Catalytic production of biodiesel from waste cooking oil using calcium silicate

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(MSc (50/50) research report)

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DECLARATION

I, Ntinugwa Ndubuisi Ebenezer; hereby declare that this research report is my own unaided work. It is being submitted for the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

_______________________________on this ***__ day of _September 2018__***

*(*Ntinugwa Ndubuisi Ebenezer*)*

ABSTRACT

The production of biofuels has witnessed a renewed interest in light of finding alternatives to fossil fuels. One such important biofuel is biodiesel. Biodiesel made from waste vegetable oil (WVO) is particularly favorable due to the availability of waste as fuel source as opposed to oil derived from food plants. Biodiesel production can therefore loom as a large economic opportunity for South Africa, whose fuel is largely imported from crude-oil rich regions in the world. Despite the environmental benefit compared to the fossil fuel, bio-fuels production at industrial level is not currently financially attractive in comparison to the conventional diesel fuel prices. The market price of the produced biofuel depends on its feedstocks, which fluctuate significantly and affect the production cost.

The purpose and aim of this research project is to combine and investigate the optimum conditions and the elementary reaction kinetics for the production of biodiesel from waste vegetable oil using a calcium silicate catalyst. The optimum conditions of interest are the methanol to oil ratio and the catalyst concentration.

There are various methods available for the production of biodiesel. For this project, transesterification was discovered to be the most suitable, and was then used throughout during the experiment. Prior to the production of biodiesel the catalyst was prepared from a reaction containing calcium hydroxide and silica gel as the reactants. The catalyst was characterized using FTIR, BET, XRD and SEM determinations. The waste vegetable oil was also characterized in order to determine its free fatty acid (FFA) content, its density and its moisture content; which are all essential to the quality of biodiesel that could be produced. The biodiesel produced was confirmed using GCMS and its quality in terms of concentration was derived from its absorbance using an absorbance vs. concentration calibration curve.

The results show that the optimum methanol to oil ratio at a constant temperature of 60 °C, with a reaction time of 180 minutes is 3:1. The optimum catalyst concentration at the same reaction temperature and time was found to be 5%. The transesterification reaction in this project correlated to an irreversible first order kinetic model. The reaction kinetics depicted this catalyst as ineffective for transesterification since low reaction rates were observed.

DEDICATION

I would like to dedicate this report to my family, especially to my wife Ntinugwa Priscilla Bongiwe and my children Emeka and Kelechi, for their unwavering love, support, encouragement, financial and understanding throughout the time spent in this project.

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NOMENCLATURE

BET	Brunauer-Emmet and Teller Surface Area Measurement
B100	100% bio-diesel
B20	20% bio-diesel.
CN	Cetane number.
DG	Diglyceride.
EDS	Energy Dispersive Spectrometry.
FAME	Fatty acid methyl ester.
FFA	Free fatty acid.
FTIR	Fourier transformation infrared spectrometer.
G	Glycerol .
HHV	Higher heating value
LMA	Law of mass action..
IV	Iodine Value.
MG	Monoglyceride.
OGProP	Oil and Gas Production and Processing.
PKO	Palm Kernel Oil.
RO^-	Alkoid ion.
ROH	Alcohol.
SV	Saponification Value.
SEM	Scanning electron microscope
TG	Triglyceride
TGA	Themogravitric analysis.

WVO	Waste vegetable oil.
XRD	X-ray diffraction.

1. INTRODUCTION

1.1 MOTIVATION

Over the years, fossil fuels have dominated as sources of fuel in many parts of the world. Developments were centered on using the energy produced by fossil fuels due to non-availability of renewable energy sources. However, the fuels sector is fast changing, introducing cleaner, greener and renewable fuel sources into the game. One such fuel is biodiesel. The generation and use of biodiesel from waste vegetable oil (WVO) has gained popularity over the years due to a number of great benefits that it offers.

Approximately 36% of the liquid fuels demand in South Africa is met by synthetic fuels, which are locally produced largely from coal and natural gas. The remaining sixty four percentage is met by locally refined products from imported crude oil (Anon., 2014). These figures show that South Africa's fuel market, hence its fuel prices, are still largely dominated by crude oil and its price in international markets (quoted in US dollars, $). Due to fluactuation in the international prices of crude oil and its effect on South Africa's economy is always felt once there are changes, therefore the dependence of fossil fuel as the only source of energy can be detrimental. To bridge the gap of locally produced liquid fuels, the South African government rolled on a Bio-fuels Industrial Strategy, which is a 5 year pilot phase from 2007 to 2013, during which 2% of bio-fuels should be added in the national liquid fuels (Department of Energy, 2014). Despite the approval of this strategy, no single large scale bio-fuels industry player has emerged to date. This was because of the fact that bio-fuels projects are not financially attractive in comparison to the current crude oil/ liquid fuel prices (Department of Energy, 2014). To ensure the success of the implementation of this strategy, regulations regarding the mandatory blending of bio-fuels, such as biodiesel, with petrol and diesel were regarded as possible tools in pursuance of this objective (Department of Energy, 2014). Hence the mass scale of the use of bio-diesel comes in the form of being mixed with crude oil derived liquid fuel, which is an economically viable option at the present stage. Should cheaper options of producing biodiesel be explored, it could be seen as a competitive fuel alternative.

Since approximately 80% of the total operating cost for the production of biodiesel is due to the feedstock, less expensive feedstock options such as waste vegetable oil (WVO) and palm kernel oil (PKO) are considered as great options in reducing the high biodiesel production costs. In 2008, the Energy Information Administration in the United States estimated that some 100 million gallons of WVO is produced per day in the USA (Chhetri et al., 2008). Assuming that this figure has increased over the past 6 years, it is clear to see the waste vegetable oil is not only a resource that is cheaper, but its availability locally. Using WVO as a source for the production of biodiesel can also significantly assist in the decrease of pollution, and is thus an excellent means of recycling and being environmental friendly.

The type of catalyst that will be used for this experiment is an alkali heterogeneous catalyst. The disadvantages of using acid-catalysts are that they require higher temperatures and longer reaction times which will not profitable if produced on a larger scale, in addition to causing undesired corrosion of the equipment (Thanh et al., 2012). This further enhances the costs associated with producing biodiesel, making it even more economically inefficient. Using a heterogeneous catalyst is preferred since homogeneous base-catalysts induce high energy consumptions, furthermore, separation of the catalyst from the reaction mixture and the purification of the biodiesel are costly (Thanh et al., 2012). Therefore to reduce the costs of the purification process, heterogeneous solid catalysts have been used recently because they can easily be separated from the reaction mixture and be reused (Thanh et al., 2012).

There are a number of environmental benefits that are associated with using biodiesel over conventional liquid fuels. Firstly, biodiesel virtually does not consist of any sulphur or aromatics, and using it in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matter (National Biodiesel Board, 2009). A study by the National Renewable Energy Laboratory conducted a life-cycle analysis on the carbon dioxide emissions of 100% petroleum diesel fuel and compared it to that of petroleum diesel comprising of 20% bio-diesel (B20) and to that of 100% bio-diesel (B100). The results were summarized in a graph shown in Figure 1, and display that pure bio-diesel reduces the carbon dioxide emissions by 78.45% as compared to pure petroleum diesel.

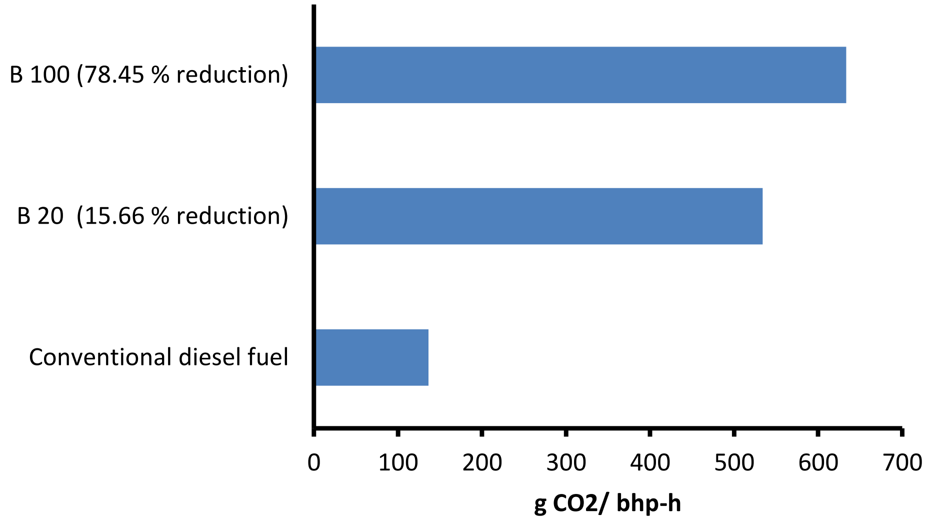


Figure 1: Comparison of net 〖CO〗_2 Life Cycle Emissions for petroleum diesel and biodiesel blends(Sheehan, Camobreco, Duffield, Graboski, & Shapouri, 1998)).

The results conducted by the same study showed that bio-diesel life cycle wastewater flows are almost 80% lower than those of petroleum diesel (Sheehan et al., 1998). Also shown was that biodiesel is responsible for only about 5% of the hazardous waste generated by petroleum diesel. Biodiesel is also reported to be non-toxic, biodegradable and safer to ship since spills do not require emergency response clean-up activities (US Department of Energy, 2014).

1.2 Problem Statement

The use of biodiesel as an alternative fuel option to crude oil derived fuels has become widespread and popular over the years. However, it has not been used commercially on a scale similar to crude oil derived fuels largely because it is not cost effective. A large contributor to the use of biodiesel not being cost efficient is the feedstock, which makes up 80% of the total operating cost (ElSolh, 2011). As a means of further reducing the production costs of biodiesel, a feasible catalyst that is both cost efficient and a viable option for the production of biodiesel must be determined.

1.3 AIM

The main aim of this research project is to investigate the production of biodiesel from waste cooking oil using calcium silicate. To meet the aim of the research project, the following objectives were investigated.

- Investigate the optimum operating conditions for biodiesel production;
- Synthesize Calcium silicate from calcium hydroxide;
- Investigate the catalytic activity of Calcium silicate for the production of biodiesel;
- Establish and review a kinetic model for biodiesel from waste vegetable oil using calcium silicate as heterogeneous catalyst.

2. LITERATURE REVIEW

2.1 TRANSESTERIFICATION

2.1.1 *TECHNIQUES FOR PRODUCTION OF BIODIESEL*

The vegetable oil used in this research has certain disadvantages namely a high viscosity, low volatility and reactivity of unsaturated hydrocarbon chains. There are four possible techniques that could be applied to solve this problem. The four techniques are dilution, micro-emulsification, pyrolysis and transesterification (Ankapong, 2010).

2.1.1.1 Dilution

Vegetable oils can be used directly or diluted with biodiesel to improve viscosity. Dilution is not a good technique because it causes engine performance problems such as injector coking and carbon deposits. Common diesel engines used in vehicles such as trucks that use the turbocharged direct injection engines encounter the problems of injector coking and carbon deposits (Ankapong, 2010).

2.1.1.2 Micro-Emulsification

Micro-emulsification is a process that involves the immersing of vegetable oil into an alcoholic solvent such as methanol or butanol. A micro-emulsification cannot be used for the synthesis of biodiesel because it leads to incomplete combustion, forms carbon deposits, has a low volumetric heating values compared to diesel produced from hydrocarbon and produces a lower cetane number compared to conventional diesel (Arifin, 2009).

2.1.1.3 Pyrolysis

Pyrolysis is a thermochemical process that heats one substance into another by using a catalyst in the absence of oxygen or air. The materials that can be used for pyrolysis is vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. There are several advantages in using pyrolysis. The oils used in pyrolysis are easier to handle and produce a consistent quality of biodiesel compared to other techniques used for the synthesis of biodiesel. The process of pyrolysis produces a clean liquid that requires no additional washing, drying or filtering. This technique also produces a high cetane number.

Pyrolysis also has many disadvantages. The viscosity of pyrolysis vegetable oil is considered to be higher than the standard used to test the biodiesel. The ash and carbon content found in the biodiesel is higher than that found in diesel made from fossil fuels. Oxygen is removed during thermal decomposition, thus eliminating one of the main ecological benefits of using oxygenated fuel (Ankapong, 2010).

2.1.1.4 Transesterification

Transesterification is a reaction of a fat or oil triglyceride and an alcohol such as methanol to form a free acid ester and glycerol. This process has been the most successful method in the production of biodiesel. Transesterification started by a scientist name Henriques, in 1898 he achieved 99% conversion of vegetable oil in methanol using a potassium hydroxide catalyst. Most of the global production of biodiesel uses this process because it meets the standards used to test biodiesel, reduces the viscosity and improves the fuel property of the vegetable oil.

In transesterification one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of free fatty acid esters. A catalyst is used to improve the reaction rate and yield. This process is a reversible reaction and the excess alcohol is used to shift the equilibrium towards the formation of esters and increase the yield of esters produced (Ankapong, 2010)

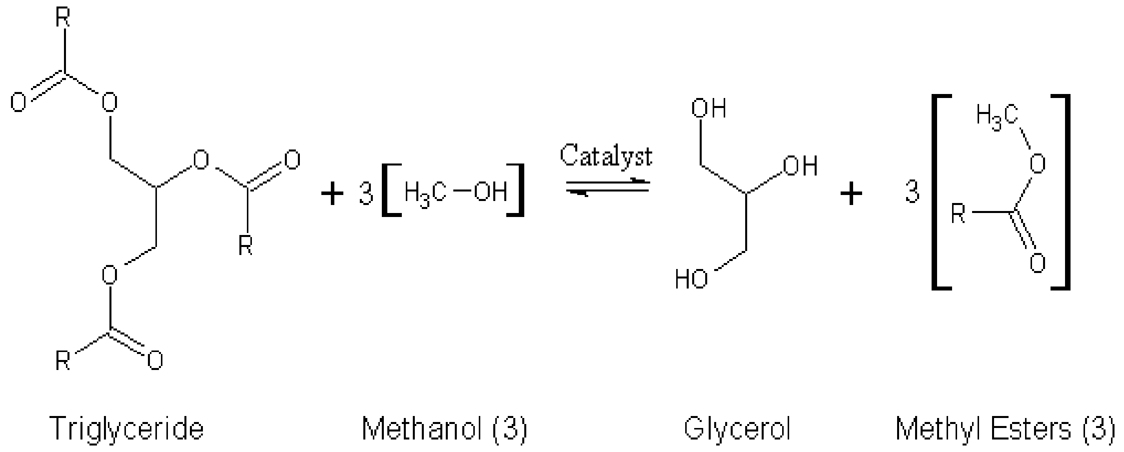


Figure 2: Transesterification Reaction (Spec Engineers and Consultants , 2010)

2.1.2 *MECHANISM OF TRANSESTERIFICATION*

The general mechanism of an alkaline -catalyzed transesterification of vegetable oils comprises of three reaction steps. The first reaction step involves the triglyceride and the alcohol, forming. The second step is the formation of a tetrahedral intermediate called monoglycerides by the nucleophilic attack at the carbonyl group of diglyceride. The third reaction step is the formation of an alkyl ester and glycerol from the reaction of monoglyceride with the third molecule of alcohol. The final products alkyl ester (biodiesel) and glycerol form an immiscible layer, the glycerol forming the bottom layer and the biodiesel the top layer (Ejikeme et al., 2009). The mechanism of transesterification is summarized in Figure 2.

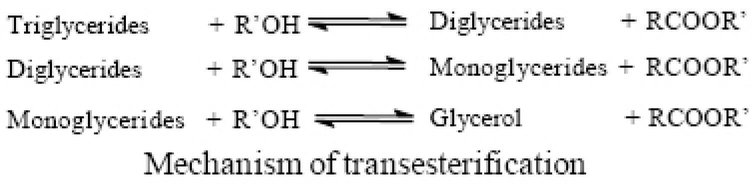


Figure 3: Mechanism of Transesterification (Ejikeme, et al., 2009)

2.1.3 *REQUIREMENTS FOR TRANSESTERIFICATION*

There are three important requirements for the success of transesterification of vegetable oils:

2.1.3.1 High Temperature

Transesterication can occur at various temperatures depending on the type of vegetable used. Since temperature has a direct impact on the reaction and yield of alkyl esters, the temperature at which transesterification takes place should be between 50 – 70 ˚C (Ankapong, 2010).

2.1.3.2 Catalyst

A catalyst is a substance that speeds up the rate of a chemical reaction by lowering the activation energy, without itself being consumed in the reaction. In the transesterification of triglycerides it is vital that catalysts can be used in the production of biodiesel. The catalysts used for transesterification are discussed below in the subsection catalyst type (Arifin, 2009).

2.1.3.3 Mechanical Mixing

Due to the difference in densities between the vegetable oil and methanol, both reactants tend to form to phases due to the effects of gravity. Hence it is vital to continuously mix the reactants in order for the reactions to begin and the production of biodiesel to take place (Chand, 2008).

