett–Teller

C = Concentration

FAME = Fatty acids methyl ester

FFA = Free Fatty Acid

FTIR = Fourier transform infrared

GC-MS = Gas Chromatography- Mass Spectrometry

h = hour

m = mass

Max = Maximum

MeOH = Methanol

Min = Minimum

PVA = Polyvinyl Acetate

SABS = South African Bureau of Standards

SEM-EDS = Scanning Electron Microscopy-Energy Dispersive Spectroscopy

V = Volume

WCO = Waste cooking oil

XRD = X-ray diffractometer

XRF = X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

The World is currently worried about the protection of the environment and the conservation of non-renewable natural resources. This therefore prompted researchers to look for alternative sources of energy to substitute the traditional fossil fuels (Anita & Dawn, 2013; Gashew & Likachew, 2014). The combustion of fossil fuels releases harmful gases into the atmosphere, which causes environmental problems like air pollution and global warming or green house effects etc. (Nikul et al., 2013). Due to this adverse effect on the environment, it is essential to find alternative energy sources; which are secure and has less environmental footprint. Biodiesel has been reported to be a potential alternative, eco-friendly fuel with less environmental impact (Agarwal et al., 2015).

Biodiesel is a fuel that is similar to the conventional diesel, except that it is formed from biological sources such as vegetable oils and animal fats. Currently, biodiesel is an alternative transport fuel made from oils and fats, which can be used directly in conventional unmodified diesel engines (Zhu et al., 2017; Endalew et al., 2011). It is biodegradable, non-toxic, safer to handle, store and transport (Tan et al., 2015). It is also environmentally friendly as it reduces greenhouse gas emissions such as CO₂, CO and unburned hydrocarbons (Borges

& Diaz, 2012; Farooq et al., 2015). In addition, biodiesel contains no sulphur, aromatic compounds and particulate materials. However, due to poor quality of biodiesel produced by many researchers thus far, the challenge pertaining to production of high quality biodiesel as an alternative fuel remains and continues to attract investigation.

Biodiesel is produced through a process called transesterification (Chopade et al., 2012). Transesterification is the process whereby triglycerides from oil or fats feedstock is reacted with alcohol in the presence of a suitable catalyst to form an ester and glyceride products (Boege & Diaz, 2012; Anastopoulos et al., 2009). It is used because of its simplicity and the biodiesel produced has been shown to be similar to that of the conventional diesel fuel (Talhi et al., 2010). The quality of biodiesel produced depends on the type of feedstock, type and amount of catalyst, reaction temperature and time, alcohol to oil molar ratio, free fatty acid and water content and the agitation speed (Jagadale & Jugulkar, 2012; Sain et al., 2017).

Homogeneous or heterogeneous base and acid catalysts or enzymes catalysts are commonly used in the transesterification reaction to produce biodiesel (Gupta et al, 2015). Heterogeneous base catalysts are more active due to inherently surface area compared to homogeneous counterpart leading to increase in biodiesel yield (Liu et al., 2018). Heterogeneous catalysts are generally more preferred for biodiesel production because they can be recycled and re-used, are relatively less expensive and are easier to separate from the final product, and also can be

continuously used without the need for further purification (Endalew et al., 2011; Kataria et al., 2019). Heterogeneous catalysts are also preferred to avoid the neutralisation and separation steps (Ramachandran et al., 2013). In the case of waste cooking oils as a feedstock for transesterification process, heterogeneous catalysts are mostly preferred based on the fact that waste cooking oils have higher amount of free fatty acids that result in the formation of saponification product. Soap formation causes reduction in the yield of transesterification reaction and hinders the biodiesel purification step (Alves et al., 2012).

Thus this research aims to investigate biodiesel production from waste cooking oil by transesterification using modified attapulgite (ATP) as a heterogeneous base catalyst in the presence of methanol. ATP is found abundantly in nature as a hydrated three dimensional magnesium aluminium silicate material with a chemical formula $[(Al_2Mg_2)Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O]$ (Wang et al., 2018). It has gained extensive use as a heterogeneous support because of its three-dimensional structure, no swelling can occur, ion exchange capacity, pore structure, large surface area, adsorption properties and low specific volume ($2.0-2,3\text{gcm}^{-3}$) (Rafiq et al., 2018).

1.2. Problem statement

Fossil fuels being the key source of energy cannot be recycled. Depletion of these fuels and their impact on the environment has given rise to the quest to find an alternative sustainable energy source. On the other hand, the dumping of waste

cooking oils from restaurants down the drain and sinks, on the ground, into garbage and into rivers leads to drain and sewer blockages and cause harmful effects on aquatic animals' life (Guerrero et al., 2011). Amongst others, biodiesel is found and considered to be the best and suitable substitute for diesel fuel. Although biodiesel has been produced successfully, its production cost is still high due to high cost of raw material and processing (Demirbas, 2009).

Currently, most commercial processes produce biodiesel from vegetable oils and animal fats in the presence of homogeneous base or acid catalysts (Ye et al., 2013). However, challenges encountered with using homogeneous catalysts, include, its separation from biodiesel and sensitivity towards oils with high amounts of free fatty acids and water give rise to the preference of using heterogeneous catalysts in biodiesel production. Therefore, the use of waste oil for the biodiesel production will consequently reduce costs. WCO is also easy to obtain and easy to handle due to low viscosity and relatively cheaper compared to vegetable oils. Hence, in this study the biodiesel is produced from waste cooking oil as feedstock in the presence of KOH supported on attapulgite clay as a heterogeneous catalyst.

1.3. Research aim and objectives

1.3.1. Research aim

The aim of this project is to produce biodiesel by transesterification of waste cooking oils using basic heterogeneous catalysts prepared by supporting potassium ions on attapulgite clay.

1.3.2. Research objectives

This study is based on biodiesel production by transesterification of waste cooking oil as a feedstock using modified attapulgite as a support. In order to achieve the aim of the research, the following objectives were set:

- To modify attapulgite clay into a base catalyst using ion-exchange method
- To investigate the effect of potassium loading (1M-5M) on the biodiesel yield
- To characterise the catalyst using BET, XRD, XRF, Hamad indicator, FTIR and SEM-EDS
- To investigate the influence of reaction parameters such as reaction time, the amount of catalyst, temperature, alcohol to oil molar ratio and stirring rate on the formation of the biodiesel using waste cooking oil.
- To investigate the physical and chemical properties of the biodiesel formed.
- To characterise the formed biodiesel using GC-MS-FID

CHAPTER 2

LITERATURE REVIEW

1.1. Introduction

Biodiesel has been investigated in the past and currently as a possible replacement of the current fossil fuels. In 1898 Rudolf Diesel discovered the diesel engine by testing peanut oil in his car engine (Dash & Lingfa, 2018). During the 1930s and 1940s, vegetable oils were utilised as diesel only during emergencies (Fangrui and Milford, 1999). However, the increase in crude oil prices, environmental pollution caused by burning of fossil fuels and depletion of fossil fuel resources resulted in the search for alternative renewable energy resources, especially for transportation fuels (Mubarak et al., 2015; Mata and Martins, 2010).

Due to the above stated challenges, biodiesel was considered to be a potential alternative fuel since it is made from agricultural materials that are produced by photosynthetic carbon fixation and for the fact that burning of these oils do not produce harmful gases (Sukjit and Punsuvon, 2013). Biodiesel is produced by transesterification of vegetable oils with methanol in the presence of homogeneous or heterogeneous catalysts (Sandesh et al., 2016, Chen et al., 2015).

2.2. Biodiesel

Biodiesel is methyl or ethyl esters of fatty acids made from vegetable oils and animal fats (Zhang et al., 2010, Zhu et al., 2017). Utilisation of vegetable oils as feedstock to alternative fuel has been investigated extensively, since the first

discovery by Rudolph Diesel who demonstrated peanut oil to work in his car engine (Ma & Hanna, 2009).

Some of the advantages of using biodiesel as a fuel include the fact that; it is produced from vegetable oils and animal fats making it a renewable fuel. It is less toxic compared to diesel fuel. It is biodegradable reducing the environmental impact caused by diesel fuel leaks. It minimises emission of carcinogenic substance such as aromatics which lowers health risks. It has a high flash point making it safe to store. It can be used in conventional diesel engine without modification.

Even though vegetable oils play important role as a feed stock for an alternative fuel (biodiesel), there have been some drawbacks associated with direct utilisation of vegetable oils in engines. The key challenge is that vegetable oils are highly viscous and have low volatility which causes the formation of deposits in engines due to incorrect vaporisation characteristics which generate incomplete combustion (Kataria et al., 2019; Verma & Sharma, 2016; Chopade et al., 2011). Other disadvantages include that vegetable oils and animal fats are made up of phospholipids, free fatty acids, water, steroids and other impurities (Ma & Hanna, 1999). To address these challenges, vegetable oils firstly need to be chemically modified using the following processes: direct use and blending, micro-emulsion process, pyrolysis and transesterification. Among these processes, transesterification is the most used process to produce a cleaner and more

environmentally friendly fuel from vegetables (Emweremadu & Mbarawa, 2009; Onokwuli et al., 2017).

2.3. PROCESSES OF PRODUCING BIODIESEL

There are four processes that are used to synthesise biodiesel, namely; direct use and blending, micro-emulsion, thermal cracking and transesterification.

2.3.1. Direct use and blending

Vegetable oils can be used directly or blended with fossil diesel for use in diesel engines. However these oils are highly viscous compared to fossil diesel, leading to problems such as incomplete combustion, poor fuel atomisation, gum formation due to oxidation and polymerisation during storage (Ma and Hanna, 1999).

2.3.2. Micro-emulsion process

This is a process in which the dispersed phase is in the form of very small droplets usually produced and maintained with the aid of surfactants and having dimension in the range of 1-150 nm. The process is also used to reduce viscosity of oils, (Agarwal et al., 2015). Micro-emulsion with solvent such as methanol, ethanol and 1-butanol have been studied (Gashaw & Teshita, 2014). It has been found that micro-emulsion of vegetable oils and alcohols are not suitable for long term use due to incomplete combustion, increasing viscosity of the lubricating oil (Mittelbach & Remschmidt, 2006).

2.3.3. Pyrolysis (thermal cracking)

This process involves heating of the feedstock at high temperatures to break the molecular bonds to produce biodiesel. However, it has been found that the viscosity of the fuel is too high and it requires high cost equipment for processing (Gashaw & Teshita, 2014).

2.3.4. Transesterification reaction

Transesterification reaction is the reaction of vegetable oils or fats with methanol in the presence of acids, base or enzyme catalysts producing esters and glycerol (Corro et al., 2013). The simplified chemical reaction of transesterification is given in **Figure 1** below:

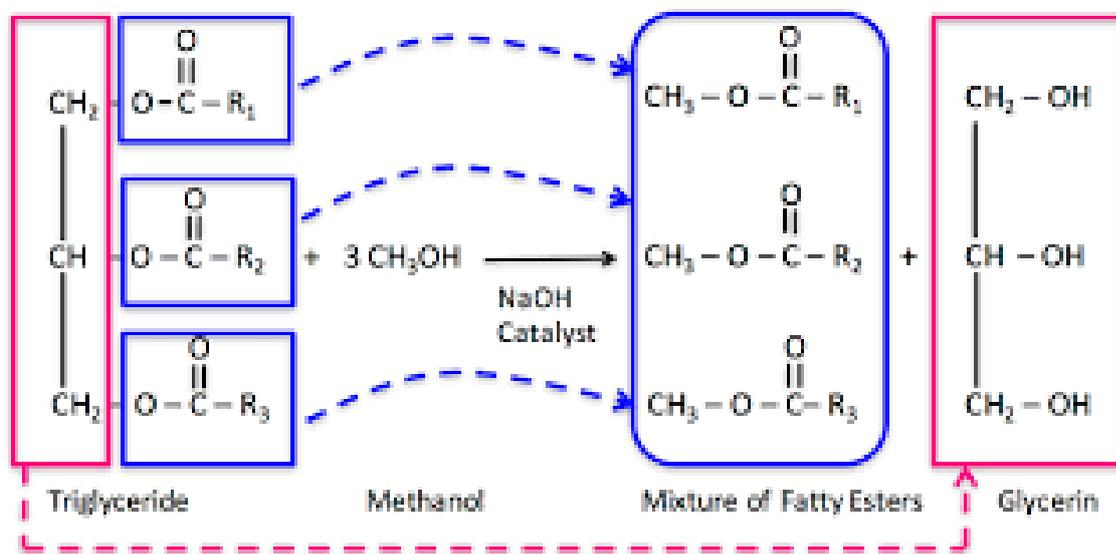


Figure 1: An example of transesterification reaction of an oil and methanol ;R₁, R₂, R₃ are fatty acids chains (Atadashi et al., 2010).

