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**Process Optimization and the Kinetics of  
Transesterification of *Jatropha curcas* Oil**

**BY**

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## **DEDICATION**

This work is dedicated to my parents; Mr Justice M M Pedavoah (of blessed memory) and Mrs Elizabeth B Pedavoah for their relentless efforts and support to give me the best of education. It is also dedicated to my beloved children Mariana and Finnian (who were both born during the course), and their dad Fidelis A Akanyani for being there when I needed them most.

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“May the Almighty richly bless all who share in the success of this work.”

## ABSTRACT

This work focused on the kinetics of production of biodiesel from *Jatropha curcas* seed oil (a non-edible oil). The oil was obtained from Busunu in the Northern Region of Ghana. Some physicochemical properties of the crude *Jatropha* oil were determined; the density was  $0.909\text{gcm}^{-3}$ , the acid value was  $6.418\text{mgg}^{-1}$  of oil and the FFA content was 3.23%. The crude oil was then transesterified using methanol and KOH at varied reaction conditions. The optimum reaction conditions were chosen based on the percentage yield obtained. Optimum conditions were found to be as follows: the optimum molar ratio of oil to alcohol was found to be 1:6, amount of catalyst of 1.2% KOH (weight by volume of oil), temperature of  $55^{\circ}\text{C}$ , time of 45min, and a stirring rate of 250rpm. Based on the optimized conditions; the order of the reaction with respect to the biodiesel was first order and an Activation Energy of 53,814 J per mol was recorded. The fuel produced had a cetane index of 54.55, kinematic viscosity of 7.9Cst, total acid number of  $0.14\text{mgKOHg}^{-1}$ , pour point of  $0^{\circ}\text{C}$ , density of  $886.4\text{kgm}^{-3}$ , basic sediments and water of 0.01 %wt, ash content of 0.001 %wt, sulphur of 0.01 %wt, Conradson carbon of 0.16 %wt and metals (Na + K) of 1.125ppm. Almost all the fuel properties were within the ASTM standard for biodiesel 2009; hence the biodiesel produced from *Jatropha* seed oil is of useful quality and can be used in any diesel engine. This work can thus serve as basic information for further research especially for biodiesel production from *Jatropha* oil from Busunu in Northern Ghana for any researcher.

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## LIST OF ACRONYMS

AOCS.....	American Oil Chemists' Society
ASTM.....	American Society for Testing and Materials
BOST.....	Bulk Oil Storage and Transport Limited
BSW.....	Basic Water and Sediment
CI.....	Cetane Index
CN.....	Cetane Number
CMO.....	One cubic mile of oil
CO.....	Carbon monoxide
CO <sub>2</sub> .....	Carbon dioxide
Ea.....	Activation Energy
EN.....	European Standard
FAME.....	Fatty Acid Methyl Ester
FFA.....	Free Fatty Acid
FFAs.....	Free Fatty Acids
FP.....	Flash Point
HC.....	Hydrocarbon
HCl.....	Hydrochloric acid
ICP.....	Inductively Coupled Plasma
KOH.....	Potassium hydroxide
MR.....	Molar Ratio
NaOH.....	Sodium hydroxide
NO <sub>x</sub> .....	Nitrogen oxides
OES.....	Optical Emission Spectroscopy
ROH.....	Alcohol
RPM.....	Revolutions per minute
S.....	Sulphur

SO <sub>x</sub> .....	Sulphur oxides
SVO.....	Straight Vegetable Oil
TAN.....	Total Acid Number
TOR .....	Tema Oil Refinery
VOs.....	Vegetable Oils
WVO.....	Waste Vegetable Oil

## CHAPTER ONE

### 1.1 INTRODUCTION

A large percentage of the world's energy needs are met through petrochemical sources, coal and natural gas. These sources are finite and at the current rate of consumption will run out within a short time. A viable alternative to these is biofuel.

Biodiesel is a form of biofuel; it is a renewable fuel that can be synthesized from edible, non-edible and waste oils. Due to diminishing petroleum reserves, vegetable oils have attracted attention as potential renewable sources for the production of alternatives to petroleum-based diesel fuel. A number of processes have been developed for biodiesel production involving chemical or enzyme catalysis or supercritical alcohol treatment (Tiwari *et. al.*, 2007).

Enzymatic transesterification of triglycerides is a good alternative to chemical processes due to its eco-friendly, selective nature and low temperature requirements (Freedman *et. al.*, 1984; 1985).

In many countries, like Ghana, where edible oils are not in surplus supply, there is a need to search for alternative starting materials, such as from non-edible oils. The oil of *Jatropha curcas* (Euphorbiaceae) is a non-edible oil and has been chosen for the present investigation. The seeds and oil are toxic due to the presence of toxic phorbol esters. *Jatropha curcas* is a low-growing tree, generally planted as a hedge for protecting crops from animals. It can be grown on barren land under harsh conditions and can be cultivated as part of the strategy for reclaiming degraded lands (Gubitz *et. al.*, 1999).

Biodiesel is produced by transesterification of triglycerides with methanol and has become more attractive recently because it is renewable and environmentally friendly (Freedman *et. al.*, 1984; 1985).

Biodiesel fuels have many attractive features such as that it is domestically produced, offering the possibility of reducing petroleum imports. It is biodegradable and the by-products of combustion have reduced levels of harmful substances as compared to petroleum.

Jatropha is grown in only some parts of the world and research is currently on-going in the cultivation and the production of biodiesel from Jatropha.

Kinetic study of transesterification in the last thirty years has been mainly on finding best fit of empirical data to simple models of reaction order. Freedman and his colleagues started work in this area in the 1980s.