2.1.4 *FACTORS AFFECTING TRANSESTERIFICATION*

2.1.4.1 Effect of Molar Ratio of Alcohol

The molar ratio of alcohol is important in biodiesel yield. Since in transesterification, 3 mol of alcohol reacts with one mole of triglycerides to form three mol of fatty acid ester and one mol of glycerol. The excess alcohol converts the oil into ester in a short period of time, thus the yield of biodiesel increases with the increase in concentration of alcohol up to a certain extent. Further increase of the alcohol concentration will not result in an increase in yield of biodiesel but just increase the cost of alcohol recovery. Since an alkali catalyst is used in this research, the molar ratio of alcohol to triglycerides requires being 6:1 (Mathiyazhagan & Ganapathi, 2011).

2.1.4.2 Concentration of Catalyst

The quality of biodiesel produced is affected with the concentration of the catalyst. The catalyst is first mixed with the methanol then added to the oil to prevent formation of water which restricts the formation of biodiesel. When the concentration of the catalyst is increased in the vegetable oil, the formation of biodiesel from triglycerides also increases. However if too little catalyst is used, it results into incomplete conversions of triglycerides into fatty acid esters. It is important to determine experimentally the optimum concentration of catalyst required because excess concentration of the catalyst leads to the formation of soaps (Mathiyazhagan & Ganapathi, 2011).

2.1.4.3 Free Fatty Acid (FFA) Content

Free fatty acids content is used to determine the viability of the vegetable oil in the transesterification process. Vegetable oil should contain little or no free fatty acids. If there are significant amount of free fatty acids in the vegetable oil, an alkaline catalyst should be used to neutralize these free fatty acids which consume the catalyst and slow down the reaction (Chand, 2008).

2.1.4.4 The Moisture Content

The moisture content is crucial in determining the viability and sustainability the biodiesel being produced. The higher the moisture in the oil results in a high probability of soap formation and lowers the efficiency of the catalyst. The presence of water also lowers the conversion of biodiesel being formed (Al-Zaini, 2012).

2.2 CATALYST

2.2.1 *HISTORY OF BIODIESEL CATALYSTS*

The historical development of the biodiesel industry has one whose advances have been driven largely by economics and politics rather than available technologies (Y.M. Sani, 2013). This has caused the developments of the catalysts used within the transesterification process to be based on reducing process economics. The transesterification process as a means of biodiesel production was first reported on August 31st 1937 in a Belgian Patent by Chavanne of the University of Brussels (P. M. Ejikeme, 2010). The original objective of the work was to establish a method for extracting glycerol during soap production since the glycerol was needed for wartime explosives production (P. M. Ejikeme, 2010). The glycerol was separable from the esters since it is insoluble in them and also has a much higher density making it easier to remove it through settling or centrifugation (P. M. Ejikeme, 2010).

Conventional industrial biodiesel processes in the past have used a homogenous catalyst system operated in either batch or continuous mode (Hillion. G, 2003). In most cases the catalysts used were sodium hydroxide or sodium methylate (Hillion. G, 2003), which were recovered after the transesterification reaction as sodium glycerate, sodium methylate and sodium soaps in the glycerol phase (Hillion. G, 2003). However the formation of the sodium soaps, from the side reactions occurring, is generally undesirable. In order to avoid catalyst removal operations and soap formation, effort has been invested towards the development of solid acid or basic catalysts that could be used in a heterogeneous catalyzed process (Hillion. G, 2003). The search for a catalyst that could yield optimum results for the biodiesel production process is still ongoing, and new technologies are constantly being researched and discovered.

2.2.2 *CATALYST TYPE*

A catalyst is a substance that speeds up the rate of a chemical reaction by lowering the activation energy, without itself being consumed in the reaction. In transesterification of triglycerides there are three types of catalysts that can be used in the production of biodiesel. The three types of catalysts are homogenous, heterogeneous and enzymatic.

2.2.2.1 Homogeneous

A homogeneous catalytic process involves a catalyst in solution with a minimum of one reagent. There are two types of homogenous catalysts, namely alkaline and acidic. Alkaline catalysts are commonly used in industry because they operate at moderate reaction conditions and allow the process to take place faster. However, the disadvantage of using a homogeneous alkaline catalyst is the formation of soaps and unwanted side-reactions. This causes the catalyst to be consumed, a reduction in biodiesel yield and complicates the procedure in separation and purification steps. Sodium hydroxide, sodium methoxide and potassium hydroxide are common examples of alkali catalysts. Acid catalysts such as sulphuric acid, hydrochloric acid and sulfonic acid do not have the problem of soap formation. Acid catalysts increase the yield of biodiesel production, but the process transesterification is slow and requires extreme pressure and temperature conditions (Arifin, 2009).

2.2.2.2 Heterogeneous

Heterogeneous catalyst can be classifies as acidic or alkaline. The type of catalysts used determines the reaction rate of transesterification. There are several advantages when using a heterogeneous catalyst. The advantages include minimal waste is produced during production, the setup is simple and requires less purification steps, since a high purity of glycerol is produced the refining and distillation process is minimize, thus reducing costs and less negative impact on the environment. The yield of biodiesel produced is similar that that of the theoretical yield. The disadvantages of this type of catalyst is that high pressure and temperature is required thus increases the utility and energy related costs. From various studies conducted on heterogeneous catalyst used in the production, it was concluded that alkaline catalyst are more effective than acidic catalysts. Alkaline catalysts contain more active sites, thus improves the performance of the catalyst in the transesterification reaction. Alkaline catalysts also produce a higher conversion and use less energy compared to acidic catalysts. Thus an alkaline catalyst, calcium silicate, is used in this study (Bobase et al., 2011).

2.2.2.3 Enzymatic

Enzymatic catalysts such as lipase can be used in the transesterification process. The advantages of using an enzymatic catalyst is that it is operational at room temperatures, enables easy separation between products, can be recycled when immobilized on a substrate and results in high selectivity. However, during immobilization the enzyme activity can be reduced thus reducing yield of biodiesel production. Other setbacks include slow reaction times of four to forty hours and the high cost of using such catalyst (Selahattin, 2008).

2.2.3 *CATALYST PREPARATION*

2.2.3.1 Preparation of Catalyst from Other Studies

This subsection covers the preparation of various catalyst used for the transesterication of vegetable oil from other studies.

A study conducted by Olivera Stamenkovic and colleagues in 2008 from a university in Serbia used a calcuim oxide catatyst for the transesterication of sunflower oil. The calcuim oxide catalyst was made from calcium chloride and potassuim hydroxide pellets. Using the process of calcination the catalyst was produced in a calcinating furnace using various temperatures ranging from 300˚C to 900˚C for a duration of two hours. Before the catalyst could be used it was cooled in a desiccator and finely ground by an electrical mill (Stamenkovic et al., 2008).

Buasri and colleages from the Silpakorn University in Thailand described the preparation of a potassuim hydroxide catalyst supported with activated carbon. A potassuim solution was obtained by dissoving pottasium hydroxide in distilled water. Portions of activated carbon were placed in the potassium solution. The solution was agitated at ambient temperature for a duration of 24 hours. When significant amount of potassium was adsorbed, the catalyst was ready to be characterised (Buasri et al., 2012).

A study conducted by Taufiq-Yap and colleagues from the Putra Univeristy in Malaysia involved the catalyst preparation of soduim hydroxide and aluminuim oxide. The catalyst was prepared by the impregnation of alumina in an aqueous solution containing various concentrations of soduim hydroxide. The impregnated alumina solution was dried in an oven for a duration of 12 hours and calcinated in air for 3 hours. The prepared catalysted was then characterised (Tayfiq-Yap et al., 2011).

2.2.3.2 Preparation of Catalyst used in Current Experiment

This subsection discusses the preparation of the calcium silicate-based catalyst used in this experiment. The catalyst is made up from two chemicals namely sodium silicate and calcium hydroxide. A silica solution is prepared from sodium silicate and distilled water. While a calcium slurry is prepared from calcium hydroxide and a weak hydrochloric acid. The silica solution and calcium slurry is combined together at room temperature, with rigorous agitation in a batch reactor forming the catalyst calcium silicate. The catalyst is then washed and dried before it can be used. A detailed discussion about the preparation of the catalyst can be found in the Methodology (McFarlane, 2007).

2.3 CHARACTERIZATION

2.3.1 *CHARACTERIZATION OF THE VEGETABLE OIL*

2.3.1.1 Free Fatty Acid (FFA) Content

Free fatty acids content is used to determine the viability of the vegetable oil in the transesterification process. The higher the acidity of the oil, the lower the conversion efficiency thus to carry the base reaction to completion a FFA value lower than 3% is needed, preferably 1% (Ankapong, 2010).

2.3.1.2 The Iodine Value (IV)

The Iodine value is used to describe the degree of un-saturation from vegetable oils and ultimately their derived biodiesel fuel. Increased IV of a particular fuel contributes to a massive reduction in fuel cetane number and long term storage oxidation stability (Ankapong, 2010).

2.3.1.3 The Saponification Value (SV)

Saponification is when an undesirable reaction occurs that consumes alkaline catalysts and promotes the reaction following an unwanted route producing soap rather than the prospective product. Increased saponification promotes a reduction in important properties in fuel such as higher heating value (HHV) and cetane number (CN). It is therefore desirable for the vegetable oil to have a relatively low SV (Ankapong, 2010).

2.3.1.4 The Moisture Content

Like the FFA content, the moisture content is crucial in determining the viability and sustainability of any biodiesel producing technology. The higher the moisture of the oil the lower the apparent yield of esters will be. This is because the presence of water within the vegetable oil leads to the formation of soap during the catalyst reaction, which is undesirable (Ankapong, 2010).

2.3.2 *CHARACTERIZATION OF THE FUEL PRODUCED*

2.3.2.1 The FAME composition

Biodiesel fuels are generally classified as fatty acid methyl esters (FAMEs). The fatty acids vary in their carbon chain length and in number of double bonds of carbons. Determining the FAME compositions is important since they affect the quality of the fuel through their influence on certain important properties of the fuel such as the cetane number, viscosity, iodine value, heat of combustion, oxidative stability and cold flow.

2.3.2.2 The Cetane number (CN)

Cetane number is indicative of the ignition characteristics of the biodiesel. It measures how easily ignition occurs and the smoothness of combustion. The higher the CN the better it is in its ignition properties, thus the higher the combustion efficiency. It affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise and emissions of CO.

2.3.2.3 Higher Heating Value (HHV)

The higher heating value of a fuel is the chemical property that reflects its energy content. It is also a measure of the heat liberated from complete combustion of a unit mass of biodiesel.

2.3.2.4 The Density

The density is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel. Different density values for different biodiesel fuels produced are due to their different fatty acid methyl ester (FAME) compositions as well as their purity. Density increases with decreasing chain length and increasing number of double bonds.

2.3.2.5 The viscosity

The viscosity of the biodiesel controls the characteristics of the injection from the diesel injector. A high viscosity of the fuel is not desirable since it often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubrication oil.

2.3.2.6 The flash point

The flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flashpoint of biodiesel is expected to be higher than that of petro-diesel, making it safe for transport purpose.

2.3.3 *CHARACTERIZATION OF THE CATALYST*

2.3.3.1 Microstructural analysis

One of the most commonly used instruments in the research and development of materials is the scanning electron microscope (SEM). Its use is widely common in a variety of fabrication plants (Leonard, 2012). Scanning electron microscopy is imperative to microstructural analysis and therefore central to research involving the processing, properties, and behaviour of materials that involves their microstructure (Leonard, 2012). Information that can be attained from the SEM is that concerning the topographical features, morphology, phase distribution, compositional differences, crystal structure, crystal orientation, and the presence and location of electrical defects on the surface of materials (Leonard, 2012). Another one of its abilities is to determine the elemental composition of micro-volumes with the addition of an x-ray (Leonard, 2012).The inherent versatility of the SEM, due to the multiple signals generated; simple image formation process; wide magnification range; and excellent depth of field, makes up its core strength (Leonard, 2012). I

2.3.3.2 Crystallographic structure

In order to determine the crystallographic structure, chemical composition and physical properties of the catalyst, different X-ray diffraction (XRD) techniques can be used. X-ray powder diffraction is defined as a rapid analytical technique primarily used for phase identification of crystalline material and can provide information on unit cell dimensions (UMDU, 2008).

2.3.3.3 Catalyst composition and calcinations temperature

In order to determine the correlation between the catalyst’s composition and calcinations temperature, characterization by Fourier transform- infrared spectrometer (FTIR) would need to be conducted.

2.3.3.4 Catalyst surface area

An important property of the catalyst is its surface area. In order to determine the surface area of the catalyst the Brunauer-Emmett-Teller method can be carried out. This method is based on adsorption of a gas on a surface. A definition of adsorption describes it as “the adhesion of atoms or molecules of gas to a surface”. It is important to point out that adsorption should not be confused with absorption, where a fluid permeates in a liquid or solid (Barron, 2014). The amount of gas adsorbed at a given pressure allows for determination of the surface area of the solid (Anon., n.d.). In a BET determination nitrogen is commonly used because of its availability in high purity and its strong interaction with most solids (Barron, 2014). It is an inexpensive method that is reliable and it is fast to implement.

2.3.3.5 Catalyst Thermal Stability

The catalyst’s thermal stability and its fraction of volatile components can be determined by Thermogravimetric analysis (TGA), which monitors the weight change that occurs as a specimen is heated (ÖNER, 2007). Usually, the measurement is carried out in air or in an inert atmosphere, such as Helium or Argon, and the catalyst weight is then recorded as a function of increasing temperature. In cases where oxidation may occur, the measurement is carried out in a lean oxygen atmosphere in order to decrease the rate at which oxidation occurs (ÖNER, 2007). Along with the weight variations, other instruments read the temperature variations between the specimen and one or more reference pans or heat flow into the specimen pan compared to that of the reference pan- which can be used to monitor the energy released or absorbed through chemical reactions during the heating process (ÖNER, 2007).

2.4 KINETIC MODEL

The study of kinetics on the transesterification of vegetable oil for production of biodiesel determines the parameters for predicting the extent of reactions at any given time under certain conditions. Kinetics involves the determination of activation energy, reaction rate equations and reaction rate constants. Even though the significance of biodiesel as an alternative fuel has grown over the last two decades, the chemical kinetics of transesterification remain controversial (Singh & Fernando, 2011). The kinetic models in literature focused on determining the best fit of empirical data to simple models of reaction order. Some of the results found in these models are contradictory (de Lama de Silver, 2009). Many research studies have been carried out on the kinetics of transesterification process using a acid and base catalysts (Jain & Sharma, 2010). In this section Freedman's Kinetic Model and Komer's Kinetic Model will be discussed in order to gain a deeper understanding of the reaction kinetics involved during transesterification using other base catalysts. The theory behind the elementary development of the reaction kinetics for transesterification using a calcium silicate catalyst will be reviewed.

2.4.1 *FREEDMAN'S KINETIC MODEL*

The first biodiesel chemical kinetic model was developed by Freedman and his colleagues in the 1980's (Freedman et al., 1986). The kinetics were determined using soybean oil with solvents of methanol and butanol to examine the alcohol type, catalyst type, reaction rate constants and concentration. Freedman's kinetic model has a limitation because it considers only one overall reaction. The overall reaction is the case where one molecule of triglyceride (TG) reacts with three molecules of alcohol (ROH) as seen in Equation 10 (Mjalli & Hussain, 2009).

$$\boldsymbol{TG} + 3ROH \rightleftharpoons G + 3E \qquad \textbf{(10)}$$

The above overall reaction occurs in three steps. Firstly the triglyceride (TG) breaks down into diglyceride (DG) and monoglyceride (MG) and producing glycerol (G) and alkyl ester (E). This is shown as Equation (11) – (13):

$$\boldsymbol{TG} + ROH \rightleftharpoons DG + E \qquad \textbf{(11)}$$

$$\boldsymbol{DG} + ROH \rightleftharpoons MG + E \qquad \textbf{(12)}$$

$$\boldsymbol{MG} + ROH \rightleftharpoons G + E \qquad \textbf{(13)}$$

It appears that Freemans's kinetic model is obtained from the application of the law of mass action to the three steps of the above reaction. The forward reactions are considered to be second order, with regards to the overall order of the forward reactions. The concentration of alcohol is considered to be constant when the molar ratio of alcohol to triglycerides is very high. The rate of reaction is only a function of the concentration of triglyceride. This is known as "pseudo-first-order". When the data does not correspond to the aforementioned model, Freedman et Al. (1986) proposed the use of a “shunt reaction” whereby three alcohol molecules simultaneously react with the triglyceride. The “shunt reactions” are fourth order and proportional to $[TG][ROH]^3$ (Mjalli & Hussain, 2009)

Freedman et Al. (1986) used two solvents namely, methanol and methanol, to investigate the transesterification of soy oil. The investigation used a molar ratio of alcohol to oil of 30:1 and 6:1 at temperatures between 20˚C - 60˚C. The investigation showed that using butanol the forward reaction is second order at a molar ratio to oil of 6:1, while a molar ratio to oil of 30:1 when the forward reaction was pseudo first order. It was found using methanol the forward reaction is fourth order at 6:1 (shunt reaction) and a ratio of 30:1 at pseudo first order. He determined the reverse reactions to be second order. Freeman used the Arrhenius to derive the reaction rate constants and activation energies (Freedman et al., 1986). The Arrhenius equation is shown in Equation (14).

$$\boldsymbol{k} = A \exp(-E_A/RT) \qquad \textbf{(14)}$$

Where:
A: frequency factor of reaction
R: universal molar gas constant
T: Temperature (K)
k: rate constant
E: activation energy

The activation energy is a function of temperature; therefore the rate constant can be determined using the following equation:

$$\ln k = \ln A - \frac{E}{RT} \qquad \textbf{(15)}$$

Equation (15) is linear and a plot of $\ln k$ vs. 1/T will result in a straight line slope of $\frac{-E}{RT}$ (Jain & Sharma, 2010).