The fatty acids chains are usually composed of stearic, oleic, palmitic, linolenic and linoleic (Leung et al., 2010). The vegetable oils and animal fats contain long chain fatty acids attached to one molecule of glycerol. These long chain fatty acids have different carbon chains, the position, orientation and the position of double bonds in these chain make the oils more viscous (Emweremadu & Mbarawa, 2009). Therefore, the transesterification reaction transforms esters from long chain fatty acids into monoalkyl esters, significantly decreasing the viscosity of the oil (Gashaw & Likachew, 2014).

This process occurs in three consecutive reversible reaction steps, producing di- and monoglycerides intermediates and converting glyceride to glycerol, giving one ester in each step (**Figure 2**). This reaction is reversible, therefore, it requires 1 mole of triglyceride and 3 moles of alcohol to shift the equilibrium to the formation of the desired product. Excess alcohol is used to enhance the ester yield and the separation of ester from glycerol easy.



Figure 2: Three consecutive and reversible transesterification reaction (Marchetti et al., 2007)

The transesterification reaction is influenced by various parameters which include reaction temperature and time, reaction temperature and time, water content and free fatty acid content, catalyst type and catalyst amount and alcohol to oil molar ratio.

The influence of these parameters is explained below from section 2.3.4.1 onwards based on the type of catalyst used. The catalyst used for transesterification can be classified as acid, base and biocatalyst (**Figure 3**).

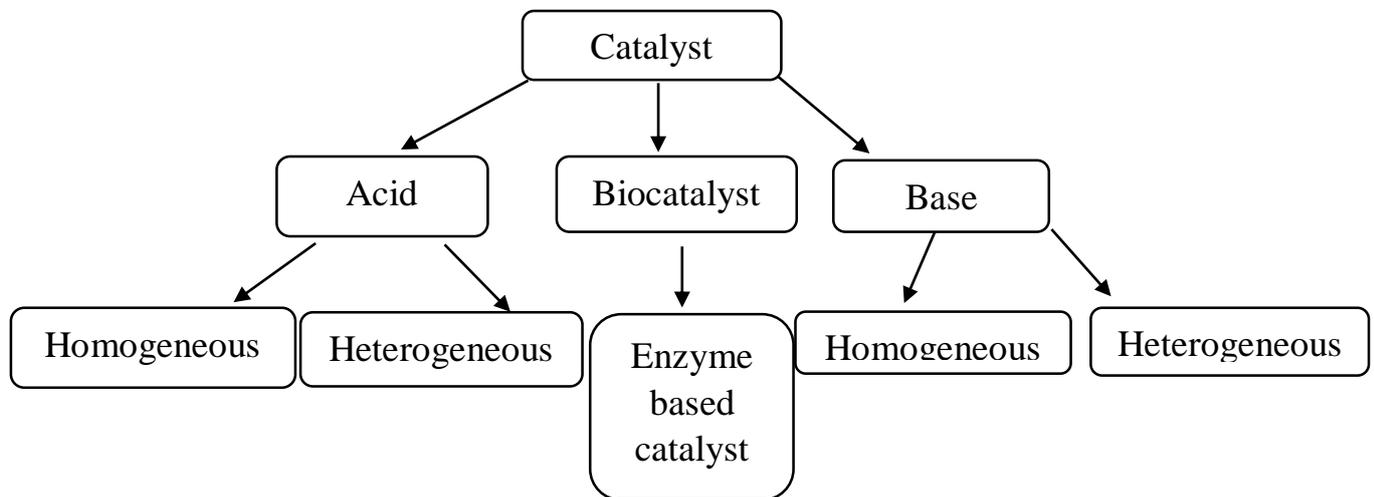


Figure 3: Classification of transesterification catalysts (Pathak, 2015)

2.3.4.1. Base catalysed transesterification reaction

Homogeneous base catalysts are catalysts that exist in the same phase as the products or reactants. These catalysts include but not limited; NaOH, KOH, KOCH₃, NaOCH₃, and NaOCH₂CH₃ (Verma & Sharma, 2016). Homogeneous catalysts are the commonly employed catalysts commercially because they produce high yields under mild conditions in short period of time (Kataria et al.,

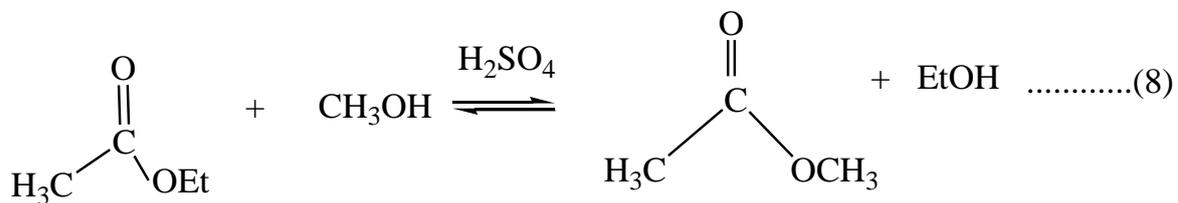
The active sites are able to bond with a second alcohol molecule, initiating another catalytic cycle. Diglyceride and monoglyceride are transformed via the same mechanism to produce a mixture of alkyl esters and glycerol.

However, there are a number of major difficulties in utilising homogeneous catalysis. These include: difficulty of homogeneous catalysts separation from the product mixture because it has the same phase as the product and large amount of waste water is produced during purification step which is not environmentally friendly. They are also affected by the quality of the oil, that is, the amount of acid value and water content present in the oil (Kataria et al., 2019; Corro et al., 2013). Homogeneous base catalysts are sensitive towards oils with high amounts of free fatty acids and water. Fatty acids and water content in oils cause the unwanted formation of carboxylates by the saponification reaction, forming stable emulsion which are difficult to separate, consequently leading to a decrease in the biodiesel yield and cannot be recycled (Gnanaprakasam et al., 2013; Said et al., 2015). Due to these challenges, homogeneous acid catalysts are often considered.

2.3.4.2. Homogeneous acid catalysis

The transesterification reaction is catalysed by Brønsted acids such as sulfuric, sulfonic acids, H_3PO_4 , HCl etc. as can be shown in **Figure 5** below for the transesterification of ethyl methyl ester. These catalysts give high yields of alkyl

esters. However, there are some drawbacks associated with the use of these catalysts.



Machanism is as follows:

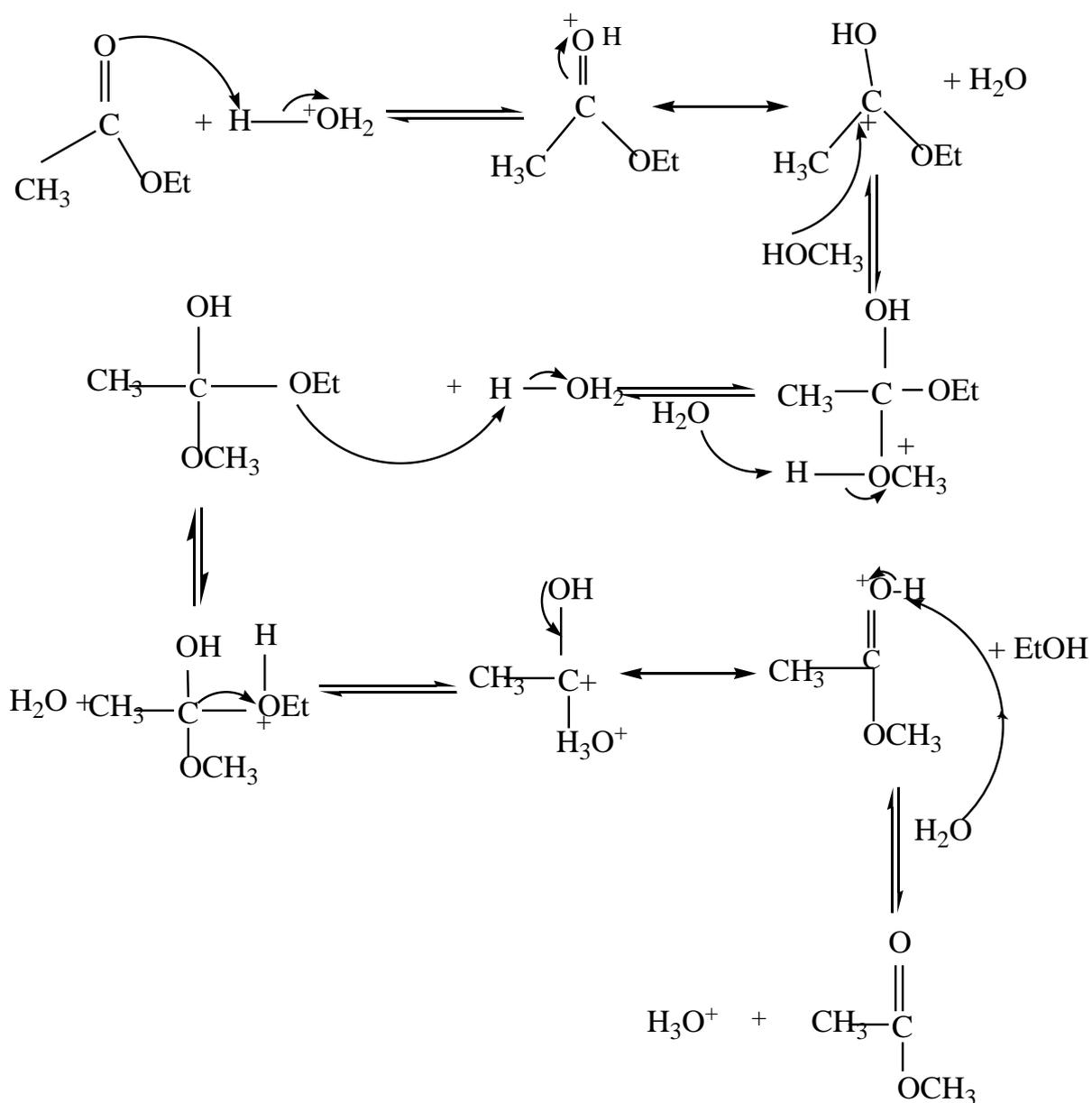


Figure 5: Mechanism of acid catalyzed transesterification

Homogeneous acid catalysts are insensitive towards oils with high amount of free fatty acids (FFA) like waste oils, *Jatropha curcas*, rubber, tobacco oils, etc., and they can catalyse the esterification and transesterification at the same time (Thanh et al., 2012). However, it has been found that acid catalysts are sensitive towards water content in oils and affect the formation of fatty acid methyl esters (FAME) yield. Therefore, homogeneous acid catalysts can be used as the pre-treatment step when it is necessary to change FFA into esters followed by base catalysed transesterification (Hincapie et al., 2011).