According to Komer the probability of a reaction can be predicted to about 78% using only kinetic factors. Kinetics is the study of rates (that is the change in concentration of reactants or products with time) of chemical reactions, it includes investigations of how different experimental conditions can influence the speed of a chemical reaction to generate information about reaction mechanisms and transition states as well as construct mathematical models. The aim of kinetic study is to make predictions about the composition of a reaction mixture as a function of time, to understand the processes that occur during the reaction and to identify what controls its rate.

This work will focus on adding knowledge to the research currently going on with Jatropha, by exploring the rate of reaction and how transesterification of Jatropha seed oil is affected by molar ratio of oil to methanol, temperature, catalyst and free fatty acids. It will also focus on determining

the kinetic parameters that control the transesterification reaction and hence help in the optimization of appropriate conditions for producing biodiesel from *Jatropha* seed oil.

## 1.2 Problem Statement

Many edible and non edible vegetable oils are currently being used in transesterification for the production of biodiesel. However, some of the raw materials are competing with food sources, the focus now should be on the non-edible oils which will not affect food production as well as its supply (Freedman *et. al.*, 1984). Research on *Jatropha curcas* has taken different dimensions with various people and organized bodies in the production of biodiesel by transesterification.

A number of factors affect the kinetics of the process of production of biodiesel: free fatty acids, water, the temperature, concentration, type of catalyst and others. These factors have a direct impact on the rate and activation energy of the reaction (Freedman *et. al.*, 1984; 1985). There are principles that govern the kinetics of a chemical reaction. A chemical reaction may be classified as either reversible or irreversible. Thus it is important to control the conditions of the reaction to favour the desired direction of conversion. Studies have shown that reaction rate drops off over time; due to both inadequate mixing and to reduced effectiveness of catalyst because of reduced polarity (Boocock, 1998). The formation of water during transesterification also favours the reverse reaction (Bikou, 1999).

Saponification reactions rob the process of transesterification of reactants that not only could be made into biodiesel but also of the catalyst needed for the reaction to proceed; that is the hydroxide ion which is the catalyst for base-catalyzed transesterification. It is also a reactant in the competing saponification reaction in which it is consumed.

This work thus seeks to produce biodiesel from the seed oil of *Jatropha curcas* by taking keen interest in the kinetics and factors stated. The fuel properties of the Jatropha biodiesel will be analyzed and compared with the ASTM standards for biodiesel.

### **1.3 Justification**

The world has shifted attention to Africa especially Ghana for the production of raw materials for biodiesel. For Africa to maximize the benefits from these projects, serious research should be done on biodiesel production in Africa so that processing of the raw material could be domesticated and biodiesel exported to the developed world.

If this is not done, Africa will remain a producer of raw materials which will be processed by the developed world and sold back to Africa at a higher price. Biodiesel has been produced from a number of sources, under various conditions, thus to optimize the yield, the best method and conditions for production should be developed (Chhetri *et. al.*, 2008).

The determination of the kinetic parameters will help establish the best method for the production of biodiesel from Jatropha compared to other sources. For the resulting biodiesel to be non-toxic it is important to ensure complete reaction, removal of glycerol, removal of catalyst, alcohol and reduced levels of FFA. This work is also intended to help maximize the efficiency of biodiesel production from *Jatropha curcas* currently under research in Ghana. With sufficient research and development, Jatropha remains a hopeful candidate for near-term fuel and energy production. This project will contribute to the promotion of Jatropha as an alternative viable source of oil for biodiesel production and hence promotion of the local economy. This work will thus seek to produce biodiesel of standard based on optimized conditions determined in the work and analyze its quality in accordance with existing fuel standards.

## **1.4 Objective**

The main objective of this work is to determine the reaction conditions that affect the transesterification of the seed oil of *Jatropha curcas* and based on that formulate parameters that affect the reaction.

### **1.4.1 Specific Objectives**

- Determine the effects of kinetic parameters on biodiesel from *Jatropha curcas*.
- Determine the Arrhenius parameters of the reaction.
- Determine fuel properties of the Jatropha biodiesel and compare with the ASTM standards.

## **1.5 Scope of Study**

This work was limited to the optimization of the production of biodiesel from crude Jatropha seed oil. Only the factors affecting rate (such as; molar ratio, amount of catalyst, temperature, time and stirring rate) and the kinetics were studied. Some fuel properties were determined and compared with the ASTM standards for biodiesel. The sustainability, environmental impact assessment of Jatropha biodiesel production and any other factor not stated are beyond the scope of this work.

## CHAPTER TWO

### 2.1 LITERATURE REVIEW

#### Introduction

The world depends largely on fossil fuel for most of its fuel needs especially in the transport sector. These sources are, however, finite and non-renewable. This has generated the interest in research into alternative energy forms; such as wind, solar, water and biofuels among others. The impact of energy sources on the environment is also very critical, thus this influences the choice of fuel. Pollutants such as CO, CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> can cause acid rain, green house effect and global warming. Diesel fuels have an essential function in the industrial economy of developing countries and used for transport of industrial and Agricultural goods and operation of diesel tractors and pump sets in the Agricultural sector. Economic growth is always accompanied by commensurate increase in the transport sector. The high energy demand in the industrialized world as well as in the domestic sector, and pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional ones. These have stimulated recent interest in alternative sources for petroleum-based fuels (Awudza, 2009). An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds (Meher *et al*, 2004).

Biofuels have been found to be environmentally friendly due to the reduction in CO and CO<sub>2</sub> production and can be domesticated for maximum benefit to producer nations. They are mainly produced from vegetable oils, algae and tallow and waste oils from industry. Countries which produce edible vegetable oil in surplus tend to use the excess while non edible oils are encouraged

for use in other nations. There is also growing concern to prevent the competition for land use between food crops and raw materials for biofuel. Stakeholders and researchers are advocating mix cropping as this will generate the needed raw materials and food resources simultaneously.