Mittelbach and Trathnigg from the University of Karl Franzen in Austria experimented on the kinetics of sunflower oil using methanolysis. Their experiment did not explore any reaction rate constants; however they determined the parameter affecting the transesterication process. Mittelbach discovered that the forward reaction of the conversion of triglycerides is not second order as found by Freedman. He showed this by the first reaction step between methanol and triglyceride forming diglyceride as the rate limiting step, as the other reaction steps occurred faster. He also found that the reaction rate is a function of temperature, however the percentage conversion is a poor function of temperature as long as the reaction takes place at a minimum duration of 10 minutes (Mittelbach & Remschmidt, 2006).

Mittelbach discovered that the reaction is a two-phase system, which is different to Freedman's discovery of a single phase system. Mittelbach found that for the first two minutes of the reaction a two-phase system occurred, thereafter complete solution took place for duration of 5 to 10 minutes. Thereafter after some time when glycerol was fully formed the two phased system occurred again. The two phase system complicates the kinetics and need to be taken into consideration (Mittelbach & Remschmidt, 2006).

Noureddini and Zhu from the University of Nebraska studied the kinetics of the transesterification of soybean oil with methanol as the solvent and NaOH as the catalyst in 1997. They used Freedman's kinetic model. Noureddini and Zhu investigated the effect of mixing intensity and temperature on the reaction rates using a molar ratio of 6:1 for methanol to soybean oil. The forward reaction was second order as proposed by Freedman. Measurements in the study were taken at different mixing intensities and Reynold's number of the stirrer. The effects of temperature were determined using the Arrhenius equation and modified Arrhenius equation as expressed in Equation (16) (Cheng, 2010)

$$\boldsymbol{k} = AT^{n}\exp(-E/RT) \qquad \textbf{(16)}$$

Where:
n = experimentally derived parameter

The authors in the study used a value of n=1. From the results of their study it was found that the shunt reaction proposed by Freedman was negligibly small. It was also found that the activation energy changed with the change in Reynolds number. Lastly it was found that the rate constant for the reverse reaction was larger than that of the forward reactions (Cheng, 2010).

A study conducted in 1988 by Boocock and colleagues from the University of Toronto found anomalies in Freedman's work. They study was investigating the formation of high purity of methyl esters using coconut oil and soybean oil using tetrahydroforan as a solvent. Their study shows that the reaction slows down considerably over time and the reaction rate drops due to inadequate mixing and the reduced efficiency of the catalyst because of the reduced polarity effect between the methanol and the non-polar oil (Boocock, 1998).

Bikou and colleagues, in 1999, from the National Technical University of Athens studied the effects of ethanolysis on cotton seed oil. The study proposed that the three reaction steps are third order with regard to ethanol. The study did not focus on the kinetic model, rather studied the effect of water on the equilibrium constants of the three reaction steps. The results showed that the presence of water shifted the three reaction steps to the left (Turner, 2005).

A study on the kinetics on the transesterification of palm was conducted in 2000 by Cheran and Darnoko at the University of Illinois. The study was conducted in a batch reactor. The study found that the best kinetic model for their data was a pseudo second order for initial stages of the reaction, thereafter the reaction follows a zero-order or first order kinetics (Darnoko & Cheryan, 2000).

At the University of Pardubice in the Czech Republic, in 2002, Kromers and his colleague developed a kinetic model for all competing reactions that take place during transesterification using vegetable oil with methanol and a potassium hydroxide catalyst. The model included the formation of methanol, methanolysis and saponification (Komers, 2002). Komers made certain assumption, these assumptions include that the vegetable oil used is purely triglyceride, the concentration of FFAs on the vegetable oil is negligibly small and saponification of FFAs does not take place during alcoholysis. This model supports Bokou's research with regard to the negative effect of water on the progress of the transesterication process. The model developed by Kromers is discussed in detailed in the following section (Bikou et al., 1999).

2.4.2 *KOMERS KINETIC MODEL*

Komers kinetic model investigates the methanolysis of rapesideseed oil using a heterogeneous alkaline catalyst, potassium hydroxide. For simplification purposes the Komer kinetic model is used for any alkyl alcohol, selected ROH and any alkaline (base) catalyst.

The modelling of kinetic models requires simplifying assumptions. For theoretical development of Komers kinetic model, the following assumptions were made (Komers, 2002):

1. The concentration of FFAs (free fatty acids) is negligibly small.
2. From the possible theoretical reactions only two reactions proceed to form products. These two reactions are the alcoholysis of glycerides (TG, DG and MG) and saponification of TG, DG and MG or E.
3. The isomers namely TG, DG, MG and E proceed at the same rate.
4. Alcoholysis is catalyzed by OH^- or RO^- (alkoxide) ions. The concentration of OH^- and RO^- ions are very small compared to the ions of TG and ROH.

Based on the assumptions above, the simplifications are represented as the possible reactions:

Formation of alkoxide:

$$\boldsymbol{ROH} + OH^- \underset{k_{1r}}{\overset{k_1}{\rightleftarrows}} RO^- + H_2O \qquad \textbf{(17)}$$

Alcoholysis:

$$\boldsymbol{TG} + RO^- \underset{k_{2r}}{\overset{k_2}{\rightleftarrows}} DG^- + E \qquad \textbf{(18)}$$

$$\boldsymbol{DG} + ROH \underset{k_{3r}}{\overset{k_3}{\rightleftarrows}} DG + RO^- \qquad \textbf{(19)}$$

$$\boldsymbol{DG} + RO^- \underset{k_{4r}}{\overset{k_4}{\rightleftarrows}} MG^- + E \qquad \textbf{(20)}$$

$$\boldsymbol{MG} + RO^{-} \underset{k_{5r}}{\overset{k_5}{\rightleftarrows}} G^{-} + E \qquad \textbf{(21)}$$

$$\boldsymbol{DG} + RO^{-} \underset{k_{6r}}{\overset{k_6}{\rightleftarrows}} MG^{-} + E \qquad \textbf{(22)}$$

$$G^{-} + ROH \underset{k_{7r}}{\overset{k_7}{\rightleftarrows}} MG^{-} + E \qquad \textbf{(23)}$$

Saponification:

$$\boldsymbol{E} + OH^{-} \overset{k_8}{\rightarrow} ROH + A \qquad \textbf{(24)}$$

$$\boldsymbol{TG} + OH^{-} \overset{k_9}{\rightarrow} DG + A \qquad \textbf{(25)}$$

$$\boldsymbol{DG} + OH^{-} \overset{k_{10}}{\longrightarrow} MG + A \qquad \textbf{(26)}$$

$$\boldsymbol{MG} + OH^{-} \overset{k_{11}}{\longrightarrow} G + A \qquad \textbf{(27)}$$

Where:
A= soap of the corresponding fatty acid chain (Komers, 2002).

If the effect of FFA content is being studied, the following Equation (28) needs to be taken into consideration. Equation (28) is considered to be a saponification reaction.

$$\boldsymbol{FFA} + OH^{-} \xrightarrow{k_{12}} A + H_2O \qquad \textbf{(28)}$$

The above reaction showing the saponification of FFA is an undesirable reaction because it consumes the reaction producing soap instead of biodiesel. Therefore the kinetic model consists of 10 components namely TG, DG, MG, G, E, M, A, OH, FFA and H_2O (Komers, 2002).

The above lists of reactions from Equation (17) – (28) are assumed to be elementary and obey the rate law called the law of mass action (LMA). Rate laws are helpful in calculating reaction rates by using the product of a rate constant and reactant concentrations. The direct use of LMA produces 13 differential equations. The number and complexity of the differential equations can be reduced by simplifying assumptions. There are two approaches that can be used. The first approach is the rate-limiting step approach. This approach is based on the assumption that forward and reverse reaction rates of the first reaction step is greater than the rate of reaction of the second reaction step. The second approach is the steady state assumption. This approach makes the assumption that the rates of change of the concentration of all reactive intermediaries are negligible. This assumption is good because the concentrations of the intermediates are low since small variables have small time derivatives on condition they do not oscillate quickly. Komers took the steady state approach because it yields accurate results (Mortimer, 2008). This assumption means the following:

$$k_2, k_{2r} \ll k_3, k_{3r} \qquad \textbf{(29)}$$

$$k_4, k_{4r} \ll k_5, k_{5r} \qquad \textbf{(30)}$$

$$k_6, k_{6r} \ll k_7, k_{7r} \qquad \textbf{(31)}$$

$$k_3, k_{3r}, k_5, k_{5r}, k_7, k_{7r} > k_8, k_9, k_{10}, k_{11}, k_{12} \quad \textbf{(32)}$$

Based on the above assumption, removing small terms and substituting them into rate equations at equilibrium the following was obtained.

$$\frac{d[H_2O]}{dt} = \frac{d[RO^-]}{dt} = \frac{d[DG^-]}{dt} = \frac{d[MG^-]}{dt} = \frac{d[G^-]}{dt} = \mathbf{0} \quad \textbf{(33)}$$

Komer normalized each species by the initial concentration of triglyceride $[TG]_0$ and alcohol $[ROH]_0$ as follows:
Let a = $[TG]_0$ and b = $[ROH]_0$.

$$\boldsymbol{TG} = \frac{[TG]}{a} \quad \textbf{(34)}$$

$$\boldsymbol{DG} = \frac{[DG]}{a} \quad \textbf{(35)}$$

$$\boldsymbol{MG} = \frac{[MG]}{a} \quad \textbf{(36)}$$

$$\boldsymbol{G} = \frac{[G]}{a} \quad \textbf{(37)}$$

$$\boldsymbol{A} = \frac{[A]}{a} \quad \textbf{(38)}$$

$$\boldsymbol{OH} = \frac{[OH^-]}{a} \quad \textbf{(39)}$$

$$\boldsymbol{W} = \frac{[H_2O]}{a} \quad \textbf{(40)}$$

$$\boldsymbol{ROH} = \frac{[ROH]}{b} \quad \textbf{(41)}$$

$$\boldsymbol{E} = \frac{[E]}{b} \tag{42}$$

The resulting differential equations for the ten reaction components (TG, DG, MG, G, E, ROH, OH, A, FFA and H_2O):

$$\frac{-dTG}{dt} = b \cdot OH \left(k_2' \cdot TG \cdot ROH - k_{2r}' \cdot DG \cdot E\right) + a \cdot OH \cdot DG \cdot E \tag{43}$$

$$\frac{-dDG}{dt} = b \cdot OH \left(-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E\right) + a \cdot OH(-k_9 \cdot TG + k_{10} \cdot DG) \tag{44}$$

$$\frac{-dMG}{dt} = b \cdot OH \left(-k_4' \cdot DG \cdot ROH + k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E\right) + a \cdot OH(-k_{10} \cdot DG + k_{11} \cdot MG) \tag{45}$$

$$\frac{-dG}{dt} = b \cdot OH \left(-k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E\right) - a \cdot OH \cdot k_{11} \cdot MG \tag{46}$$

$$\frac{-dROH}{dt} = \frac{dE}{dt} = a \cdot OH \left(-k_2' \cdot TG \cdot ROH + k_{2r}' \cdot DG \cdot E + k_4' \cdot DG \cdot ROH - k_{4r}' \cdot MG \cdot E + k_6' \cdot MG \cdot ROH - k_{6r}' \cdot G \cdot E - k_8 \cdot E\right) \tag{47}$$

$$\frac{-dH_2O}{dt} = \frac{dFFA}{dt} = a \cdot k_{12} \cdot FFA \cdot OH \tag{48}$$

$$\frac{-dOH}{dt} = \frac{dA}{dt} = b \cdot OH \cdot k_8 \cdot E + a \cdot OH \cdot (k_9 \cdot TG + k_{10} \cdot DG + k_{11} \cdot MG) \tag{49}$$

Where:

$k_1\ to\ k_{12}$ = reaction rate constants (Lmol^{-1} s^{-1})

The above reaction constants have the following definitions:

$$k_2' = k_2 \cdot \frac{K_1}{W} \qquad \textbf{(50)}$$

$$k_{2r}' = k_{2r} \cdot \frac{K_1}{K_3 \cdot W} \qquad \textbf{(51)}$$

$$k_4' = k_4 \cdot \frac{K_1}{W} \qquad \textbf{(52)}$$

$$k_{4r}' = k_{4r} \cdot \frac{K_1}{K_5 \cdot W} \qquad \textbf{(53)}$$

$$k_6' = k_6 \cdot \frac{K_1}{W} \qquad \textbf{(54)}$$

$$k_{6r}' = k_{6r} \cdot \frac{K_1}{K_7 \cdot W} \qquad \textbf{(55)}$$

And:

$$K_1 = \frac{k_1}{k_{1r}} = \frac{[RO^-][H_2O]}{[ROH][OH^-]} \qquad \textbf{(56)}$$

$$K_2 = \frac{k_2}{k_{2r}} = \frac{[DG^-][E]}{[TG][RO]} \qquad \textbf{(57)}$$

$$K_3 = \frac{k_3}{k_{3r}} = \frac{[DG][RO^-]}{[DG^-][ROH]} \qquad \textbf{(58)}$$

$$K_4 = \frac{k_4}{k_{4r}} = \frac{[MG^-][E]}{[DG][RO^-]} \qquad \textbf{(59)}$$

$$K_5 = \frac{k_5}{k_{5r}} = \frac{[MG][RO^-]}{[MG^-][ROH]} \qquad \textbf{(60)}$$

$$K_6 = \frac{k_6}{k_{6r}} = \frac{[G][E]}{[MG][RO^-]} \qquad \textbf{(61)}$$

$$K_7 = \frac{k_7}{k_{7r}} = \frac{[G][RO^-]}{[G^-][ROH]} \tag{62}$$

The rate of reactions can be represented in a balance equation as follows:

$$\mathbf{1} = TG + DG + MG + G \tag{63}$$

$$\boldsymbol{ROH} + E = 1 \tag{64}$$

$$\boldsymbol{OH} + A = p \tag{65}$$

$$\boldsymbol{p} = [OHJ]_o/[TG]_0 \tag{66}$$

$$\boldsymbol{n} \cdot E + 3 \cdot TG + 2 \cdot DG + MG + A = 3 \tag{67}$$

$$\boldsymbol{n} = [ROH]_0/[TG]_0 \tag{68}$$

The initial concentrations from the above equations are as follows:

$$[TG]_0 = 1 \tag{69}$$

$$[ROH]_0 = 1 \tag{70}$$

$$[OH]_0 = p \tag{71}$$

$$[DG]_0 = [MG]_0 = [E]_0 = [A]_0 \tag{72}$$

Komer defined new Equilibrium constants by combining the product of pairs of original equilibrium constants as the following:

$$K_2' = K_2 \cdot K_3 = \frac{[DG][E]}{[TG][ROH]} = \frac{k_2'}{k_{2r}'} \tag{73}$$

$$K'_4 = K_4 \cdot K_5 = \frac{[MG][E]}{[DG][ROH]} = \frac{k'_4}{k'_{4r}} \tag{74}$$

$$K'_6 = K_6 \cdot K_7 = \frac{[G][E]}{[MG][ROH]} = \frac{k'_6}{k'_{6r}} \tag{75}$$

The values of the intermediaries directly lead to:

$$\boldsymbol{DG} = K'_2 \cdot TG \cdot \frac{(1-E)}{E} \tag{76}$$

$$\boldsymbol{MG} = K'_4 \cdot DG \cdot \frac{(1-E)}{E} = K'_2 \cdot K'_4 \cdot TG \cdot \left(\frac{(1-E)}{E}\right)^2 \tag{77}$$

$$\boldsymbol{G} = K'_6 \cdot MG \cdot \frac{(1-E)}{E} \tag{78}$$

$$= K'_2 \cdot K'_4 \cdot K'_6 \cdot TG \cdot \left(\frac{(1-E)}{E}\right)^3 \tag{79}$$

Combining Equations (57), (59), (61) and Equations (63) – (68) a relation between TG and E is formed and is represented in the following equations:

$$\boldsymbol{TG} = \frac{1}{1 + K'_2 \cdot \frac{(1-E)}{E} + K'_2 \cdot K'_4 \cdot \left(\frac{(1-E)}{E}\right)^2 + K'_2 \cdot K'_4 \cdot K'_6 \cdot \left(1 + K'_6 \cdot \frac{(1-E)}{E}\right)^3} \tag{80}$$

The desired result for the initial molar ratio of alcohol to triglyceride is obtained by substituting Equation (80) and Equations (73) - (75) into Equation (68). The equation is expressed as follows:

$$n = \frac{1}{E}\left[P + 3 - \frac{3 + 2K_2' \cdot \frac{(1-E)}{E} + K_2' \cdot K_4' \cdot \left(\frac{(1-E)}{E}\right)^2}{1 + K_2' \cdot \frac{(1-E)}{E} + K_2' \cdot K_4' \cdot \left(\frac{(1-E)}{E}\right)^2 + K_2' \cdot K_4' \cdot K_6' \cdot \left(1 + K_6' \cdot \frac{(1-E)}{E}\right)^3}\right] \quad (81)$$

Where:

P= molar ratio of base catalyst to triglyceride

With the use of Equations (73) – (75) and Equation (80), it is possible to calculate the values n, DG, TG, G and MG for every alkyl ester selected. The value of the alcohol can be determined using equation (64).