Disadvantages of acid catalysts are that they need long reaction time at high temperature, require high amount of methanol and cause the equipment corrosion. Schuchard et al., (1997), produced higher than 99 % biodiesel from soybean using 1 % of sulphuric acid with and alcohol to oil molar ratio of 30:1 at 65 °C in 50 h of reaction time.

Therefore, heterogeneous acid or base catalysts are found and considered to be the most suitable catalysts for transesterification. This is because they can be easily separated from the reaction mixture, inexpensive, less corrosive towards process equipment, no salts formation in the neutralisation step (Vedrine, 2019; Khoury et al., 2019).

2.3.4.3. Heterogeneous solid catalyst

Heterogeneous solid catalysts are catalysts that are in a different phase from that of the reactants. To overcome the challenges associated with the use of homogeneous catalysts in biodiesel production, heterogeneous solid catalysts are found to be a likely solution (Atadashi et al., 2012). Heterogeneous solid catalysts are categorised into three groups: acidic, basic catalysts and enzyme catalysts (Diamantopoulos et al., 2015). Heterogeneous solid catalysts are non-corrosive towards process equipment and are considered to be environmentally friendly (Kumar et al., 2012). They can be reused, easily separated from the reaction mixture and require no washing step. The high selectivity and activity of heterogeneous catalysts is largely impacted by the surface properties of heterogeneous catalysts (Gera et al., 2009).

Heterogeneous solid acid catalysts have high tolerance to oils with high level of FFA since they can catalyse esterification and transesterification reaction simultaneously. Pukale et al. (2015) reported the use of different heterogeneous catalysts such as K_3PO_4 , Na_2PO_4 , $NaHPO_4$, K_3HPO_4 and NaH_2PO_4 for transesterification reaction of waste cooking oil. The experimental conditions used in the study were 1:6 oil to methanol molar ratio, at 60 °C of reaction temperature, and 2% catalyst concentration for a period of 120 min. For K_3PO_4 catalyst, a relatively high amount of 70,5% biodiesel yield was obtained. This was due to the higher basicity of K_3PO_4 than other catalysts used.

General, acid catalysts, either homogeneous or heterogeneous, require long reaction times and high temperature. Their catalytic activity is low. Additional challenge include their sensitivity towards water which retards catalyst activity of the transesterification reaction leading to unwanted side reactions.

2.3.4.4. Heterogeneous solid base catalysts

These catalysts include single component metal oxides, zeolites, supported alkali metals, clays and non-oxides. Generally, these catalysts are more active compared to solid acid catalysts. They exhibit high catalytic activity, long catalyst life time, and can operate under mild reaction conditions. The highly active alkoxide ion (RO^-) describes the high activity of the base catalyst when reacting with alcohols (Dai et al., 2018; Shokouhimehr et al., 2018; Najaiva et al., 2018).

2.3.4.4.1. Metal oxides

They include: calcium oxide (CaO), magnesium oxide (MgO), aluminium oxide (Al_2O_3), tin oxide (SnO_2), titanium dioxide (TiO_2), etc. These catalysts have a great influence on biodiesel production because they have high catalytic activity, long catalytic life time and can operate under mild reaction conditions (Borges & Diaz, 2012). However, using metal oxides on biodiesel production poses some challenges, which include slow reaction rate, and can have similar effect as homogeneous catalysts by forming stable emulsions and metal glycerides (Narasimharao et al., 2007).

Kouzu et al. (2008), in another study used CaO, Ca(OH)₂ and CaCO₃ as solid base catalysts for transesterification of edible soybean oil. It was observed that 93% FAME yield was obtained using CaO, 12% for Ca(OH)₂, and 0% with CaCO₃ at 1hr reaction time. They further used CaO for transesterification of WCO and 99% of FAME yield was obtained in 2 h reaction time. However, calcium carboxylate formation was also observed.

2.3.4.4.2. Zeolites

Zeolites are crystalline solids structures made of silicon, aluminium and oxygen atoms that form frameworks with cavities and channels inside where cations, water and small molecules may reside. Many zeolites occur naturally as minerals. However, they can be synthesised (Baerlocher et al., 2007). Synthetic zeolites have an important advantage due to the purity of crystalline products and the uniformity of the crystals (Breck, 1974 & Szoztack, 1998). However, synthesis of zeolites from chemical sources of aluminium and silicon is expensive. The cost of the zeolite material can be relatively reduced by the use of material such as natural clay minerals, volcanic glass, rice husks, diatoms, fly ash or paper sludge as starting material (Tanakal et al., 2004; Adamczyk and Bialecka, 2005;). The increase in the electropositive nature of the exchanged cation of the alkali ion exchanged zeolite increases the basic strength of catalyst (Helelweni et al., 2009). The metal oxides cluster in zeolites cages through decomposition of impregnated metal salts results in high basicity of the catalysts (Philippou &

Anderson, 2000). Hassani et al. (2014), prepared a zeolite-based catalyst using zeolite powder, kaolinite and polyvinyl acetate (PVA), and used it for transesterification of WCO. They obtained a maximum yield of 46% at a reaction temperature of 70 °C, 5:1 methanol: oil molar ratio for 6 h of reaction time.

2.3.4.4.3. Supported alkali and alkaline earth metals

Alkali and alkaline earth metals are used as the source of basicity and as active species of supported catalysts. They are either used in a metallic form or as different ionic forms of halides, carbonates, hydroxides and nitrates like K^+ , Li^+ , La^{3+} , KOH, NaOH, KF, etc, (Vyas, 2009). Most used supports are alumina, zinc oxide, silica, zirconium and zeolites. Moreover, the basicity of the catalyst has the main influence on the catalyst activity, followed by the specific surface area and pore volume of the catalysts (Sun et al., 2008). On the other hand, the support helps to improve the basicity of the catalyst by providing more surface area and pores for active sites in the catalyst (Refaat, 2011).

Hamad et al. (2010) also prepared a catalyst by supporting potassium and caesium ions on zirconium oxide support. The catalyst was then applied in transesterification of rapeseed oil. The reaction conditions used were 6:1 methanol to rapeseed oil molar ratio, 3% of catalyst amount, 5 h of reaction time and at 65 °C reaction temperature. The highest amount of biodiesel was obtained for potassium cations supported on zirconium oxide at 91% yield.

2.3.4.4.4. Clay minerals

Clay minerals used as heterogeneous catalyst are generally hydritalcite. This comprises nanoparticles with layered structures and a molecular formula of $\text{Mg}_6\text{Al}_3(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Helwani et al., 2009). These layers have net negative charges that are neutralised by cations like Na^+ , K^+ , Ca^{2+} , etc., which occupy the interlameller space. These interlameller cations can be easily replaced by other cations or molecules during clay modification, changing the properties of the clay like acidity, pore size, surface area, polarity, stability, etc. (Nagdrappa, 2011).

They have extensive applications due to their ability to expand, adsorbent capacity and ion exchange properties and high surface area (Das et al., 2002).

They find application in industry as catalysts or catalyst support, adsorbent, ion exchangers, etc., depending on their specific properties (Wang et al., 2001; Morato et al., 2001). Their crystalline structure, the ability to modify the original crystalline structure in a controlled way and small size of their particles make them useful as catalyst for transesterification reaction (Goa et al., 2010).

Ye et al. (2013) prepared a basic catalyst by loading K_2CO_3 on attapulgite through impregnation. The prepared K:ATP catalyst was used in the transesterification of soybean oil with excess methanol. The reaction conditions were 22:1 methanol to oil molar ratio, 8wt% of catalyst, 60 °C reaction temperature, 3 h reaction time to yield 93.4% of biodiesel product. It was observed that K:ATP had high catalytic activity, catalyst longer life time and stable after being used five times.

Modiba et al. (2015), prepared Diatomite-KOH by impregnation and used it for the transesterification of WCO and methanol. They obtained 90% biodiesel yield under the following conditions; the reaction conditions were 30% MeOH: oil mass, 5wt% catalyst loading, 4 h at reaction temperature of 75 °C. Diatomite-KOH showed no significant impact on catalyst activity after .three recycle intervals.

In a separate study, Takase et al., (2018), prepared KF-ATP by Ion-exchange method and used it for the transesterification of non-edible oil with methanol. The reaction conditions were 12:1 oil: MeOH molar ratio, 12% catalyst loading, 65 °C and 5 h to afford 93,5% biodiesel yield. They observed that the catalyst could be used repeatedly with consistent catalytic activity positioning the catalyst as good potential for biodiesel production.

2.3.4.5. Enzymes (biocatalyst)

Recently, research activities have focused on enzyme catalysed transesterification reaction of oils as a lever to overcome the challenges associated with pollution and separation of by-products from the reaction mixture when conventional catalysts are used (Fukuda, 2001, Royon, 2007, and Talha & Sulaiman, 2016). Advantages of using enzyme catalysts are that, they do not produce by-products and this simplifies recovery of products, they are insensitive towards oils with high amount of FFA and they are reusable (Shimad et al., 2002). However, there

are some drawbacks associated with the utilisation of enzyme catalysts, which include catalyst cost, ultimately resulting in an increase in biodiesel price, their reaction rate is slow and enzymes are susceptible to high temperatures. (Royon 2007 & Tan 2010).

Kaieda et al. (2001) investigated transesterification of soybean oil with methanol using lipases from different microorganism (*Candida rugosa*, *Pseudomonas cepacia* and *Pseudomonas fluorescens*) in a water containing system without an organic solvent. Lipases from *C. rugosa*, *P. cepacia* and *P. fluorescens* showed high catalytic activity. However, for *C. rugosa* and *P. fluorescens* lipases, there was a decrease in biodiesel yield when water content was low. This was due to water inhibiting the inactivation of these lipases by methanol. In contrast, *P. cepacia* showed high activity even when water content was low. In the reaction mixture up to 2 or 3 molar equivalents of methanol to oil, *P. cepacia* gave high methyl ester content and that was attributed to *P. cepacia* significant methanol tolerance.

2.4. Biodiesel feedstock

Vegetable oils are a promising alternative feedstock for biodiesel because they are renewable in nature, environmentally friendly and can be produced in huge scale locally (Patil et al., 2009, Leung et al., 2010). They are categorised into edible oils and non-edible oils. Edible oils include sunflower oil, soybean oil, rapeseed oil, olive oil, corn oil, coconut oil, etc. Non-edible oils include *Jatropha*

curcas, linseed, tobacco, *Pongamia glabra*, to name but few (Atabani et al., 2013). Edible oils are the most used feedstock for biodiesel production due to their availability and ability to produce biodiesel that has the potential to substitute fossil derived diesel fuel. However there exist a competition between the food industry and energy industry when edible oils are used, leading to potential food shortages and consequential increase in the oil price and derived biodiesel (Kansedo et al., 2009).

Use of edible oils also leads to deforestation as a result of forests being cut for plantation purposes disturbing the ecosystem balance of both plants and animals (Avhad & Mirchetti, 2015). Thus, research has been conducted on how to address the challenge by using non-edible oils. Instead researcher have discovered that the non-edible oils contain high amount of FFA (14 wt%) and requires large land area for plantation (Gui et al., 2008). Therefore the use of waste oils presents an attractive opportunities to be explored.

2.4.1. Waste cooking oil

Waste cooking oil is an attractive, alternative source of triglycerides for biodiesel production because it is inexpensive, has low viscosity and readily available as raw material. It further contributes to reduction of environmental pollution since waste cooking oils used in restaurants are generally dumped irresponsibly (Balakrishnan et al., 2013), down the drain and sinks, on the ground, into garbage

and into rivers which leads to drain and sewer blockages and cause harmful effect on aquatic animal's life (Guerrero et al., 2011).