There are several oil plants currently being investigated for use in fuel production: soybean, tiger nut, Jatropha, peanut, sun flower among others. For purposes of this work, the seed oil of *Jatropha curcas* will be used. Research has shown that climate and location can affect the quality of oil.

The mineral diesel fuel is a complex mixture with carbon atoms ranging between 12 and 18, whereas vegetable oils are a mixture of organic compounds ranging from simple straight chain compounds to complex structures of proteins and fat soluble vitamins which are commonly referred to as triglycerides (Barnwal and Sharma, 2005; Srivastava and Prasad, 2000). Vegetable oils are usually triglycerides, generally with a number of branched chains of different lengths and different degrees of saturation. Vegetable oils have about 10% lower heating value than mineral diesel due to the oxygen present in their molecules. The viscosity of vegetable oil is several times higher than that of mineral diesel due to its large molecular mass and chemical structure. The cloud point and pour point are higher, and the cetane number is comparable to that of mineral diesel (Barnwal and Sharma, 2005; Srivastava and Prasad, 2000). The inefficient mixing of fuel with air contributes to incomplete combustion. The high flash point and lower volatility characteristics of mineral oil result in increased carbon deposit formation, injector choking, lubricating oil dilution and degradation. With vegetable oil as fuel, short term engine performance results are comparable to those with mineral diesel, but long term results with vegetable oil or blends with mineral diesel lead to severe engine deposits, piston ring sticking, and injector coking and thickening of the lube oil. High viscosity, low volatility and a tendency to polymerize within the cylinder is the root of many problems associated with direct use of vegetable oils as fuel (Barnwal and Sharma, 2005; Peterson,

1983). Because of these problems, vegetable oils need to be modified to bring their combustion related properties closer to those of mineral diesel. The fuel modification is mainly aimed at reducing the viscosity and increasing the volatility. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon fuels. The methods employed include pre-heating the oil, pyrolysis, microemulsion, blending and transesterification (Srivastava and Prasad, 2000). From various studies (Al-widyan and Al-shyoukh, 2002; Antolin *et al.*,2002; Altin *et al.*,2001), it is found that the best way to make vegetable oil compatible with existing engines is to convert it into ester (biodiesel). In comparison to mineral diesel, biodiesel has a more favorable combustion and emission profile. Emissions of CO, CO<sub>2</sub> and particulate matter decrease by 45%, hydrocarbon (HC) emissions decrease by nearly 70% but NO<sub>x</sub> emissions increase by 10% with 100% biodiesel (B100) as a fuel (Anon,2002). The carbon cycle time for fixation of CO<sub>2</sub> from biodiesel is quite small compared to mineral diesel. It means that biodiesel usage reduces greenhouse gas emissions compared to mineral diesel. Biodiesel has a relatively high flash point, which makes it safer to handle. Agarwal *et al.* (2003) have found that biodiesel provides good lubricating properties that can reduce component wear and enhance engine life. The physical wear of various vital parts and carbon deposits were found to be substantially lower in the case of 20% biodiesel fuelled engine. Hence, vegetable oil is a potential alternative for mineral diesel if it is converted to biodiesel. Biodiesel usage not only improves emissions but also improves engine life. Several experimental researches have shown that the fuel properties of vegetable oils can be improved by transesterification, and this is the method of choice in the current study.

Transesterification is the most common and well established chemical reaction in which alcohol reacts with the triglycerides of fatty acids (vegetable oil) in the presence of a catalyst. It is a

reversible reaction of fat or oil (triglyceride) with a primary alcohol to form esters and glycerol. The alcohol combines with the triglycerides to form glycerol and esters. The reaction is 3:1 molar ratio of alcohol to oil, however, since the reaction is reversible, in practice, excess alcohol (6:1) is required to shift the equilibrium to the products side to raise the product yield (Agarwal *et al* ; 2003).

Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides, and NaOH gets easily dissolved in it. For an alkali catalyzed transesterification, the triglycerides should have lower free fatty acid (FFA) content, and the alcohol must be substantially anhydrous because water can partially change the reaction to saponification, which produces soap. Soap formation lowers the yield of esters and renders the separation of esters and glycerol as well as water washing of esters difficult (Freedman *et al* 1984; Muniyappa *et al* 1996).

For oils with up to about 5% FFA, the reaction can be catalyzed using an alkali catalyst (Carracetto *et al* 2004).

Acid catalysts (HCl, H<sub>2</sub>SO<sub>4</sub>) are advantageous for oil having high FFA content, as acids catalyze the FFA esterification to produce fatty acid methyl ester, increasing the biodiesel yield, but the reaction time and alcohol requirement is very high (Al-widyan and Al-shyoukh, 2002). Boocock *et al.* proposed the addition of a co-solvent (tetrahydrofuran and methyl tertiary butyl ether) to create a single phase, and this accelerates the reaction so that it reaches substantial completion in a few minutes. The primary concerns with this method are the additional complexity of recovering and recycling the co-solvent and the hazard level associated with the proposed co-solvents. Several researchers (Demirbas 2003, Saka and Kusdiana, 2001; 2004) tried

transesterification without using any catalyst in supercritical methanol, which eliminates the need for the water washing.

Saka and Kusdiana, (2001; 2004) found that in supercritical methanol, the reaction requires only four minutes, and also, the presence of water did not effect the yield of ester, but very high pressure (45–65 bar), temperature (350°C) and very high molar ratio of alcohol to oil (42:1) were required. Enzymes like lipases can also be used as biocatalysts for transesterification, but the cost is the main hurdle in commercializing enzymes as catalysts (Fukuda *et al*, 2001).