Komers kinetic model helps to predict the concentration of the end products using analytical expressions. The model also assists in telling us how the reaction conditions are affected by the concentrations of the reactions. An example is the increase in the concentration of ROH increases the total reaction rate (Komers, 2002).

2.4.1 *ELEMENTARY KINETICS FOR CALCIUM SILICATE AS A CATALYST*

The basis of the reaction kinetics reviewed in this project is the Arrhenius law, which is described as shown in equation (14). Within the Arrhenius law, the activation energy acts as a “barrier”, since it represents the minimum energy required for a reaction to take place. Therefore, the higher the reaction temperature, the more molecules have enough energy to make it over the barrier. This phenomenon can be described by the Boltzmann Distribution, which is shown as Figure 4 below.

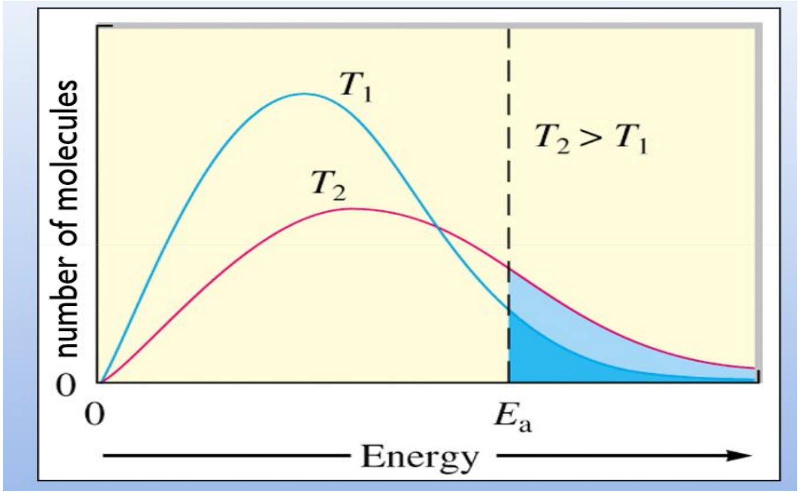


Figure 4: Boltzmann distribution showing the effect of temperature on the activation energy (Bout, 2014)

An assumption was made that transesterification catalyzed by calcium silicate will correlate an irreversible first order kinetic model as follows:

$$\text{Rate of Methyl Ester formation} = k[ME] \tag{82}$$

Where

k=reaction rate constant;

[ME]= concentration of Methyl Ester formed

Equation (82) can be re-written as follows:

$$Rate\ of\ Methyl\ ester\ formation = \frac{d[ME]}{dt} = k[ME] \tag{83}$$

Since the initial [ME] value is zero, equation (83) is integrated to give:

$$\ln([ME]) = kt \tag{84}$$

Therefore the experimental data from this project should display a linear relationship between ln ([ME]) and time (t) for the assumption regarding the order of the reaction to be justified.

As part of fulfilling the purpose of this project, the activation energy will be obtained for transesterification using calcium silicate as a catalyst, from the Arrhenius plot, and compared to one obtained from literature.

The rate constant (k) for transesterification at different reaction temperatures will be obtained from a model simulated in Matlab which uses a numerical method to calculate k from different methyl ester (biodiesel) concentrations obtained with the change in time for each temperature.

3. EXPERIMENTAL PROCEDURES AND ANALYTICAL TECHNIQUES

3.1 PROCESS FLOW DIAGRAM

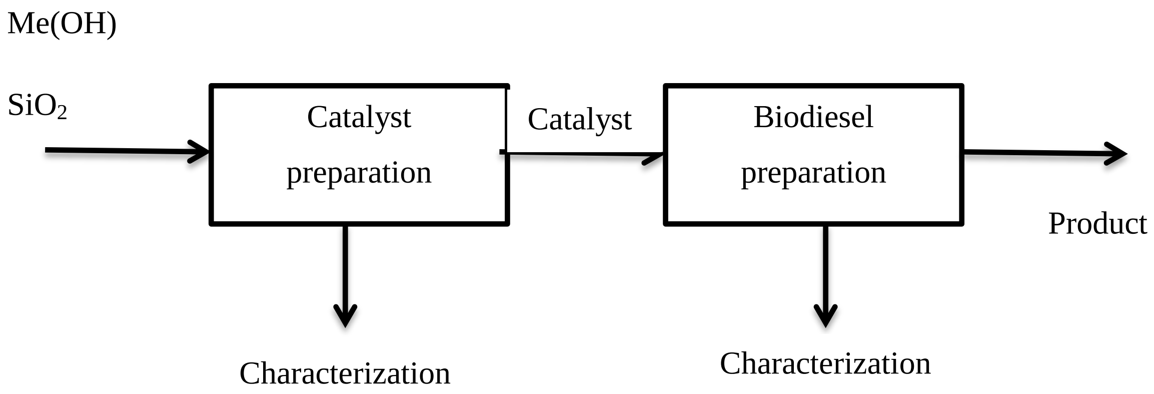


Figure 5: Schematic diagram of biodiesel production

3.2 CATALYST PREPARATION

The production of calcium silicate is prepared in a batch vessel on a hot plate. Firstly distilled water was heated to a temperature of 50℃ using a small steel bowl. Thereafter silica gel was added to the water. The mixture was gently stirred, whilst the calcium hydroxide powder was gradually added to form a thick slurry. The slurry was then continuously stirred for 20 minutes on the hot plate, maintaining a temperature of 50℃. This is done in order to prevent adhesion of the catalyst to the steel bowl. Once the 20 minute period had elapsed, the slurry was put into a crucible which was placed in a furnace for 150 minutes at a temperature of 480 ℃. The aim of using a temperature of 480 ℃ is to ensure that all the moisture is removed.

The details of the contents used to create the catalyst are shown in Table 1 below

Table 1: Details of preparing Calcium Silicate catalyst.

MATERIAL	WEIGHT (g)	VOLUME (mL)	Mol
Silica gel (SiO_2)	12	4.53172	0.20
Calcium Hydroxide ($Ca(OH)_2$)	16	7.23982	0.22
Water (H_2O)	40	40	2.22

Figure 6: Illustration of the calcium silicate catalyst produced.

3.3 ANALYTICAL TECHNIQUES FOR CATALYST CHARACTERIZATION

3.3.1 *FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)*

A Brüker Tensor 27 Fourier Transform Infrared spectrometer was used to analyze the surface functionalities and the type of functional groups present on the materials. All the samples analyzed were in powder form. The spectra were recorded in the range of 600-4000 cm^{-1}.

3.3.2 *SCANNING ELECTRON MICROSCOPE (SEM)*

The SEM analysis was performed using the Carl Zeiss FE-SEM. Before the sample was placed in the microscope, it was splutter coated with palladium and gold to increase conductance of the sample.

3.3.3 *BRUNAUER-EMMET AND TELLER SURFACE AREA MEASUREMENT (BET)*

A Micromeritics Tristar-Surface area and Porosity analyzer was used, to determine the surface areas and pore volumes of the materials. Sample with an approximate mass of 0.2 g was degassed under the flow of nitrogen gas at 150 ℃ for 4 h prior to analysis using a Micromeritics flow Prep 060, sample degas system.

3.3.4 *X-RAY DIFFRACTION (XRD)*

All samples were top loaded into the sample holders followed by pressing into place with a smooth glass slide. Powder X-ray diffraction patterns were collected on a Bruker D2 Phaser desktop diffractometer. This diffractometer employs a sealed tube Co X-ray Source (Co = 1.78897 Å) and is equipped with a Bruker Lynxeye PSD detector using primary and secondary beam Söller slits and a secondary beam Ni filter.

3.4 WASTE VEGETABLE OIL CHARACTERIZATION

3.4.1 *DETERMINING FREE FATTY ACID (FFA) VALUE*

Weigh out 0.5g of sample of vegetable oil into a 250ml conical flask. Then 50ml of ethanol is added to form a mixture. In a water bath the mixture is heated to dissolve the sample into the ethanol solution. The solution is titrated using 0.1M KOH with using phenolphthalein as an indicator. The acid values determined using the following equation (Ankapong, 2010):

$$Acid\ Value = \frac{A \times M \times 56.1}{W} \tag{85}$$

Where:
A: ml of 0.1M consumed by sample
M: Molarity of KOH
W: Weight of sample (grams)
56.1: Molar mass of KOH

Using the acid value obtained from Equation 1, the FFA content is determined as follows:

$$FFA = \frac{Acid\ Value}{2} \tag{86}$$

3.4.2 DETERMINING THE SAPONIFICATION VALUE (SV)

One gram of WVO was added in a beaker prior addition of 5ml of WVO solvent (ethanol) mix well and add the contents into a round bottom flask. Rinse the beaker with 5ml of the WVO solvent and transfer to the round bottom flask. Mix well so that the WVO dissolves completely in the ethanol and label the flask “Test”. Now add 25 ml of 0.5M of ethanoic KOH (KOH dissolved in ethanol) to the round bottom flask. The blank is prepared by adding 10ml of the WVO solvent and 25 ml of 0.5M ethanoic KOH into a separate round bottom flask. Label it as “Blank”. Reflux both for 30 minutes and allow them to cool afterwards. Add 1-2 drops of phenolphthalein indicator into both the flasks. The contents of the flasks are then titrated against 0.5M HCl. The end point of the titration is indicated by the decolourization of pink solution in the round bottom flask.

The Saponification Value (SP) is calculated using the following equation (Ankapong, 2010):

$$SP = \frac{(B - S) \times M\ of\ HCl}{weight\ of\ sample} \tag{87}$$

Where:
B: ml of HCl required by blank
S: ml of HCl required by sample
M: Molarity of HCl

3.4.3 DETERMINING THE DENSITY (ρ)

A sample of vegetable oil is used to measure the density. The mass of the sample is measured using a scale. The volume of the sample will be determined using a measuring cylinder.

$$\rho = \frac{m}{V} \tag{87}$$

Where:
m: Mass of sample (g)
V: Volume of sample (ml)

3.4.4 *DETERMINING MOISTURE CONTENT*

A sample of vegetable oil is weighed in a moisture pan. The weight of the oil and pan was taken and placed into an oven for three hours at 50˚C. After every hour the sample is cooled and weighed until the weight before and after is equal (Ankapong, 2010).

3.5 BIODIESEL PRODUCTION

3.5.1 *GENERAL TRANSESTERIFICATION PROCEDURE*

A proportionate amount of the catalyst, the methanol and vegetable oil are mixed by being added into a 250ml 3-neck round bottom flask. The contents of the flask are then heated to a temperature of 60℃ and stirred using a hotplate and magnetic stirrer by placing the flask in a water bath. The reason for adding the alcohol-catalyst solution to the vegetable oil whilst it is being stirred is due to the fact that the reaction is relatively slow at the beginning because of mixing and dispersion of alcohol into feedstock. The mixing of the reactants thus increases the reaction rate along with the ester conversion. Upon the completion of the reaction, the product mixture is separated into a crude ester layer and denser glycerol layer through a separating funnel. The glycerol is then flowed out of the separating funnel (Ankapong, 2010).

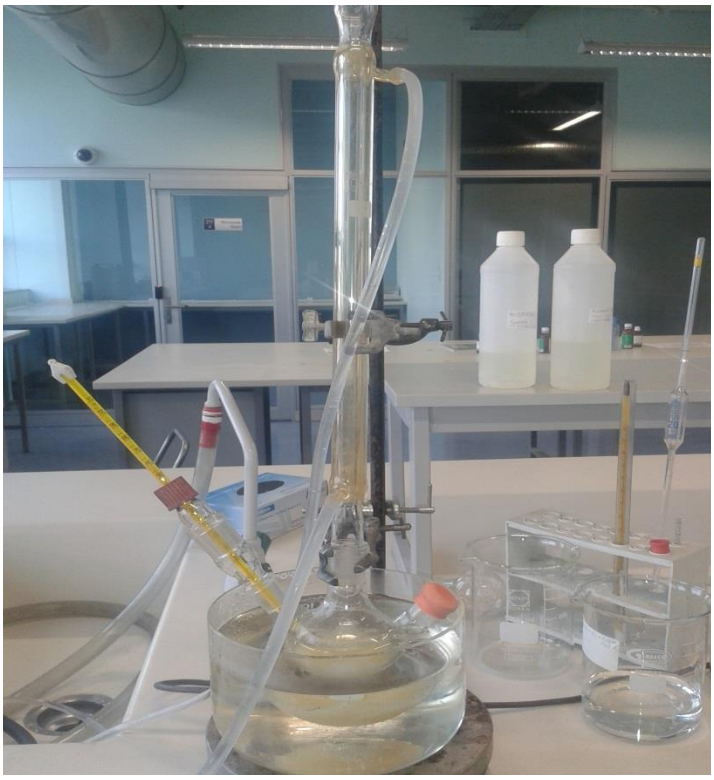


Figure 7: Apparatus Set-up for Biodiesel Production

3.5.2 EFFECT OF CATALYST CONCENTRATION

A measured volume of the vegetable oil is preheated to a temperature of 60℃ on a heating plate. A constant methanol-to –oil ratio of 6:1 is used. This value, recommended from literature as the optimum for transesterification of WVO using a heterogeneous catalyst, was used as the basis for this part of the experiment. The catalyst, at a concentration of 0.5% relative to WVO, is then added to the 3-neck round bottom flask along with methanol and WVO (Ankapong, 2010).

The reaction is timed from the moment the contents of the flask reach the desired reaction temperature of 60℃. The flask contents are stirred continuously for 180 minutes to ensure that the conversion of the fatty acids into fatty acid methyl esters is complete. The mixture is then poured into a separating funnel and left for an hour to allow for the gravity separation of glycerol from the ester layer (Ankapong, 2010).

The procedure is repeated for catalyst concentration values of 2%; 3.5%; 5% and 6.5%. This is done to determine which of these concentrations would be optimal for producing biodiesel using a calcium silicate catalyst (Ankapong, 2010).

3.5.3 *DETERMINING EFFECT OF METHANOL-TO-OIL RATIO*

A measured volume of the vegetable oil is preheated to a temperature of 60℃ on a heating plate. A constant catalyst concentration of 4% is used. This value is the average of the range used when determining the optimum catalyst concentration. The catalyst is then added to the 3-neck round bottom flask along with methanol and WVO, which are added at a ratio of 3:1. (Ankapong, 2010).

The reaction is timed from the moment the contents of the flask reach the desired reaction temperature of 60℃. The flask contents are stirred continuously for 180 minutes to ensure that the conversion of the fatty acids into fatty acid methyl esters is complete. The mixture is then poured into a separating funnel and left for an hour to allow for the gravity separation of glycerol from the ester layer (Ankapong, 2010).

The procedure is repeated for methanol to oil ratios of 6:1; 9:1 and 12:1. This is done to determine which of these ratios would be optimal for producing biodiesel using a calcium silicate catalyst (Ankapong, 2010).

3.6 BIODIESEL CHARACTERIZATION/ANALYSIS

3.6.1 *GAS CHROMATOGRAPHY AND MASS SPECTROMETER (GSMS) ANALYSIS*

GCMS Analysis was used to identify if and the FAME present in the unknown sample.

3.6.1.1 Reference Material used for GCMS Analysis

Commercial biodiesel made from WVO and methanol using a potassium hydroxide catalyst was used as reference material when analyzing unknown samples from the experiment.

3.6.1.2 GCMS analysis

The GCMS instrument used was the QP-1000 Ultra by Shimadzu. Trial and error was used to determine the optimum experimental condition of the GCMS. The optimum conditions can be found in Appendix A. The commercial biodiesel is used as a basis in the analysis to determine if the unknown sample is biodiesel or not. The instrument was not used to determine the concentrations of the different types of fatty acid methyl ester compositions due to technical problems with the instrument at the time.