The use of waste oils in biodiesel production also helps to minimise cost of production which results in the decrease in biodiesel price (Kataria et al., 2019). However, waste oils generally contain high amount of FFA and water, which results in emulsification of oil and water when homogeneous catalysts are used for the biodiesel production. This limitation can be sufficiently mitigated by pre-treatment of oils to convert all the FFA to esters and the use of heterogeneous catalysts, since they are insensitive towards FFA (Lam et al., 2010).

2.5. Physical and chemical properties of biodiesel

Before the biodiesel is used, it is necessary to determine its chemical and physical properties to ensure its quality and risk associated with its use. These properties differ depending on the type of the feed stock used for the production of that specific biodiesel. They are usually compared with biodiesel fuel standards and the most used standards are the American Standard for Testing Materials (ASTM) and European Standard (EN 14214). Below are some of the chemical and physical properties of biodiesel:

2.5.1. Density

Density is defined as the mass per unit volume of liquid and can be showed by specific gravity (g/L) which varies from 848-885g/L. Density is an important factor which influences the engine performance features (Demirbas et al., 2008).

The denser the biodiesel the higher the energy content resulting in better mileage and increased power (Alptekin & Canakci, 2008).

2.5.2. Viscosity

Viscosity is defined as the resistant of a liquid to flow. Viscosity is a very important property because it affects the fuel atomisation lubrication especially at low temperatures (Demirbas et al., 2008). The higher the viscosity of the fuel, the poorer the atomisation of the fuel spray and there will be an increase of fuel droplets on the engine leading to an efficient cold start (Atabani et al., 2013). Vegetable oils have high viscosity hence they are not used directly in engines. Transesterifying these vegetable oils lowers the viscosity of the biodiesel (Alptekin & Canakci, 2008).

2.5.3. Acid value/number

Acid number determines the acid content of a fuel (Gashew & Lakachew, 2014). This acid value can be raised by acids used that are not totally separated in the production process or has undergone oxidative degradation (Sanjay 2013). High acid value in fuel can corrode the fuel supply system and hinder the transesterification reaction leading to soap formation (Atabani et al., 2012).

2.5.4. Flash point

Flash point is a temperature at which a fuel gives off sufficient vapour to ignite in air. The higher the flash point, the lower the fire hazards indicating good transportation, handling and storage of fuel (Atabani et al., 2013).

2.5.5. Cloud point

Cloud point is the temperature whereby the fuel or oil to starts form wax crystals (Tan et al., 2018). It is a temperature used to check the lowest temperature performance of biodiesel (Kirubakaran & Selvan, 2018). It also depends on the bond saturation of the feedstock used. The more saturated the feedstock is, the higher the cloud point (Sakthivel et al., 2018; Giakoumis et al., 2018).

2.5.6. Pour point

Pour point is the lowest temperature at which the fuel remains pourable, that is, it still has a potential to flow. The increase in pour point of biodiesel is due to the presence of the impurities in the biodiesel (Kirubakaran & Selvan, 2018). It gives information based on the use of the fuel in cold weather.

2.5.7. Oxidative stability

Oxidative stability shows the level of oxidation, possibility to react with molecular oxygen in the air and can determine the need for antioxidants (Giakoumis et al., 2013). Oxidation is affected by the presence of air, peroxides, light, heat, traces of metals and double bonds present in the compound (Atadashi et al., 2010; Atabani et al., 2010). When the oxidation stability is low, the use of antioxidant is required to meet the standard specifications (Atabani et al., 2012).

2.5.8. Iodine number

It is number of iodine absorbed by an oil in grams. It measures the number of double bonds present in fatty acid chains, meaning, it is associated with the saturation of fatty acids chains (Kirubakaran & Selvan, 2018). It is also used as measure of the chemical stability properties of biodiesel fuel against oxidation. Iodine absorption only takes place where there are double bonds present, that is, the more the double bonds the higher the iodine number and the greater its ability to polymerise and/or become less stable (Kirubakaran & Selvan, 2018).

CHAPTER 3

EXPERIMENTAL

3. Materials and Methods

3.1. Chemicals and reagents

Table 1: Chemicals and their purity used

Chemicals	Source	Purity
Potassium hydroxide	Promark chemicals	85.00%
Potassium nitrate	Sigma Marck	99.99%
Potassium cyanide	Sigma Merck	96.00%
Potassium iodate	Sigma Merck	99.00%
Hydrochloric acid	Glassworld	32.00%
Methanol	Glassworld	99.00%
Methyl lineate	Sigma Merch	99.00%
Methyl palmitate	Sigma Merch	99.00%

3.2. Methodology

3.2.1. Waste cooking oil analysis

Waste cooking oil (WCO) which was originally sunflower oil was sourced from the Vaal University of Technology cafeteria in Vanderbijlpark. Pre-treatment of WCO was performed to remove any impurities like food and other particulate

materials by filtration and subsequently water removal. Dehydration- was done by heating WCO to remove traces amounts of water at 110 °C for 3 h. Filtration was done to remove solid materials present in the WCO using a sieve.

The acid value (AV) and free fatty acids (FFA) of WCO were examined by the use of a titration method. It was done by mixing 1.0g of WCO and 10.0g of methanol and 5 drops of phenolphthalein indicator were then added to the solution. The solution was then titrated with potassium hydroxide solution (1.0g per 100 mL) until a pink colour appeared showing the completion of the reaction and this was repeated in triplicates. The average titre volume was recorded. The acid value (AV) of the WCO was calculated using the **eq. 9** below:

$$AV = \frac{56.1 \times V \times C}{m} \dots \dots \dots (9)$$

where 56.1g/mol is molecular weight of KOH, V (ml) is the average titre volume, C (M) is the concentration of KOH and m is mass of tested WCO percentage (Jena et al., 2010).

The FFA content was determined utilising **eq. 10** below

$$FFA = \frac{28.2 \times V \times C}{m} \dots \dots \dots (10),$$

Where V, C and m are as described above in (**eq. 9**) (Rukunudin et al., 1998).

3.2.1. Catalyst preparation

3.2.1.1. Acid treatment

Firstly ATP was pulverised into small particles and then sieved to a particles size of less than 90 μm . The ATP was then treated with hydrochloric acid to remove impurities. The acid treatment was as follows: the ATP was deposited into a 100 ml of 2 M HCl solution and stirred with a magnetic stirrer bar for 100 min at 60 $^{\circ}\text{C}$. The solution was then sonicated for 10 min in an ultrasonic bath followed by centrifugation. The supernatant was decanted and the suspended residue was washed with deionised water until neutral, $\text{pH} = 7$. It was then dried in an oven at 100 $^{\circ}\text{C}$ for 12 h. The acid treated ATP obtained was stored in a desiccator.

3.2.1.1. Preparation of catalyst by ion exchange method

The catalyst was prepared by ion exchange method with different concentration of KOH ranging from 1 M -5 M. A mass of 10g acid treated ATP was deposited into a required KOH concentration solution and soaked for 24 h to ensure it is fully coated. Then the solution was centrifuged and the supernatant was decanted. The residue was dried in an oven at 100 $^{\circ}\text{C}$ for 12 h to remove excess water and to ensure adequate coating of metal onto the surface of the support and then calcined at 400 $^{\circ}\text{C}$ for 12 h in a furnace.

3.2.1.2. Characterisation techniques

3.2.1.2.1. Hammett indicator

The catalyst was characterised using Hammett indicator to determine the basic strength of the formed catalyst. It was done as follows: 300 mg of the formed catalyst was mixed with 1 ml of phenolphthalein indicator (H_9.3) and 10 ml of methanol was added. It was then allowed to settle down for 2 h and the colour change was noted.

3.2.1.1.1. XRF

The solid samples of the support and the 5MKOH/ATP was analysed using Malvern Panalytical-Benchtop X-Ray Fluorescence Spectrometer-Epsilon 1. The samples were placed inside a disposable cylindrical polymer sample cells covered with thin film for X-Ray Fluorescence transmission. The analysis was done by irradiating the sample with X-Rays through the film.

3.2.1.1.2. FTIR

FTIR spectra were recorded on Nicolet iS50 FT-IR in the range of 400-4000 cm^{-1} . The samples were solid samples and they were analysed as such. Firstly, the diamond ATR accessory was cleaned with acetone. The samples were then placed on the diamond and pressed with pressure handle.

3.2.1.1.3.XRD

The X-ray diffraction data was collected using MAXim_X XRD-7000. The measurements conditions of the instrument were: CuK α ($\lambda = 1.154056\text{\AA}$) radiation source, voltage and current set at 30 mA and 40 KV. The XRD patterns were recorded in the range of $2\theta = 10\text{--}80^\circ$ with a scanning rate of $2^\circ/\text{min}$. The solid samples of the ATP support and 5MKOH/ATP were placed in a sample holder and cautiously placed in the fitting XRD slot.

3.2.1.1.4.SEM-EDX

A small amount of a solid sample was first dispersed in hexane and sprinkled on an aluminium SEM stub coated with carbon tape glue. Excess sample was gently blown off with compressed air. The samples were then coated in an evaporation coater with a thin layer of carbon to make the sample conductive. The samples were viewed in an FEI Nova NanoSEM 320 with a field emission gun. The viewing conditions (KV, working distance and spot size are all on the data bar at the bottom of the image). The elemental analysis was carried out using an Oxford X-max detector and Inca software.

3.2.2. Transesterification

Transesterification was carried out in a three necked flask equipped with a condenser, thermometer and immersed in a hot water bath, with test carried out at various temperatures: 45, 50, 55, 60, 65 and 70 °C. The molar ratio of oil to methanol were 1:3, 1:6, 1:9, 1: 12, 1:15, 1:18, respectively. The catalyst amount

was measured in % wt with respect to the amount of WCO feed added. The parameters evaluated includes reaction time (1 h, 2 h, 3 h, 4 h, 5 h and 6 h) and varying stirring rate (100 rpm, 200 rpm, 300 rpm, 400 rpm, 500 rpm and 600 rpm) using a magnetic stirrer bar.

The transesterification reaction was carried out as follows: firstly, the WCO was added into a three necked flask and heated to the desired temperature at a specific stirring rate. When the target temperature was reached, the required amount of methanol and catalyst were added. The point was noted as the start time for the reaction. When the predetermined reaction time was reached, the solution was allowed to cool down. The resulting reaction mixture was then centrifuged and the catalyst was separated from the biodiesel product solution. The glycerol layer was also separated from the resultant biodiesel using a separating funnel. The obtained biodiesel was analysed using GC-MS and the yield of the biodiesel produced was calculated using the equation 14 below:

$$\%Yield = \frac{\text{mass of biodiesel}}{\text{mass of WCO}} \times 100\% \dots \dots \dots (11)$$

3.2.3. Catalyst reusability

The 5MKOH/ATP catalyst was removed from the reaction mixture and washed with methanol five times. The recovered catalyst was dried in an oven for 12 h at 100 °C and re-calcined at 400 °C for 12 h in a furnace. The recovered catalyst was

used to catalyse the transesterification reaction and the process was repeated three times. The percentage yield for each run was calculated using (eq.11) above.

3.2.4. Biodiesel characterization

The methods above used to determine the AV (eq. 9) and FFA (eq. 10) content on WCO were also used to determine the AV and FFA for the formed biodiesel.