Marchetti *et al*. (2007) compared the different technologies. More recently, there has been an increase in the development of heterogeneous catalysts (enzymes and solid catalysts) because their utilization in the transesterification reaction greatly simplifies and economizes the post-treatment (separation and purification) of the products. The use of heterogeneous catalysts does not produce soaps through fatty acid neutralization and triglyceride saponification. However, heterogeneous catalyzed reaction also requires extreme reaction conditions, while the methyl ester yield and the reaction time are still unfavorable compared to the alkali catalysts (Vicente *et al*, 2004).

In summary, base catalysts are most common, since the process is faster and reaction conditions are moderate. Although it is a well-known process, the proportions of reagents affect the process in terms of conversion efficiency, and this factor differs according to the vegetable oil type. Several researchers have identified the most important variables that influence the reaction, namely, reaction temperature, type and amount of catalyst, quantity of alcohol, stirring rate and reaction time (Ma and Hanna, 1990; Freedman *et al*, 1984; and Dorado *et al*, 2004).

Depending upon the climate and soil conditions, most nations are looking into different vegetable oils as potential diesel fuel replacement. America mainly producing biodiesel from maize, however, most countries in Europe use soybean, sunflower, saffola, rapeseed, palm oil, etc. for production of biodiesel and investigations on engines (Korbitz, 1999; Dorado *et al*, 2005, Bozbas, 2005). These oils are edible in nature and developing countries like Ghana cannot afford edible oils as a fuel substitute.

The use of such edible oils to produce biodiesel in Ghana is not feasible in view of a big gap in the demand and supply of such oils in the country for dietary consumption. Increased pressure to augment the production of edible oils has also put limitations on the use of these oils for production of biodiesel. To extend the use of biodiesel, the main concern is economic viability of producing biodiesel. The price of feedstock (vegetable oil) is one of the most significant factors, which consists of approximately 75%–88% of the total biodiesel production cost

(Dorado *et al*, 2005, Bozbas, 2005; Hass *et al* 2006). Obviously, developing nations have to focus their attention on oils of non-edible nature, which are cheaper.

## **2.2 History of biodiesel**

The diesel engine was invented by Otto Diesel in 1892. His engine was designed to run on a wide variety of fuels. Although he demonstrated a diesel engine running on peanut oil at the Paris Exhibition of 1900, the first commercial diesel engines run on kerosene. Due to their large size, diesel engines were first used in manufacturing plants. The new engine first appeared in transportation vehicles in ships in the 1900's. They showed up in trains in 1914, but did not seriously displace the steam engine until after World War II. Diesels were first used in automobiles in 1924 (Pahl, 2005).

Chemically, biodiesel is a mixture of fatty alkyl esters, or esters formed by fatty acids and an alcohol. Alkyl esters are commonly made from vegetable oil through a chemical reaction called transesterification. Although this process has had long use in making detergents, the resulting compound was first used as a diesel fuel by Austrian researchers around 1980 (Mittelbach, 1983). Mittelbach's group is also responsible for using waste vegetable oil as an inexpensive alternative to virgin oil as the fuel stock for biodiesel.

The major reasons to make biodiesel (as opposed to simply burning a good vegetable oil) are several: some of which include;

- Biodiesel is lower in viscosity and gelling temperature than the oils and fats it can be made from. This makes it pourable and jumpable at lower temperatures. The lower viscosity is particularly important to diesel injectors on smaller engines.
- Biodiesel is less biodegradable than the oils and fats - it stores better.
- Biodiesel is a better lubricant, and has higher cetane rating. Engines wear less and run better.
- The Biodiesel conversion (particularly when the result meets National specifications) removes some species found in fats and oils (particularly in waste fats and oils) which are gummy or acidic.
- Biodiesel can be made from a wide range of fats and oils which are very unattractive as diesel fuels, to yield a fuel with much more desirable and uniform properties.

All of these advantages are largely diesel-specific. It is not really very sensible to demand biodiesel conversion for fuels which will be burned in simple continuous burners (e.g. for heating oil) unless

gelling temperature depression is a major concern (and in this case the rest of the specifications of biodiesel could be relaxed and a less expensive process achieved). In this connection it should be remembered that biodiesels have lower heats of combustion (both by volume and by mass) compared to alkanes and alkenes because they are oxygenates (and so are the fats and oils they come from). In diesel engines the fuel value of the biodiesel is improved (compared to typical petrodiesels) because the cetane number is higher: the fuel burns faster. This allows more of the heat energy to be delivered near the top of the compression cycle, where more expansion work can be extracted from it.

### **2.3 Vegetable oil as fuel**

There are at least three ways to run a diesel engine on vegetable oil:

- Mix it with petroleum diesel fuel, or with a solvent, or with gasoline;
- Use the oil just as it is -- usually called SVO fuel (straight vegetable oil) or PPO fuel (pure plant oil);
- Convert it to biodiesel

Vegetable oil is much more viscous (thicker) than either petro-diesel or biodiesel. The purpose of mixing or blending straight vegetable oil (SVO) with other fuels and solvents is to lower the viscosity to make it thinner, so that it flows more freely through the fuel system into the combustion chamber. Mixing SVO with petro-diesel is a process that still uses fossil-fuel; this may be cleaner than pure fossil fuel, but still not clean enough. For every gallon of SVO used, one gallon of fossil-fuel is saved, and that much less climate-changing carbon dioxide in the atmosphere. People use various mixes, ranging from 10% SVO and 90% petro-diesel to 90% SVO and 10% petro-diesel.