3.6.2 *SPECTROPHOTOMETER*

A spectrophotometer is used to determine the FAME in the samples produced during the experiment.

3.6.2.1 Determining Optimum Wavelength

A sample of commercial biodiesel is measured using a single beam, spectrophotometer. The absorption spectrum is varied within the wavelength range of $330 - 500\mu m$ for the commercial biodiesel, using standard 1 cm quartz cuvettes. Each wavelength corresponds to a certain absorbance. The optimum wavelength value corresponds to the highest absorbance.

3.6.2.2 Preparing Standards

Ten standards of commercial biodiesel are prepared with varying concentrations. The standards are made by diluting the commercial biodiesel with n-heptane.

3.6.2.3 Calibration Curve

Using the optimum wavelength, the ten standards with varying concentrations are placed in the spectrophotometer, one at a time, in order to determine the absorbance of each. A calibration curve is drawn by plotting absorbance against concentration.

3.6.2.4 Determining the concentration of the unknown sample

Each unknown sample is placed in the spectrophotometer to determine its absorbance. The biodiesel concentration of each unknown sample is determined using the calibration curve.

3.6.3 *DETERMINING THE DENSITY*

An empty disposable 15ml graduated plastic beaker is weighed. The beaker is filled to the 15ml line with the biodiesel product and the mass of the beaker and fuel together is recorded. Using this information the density of the biodiesel can be determined by calculation through equation (8) (Hoffman, 2011):

$$\rho = \frac{mass}{volume} \tag{8}$$

3.7 REACTION KINETICS

In order to gain knowledge of the kinetics of transesterification catalyzed by calcium silicate a series of experiments were performed with 3 main operating variables; namely methyl ester (biodiesel) concentration, reaction time and reaction temperature. The following procedure was carried out:

A constant methanol-to –oil ratio of 6:1 is used. This value, recommended from literature as the optimum for transesterification of WVO using a heterogeneous catalyst, was used as the basis for this part of the experiment. The catalyst, at a concentration of 2% relative to WVO, is then added to the 3-neck round bottom flask along with methanol and WVO (Ankapong, 2010). The reaction is timed from the moment the contents of the flask reach the desired reaction temperature. The starting desired reaction temperature is $40^{\circ}\mathrm{C}$. The flask contents are stirred continuously to ensure that the conversion of the fatty acids into fatty acid methyl esters is complete. The starting reaction time is 30 minutes. The mixture is then poured into a separating funnel and left for an hour to allow for the gravity separation of glycerol from the ester layer (Ankapong, 2010).

The procedure is repeated for the following reaction temperatures: $45^{\circ}\mathrm{C}, 50^{\circ}\mathrm{C}, 55^{\circ}\mathrm{C}\ and\ 60^{\circ}\mathrm{C}$ increasing the reaction time to 60 minutes, 90 minutes 150 minutes, 180 minutes and 240 minutes, respectively for each reaction temperature. This should amount to a total of 35 experiments.

4. RESULTS AND DISCUSSION

4.1 CATALYST CHARACTERISATION

4.1.1 *FTIR ANALYSIS*

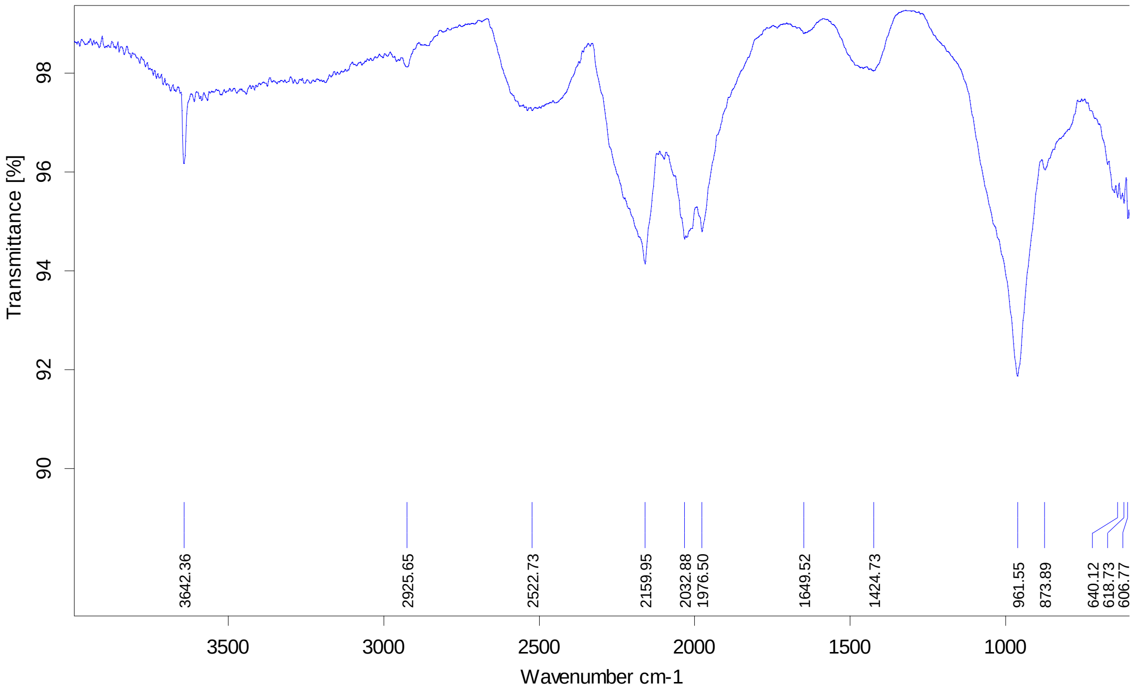


Figure 8: FTIR Spectra for Calcium Silicate Sample dried at 240˚C

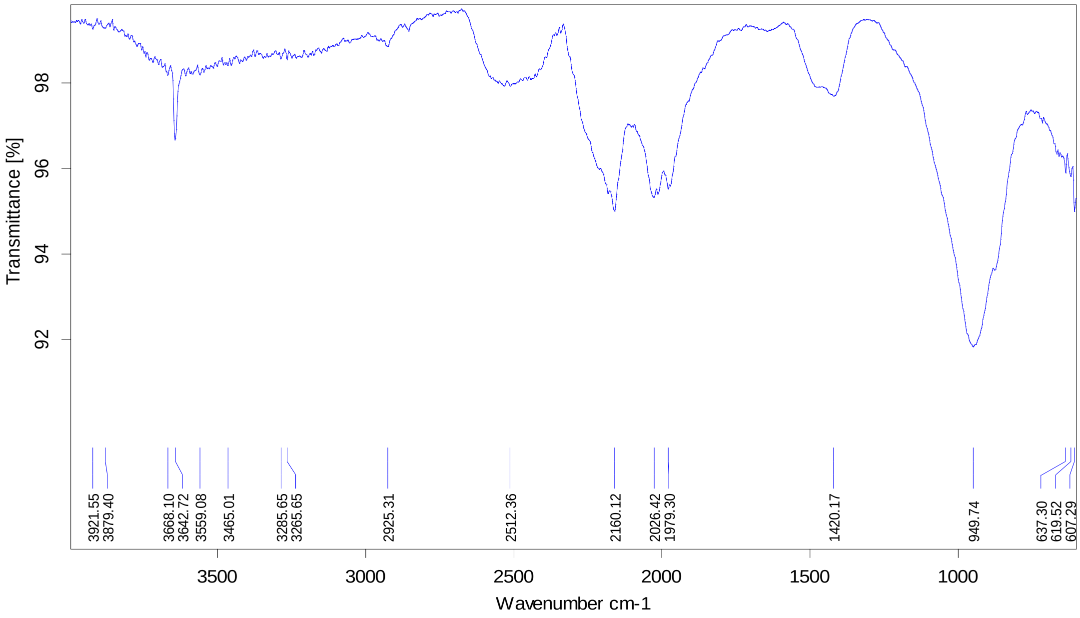


Figure 9: FTIR Spectra for Calcium Silicate Sample calcinated at 240˚C

Figure 8 shows the FTIR Spectra of the calcium silicate catalyst produced from calcium hydroxide and silica gel after drying the catalyst at 240℃ and Figure 9 displays the FTIR Spectra of the same catalyst calcined at 480℃.

Table 2 compares the wavelengths of the catalyst produced to the wavelengths to that found in literature (Baciu & Simitzis, 2007).

Table 2: Groups and Wavenumbers of the FTIR Spectra for Calcium Silicate

Group	Wavenumber (cm^{-1}) Literature	Wavenumber (cm^{-1}) Catalyst dried at 240℃	Wavenumber (cm^{-1}) Catalyst calcinated at 480℃
$Si-O-Si$	600-800	$606.77-640.12$	$607.77-637.30$
$O-Si-O$	$750-900$	873.89	$-$
$Si-0-Ca$	$900-1000$	961.55	947.74
$Si-0-Si$	$1100-1500$	1424.73	1420.17
$Ca-O$	$1600-2500$	1649.52	1979.30
$Carbonate\ Ion\ (CO_3)^2$	1798-2982	$2032.88-2925.65$	2160.12 -2925.31
$Water\ (H_20)$	3437	3642.36	3265.65 -3921.55

The FTIR spectrum for catalyst dried at 240 ℃ in Figure 8 was recorded in the range of $600\ cm^{-1}$ and $4000\ cm^{-1}$. The FTIR spectrum shows peaks at 606.77, 618.13 and $640.12\ cm^{-1}$ are the characteristic peaks of $Si-O-Si$.. The strong peak at $873.89cm^{-1}$ in the range of $750-900cm^{-1}$ is the characteristic of $O-Si-O$. The strong peak at $1424.73cm^{-1}$ is the characteristic of $Si-O-Si$. These peaks confirm the presence of silica in the sample. The band observed in the range of $900-1000cm^{-1}$ is due to the $Si-0-Ca$ bonds, indicating the presence of calcium in the sample. The bands in the range of $1600-2500\ cm^{-1}$ indicate the presence of unreacted calcium hydroxide. The bands in the range of

$2032.88 - 2925.65\ cm^{-1}$ correspond to the $C = O$ from carbonate ion $(CO_3)^{2-}$. The narrow band at $3642.36\ cm^{-1}$ indicates the presence of water.

The FTIR spectrum for catalyst calcined at $480\ ℃$ was also recorded in the range of $600\ cm^{-1}$ and $4000\ cm^{-1}$. The FTIR spectrum shows peaks between $606.77 - 619.55\ cm^{-1}$ are the characteristic peaks of $Si - O - Si$ which are similar to that observed in Figure 8. There are no peaks found in of characteristic of $O - Si - O$ in the range of $750 - 900 cm^{-1}$. The strong peak at $1420.17 cm^{-1}$ in the range of $1100 - 1500 cm^{-1}$ is the characteristic of $Si - O - Si$. These peaks confirm the presence of silica in the sample. The band observed in the range of $900 - 1000 cm^{-1}$ is due to the $Si - 0 - Ca$ bonds, indicating the presence of calcium in the sample. The bands in the range of $1600 - 2500\ cm^{-1}$ indicate the presence of unreacted calcium hydroxide. The bands in the range of $2160.12 - 2512.36\ cm^{-1}$ correspond to the $C = O$ from carbonate ion $(CO_3)^{2-}$. When observing the wavelengths from $3265.65 - 3921.55\ cm^{-1}$ there is a high level of noise caused by the presence of water. However, when looking at the spectrum a narrow band is noticed at a wavelength of $3668.10\ cm^{-1}$.

Figure 8 and Figure 9 present similar findings. In order to have a clear distinction between which temperature provides a better catalyst, XRD analysis is required.

4.1.2 *XRD ANALYSIS*

The XRD characterization was conducted for calcium silicate samples at 240℃ and 480℃. Figure 10 is the analysis of the sample at 240℃ and Figure 11 at 480℃. The labels of the different compounds were obtained from literature (Jayakumar & Saravanane, 2009).

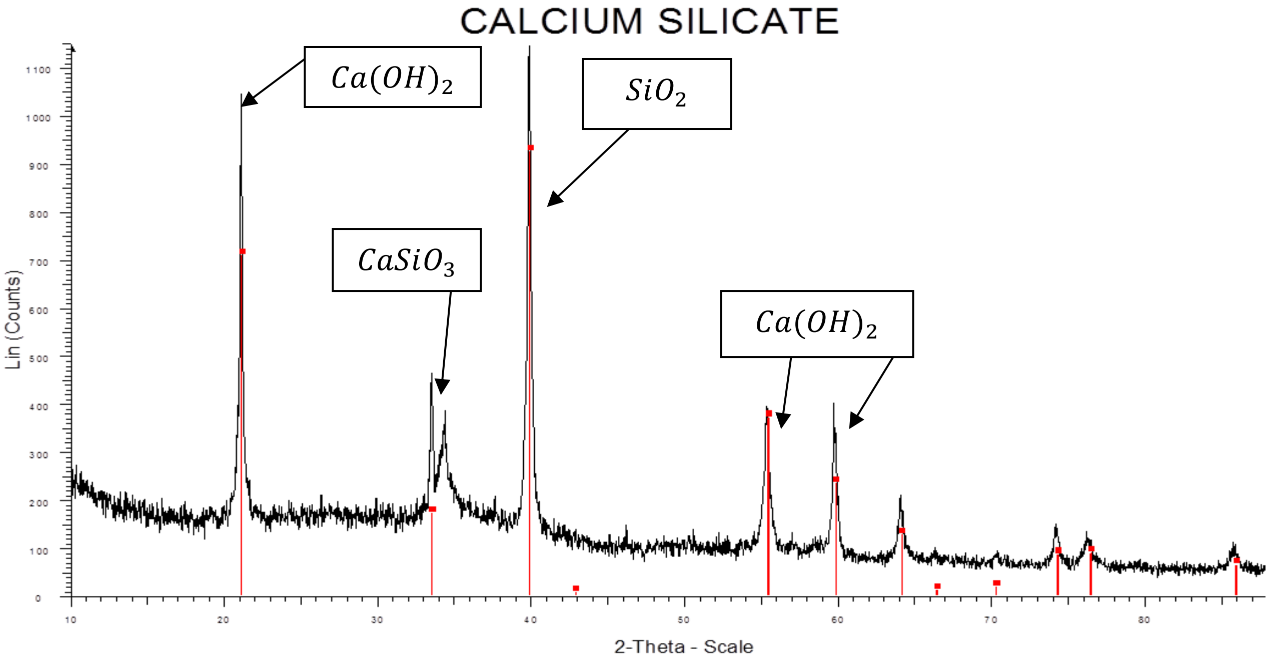


Figure 10: X-RD Characterization of Calcium Silicate Sample dried at 240℃

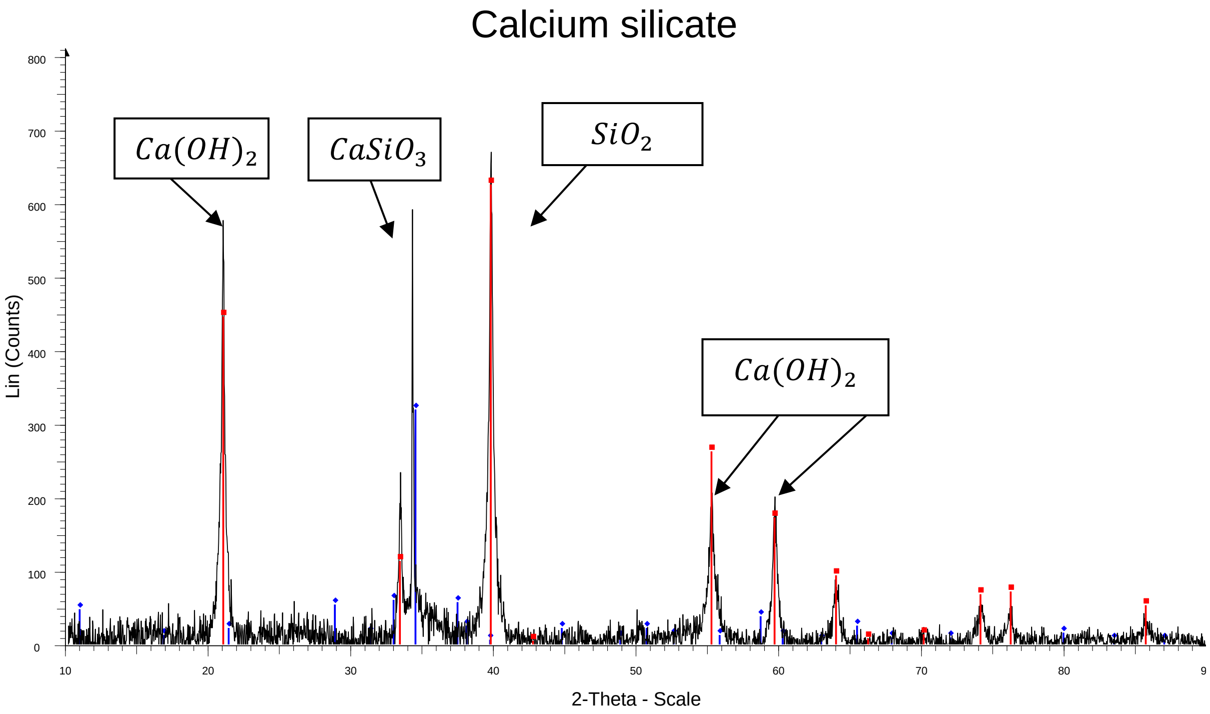


Figure 11: X-RD Characterisation of Calcium Silicate Sample calcined at 480℃

The XRD scan shows a similar pattern for both samples at the different temperatures; however the intensity and number of peaks vary. Both analyses show a significant amount of the reactants calcium hydroxide and silica gel that have not reacted. At a temperature of 480℃ there is a greater peak of calcium silicate as seen in Figure 11 as compared to 240℃ in Figure 10. Increasing the temperature indicates an increase in the conversion to form calcium silicate and a decrease in reactants which have not reacted. The minor peaks between 70 and 80 on the Theta Scale indicate the formation of an unwanted product called Riversideite, $Ca_5Si_6O_{16}(OH)_2$.