3.2.4.1. Gas Chromatography-Mass Spectrometry

The samples and reference samples were analysed using Perkin Elmer Clarus 500 Gas Chromatography-Mass Spectrometry equipped with flame-ionisation detector (FID) and capillary column (30 m × 250 μm). The carrier gas was nitrogen. The oven temperature ramp program was 135 °C for 10 min, 170 °C at 2 °C/min (ramp 1), 280 °C at 10 °C/min (ramp 2) and both held for 10 min. The flow rate of hydrogen and air were 45 mL/m and 450 mL/m. The injector temperature and detector temperature were 230 °C and 250 °C, respectively. The injection was performed in a split mode with a split ratio of 19:1. Biodiesel was analysed by dissolving 200 μL of a sample into 300 μL of hexane and injecting 1.0 μL of the resulting solution in the GC-MS instrument.

3.2.5. Determination of reaction kinetics

To determine the kinetics of the reaction, the effect of reaction time was evaluated. The catalyst quantity with respect to oil was assumed to be enough to move the equilibrium of the reaction to the formation of biodiesel. Thus, the

reverse reaction was neglected and the change in the amount of the catalyst throughout the course of reaction can be assumed to be unimportant (Birla et al., 2012)

The first order transesterification reaction was assumed and the rate law of the forward reaction was expressed as:

$$-r_a = d[\text{TG}]/dt = k[\text{TG}][\text{MeOH}]^3 \dots\dots\dots(12)$$

Where, k is the equilibrium rate constant, [TG] is the concentration of triglycerides (oil) and [MeOH] is the concentration of methanol.

Since methanol was in excess during the transesterification reaction, its concentration was assumed to be constant. Meaning, the effect of methanol concentration did not change the order of the reaction (Kusdiana & Saka, 2001).

Therefore, the rate law can be expressed as:

$$-r_a = -d[\text{TG}]/dt = k[\text{TG}] \dots\dots\dots(13)$$

Intergration of **eq. 13** resulted into **eq. 14** and **15**

$$\ln[\text{TG}]_0 - \ln[\text{TG}]_t = kt \dots\dots\dots(14)$$

or

$$-\ln(1 - X_{\text{ME}}) = kt \dots\dots\dots(15)$$

Where, $[TG]_0$ is the initial concentration of triglycerides at $t=0$, $[TG]_t$ is the concentration of biodiesel at final time and X_{ME} is the conversion of the methyl ester.

CHAPTER 4

RESULTS AND DISCUSSION

The results investigated in this work are presented and discussed in this chapter.

4.1. Catalyst characterization

Hammett indicator and instruments like Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF), Brunauer–Emmett–Teller (BET), X-ray diffraction spectroscopy (XRD), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX) were used to examine the basicity, functional groups, crystallinity phase, components and the morphology of the formed catalyst.

4.1.1. Hammett indicator

A mass of 300 mg of the formed catalysts were weighed, mixed with 1 ml of phenolphthalein indicator and 10 ml of methanol. They were then allowed to settle down for 2 h and the colour change was noted.

The catalyst that undertook the strongest colour change was taken to have a high basic strength. Attapulgite was loaded with different potassium compounds: KI, KSCN, KNO₃, and KOH at ratio of 1: 2. Attapulgite, ATP/KI and ATP/KSCN showed no colour change but ATP/KOH exhibited the strongest colour change compared to ATP loaded with KNO₃. Furthermore, the ATP was loaded with different concentration of KOH ranging from 1-5 M. The ATP loaded with 5 M

KOH showed the highest basic strength. Therefore, the solid base catalyst ATP/5MKOH was chosen as further studied as a catalyst for transesterification of waste cooking oil to biodiesel. Tables 1 and 2 bellow shows the observed colour changes.

Table 1: Basic strength of ATP loaded with different potassium precursor compounds

Catalyst	Observed colour change
ATP	No colour change
ATP/KI	No colour change
ATP/KSCN	No colour change
ATP/KNO ₃	Light pink
ATP/KOH	Strong pink

Table 2: Basic strength of ATP loaded with different KOH concentrations

Catalyst	Observed colour change
ATP/1MKOH	Very Light pink
ATP/2MKOH	Light pink
ATP/3MKOH	Light pink
ATP/4MKOH	Pink
ATP/5MKOH	Strong pink

4.1.2. XRF Results

The chemical composition of ATP and 5MKOH/ATP catalyst were determined using XRF. The results in Table 3 below show an increase in K_2O species as 5M KOH was introduced from 1,876 % TO 8,995 %. This increase in K_2O after loading of KOH indicates the incorporation of potassium onto the surface of ATP. In addition, there are basic and acidic oxides present in the catalyst. The basic oxides increases the catalyst's basic strength (Birl et al., 2012) whereas the acidic oxides molecules have an ability to indirectly connect esterification of the feedstock's FFA content (Boey et al., 2011).

Table 3: XRF results for ATP and 5MKOH/ATP

ID	ATP (%)	5MKOH/ATP (calcined at 400 °C) (%)
Na ₂ O	0.825	1.269
MgO	6.087	9.695
Al ₂ O ₃	5.526	9.384
P ₂ O ₅	0.071	0.108
SiO ₂	29.540	47.068
K ₂ O	1.876	8.995
CaO	2.465	7.428
Fe ₂ O ₃	5.623	2.992

4.1.3. BET Results

The physical properties of the raw ATP and 5MKOH/ATP are recorded in Table 4. The results showed that the surface area of ATP was 39.99 m²/g, which decreased to 0.07 m²/g for the potassium supported ATP clay catalyst (5MKOH/ATP) after the addition of 5 M KOH solution and calcination at 400 °C for 12 h. Also, there was a decrease in the pore volume and pore diameter/size of ATP and 5MKOH/ATP from 0, 20 m²/g to 0 m²/g and 20. 15 nm to 0 nm. This decrease may be attributed to either potassium species occupying and blocking the internal pores of the ATP clay resulting in pore structure collapse due to calcination conditions adopted (Huo and Yang, 2010; Takase et al., 2018).

Table 4: BET results showing physical components of ATP and 5MKOH/ATP

	ATP	5MKOH/ATP
Surface area (m ² /g)	39.99	0.07
Pore volume (m ² /g)	0.20	0.00
Pore size (nm)	20.15	0.00

4.1.4. FTIR Results

The pure ATP sample analysed was taken raw without it being calcined and the 5MKOH/ATP catalyst sample was calcined at 400 °C for 12 hrs. **Figure 6** below showS the FTIR spectra of ATP and 5MKOH/ATP catalyst. The absorption band observed at 1101 cm⁻¹ on the spectra of ATP was attributed to strong Si-O stretch and Si-O-Si bands (He et al., 2011; Modiba et al., 2015) and a clear shifted to lower wavelength of 941 cm⁻¹ was odserved when KOH was loaded. This could be attributed to either interaction between the surface of ATP and K⁺ ions as a results of calcination at 400°C. The FTIR spectra of 5MKOH/ATP showed an absorption band at 669 cm⁻¹ associated with K₂O which is absent on the spectra of pure ATP. The presence of K₂O is attributed to the decomposition of KOH to K₂O during calcination (Ye et al., 2013). New absorption band is observed on the spectra of 5MKOH/ATP at 1375 cm⁻¹ assigned to symmetric and asymmetric stretching vibrations of Si-O-K because of K⁺ ions substituting Si in the Si-O-Si groups after calcination (Modiba et al., 2015; Takase et al., 2018).

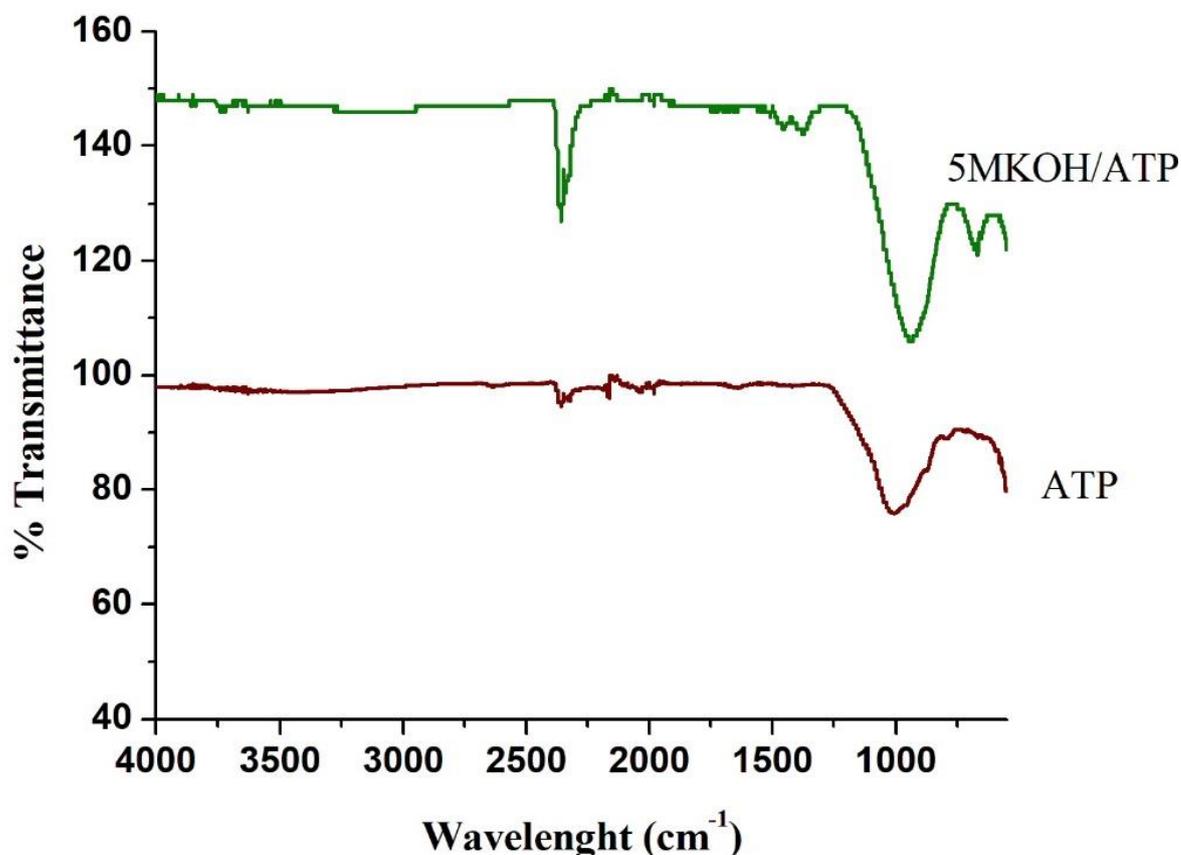


Figure 6: FTIR results for ATP and 5MKOH/ATP

4.1.5. XRD Results

X-ray diffraction was used to determine possible composition changes in the catalyst crystalline phases (**Figure 7**). The particular diffraction peaks at $2\theta = 10^\circ$, 20° , 25° and 31.9° matches the diffraction plane of (110), (200), (040) and (400) of the ATP clay, respectively (Xu et al., 2007, Takase et al., 2018). However, the diffraction peaks in XRD diffractogram of pure ATP disappeared on adding 5 M KOH and calcining. This could be attributed to the absorption of K^+ active sites into the pores in the structure of ATP support and the excellent interaction

between KOH and ATP support (Ye et al., 2013). Furthermore, development of new diffraction peaks at $2\theta=29^\circ$, 35° and 55° in the diffraction pattern of 5MKOH/ATP and these diffraction peaks were attributed to the presence of K_2O and ATP-O-K molecules. The XRD diffraction pattern of the 5MKOH/ATP showed poor crystallinity (amorphous) when compared to that of pure ATP. This finding support structural collapse observed with BET results, indicating that after the loading of potassium species and subjecting material to high temperature (calcination). Hence the crystalline structure of pure ATP was demolished (Chen et al., 2016).