Some people just use it that way, start up and go, without pre-heating it (which makes vegetable-oil much thinner). Some even use pure vegetable oil without pre-heating it. Blends of SVO with various solvents, such as mineral turpentine (white spirit), or with various ingredients, such as naphthalene (mothballs) and xylol (paint-stripper), or with unleaded gasoline, are experimental at best, however little or nothing is known about the effects of these additives on the combustion characteristics of the fuel or their long-term effects on the engine.

Higher viscosity is not the only problem with using vegetable oil as fuel. Vegetable-oil has different chemical properties and combustion characteristics from the petro-diesel fuel that diesel engines and their fuel systems are designed to use. Diesel engines, especially the more modern, cleaner-burning diesels, are high-tech machines with precise fuel requirements. Mixes and blends are generally a poor compromise. But mixes can have an advantage in cold weather: as with biodiesel, some winterized petro-diesel mixed with straight vegetable oil lowers the temperature at which the SVO starts to gel. Vegetable oil fuel systems can be a clean, effective and economical option. Unlike biodiesel, which runs in any diesel without modification, there is the need to modify the engine to use SVO. The best way is to fit a professional single-tank SVO system with replacement injectors and glow plugs optimized for vegetable oil, as well as fuel heating. With the Elsbett single-tank SVO system it can use petro-diesel, biodiesel or SVO, in any combination. Just start up and go, stop and switch off, like any other car. There are also two-tank SVO systems which pre-heat the oil to make it thinner. This involves starting the engine on ordinary petro-diesel (or biodiesel) in one tank and then switch to SVO in the other tank when the vegetable-oil is hot enough (i.e. thin enough), and switch back again to the petro-diesel tank before stopping the engine, otherwise it will choke up the injectors.

The production of biodiesel, or alkyl esters, is well known. There are three basic routes to ester production from oils and fats:

- Base catalyzed transesterification of the oil with alcohol,
- Direct acid catalyzed esterification of the oil with methanol and
- Conversion of the oil to fatty acids, and then to Alkyl esters with acid catalysis.

The majority of the alkyl esters produced today is done with the base catalyzed reaction because it is the most economic for several reasons such as:

- Low temperature and pressure processing.
- High conversion with minimal side reactions and reaction time.
- Direct conversion to methyl ester with no intermediate steps.
- Exotic materials of construction are not necessary.

#### **2.4 Environmental Impact assessment of Biodiesel Production**

For complete analyses of the environmental impact of biodiesel, the effects of production, conversion, transport and usage have to be critically studied. The aim of a Life Cycle Assessment (LCA) is to compare certain ecological impact categories of a renewable energy source and the finite energy resource that can be replaced. These include impact potentials such as; global warming, acidification potential, contribution to eutrophication, ozone depletion, and toxicity to human and ecosystem.

Various approaches have been developed for the assessment of the ecological risk of biodiesel. In the 1980s, different energy sources were compared according to their relationship between fossil energy input and usable energy output (Mittelbach and Rernschmidt, 2004).

A more efficient method was developed in the 1990s from the previous, which is an extension of the later; the Life Cycle Assessment (LCA).

The LCA approach compares the demand for finite resources and the emission of certain ecologically relevant compounds throughout the entire life cycle (Worgetter *et al.*, 1999). This method is, however, producing controversial results because the techniques and interpretations used by different teams are not uniform. The system boundaries and reference scenarios are also rarely similar. Efforts have been made to standardize the LCAs procedures, but there is still much to be desired.

## **2.5 Non Edible Oils for Biodiesel**

It has been found that one way of reducing cost of production for biodiesel is the use of non edible oils, which tend to be considerably cheaper than edible vegetable oils (Srivastava and Prasad, 2000). A number of plant oils contain substances which make them unsuitable for consumption; coaster oil has ricin, a highly toxic lectin. It is also not suitable for consumption due to its laxative effects which is ascribed to its property that about 90% of the oil is ricinoleic acid. *Jatropha* (physic nut) cannot be used for food purposes because of its content of a toxalbumine called curcine and the presence of various toxic phorbol esters. Other oils such as karanja, crambe, neem and rubber seed oils are all non edible and can be used as feedstock. In some cases these toxic substances can be removed by refining. However, in many cases the removal of toxic components from the fatty material has not been accomplished or even attempted yet (Mittelbach and Rernschmidt, 2004).

### **2.5.1 Characterization of *Jatropha***

The scientific name of the oil plant under study is *Jatropha curcas L.*, its common names include; physic nut and purgic or purging nut (English). It belongs to the family Euphorbiaceae. *Jatropha* grows in the tropics and sub-tropics and in dry to wet climates. *Jatropha* is a shrub or tree of up to

6m in height, it has milky sap from the branches, deciduous leaves, yellowish flowers (bell-shaped) growing readily from seeds or cuttings and has oil containing seeds.

The leaves of *Jatropha* are fly repellent for livestock, the bark is used as fish poison, the sap is used for making linen, and the fruits are used as purgative and contraceptives. The oil is used for illumination, lubrication, and soap production and as fuel in engines. All the plant parts are toxic.

One tonne of *Jatropha* fruits can yield about 270Kg of oil and has lower heating value of about 39.5MJ/Kg (Daimler, 2007).