4.1.3 *BET CHARACTERIZATION-DISCUSSED*

Table 3 below displays the summary of the results obtained from the BET determination of the calcium silicate catalyst.

Table 3: Summary of BET results for Calcium Silicate

Surface Area	
Single point surface area at P/Po = 0.275444769:	58.0117 m²/g
Pore Volume	
Single point adsorption total pore volume of pores less than160.6507 nm diameter at P/Po =0.987810680	0.248916 cm³/g
Pore Size	
Adsorption average pore width (4V/A by BET):	16.88770 nm

Mesoporous materials have an intermediate pore size range, between 2 – 50 nm. From Table 3 it can be seen that the pore size of the catalyst is 16.89nm, which classifies it as a mesoporous material. Advantages of mesoporous materials include narrow pore size distributions, simple functionalization strategies with organics, biocompatibility and low toxicity (Raw, 2014). The results obtained from the BET determination are as one would expect since it is typical for materials which include some kind of silica to be mesoporous (Raw, 2014). However, even though mesoporous materials are renowned for consisting of high surface areas (>500 m^2/g) (Raw, 2014), the results depicted in Table 3 show the catalyst’s surface area to be relatively low. This could be unfavourable to a certain extent since the surface are of the catalyst is an important factor in catalytic activity. A high and easily accessible surface area indicates efficiency during the application of materials as catalysts since the actual catalytic act takes place in the thin surface layer (Brunauer, 1938).

A low pore volume is also observed. These results could negatively affect the transesterification synthesis, leading to lower biodiesel conversions.

4.1.4 *SEM ANALYSIS*

For this experiment the SEM was used to perform analyses of selected point locations on the catalyst sample. The aim of this approach is to determine the elements present and the crystal sizes and orientations within the sample. There was no significant difference noted between the results of the calcium silicate dried at 240℃ and the calcium silicate calcined at 480 ℃. The calcium silicate analysed for this discussion is that calcined at 480 ℃.

Figure 10 shows the scanning electron micrograph which depicts the morphology of the calcium silicate catalyst analysed. The micrograph consists of different spectrums indicated on it. These spectrums represent randomly selected points on the sample upon which Energy Dispersive Spectrometry (EDS) analysis was done in order to determine the elemental composition of the sample. The EDS results obtained were then compared to that from an experiment conducted by Marujiwat & Puntharod (2013) which shows the EDS of calcium silicate made from rice husk and egg shell. Since the catalytic act occurs on the surface of the catalyst, the objective is to obtain a high elemental composition of the three elements that make up calcium silicate i.e. calcium, silicon and oxygen.

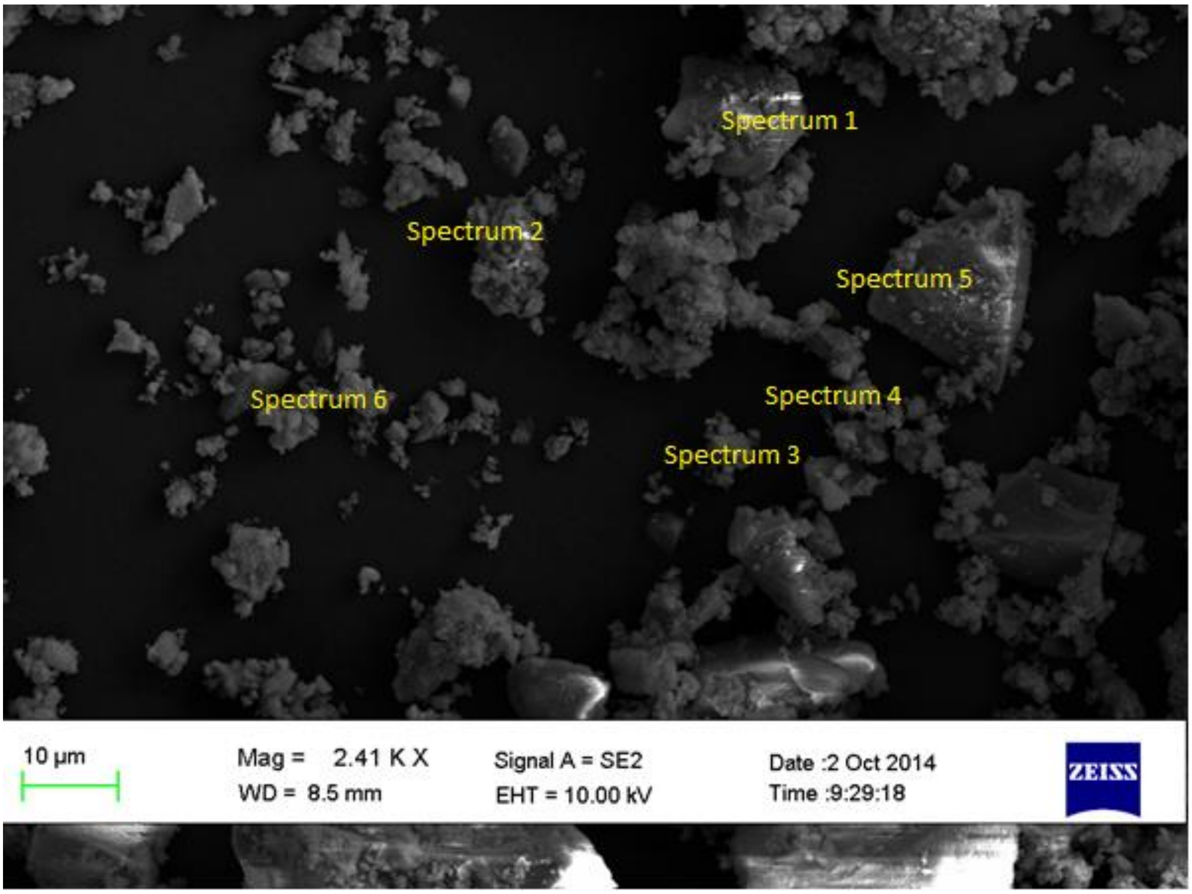
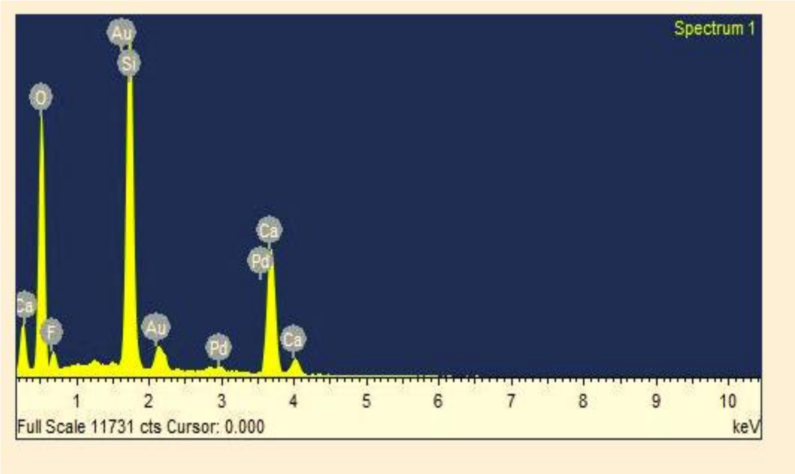


Figure 12:The SEM showing the Morphology of Calcium Silicate calcined at $480℃$

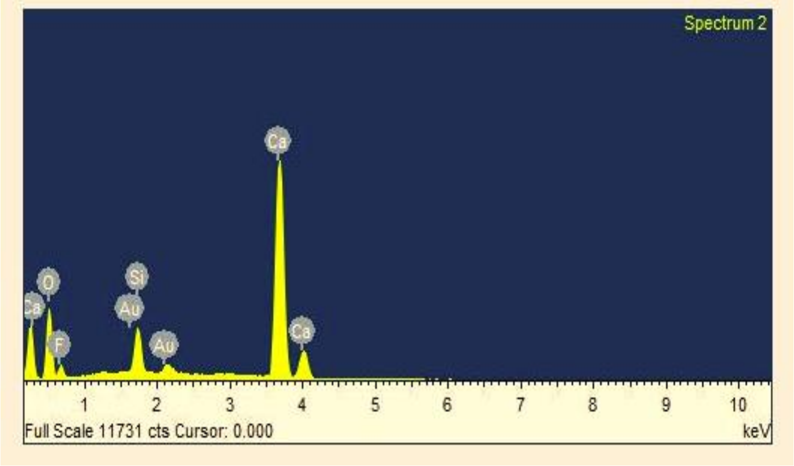
The calcium silicate particles, irregular in shape, typically ranged in size from approximately $2.5\mu m$ to $25\mu m$. Figures 11 to 16 show the EDS results along with the table containing the elemental compositions present in the sample. From the graphs shown in all the spectrums, the catalyst sample consisted mostly of elements calcium, oxygen and silicon, but had a significantly lower composition of silicon as compared to calcium and oxygen. It can also be noted that compared to the EDS graph obtained from the experiment conducted by Marujiwat & Puntharod (2013), Figure 17, where the Ca, O and Si peaks are clearly defined, there is a high level of impurity elements such as Au and F that are present on the surface of the catalyst sample. The gold (Au) element could be as a result of the sputter coating added on top of the catalyst sample prior to SEM analysis.

These findings could indicate that the calcium silicate formation was not uniform, and it is possible that some of the reagents did not completely react.



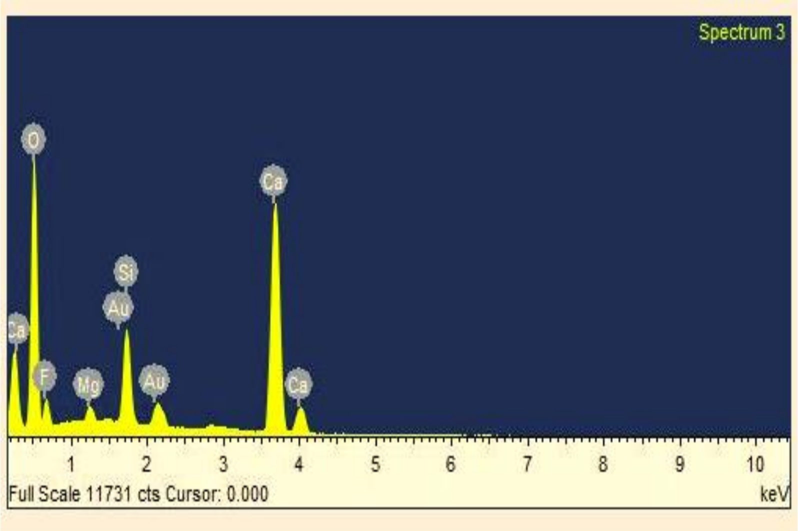
Element	Weight%	Atomic%
O K	39.98	60.10
F K	3.62	4.58
Si K	21.50	18.41
Ca K	26.16	15.70
Pd L	1.32	0.30
Au M	7.42	0.91
Totals	100.00	

Figure 13: An EDS of spectrum 1



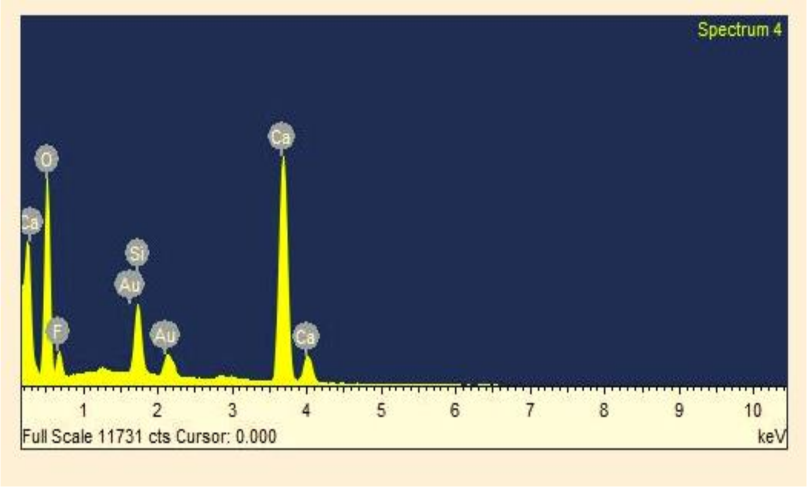
Element	Weight%	Atomic%
O K	24.81	44.17
F K	4.13	6.19
Si K	4.03	4.09
Ca K	63.35	45.02
Au M	3.67	0.53
Totals	100.00	

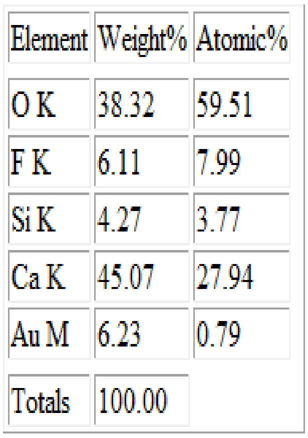
Figure 14: An EDS of spectrum 2



Element	Weight%	Atomic%
O K	42.02	62.94
F K	5.34	6.73
Mg K	0.78	0.77
Si K	5.16	4.40
Ca K	40.89	24.45
Au M	5.82	0.71
Totals	100.00	

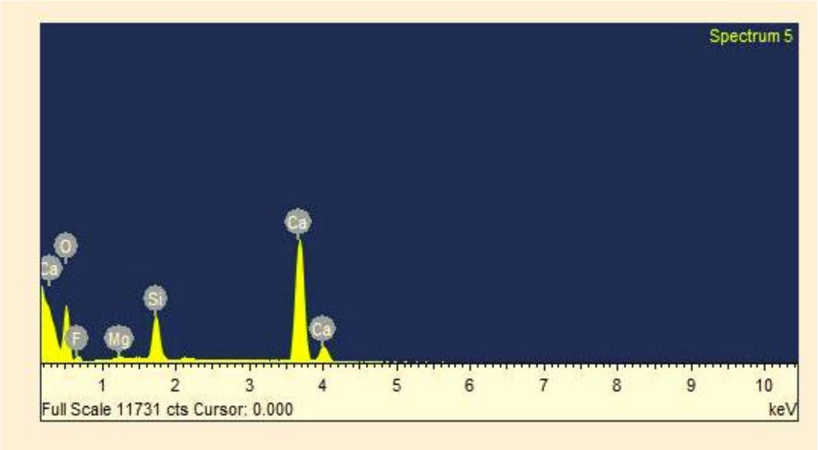
Figure 15: An EDS of spectrum 3

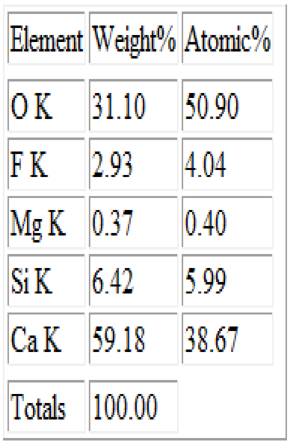




Element	Weight%	Atomic%
O K	38.32	59.51
F K	6.11	7.99
Si K	4.27	3.77
Ca K	45.07	27.94
Au M	6.23	0.79
Totals	100.00	