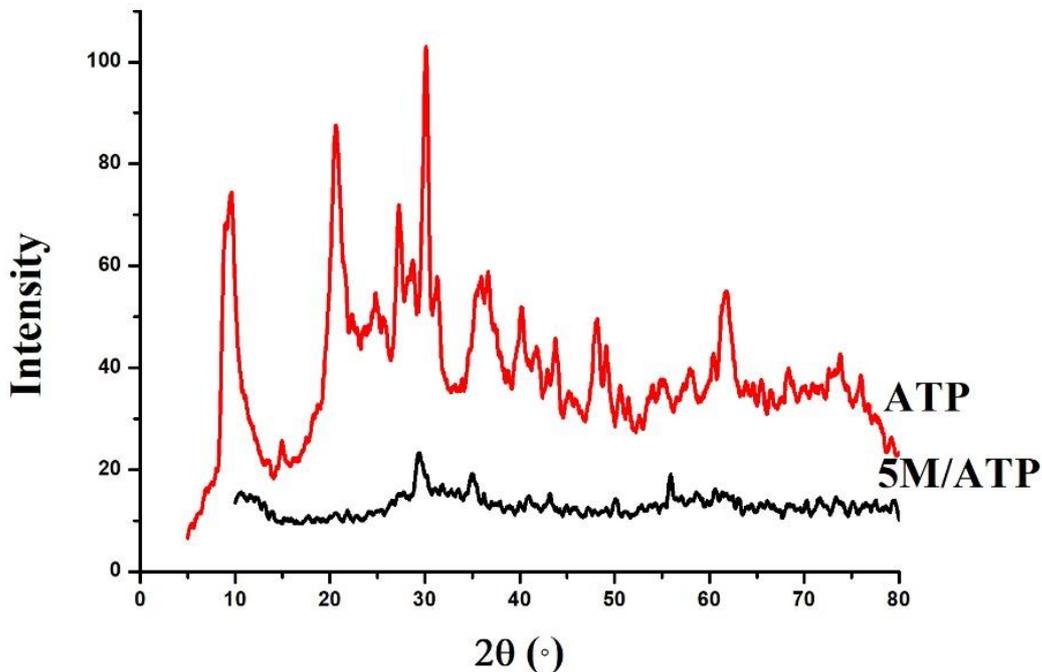


Figure 7: XRD graphs for ATP and 5MKOH/ATP

4.1.6. SEM Images and EDS results

Scanning Electron Microscopy was used to determine the morphological changes on the clay surface. **Figure 8** below shows the SEM images of (a) ATP and (b) 5MKOH/ATP catalyst. SEM images of ATP shows that the surface of the ATP was smooth with pores. However, after loading 5 M KOH on the surface and calcination, the surface became rough. This roughness suggest that there are new species formed and scattered on the surface of ATP (Ye et al., 2013). In addition, with the newly formed species it was not easy to establish consistency in their distribution on the surface of ATP.

Table 6 shows the EDS results of the raw ATP and 5MKOH/ATP catalyst. The cross-sectional surfaces of both samples were examined at three different positions using SEM-EDS and the data average. The high amount of carbon is attributed to amount added over the sample to make it conductive. Moreover, the potassium content on the surface of 5MKOH/ATP increased from 0 % to 5.13 %. This increase is attributed to successful addition of potassium species on the ATP surface (Ye, et al., 2018). It was also observed in Table 6 that there was no calcium present and that suggest that there was an exchange of potassium ions with that of calcium ions. However, the EDX results contradicts the XRF results, and this could be due to the sensitivity of the XRF technique related to EDS. In addition, sample preparation during SEM-EDS have shown that 5MKOH/ATP

was not homogeneous enough and contained grains which could contribute to the observed inconsistency in the results measured.

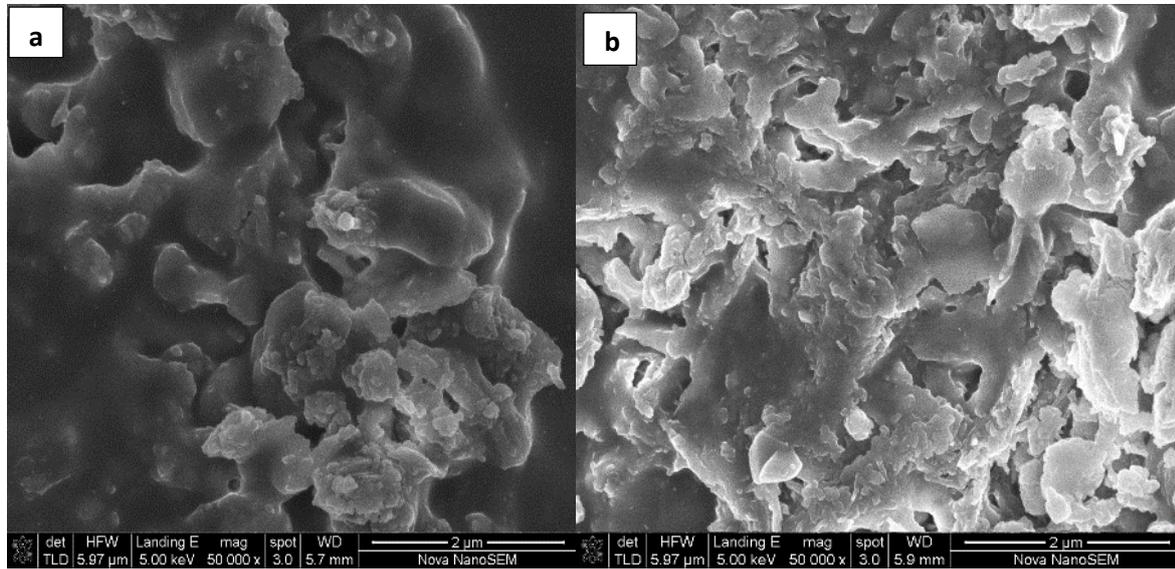


Figure 8: SEM images of (a) ATP and (b) 5MKOH/ATP

Table 6: EDX data for (A1) ATP and (A2) 5MKOH/ATP

Components	ATP (%)	5MKOH/ATP (%)
C	21.47	36.09
O	47.58	42.71
Mg	3.59	1.45
Al	4.73	2.22
Si	18.55	10.69
Ca	1.49	-
K	-	5.13
Fe	2.58	1.70
Total	100.00	100.00

4.2. Effect of reaction parameters on biodiesel yield

The percentage yield was calculated using (eq. 14) above.

4.2.1. Biodiesel product composition

The biodiesel produced was composed of methyl myristate, methyl palmitate, methyl oleate and methyl stearate (Table 7 below). Biodiesel produced was

mainly characterized by the presence of methyl oleate and methyl palmitate as the major product.

Table 7: Biodiesel composition at 1:15 oil:MeOH molar ratio, 3wt% catalyst amount, at 65 °C for 3 h and stirring rate of 200 rpm.

FAME	Structure	Composition (%)	Retention time (h)
Methyl myristate	C15:0	1.13	8.19
Methyl palmitate	C17:0	44.73	17.57
Methyl oleate	C18:1	47.99	25.47
Methyl stearate	C19:0	6.16	26.51

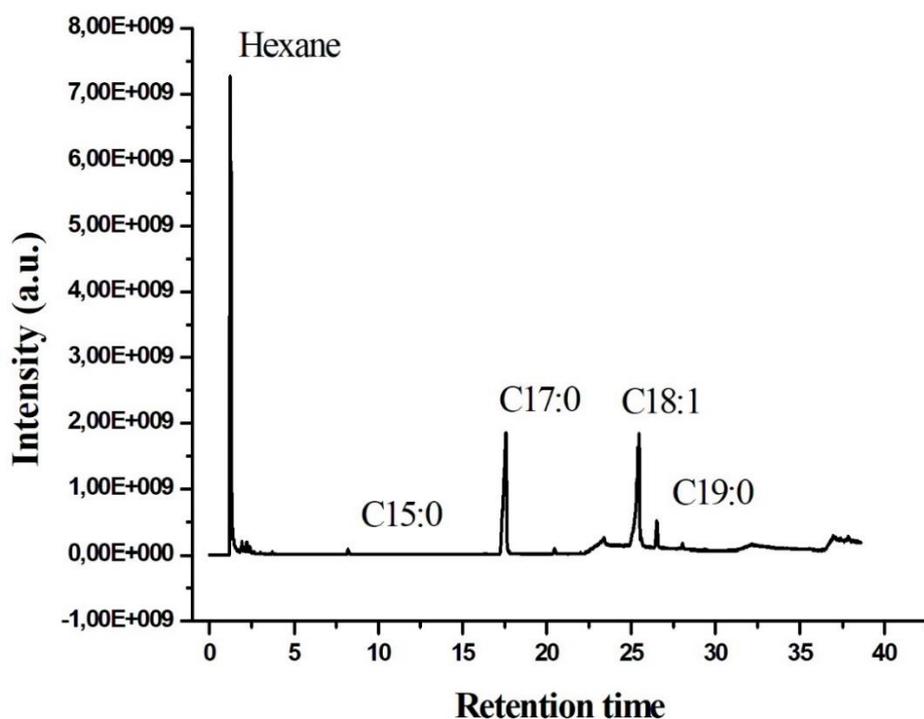


Figure 9: GC Chromatogram of the formed biodiesel at 1:15 oil:MeOH molar ratio, 3wt% catalyst amount, at 65 °C for 3 h and stirring rate of 200 rpm.

4.2.2. Kinetics studies on biodiesel yield

The reaction was carried out for a time of 7 h. The samples were collected every 1 h and the catalyst loading was 2wt%. It was observed that there was increase in biodiesel yield to 88.31 % after 3 h reaction time and slowly decreased from 86.12% to 84.39 % after subsequent sampling time of 4 h to 7 h (**Figure 10**), and that was attributed to saponification reaction taking place (Gashew & Teshita, 2014).

The rate constant was found to be $1.94 \times 10^{-4} \text{ s}^{-1}$ and it was calculated using (**eq. 12**) and the reaction followed a first order model.