## 2.6 Biodiesel production

Biodiesel production is the act of producing biodiesel through transesterification or alcoholysis. The process involves reacting vegetable oils or animal fats catalytically with short-chain aliphatic alcohols (typically methanol or ethanol). There are a number of methods used in the production of biodiesel; the three most widely used technologies in this context are pyrolysis, micro emulsification and transesterification (Schwab *et al.*, 1987). A typical production process is shown in Figure 1

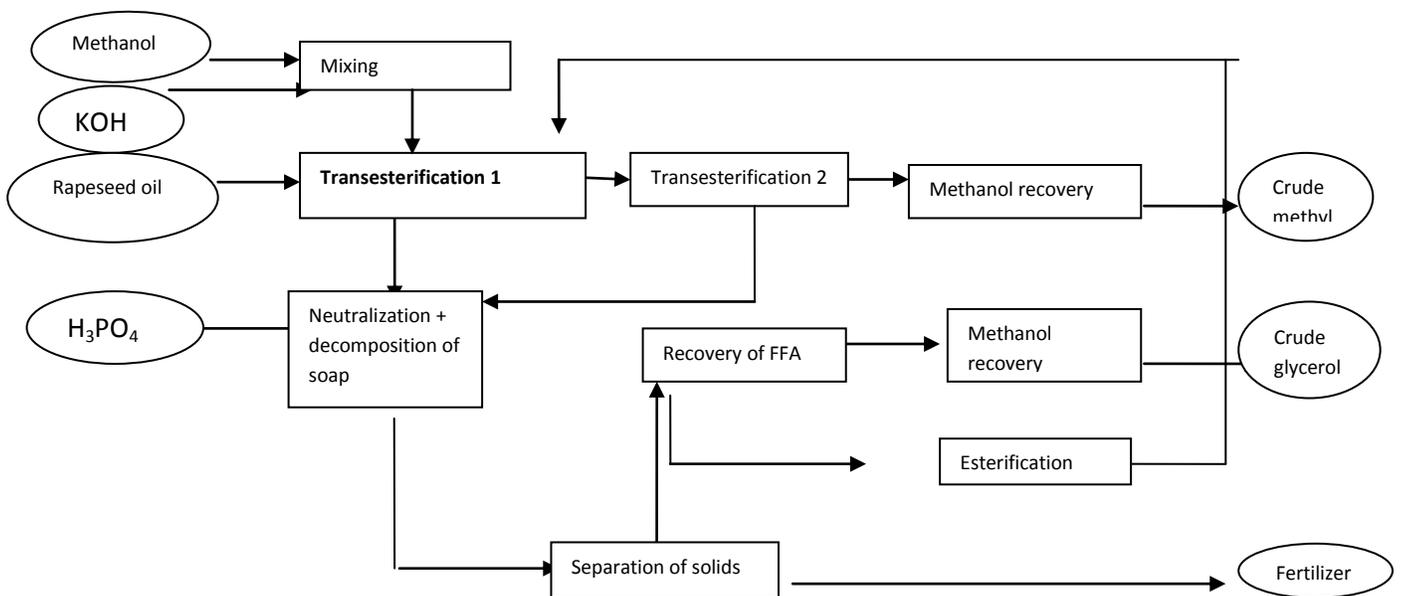


Figure 1: Schematics of a typical biodiesel production process (Mittelbach and Rernschmidt, 2004).

### 2.6.1 Feedstock for Biodiesel Production

There are different feedstocks in use depending on the availability and economic benefits. The predominant feedstock used in the United States is soybean oil, while rapeseed oil is mainly used in Europe. Other vegetable oils, such as corn, cottonseed, flax, sunflower and peanut, also can be used. These seed oils generally are more expensive than soybean oil. Palm oil and palm kernel oils have also been used successfully by Awudza and Lawer (2009).

Animal-derived products such as tallow, choice white grease (lard), poultry fat and yellow grease are also triglycerides and are used as a biodiesel feedstock. These products, when compared to plant-derived oils, often offer an economical advantage as a feedstock. There is also some indication that these sources, which are high in saturated fats, produce less nitrous oxide compared to plant oils.

The third main source of triglycerides is recycled oil and grease, usually from restaurants and food processing plants. Although more pre-treatment is required for this feedstock compared to virgin vegetable oils, economically it can be a very attractive feedstock. The use of a recycled product such as used cooking oil is an environmentally friendly process since it solves a waste disposal problem.

### 2.6.2 Feedstock Pretreatment

Before transesterification, the feedstock or oil has to usually undergo a number of treatment stages to get rid of impurities such as phosphatides, free fatty acids, waxes, tocopherols or colorants, which may interfere with the reaction. The process of degumming is usually used to remove phosphatides which make the oil turbid during storage and enhances the accumulation of water in the biodiesel. Degumming could be water or acid based. Soluble phosphatides are removed by adding water to the oil at a temperature of 60°- 90°C and centrifuging. The insoluble

phosphatides are removed adding acid solutions to decompose the material (Gutsche, 1997). A recent development for effectively getting rid of both soluble and insoluble phosphatides is the use of enzymatic hydrolysis (Dahlke and Buchold, 1995).

Deacidification is used in treating edible oils to prevent the rancid flavor in the product. For transesterification the removal of excess amount of Free Fatty Acids (FFA) is vital. This is because they favour soap formation and impede the separation of glycerol phase due to emulsifying effects of soaps. In extreme cases the oil might gel after the addition of base catalyst when FFA is greater than 5%. Deacidification is achieved by neutralization with alkali. Solvent extraction and distillation have both proved successful in deacidification.

If waste vegetable oil (WVO) is used, it is filtered to remove dirt, charred food, and other non-oil material often found. Water is removed because its presence causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of undergoing transesterification to give biodiesel.

### 2.6.3 Effect of water and Free Fatty Acids

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and water washing difficult. The glycerol is then removed by gravity separation and remaining ester is mixed with hot water for separation of catalyst. Moisture can be removed using silica gel. Saponification reaction also takes place simultaneously along with transesterification process but soap formation is not a major problem if the presence of water is less than 1% (Ma and Hanna, 1999). Material used for alkali-catalyzed transesterification of

triglycerides must meet certain specifications. The glyceride should have an acid value less than one and all reactants should be substantially anhydrous. If the acid value was greater than one, more catalyst is required to neutralize the FFA. Freedman *et al*, (1984) found that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness (Freedman *et al*, 1984). A sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of free fatty acids (carboxylic acids) present in the waste vegetable oil sample. These acids are then either esterified into biodiesel, esterified into bound glycerides, or removed, typically through neutralization. This process is also referred to as pretreatment in some materials.