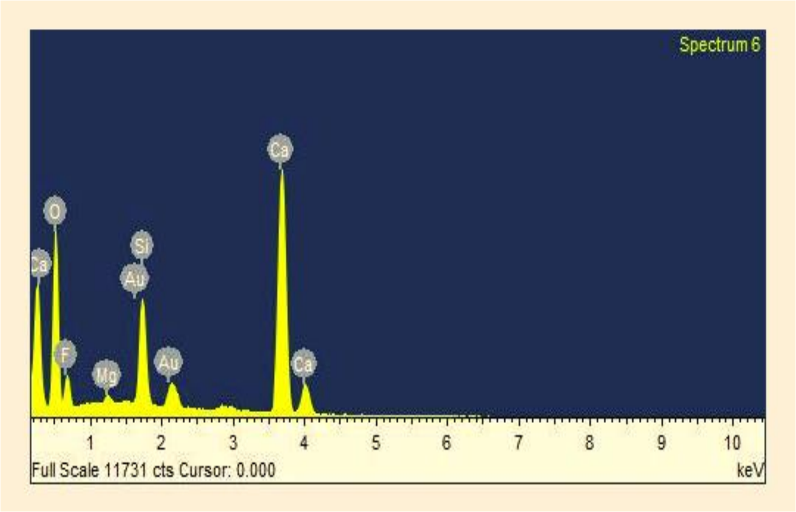
Figure 16: An EDS of spectrum 4

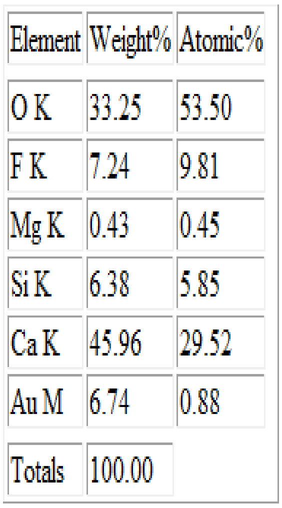




Element	Weight%	Atomic%
O K	31.10	50.90
F K	2.93	4.04
Mg K	0.37	0.40
Si K	6.42	5.99
Ca K	59.18	38.67
Totals	100.00	

Figure 17: An EDS of spectrum 5





Element	Weight%	Atomic%
O K	33.25	53.50
F K	7.24	9.81
Mg K	0.43	0.45
Si K	6.38	5.85
Ca K	45.96	29.52
Au M	6.74	0.88
Totals	100.00	

Figure 18: An EDS of spectrum 6

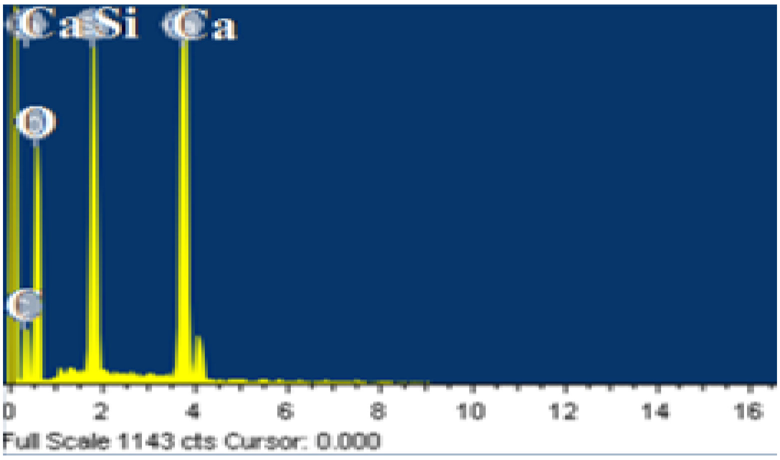


Figure 19: An EDS of calcium silicate made from rice husk and egg shell (Murujiwat, 2013)

4.2 WASTE VEGETABLE OIL CHARACTERIZATION

4.2.1 *FREE FATTY ACID (FFA)*

The FFA value of the WVO used in the experiment was calculated as 3.53% (Appendix B.1). Dorado et al. (2004) report that transesterification would not occur if the FFA value was above 3%. However (Van Gerpan, 2006) reported that the transesterification reaction using a alkali catalyst would occur with an FFA value of up to 5%. Oils with a FFA value above 5% decrease the transesterification yield and increase the formation of soaps. Based on the work of Van Gerpan (2006) and the use of an alkali catalyst, calcium silicate, the WVO used in this experiment lies below the 5% FFA value, therefore the WVO used in this experiment is sufficient for the production of biodiesel. The FFA value greater than 1% allows the use of the heterogonous alkaline catalyst, thus this substantiates the use of calcium silicate.

4.2.2 *SAPONIFICATION VALUE (SV)*

The SV was calculated as 195.42 (Appendix B.2). The typical SV for WVO is 198.50 (Shannon et al., 2009). The SV of WVO used in the experiment is similar to that found reported by Shannon *et al* (2009). When comparing the oils commonly found in literature for the production of biodiesel such as palm oil and jatropha oil, the SV of WVO is lower. Therefore WVO is desirable for the production of biodiesel.

4.2.3 *DENSITY*

The density of the WVO at standard temperature used in the experiment was calculated as $0.814 g/ml$ (Appendix B.3). Nyayieka (2010) reports that the density of WVO is approximately $0.845 g/ml$ at standard temperature.

4.2.4 *MOISTURE CONTENT*

According to (Lin & Lin, 2012) the moisture content should be less than 0.06 wt %. The moisture content of the WVO used in this experiment was 0.45 wt % (Appendix B.4). Due to the high moisture content in the WVO, it was heated at 50℃ for approximately two hours in order to reduce the moisture content to below 0.06 wt%.

Table 4: Summarizing the characterization of WVO

WVO Characterization	Literature	Experimental
FFA	3%	3.53%
SV	195.42	198.5
Density	$0.845 g/ml$	$0.814 g/ml$
Moisture Content	0.06 wt %.	0.45 wt %

4.3 BIODIESEL CHARACTERIZATION AND ANALYSIS

4.3.1 *GCMS ANALYSIS*

In order to determine if the product produced from transesterification using a calcium silicate catalyst was indeed biodiesel, it was analyzed using GCMS against a reference material, commercial biodiesel. Samples of the product were prepared and ran in SIM mode to identify the fatty acid methyl ester (FAME). The SIM mode allows the specification of the molecular mass of the FAME required. The FAME and its molecular weight that were specified in the GSMS analysis can be found in Table 5:

Table 5: Molecular Mass of the specified FAME (Gopinath et al., 2010)

FAME	Molecular Mass $\left(\frac{g}{mol}\right)$
Lauric Acid	200.32
Myristic Acid	228.34
Palmitic Acid	256.42
Linolenic Acid	278.43
Linoleic Acid	280.45
Oleic Acid	282.46
Stearic Acid	284.48

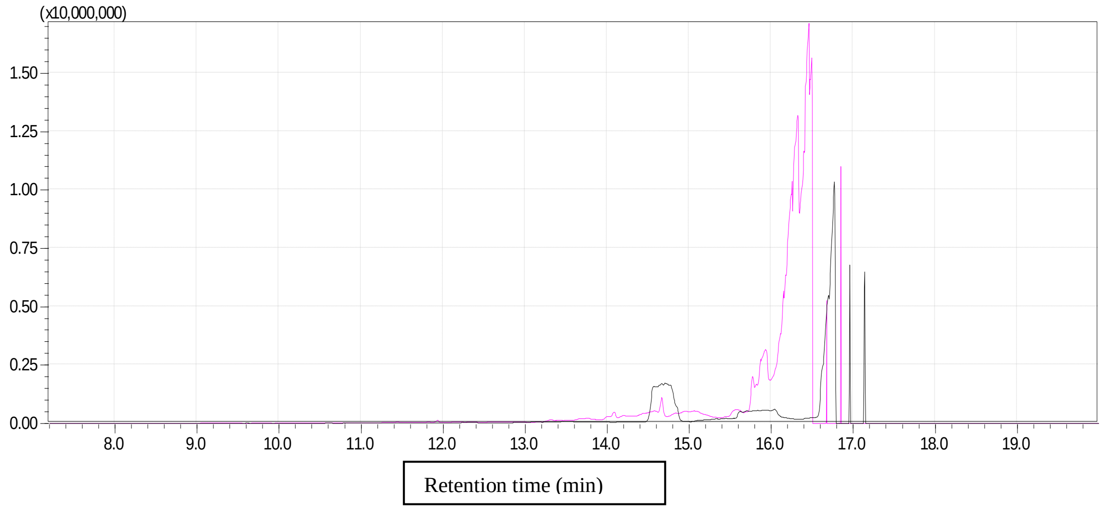


Figure 20: Chromatogram Random unknown sample (pink) with experimental conditions at 4% catalyst, reaction time of 90 minutes and temperature of 40℃ vs. commercial biodiesel (black)

Figure 20 shows the chromatogram between a random unknown sample and commercial biodiesel. The peaks between the unknown sample and commercial biodiesel are very similar, the only difference is the peaks for the both the commercial biodiesel and unknown sample occur at different retention times.

The peaks of the compounds identified in the unknown sample as observed in **Error! Reference source not found.** are described in Figure 21.

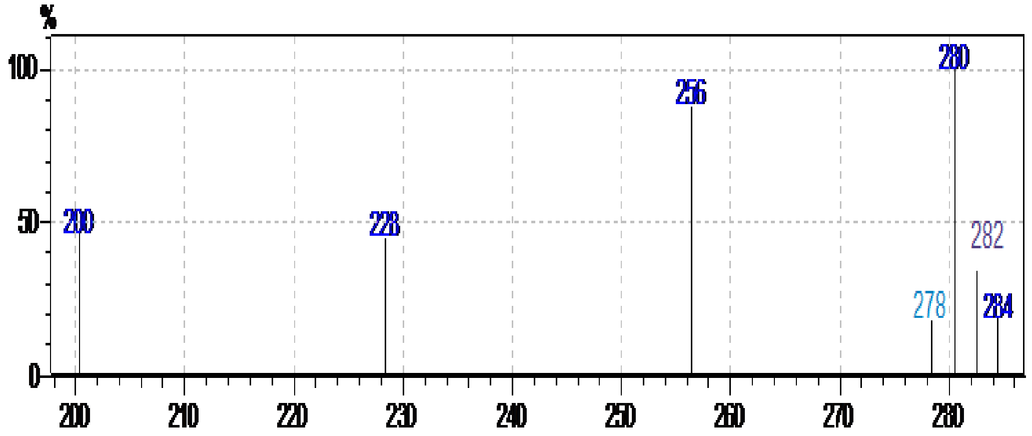


Figure 21: Molecular Mass of the Peaks of Unknown Sample

Figure 21 shows the molecular mass of the compounds present in the unknown sample. These molecular masses correspond to the FAME found in Table 5. Therefore this proves that the unknown sample is biodiesel.

4.3.2 OPERATING CONDITIONS FOR OPTIMUM BIODIESEL CONCENTRATION

One of the key deliverables for this experiment is to determine the operating conditions that would produce an optimum (maximum) concentration of methyl ester (biodiesel) in the product. In order to achieve this, a spectrophotometer was used to measure the absorbance of eight (8) standards of different concentrations. The optimum wavelength for the spectrophotometer is the one that corresponds to the highest absorbance (Appendix C.1). As a result, the optimum wavelength was found to be 350nm, as can be seen from Figure 22. The calibration curve of absorbance vs. concentration was created as shown in Figure 23 (Appendix C.2)

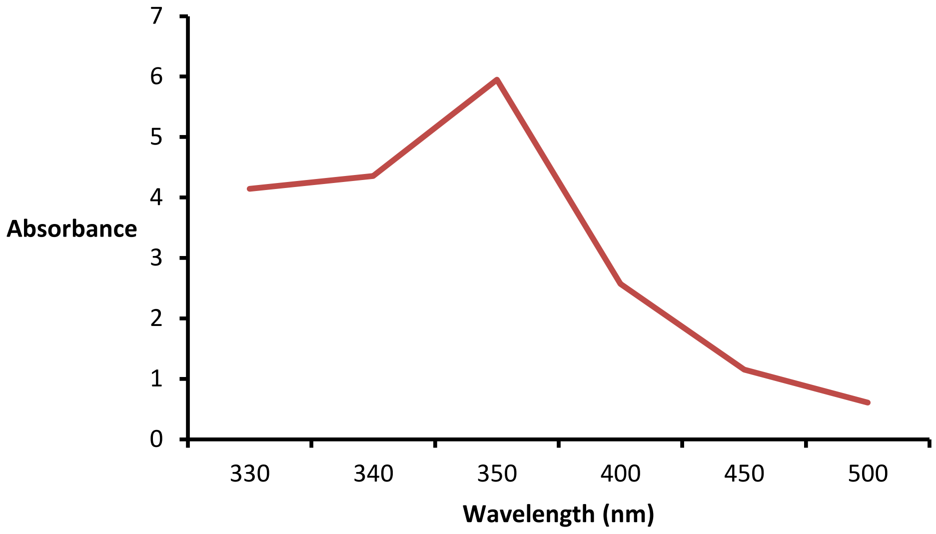


Figure 22: Absorbance vs. Wavelength graph for commercial biodiesel

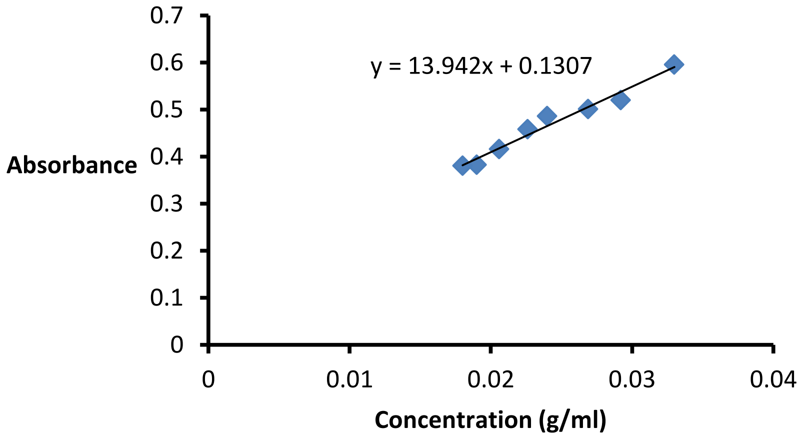


Figure 23: Calibration curve used to determine the concentration of biodiesel in the product samples.

Determining the optimum catalyst concentration

For the following set of results a methanol to oil ratio of 6:1 at 60°C was used. The reaction duration was 180 minutes.

Table 6: The biodiesel concentrations relating to different catalyst concentrations

Catalyst Concentration	Absorbance	Biodiesel Concentration (g/ml)
0.5%	0.339	0.015
2%	0.328	0.014
3.5%	0.3	0.012
5%	1.108	0.070
6.5%	0.324	0.014
8%	0.272	0.010

From

Table 6 it can be seen that the optimum catalyst concentration is 5% since it produces the highest methyl ester (biodiesel) concentration in the product.

Determining the optimum methanol to oil ratio

For the following set of results a catalyst concentration of 4% at 60°C was used. The reaction duration was 180 minutes.

Table 7: Biodiesel concentrations relating to different methanol to oil ratios.

Methanol to oil ratio	Absorbance	Biodiesel Concentration (g/ml)
3:1	0.413	0.020
6:1	0.297	0.012
9:1	0.259	0.009
12:1	0.243	0.008

From Table 7 it can be seen that the optimum methanol to oil ratio using a calcium silicate catalyst is 3:1, since it is at this ratio that the highest biodiesel concentration is produced.

4.4 REACTION KINETICS

Figure 24 below shows the methyl ester concentration vs. time graphs for different reaction temperatures (Appendix C.3).

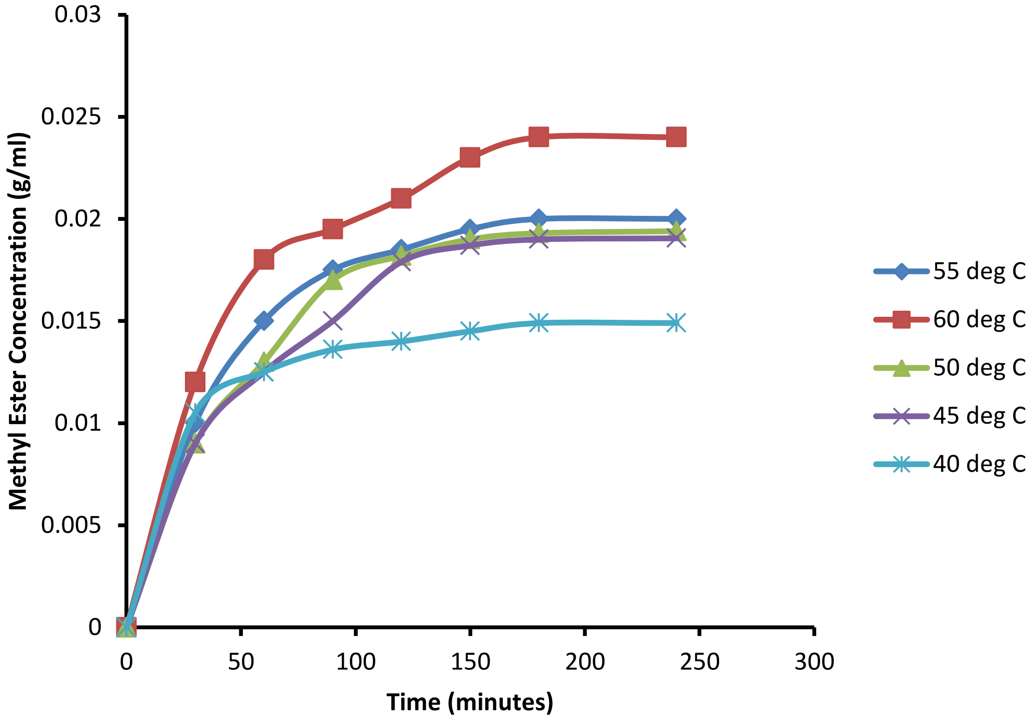


Figure 24:Methyl ester concentration vs. time graphs for the different reaction temperatures

Figure 24 below, shows the Excel Solver plot of simulated fatty acid methyl esters using least squares method, E^2 min = 0.004 and R^2 = 0.86, obtained from (Okullo, 2012). What can be noted from this graph is the similarity of the relationship between methyl ester concentration and time with the results obtained from this project.