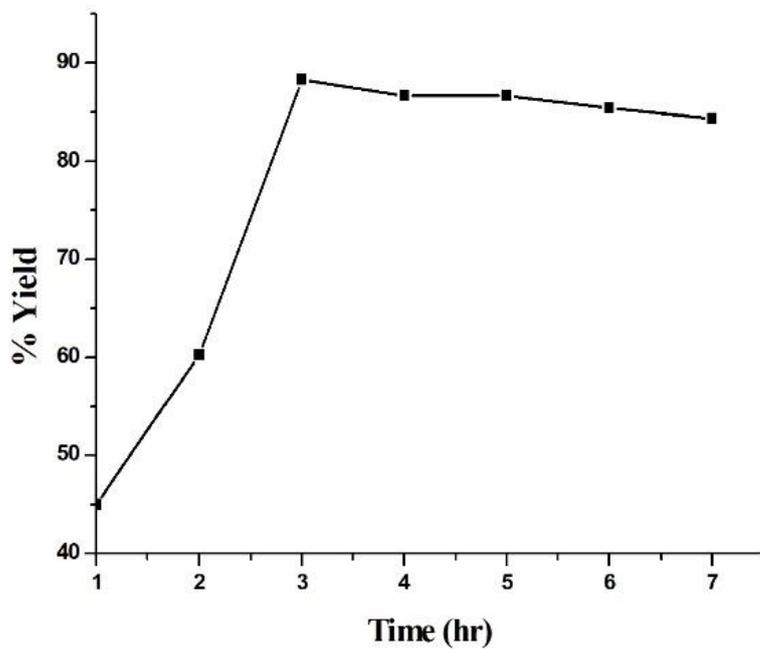


Figure 10: *The biodiesel yield at different reaction time intervals.*

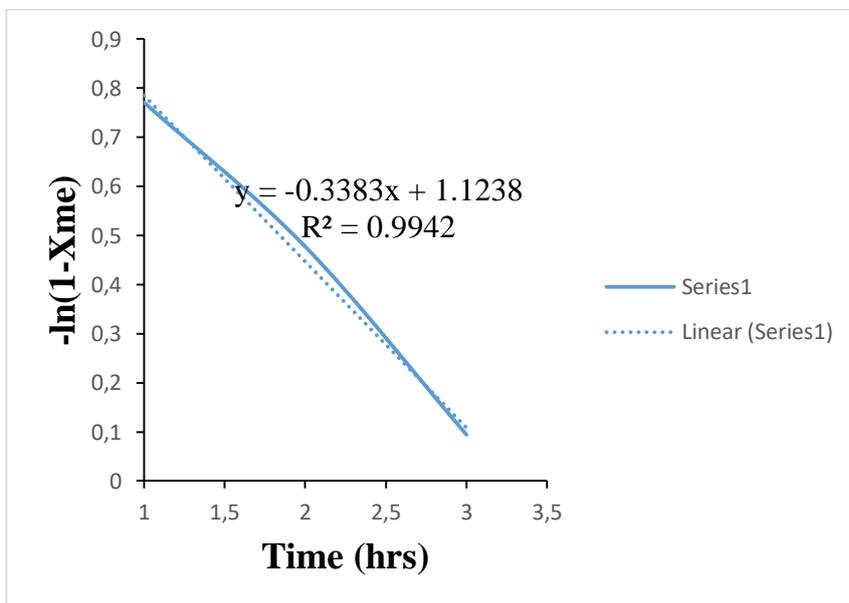


Figure 11: *The relation curve of $-\ln(1-X_{ME})$ vs time.*

4.2.3. Effect of potassium on biodiesel yield

The effect of concentration of KOH in the solid base catalyst and their catalytic activity calcined at 400 °C for 12 h were investigated. The concentration of KOH investigated ranged from 1 M to 5 M KOH and the results are shown in **Figure 12** below. The pure ATP did not show any catalytic activity, and that was attributed to ATP having no active basic sites present on the surface to catalyze transesterification (Takase et al., 2018). However, after loading KOH on the surface of ATP, there was a drastic increase in biodiesel yield as a result of increased basicity. Furthermore, an increase in biodiesel yield was observed with increasing KOH concentration which agrees to Hammett indicator results.

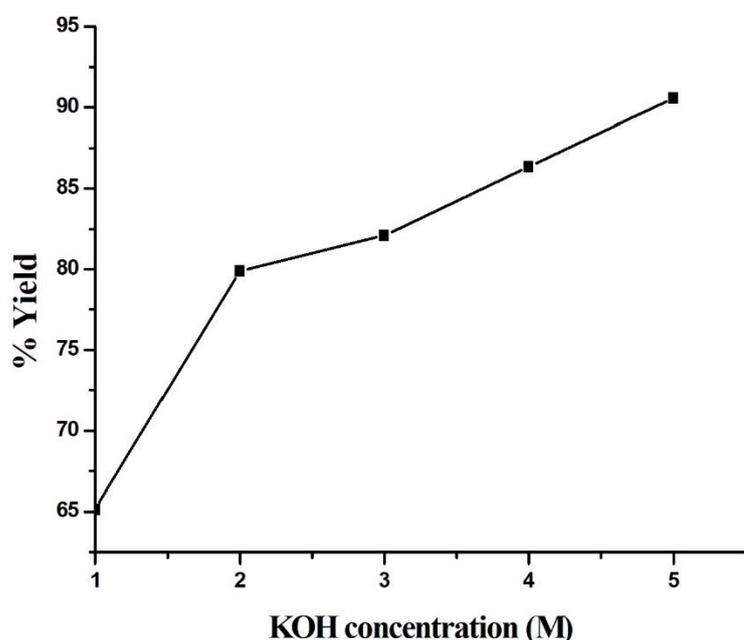


Figure 12: *Effect of K loading on WCO transesterification with MeOH at ratio 1:6, 65 °C, 3 h, 3 wt% and 300 rpm.*

4.2.4. Effect of alcohol to oil mole ratio

Alcohol to oil molar ratio is one of the most important parameters that affect the conversion effectiveness and the product yield. Since the transesterification reaction is reversible, excess methanol is required to drive the reaction forward. Theoretically, transesterification reaction requires three moles of methanol and one mole of crude oil to drive the reaction towards completion.

Figure 13 below shows the results of percentage yield from various molar ratios of methanol to oil. The ratios investigated were 3:1, 6:1, 9:1, 12:1, 15:1 and 18:1 methanol to oil ratio and the reaction temperature, reaction time, catalyst amount and a stirring rate were kept constant at 65 °C, 5 h, 3wt% 5MKOH/ATP catalyst amount and at a stirring rate of 500 rpm, respectively. The **Figure 5** shows the highest yield of biodiesel was obtained at a molar ratio of 15:1. As the molar ratio is increased from 3:1 to 15:1, an increase in biodiesel yield was observed and an optimum yield of 80.78 % was recorded. This increase was attributed to the fact that, as the molar ratio was increased the equilibrium shifted forward, favouring the formation of biodiesel product. Further increase of molar ratio resulted in a decrease in biodiesel yield and that is attributed to excess methanol causes an increase in viscosity of the reactants which results in formation of monoglycerides. The formed monoglycerides causes solubility of glycerol in biodiesel leading to decreased biodiesel yield (Ye et al., 2013 & Intarapong et al., 2014).

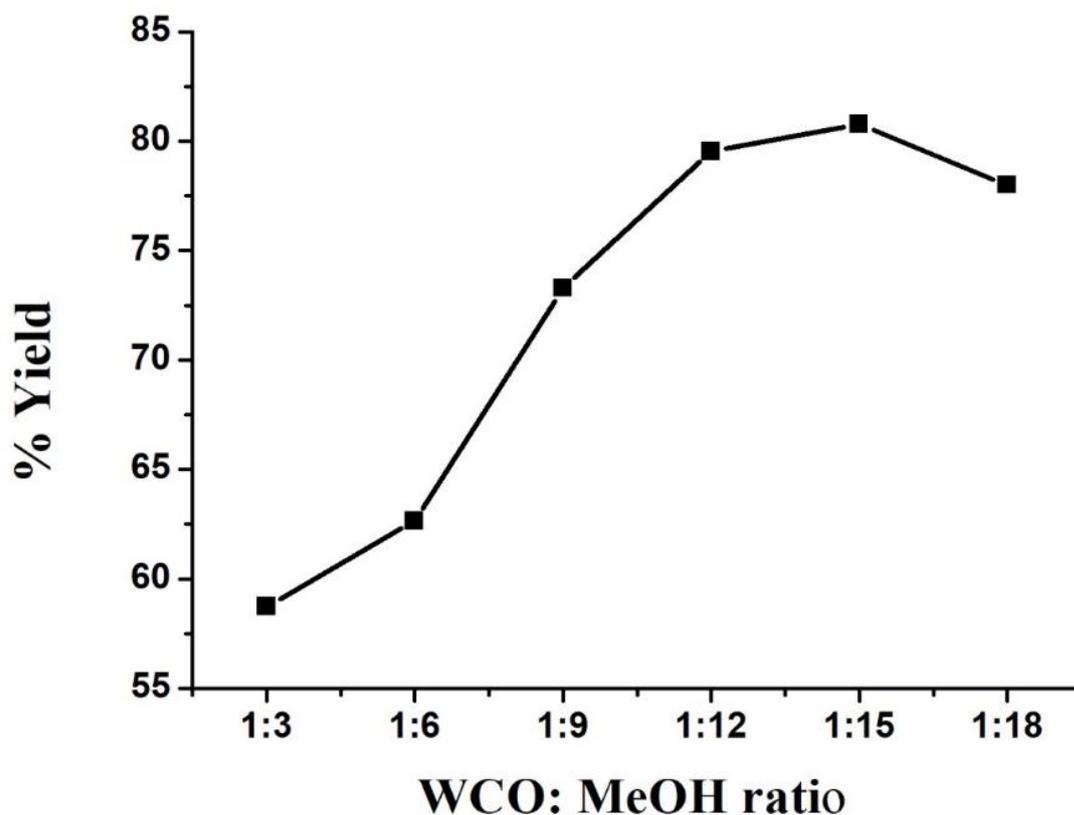


Figure 13: *The effect of WCO/methanol molar ratio on biodiesel yield*

4.2.5. Effect of catalyst loading on biodiesel yield

A catalyst has a significant role in the transesterification reaction. The catalyst and its amount improves the reaction rate and the yield. The catalyst amount was varied from 1% to 3.5% based on the amount of oil added and at 1:15 WCO:MeOH molar ratio, at 500 rpm, at 65°C for 3 h reaction time. **Figure 14** shows that as the catalyst amount was increased from 1 % to 2 %, there was also an increase in biodiesel yield from 78.58% to 94.13%. The increase in biodiesel yield is attributed to an increase in catalyst amount due to an increase in the availability of active sites (Soetaedjo et al., 2011). Further increase of catalyst

amount beyond 2wt% resulted in decrease in biodiesel yield. The decrease was attributed to excess catalyst causing an increase in viscosity of the reaction mixture resulting in further decreases the cavitation events (Gupta et al., 2015) and also excess catalyst causes formation of a slurry giving rise to mixing problem hence the decrease in biodiesel yield (Cheng et al., 2014).

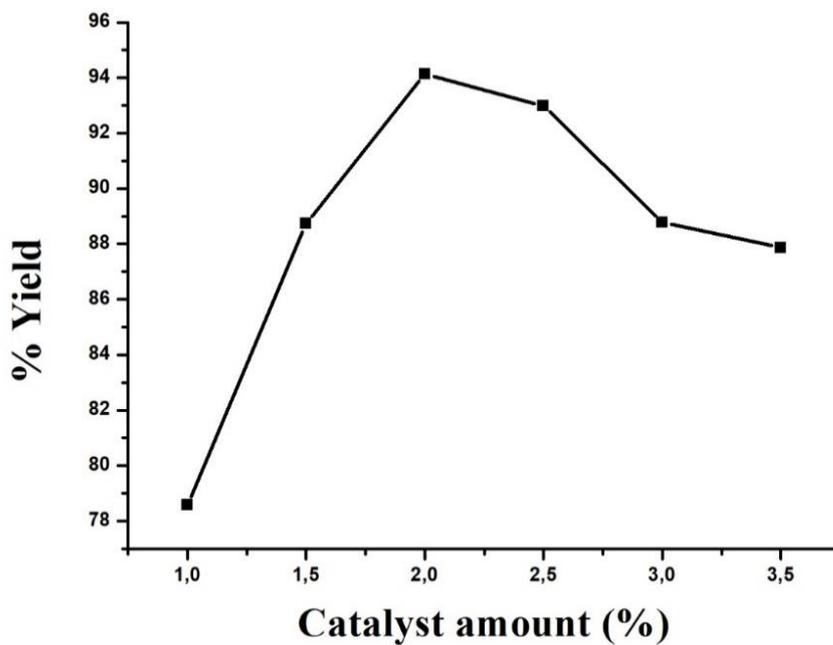


Figure 14: *The effect of catalyst amount on biodiesel yield*

4.2.6. Effect of reaction temperature

Figure 15 below shows the results of the effect of temperature on biodiesel yield. The temperature was varied from 45-70 °C and the catalyst amount, methanol/oil molar ratio, time and stirring rate were kept constant at 3wt%, 1:15, 5 h and 500 rpm stirring rate. As shown in the **Figure 15** below, as the temperature was increased from 45-65 °C, there was an increase in biodiesel yield. This increase

was attributed to the fact that, as the temperature increase there was a decrease in viscosity of the molecules leading to high diffusion between the molecules. Also as the temperature increases, there is an increase in a reaction rate and kinetic energy of the molecules leading high biodiesel yield. However, the reaction temperature above the boiling point of methanol (65 °C) resulted in decrease in viscosity resulting from evaporation of the methanol, shift in ration and diffusion challenges hence the decrease in biodiesel yield ((Birla et al., 2012; Tariq et al., 2012). Moreover, methanol above 65 °C could evaporate leading to cavitation which prevents the reaction at the interface (Ye et al., 2013).