#### 2.6.4 Mechanism for Transesterification

In organic chemistry, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. The reactions are often catalyzed by an acid or a base. Transesterification is crucial for producing biodiesel from biolipids. The transesterification process is the reaction of a triglyceride (fat/oil) with a bio-alcohol to form esters and glycerol. In the transesterification of different types of oils, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerin as shown in Figure 2, where  $R_1$ ,  $R_2$ ,  $R_3$ : are alkyl group.

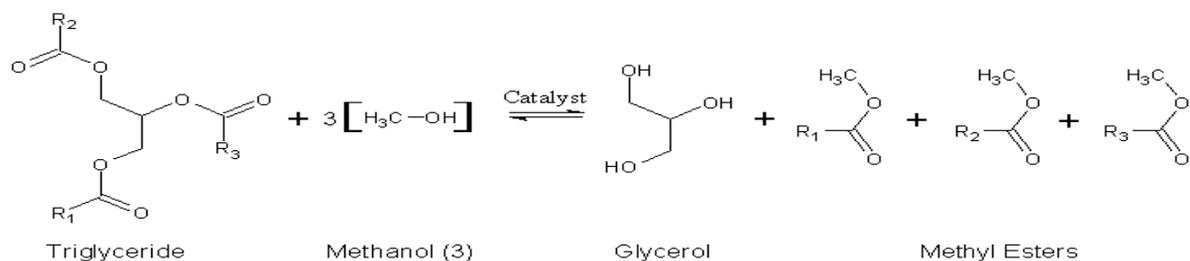


Figure 2: Reaction for transesterification of triglycerides

To make the reaction possible, a catalyst is added to the reaction (Miguel *et al*, 2001). During reaction while adding the base, a slight excess is factored in order to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide or potassium hydroxide) is added slowly to the alcohol and the mixture is stirred until the catalyst dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess of usually six parts alcohol to one part triglyceride (1:6) is added to drive the reaction to completion. Animal and plant fats and oils are typically made of triglycerides which are esters of free fatty acids with the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. The reaction has no other inputs than the triglyceride and the alcohol. Normally, this reaction will proceed either exceedingly slowly or not at all. Heat, as well as an acid or base are used to help the reaction proceed more quickly. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants but catalysts.

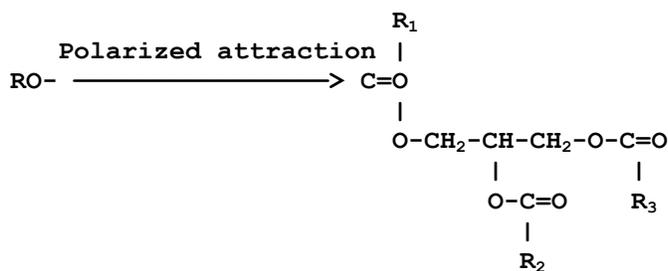
The base catalyzed reaction will be considered in this work. Any strong base capable of deprotonating the alcohol will do (e.g. NaOH, KOH, Sodium methoxide, etc.). Commonly, the base (KOH, NaOH) is dissolved in the alcohol (forming the methoxide) to make a convenient method of dispersing the otherwise solid catalyst into the oil. The ROH needs to be very dry. Any water in the process promotes the saponification reaction, thereby producing salts of fatty

acids (soaps) and consuming the base, and thus inhibits the transesterification reaction. Once the alcohol mixture is made, it is added to the triglyceride. The reaction that follows replaces the alkyl group on the triglyceride in a series of steps.

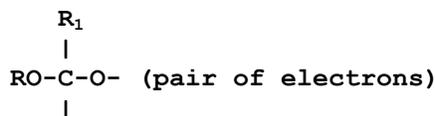
During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkali (NaOH, KOH, or Alkoxides). The main reason for doing a titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification.

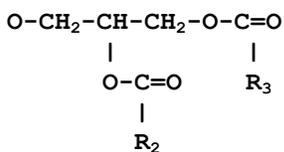
### 2.6.5 Base-Catalyzed Transesterification mechanism

In the base-catalyzed process, a mixture of the alcohol and the catalyst is made, which is then added to the triglyceride. The  $S_n2$  reaction that follows replaces the alkyl group on the triglyceride in a series of reactions. The carbon on the ester of the triglyceride has a slight positive charge, and the oxygens have a slight negative charge, most of which is located on the oxygen in the double bond. This charge is what attracts the  $RO^-$  to the reaction site;

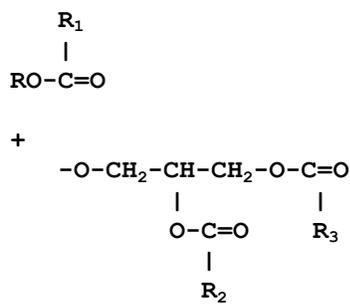


This yields a transition state that has a pair of electrons from the C=O bond now located on the oxygen that was in the C=O bond.





These electrons then fall back to the carbon and push off the glycol forming the ester.



Then two more RO groups react via this mechanism at the other two C=O groups. This type of reaction has several limiting factors. RO<sup>-</sup> has to fit in the space where there is a slight positive charge on the C=O. So MeO<sup>-</sup> works well because it is small. As the R on RO<sup>-</sup> gets bigger, reaction rates decrease. This effect is called steric hindrance. This is why methanol and ethanol are typically used.