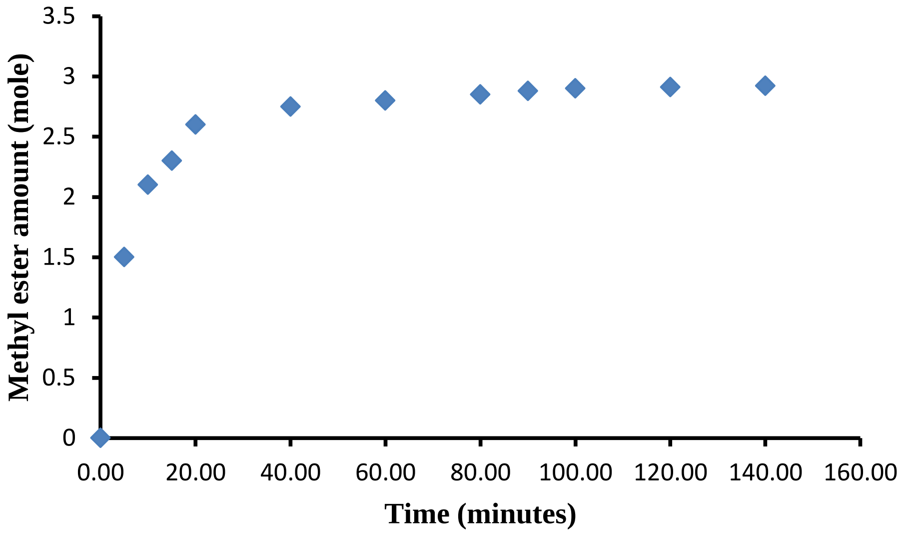


Figure 25: Excel Solver plot of simulated fatty acid methyl esters using least squares method (Okullo, 2012)

In order to confirm whether the assumption that transesterification catalyzed by calcium silicates correlated a first order irreversible kinetic model, the natural log of the methyl ester concentrations were plotted against time for one of the given temperatures. The linearity of the plot would confirm this assumption. Figure 25 shows ln [ME] vs. time at a temperature of 60℃.

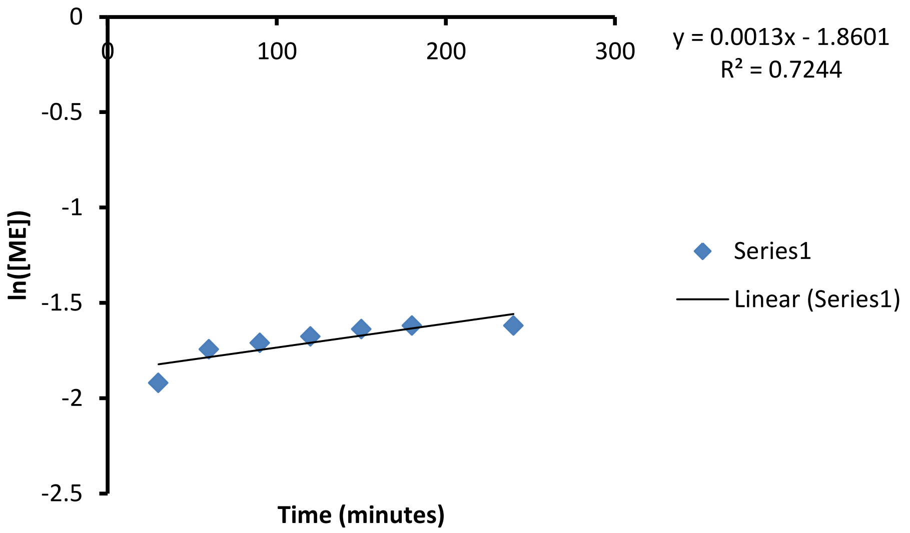


Figure 26: ln[ME] vs. time at a temperature of 60℃.

A linear trend line was added over the data points, which fits the data with a regression of 0.7244. This shows a relatively strong relationship between the data and the linear equation. Therefore, the earlier assumption is fairly justified.

Since the initial biodiesel concentration is zero (0), the linear plot cannot be used to approximate the reaction rate constant. Thus, from the methyl ester concentration values at different reaction durations a code simulated on Matlab (Appendix D) calculated the reaction rate constant for transesterification at each temperature. Table 8 below shows the reaction rate constants obtained for each temperature.

Table 8: The reaction rate constants obtained for each reaction temperature.

Temperature (K)	k
313.15	1.67E-05
318.15	2.67E-05
323.15	2.67E-05
328.15	3.33E-05
333.15	6.67E-05

From the values obtained in Table 8, the Arrhenius plot, shown as Figure 27 below was constructed on Excel.

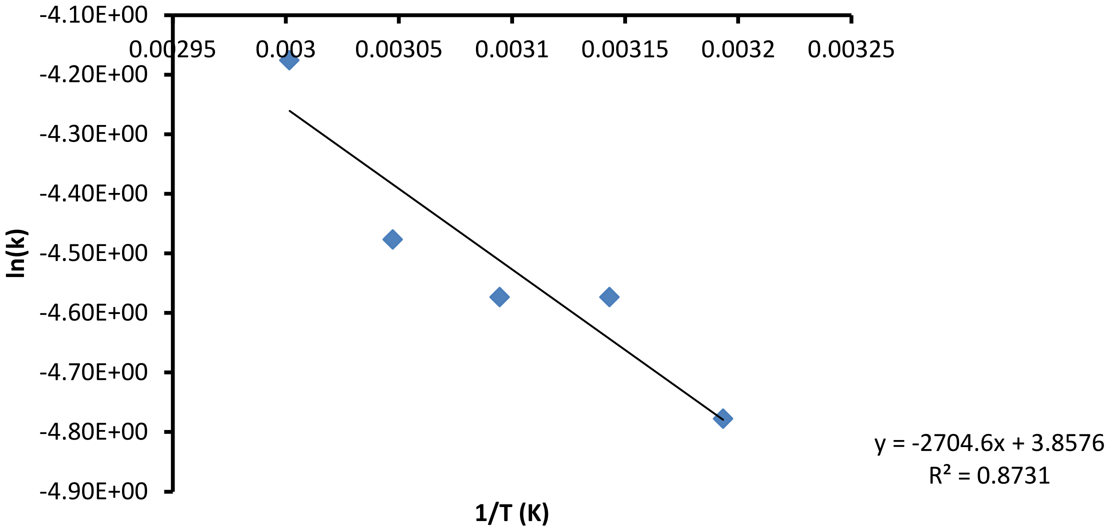


Figure 27: Arrhenius plot for Transesterification catalyzed by calcium silicate

From the Arrhenius plot the activation energy was calculated to be 22.486 kJ/mol. This value was relatively comparable to that obtained from an experiment conducted by (Ghoreishi & Moein, 2013) whose experimental data also correlated to an irreversible first order kinetic model (Ghoreishi & Moein, 2013) obtained an activation energy of 31.71 kJ/mol

From Table 8, it can be seen that the reaction rate constant increases with temperature, is an expected result. However, the reaction rate constants are relatively low along with the methyl ester (biodiesel) concentrations, meaning that the reaction rate is also low as a result. The ratio of the activation energy to the average kinetic energy (RT) plays a great role in determining the size of the rate constant-the larger this ratio, the smaller the rate. This means that high temperature and low activation energy favours large rate constants, and thus speeds up the reaction (ChemWiki, 2014). Since it not favourable to increase the reaction temperature, because at temperatures higher than 60℃ the methanol may boil and evaporate, a lower activation energy should be achieved for higher reaction rates. As mentioned earlier in the report, the role of a catalyst is to decrease the activation energy in order to increase the reaction rate. From these results it is clear to see that calcium silicate was not effective as a catalyst for transesterification. A number of reasons could be stated to justify this. Firstly the catalyst characterizations show that a fair amount of what was used to catalyse the reactions was unreacted calcium hydroxide and silica gel. This can be seen from the FTIR analysis. Also the FFA value could have also played an effect in the results. Alptekin (2011) states that the FFA value should be reduced to a level below 1% in order to avoid the formation of soap using an alkaline catalyst. Based on this one can assume that the FFA value of 3.53% was too high and may have led to the formation of soap rather than biodiesel.

5. CONCLUSION AND RECOMMENDATIONS

The transesterification reaction using waste vegetable oil (WVO) was carried using calcium silicate- an alkali heterogeneous catalyst. The main aim was to investigate the optimum reaction conditions and the reaction kinetics for transesterification using this catalyst.

The optimum methanol to oil ratio was found to be 3:1 and the optimum catalyst concentration was found to be 5% wt. The reaction kinetics depicted this catalyst as ineffective for transesterification since low reaction rates were observed. Furthermore, the activation energy, even though it was fairly comparable to that obtained from literature (Ghoreishi & Moein, 2013), was relatively high leading to lower reaction rate constants. This could be due to a number of factors. Firstly, the catalyst characterizations showed that much of what was used as the catalyst for the reaction was unreacted calcium hydroxide and silica gel. Secondly the FFA value of the oil may have been too high at 3.53%, thus leading to the formation of soap rather than methyl ester.

Since the reaction to form calcium silicate did not go on to completion, it is recommended that a longer reaction time be used during the catalyst formation process. Another recommendation is the investigation of other methods in which calcium silicate can be made, such the one used by (Murujiwat, 2013) where rice husk and egg shell were used as reagents. Vegetable oil with a lower FFA level (preferably below 1% as a precaution) should be used.

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APPENDICES

APPENDIX A: OPTIMUM CONDITIONS FOR GCMS ANALYSIS

Table 9: GC Optimized Experimental Conditions.

Optimised Experimental Conditions for GC	
Column	$30m\ x\ 0.25mm\ x\ 0.25\mu m$
Column Oven Temperature	50℃
Injector Temperature	220℃
Injection Mode	Splitless
Sampling Time	1.00
Carrier Gas	Helium
Carrier Gas Flow	0.2 mL/min
Oven Programme	50℃ hold for 1 min. 10℃/min 260℃ for 3 min 10℃/min 270℃ for 3 min 10℃/min 280℃ for 3 min 10℃/min 290℃ for 3 min 10℃/min 300℃ for 3 min
Injection Volume	$0.1\mu l$
Row Control Mode:	Linear
Pressure	106.1 kPa
Total Flow	5.1 mL/min
Column Flow	1.79 mL/min
Linear Velocity	48.6 cm/s

Table 10: MS Optimised Experimental Conditions.

Optimised Conditions for MS	
Ionisation Mode	EI
Detector Voltage	0.2kV
Interface Temperature	260℃
Scan Range	SIM

APPENDIX B: CHARACTERISATION OF WVO

B.1: CALCULATION OF FREE FATTY ACID (FFA)

Firstly the Acid Value was determined through titration using the following formula

$$Acid\ Value = \frac{A\ \times M\ \times 56.1}{W}$$

Three runs were performed and the average value was used.

A sample calculation of the Acid Value was determined as follows:

$$Acid\ Value = \frac{A\ \times M\ \times 56.1}{W}$$

$$Acid\ Value = \frac{0.63\ \times 0.1\ \times 56.1}{0.5}$$

$$Acid\ Value = 7.07$$

The FFA content was determined as follows:

$$FFA\ \% = \frac{Acid\ Value}{2}$$

$$FFA\ \% = \frac{7.07}{2}$$

$$FFA\ \% = 3.53\%$$

The table below summarises the calculation of FFA content.

B.2: CALCULATION OF SAPONIFICATION VALUE (SV)

The Saponification Value (SV) was determined using titration and calculated as follows:

$$SV = 56.1\ \times \frac{(B - S) \times M\ of\ HCl}{weight\ of\ sample}$$

Three runs were conducted and the average value was used.

A sample calculation of the average SV was calculated as follows:

$$SV = 56.1 \times \frac{(B - S) \times M\ of\ HCl}{weight\ of\ sample}$$

$$SP = 56.1 \times \frac{(11.57 - 4.6) \times 0.5}{1}$$

$$SP = 195.81$$

The table below summarises the calculation

Table 11: Table Summarizing the Calculation of SV

RUN	Blank Sample (B) (ml)	Sample (S) (ml)	M of HCL	Weight of Sample (g)	Saponification Value (SV)
Run 1	12.6	6.8	0.5	1	162.69
Run 2	11.2	3.3	0.5	1	221.595
Run 3	10.9	3.7	0.5	1	201.96
AVERAGE	**11.57**	**4.6**	**0.5**	**1**	**195.415**

B.3: CALCULATION OF DENSITY

The density of the WVO was calculated as follows:

$$\rho = \frac{m}{V}$$

$$\rho = \frac{8.14g}{10ml}$$

$$\rho = 0.814\ g/ml$$

B.4 CALCULATION OF MOISTURE CONTENT

The method of calculating the moisture content in WVO follows that described in the experimental procedure.

The table below shows the moisture content in the WVO over a period of three years.

Table 12: Moisture Content in WVO

		Moisture Removed (g)
Initial Mass (g)	49.42	0
Mass after 1 hour	49.35	0.07
Mass after 2 hours	49.2	0.15
Mass after 3 hours	49.2	0

From the above table it can be seen that it takes approxiamately 2 hours for the moisture to be removed. The amount of moisture in the oil is calculated as follows:

$$\%\,Moisture = \frac{0.07 + 0.15}{49.42} \times 100 = 0.45\%$$

APPENDIX C

C.1 OPTIMUM WAVELENGTH

The data for determining the optimum wavelength are shown in the table below:

Table 13: Data showing the absorbance for different wavelengths of commercial biodiesel.

Wavelength (nm)	Absorbance
330	4.143
340	4.356
350	5.948
400	2.569
450	1.1515
500	0.604

From the above table it can be seen the highest absorbance of 5.948 corresponds to a wavelength of $350nm$.

C.2: DATA FOR CALIBRATION CURVE

Table 14: Data for Calibration Curve

Standards	Concentration (g/ml)	Absorbance
Standard 1	0.033	0.596
Standard 2	0.0292	0.52
Standard 3	0.0269	0.501
Standard 4	0.024	0.486
Standard 5	0.0226	0.458
Standard 6	0.0206	0.416
Standard 7	0.019	0.383
Standard 8	0.018	0.381

C.3: DATA OF BIODIESEL SAMPLES

Table 15: Data relating absorbance and concentration to the biodiesel samples at different times and temperatures

Absorbance	Concentration (g/ml)	Time (min)
Temperature: 40℃		
0	0	0
0.457	0.0105	30
0.485	0.0125	60
0.500	0.0136	90
0.506	0.014	120
0.513	0.0145	150
0.518	0.0149	180
0.518	0.0149	240
Temperature: 45℃		
0	0	0
0.436	0.009	30
0.485	0.0125	60
0.520	0.015	90
0.560	0.0179	120
0.571	0.0187	150
0.576	0.019	180
0.576	0.01905	240
Temperature: 50℃		
0	0	0
0.436	0.009	30
0.492	0.013	60
0.548	0.017	90
0.564	0.0182	120
0.576	0.019	150
0.580	0.0193	180
0.581	0.0194	240
Temperature: 55℃		
0	0.01	30
0.520	0.015	60
0.555	0.0175	90
0.569	0.0185	120
0.583	0.0195	150
0.590	0.02	180
0.590	0.02	240
Temperature: 60℃		
0	0	0
0.478	0.012	30
0.562	0.018	60
0.583	0.0195	90
0.603	0.021	120

0.631	0.023	150
0.645	0.024	180
0.645	0.024	240

APPENDIX D

D.1 MATHLAB CODE TO DETERMINE REACTION KINETICS

A numerical method was used to determine the reaction rate, *k* which is the slope of the concentration vs. time curve. The slope of the curve was determined using a simple method called the finite difference. The finite difference method is determined usinf a two-point estimation by computing the slope of a nearby secant line through the outer points of the curve (Lonngren et al., 2007).

A mathlab code was developed to determine the slope of the curve. Below is the code used to determine the slope of the curve (Bergara, 2000).

```
plot(x,y);
hold all;

% first sort the points, so x is monotonically rising
[x, sortidx] = sort(x);
y = y(sortidx);

% this is the x point for which you want to compute the slope
xslope = (x(1)+x(end))/2;

idx_a = find(x<xslope,1,'last');
idx_b = find(x>xslope,1,'first');
% or even simpler:
idx_b = idx_a+1;
% this assumes min(x)<xslope<max(x)

xa = x(idx_a);
xb = x(idx_b);
slope = (y(idx_b) - y(idx_a))/(xb - xa)
```