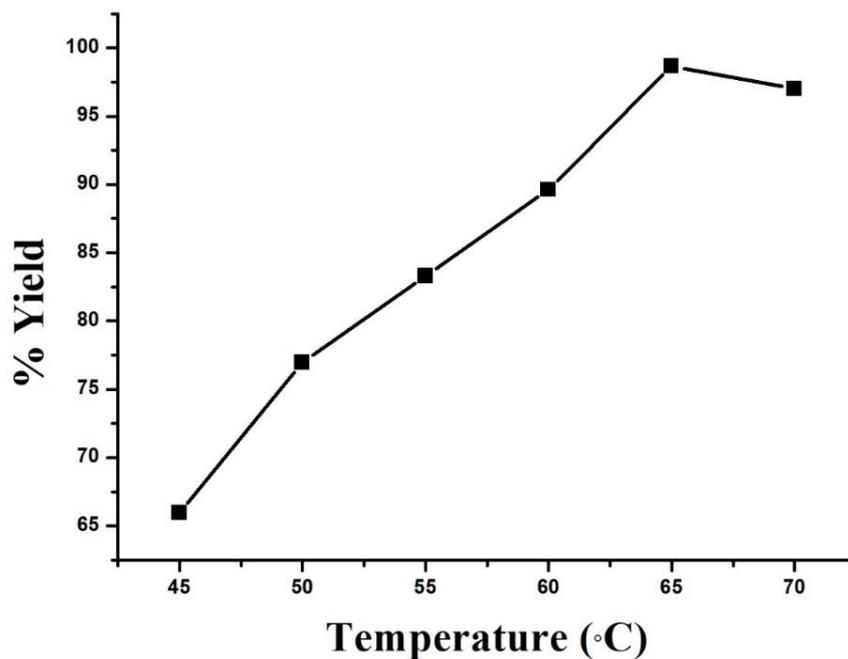


Figure 15: *The effect of temperature on biodiesel yield*

4.2.7. Effect of stirring rate

Mixing rate is very important for transesterification reaction to overcome mass transfer limitation because oils and alcohols are immiscible liquids. The reaction can occur only in the interfacial region of the two liquids causing the reaction to be slow (Sain et al., 2017). Therefore, to stimulate interaction between these two liquids, enough mixing is required to assist transesterification to take place (Jagadale & Jugulkar, 2012). The mixing rate can be varied depending on basic requirements of the transesterification reaction. It must be increased to ensure sufficient and constant mixing of the two liquids (Gashaw & Teshita, 2014). The **Figure 16** below shows graph of the effect of stirring rate on biodiesel yield. As seen from the graph, there is an increase in biodiesel yield as the stirring rate is increased from 100 rpm to 200 rpm. Further increase of stirring rate above 200 rpm caused a decrease in biodiesel yield. The decrease in biodiesel yield was attributed to the fact that higher stirring rate favours emulsification of oils and water (Gashaw & Teshita, 2014).

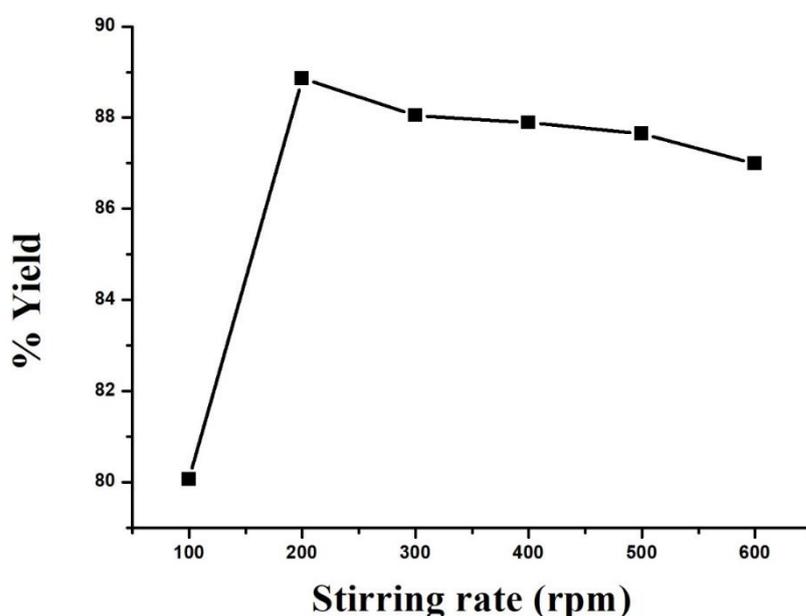


Figure 16: *The effect of stirring rate on biodiesel yield at 1:15 WCO:MeOH molar ratio, catalyst loading of 2wt% and at 65 °C for 3 h of reaction time.*

4.2.8. Catalyst reusability

Reusability and stability of heterogeneous catalysts are very crucial factors for industrial application for biodiesel production (Intarapong et al., 2014). **Figure 17** below represents the yield data of catalyst reusability after each catalyst recycle. The experimental conditions were 65 °C reaction temperature, 1:15 oil to methanol molar ratio, 3wt% catalyst load and at a reaction time of 3 h. Recycle of the catalyst was done according to the procedure described in section 3.3.3. It was observed that there was a decrease in biodiesel yield with each recycle from 93.65% to 84.49%. The decrease was attributed to the layering of organic molecules on the surface of the catalyst during transesterification reaction,

resulting in blockage of the active sites (Soetaredjo et al., 2011). Similar results were observed by Ye et al., (2013) and Takase et al., (2018) where they observed that deactivation of a catalyst was due to leaching of the active species (K_2O) from the catalyst.

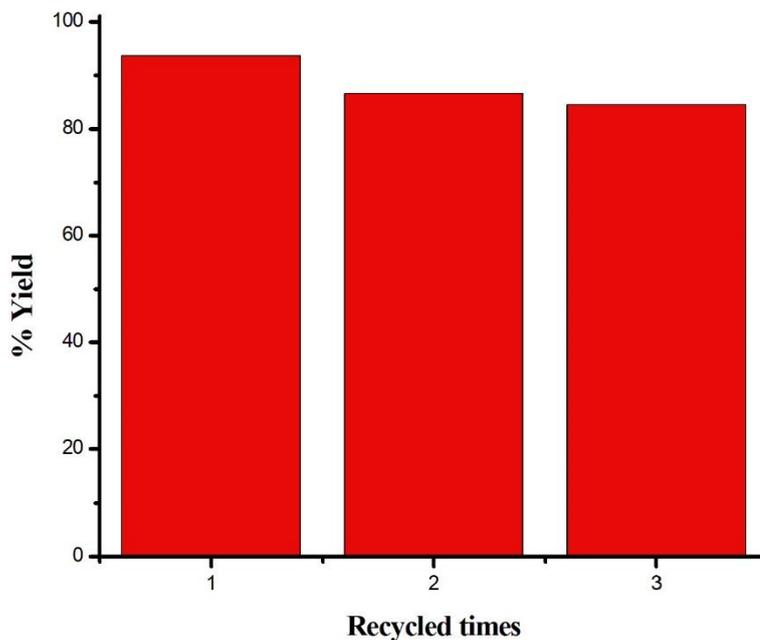


Figure 17: *The effect of recycle times on biodiesel yield*

4.2.9. Biodiesel properties

In order to evaluate the potential of biodiesel as a substitute to diesel fuel, properties of the produced biodiesel such as density, viscosity, flash point, water content, acid value, free glycerol and total glycerol were determined. These biodiesel properties were compared to the ASTM biodiesel standards as showed in Table 8 below. The biodiesel viscosity showed a significant decrease compared to that of oil showing an improvement in biodiesel properties after the

transesterification reaction. However, the biodiesel properties of the formed biodiesel does not conform to the SABS specification or EUROPE EN 14214. This might be due to oxidation of the biodiesel due to long storage. As a result of oxidation the fuel increases its viscosity, water content and become more acidic. The oxidative process can be affected by a number of factors such as temperature, heat, light, traces of metal, air and fatty acids chains (presence of double bonds) (Kapilan et al., 2009; Lin & Lin, 2012; Ong et al., 2013).

Table 8: Comparison of the obtained biodiesel properties with biodiesel standards of Europe

	Oil sample	Biodiesel sample	EUROPE EN 14214
Density @ 15 °C (kg/L)	0.915	0.915	0.860-0.900
Viscosity @ 40 °C	10.5	7.5	3.5-5.5
Flash point °C	200+	200+	120 MIN
Water content %	0.6	0.5	0.05 MAX
Acid value mg KOH/g	0.005	0.009	0.5 MAX
Saponification value	-	289	-
Free glycerol %	-	0.85	0.02 MAX
Total glycerol %	-	1.67	0.25 MAX

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

4.1. Conclusion

Most of the energy used worldwide is derived from fossil fuels (coal, natural gas and petroleum). However, these fossil fuels will be depleted in the near future due to high consumption and population growth. Therefore, finding an alternative and renewable fuel for diesel engines has grown more attraction in recent years. Biodiesel is found to be an appropriate substitute and renewable fuel. Biodiesel is described as a diesel fuel which contains mono alkyl esters of long chain fatty acids derived from renewable oil sources. It can be produced using transesterification reaction in the presence of acid, base or enzyme catalyst to minimise the viscosity of oils or fats with methanol. Moreover, the transesterification reaction can be strongly influenced by catalyst amount, reaction temperature, reaction time and oil to methanol molar ratio. The major biodiesel disadvantage is due to its carbon neutrality, making it environmental friendly.

Thus, this study aimed to evaluate the biodiesel production from waste cooking oil using a heterogeneous catalyst. In order to optimise the transesterification process, the effect of reaction temperature, time, catalyst amount, waste cooking oil to methanol molar ratio and stirring rate were investigated.

The 5MKOH/ATP catalyst was prepared by supporting KOH on ATP clay support using ion exchange method followed by drying and calcination at a temperature of 400 °C. XRD analysis showed that the crystallinity of the prepared catalyst was low, signifying that impurities were removed during acid treatment process. SEM image of 5MKOH/ATP showed that the addition of K species on the ATP surface did not cover the pores of the formed catalyst and that is important for the activity of the catalyst.

The prepared catalyst when tested for transesterification of waste cooking oil with methanol showed a good catalytic activity. The optimal reaction conditions were reaction temperature of 65 °C, 3wt% catalyst amount, 3 h of a reaction time, 1:15 waste cooking oil to methanol molar ratio and at stirring rate of 200 rpm.

According to ASTM standards or EUROPE EN 14214, the properties of the produced biodiesel did not meet the required properties. Therefore, the quality of the biodiesel produced was poor quality.

5.2. Recommendations

Future work should explore ways to improve the properties of biodiesel formed from WCO and ways reduce the amount of methanol utilised during transesterification. It should thoroughly develop and investigate the chemistry of heterogeneous catalysis in biodiesel production with other supports. Lastly, evaluate ways to improve the supported catalysts especially clays as a support.

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