## 2.6.6 Chemical Principles of Transesterification

In transesterification or alcoholysis reaction, one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of a fatty acid alkyl ester. The reaction proceeds in three reversible steps; the triglyceride molecule is converted step by step to diglyceride, monoglyceride and glycerol. One mole of alcohol is consumed and one mole of ester liberated in each step. In order to shift the equilibrium to the right, alcohol is added in excess over the stoichiometric amount in most commercial biodiesel production plants. The two main products (glycerol and fatty acid alkyl ester) of transesterification are immiscible thus can be easily separated by phase separation (Mittelbach and Remschmidt, 2004). According to Mittelbach and Trathnigg

(1990), the first reaction of methanol and triglyceride forming diglyceride and one mole of alkyl ester is the rate limiting step. The other two occur much faster.

## **2.7 Alcohol for Biodiesel Production**

In transesterification, the reactivity is greatly correlated to the alcohol: the longer the alkyl chain of alcohol, the longer the reaction treatment while in alkyl esterification of fatty acids, the conversion does not depend on the alcohol type because they have a similar reactivity. Therefore, the selection of alcohol in biodiesel production should be based on consideration of its performance properties and economics.

Various alcohols such as methanol, ethanol, propyl alcohol and butanol can be used for the process of transesterification, however; in most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters). This is because of its low price and high reactivity as compared to longer-chain alcohols (Lang, *et al* 2001a). Alkali catalyzed methanolysis can be conducted at room temperature and gives ester yields of more than 80% even after as little a reaction time as five minutes (Mittelbach, 1989). Also the separation of alkyl ester and glycerol proceeds fast and completely. Furthermore methanol is easily in the absolute form (ie has higher purity), compared to ethanol hence hydrolysis and soap formation due to water contained in the alcohol can be minimized.

## **2.8 Molar Ratio of Oil to Alcohol**

The optimum molar ratio between methanol and oil depends on the type of catalyst used. From the stoichiometry of transesterification, the reaction requires three moles of alcohol per mole of triglyceride (Mittelbach and Remschmidt, 2004). However, in order to shift the equilibrium to the right, an excess of the alcohol is frequently recommended. A molar ratio of 6:1 was suggested by

Freedman *et al.*, (1986) for the transesterification of soybean oil for alkali-catalyzed reaction in order to obtain the maximum ester yields. It has been found that higher amounts of alcohol in the reaction mixture are likely to interfere in the separation of the glycerol phase (Srivastava and Prasad, 2000). However, molar ratios of up to 30:1 have been frequently reported for acid catalyzed transesterification (Freedman *et al.*, 1984).

## 2.9 Amount of Catalyst

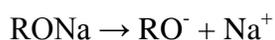
At high enough temperatures and pressures, transesterification of triglycerides with lower alcohols can proceed in the absence of a catalyst. The advantage of not using a catalyst is that high purity esters and glycerol are produced. The use of supercritical methanol without catalyst has been reported, this is, however, not economical due to the high energy requirements (Kusdiana and Saka, 2001). Thus to achieve satisfactory ester yields under mild reaction conditions, biodiesel production is generally done in the presence of some type of catalyst; alkaline and acid materials as well as transition metal compounds, silicates and lipases (Mittelbach and Remschmidt, 2004).

A catalyst is usually used to generate an alternative pathway for a reaction to occur, in transesterification an acid, alkaline or enzyme may be used as a catalyst. Alkaline catalysis is by far the most commonly used reaction type for biodiesel production. This method has the advantage over the acid-catalyzed transesterification due to its high conversion under mild conditions in comparatively short reaction time (Freedman *et al.*, 1986).

### 2.9.1 Homogenous Alkaline Catalysis

Alkoxide ions required for transesterification can be produced by either

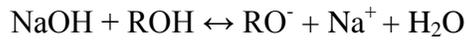
1. directly dissolving an alkali alcoholate in the alcohol;



2. by reacting the alcohol with pure alkali metal



3. or by adding an alkali hydroxide to the alcohol



1 and 2 have been mostly used in transesterification whereas 3 has been observed to favour the irreversible formation of soaps.

Unfortunately, though the alcoholates and alkali metals enable high conversion, they are expensive and pose a safety risk, thus, unattractive for commercial biodiesel production. According to Mittelbach et al., (1983), alkali hydroxides might be the promising alternative which is cheaper and easier to handle. Caldin and Long (1954) also showed that alkali catalyzed hydrolysis and soap formation played an insignificant role in water free alcohols.

Also in methanolysis, the fast separation of the glycerol phase removes most of the catalyst from the reaction mixture, thus the produced esters will hardly come in contact with hydroxides. This is common with KOH than NaOH, as it increases phase separation by increasing the density of the glycerol layer due to its higher molecular weight (Mittelbach, 1989). Ester losses are also reduced due to decrease in the amount of methyl esters dissolved in the glycerol phase.

The by product, such as; potassium dihydrogen can be processed into fertilizers, whereas the byproduct of NaOH transesterification processes are faster and NaOH is cheaper than KOH.

The major disadvantages of homogenous catalysts are that they cannot be reused and catalyst residues have to be removed by a series of washings, which increases production cost.

### 2.9.2 Heterogeneous alkaline catalysis

Heterogeneous catalysts have been introduced due to the disadvantages associated with the homogeneous ones. Mostly alkali metals and alkaline earth metal carbonates ( $K_2CO_3$ ,  $CaCO_3$ ) and their oxides ( $K_2O$ ,  $CaO$ ) are used as heterogeneous catalysts. Ashes of crop waste (such as cocoa husks and plantain peels) have also been recommended (Awudza and Mensah, 2009).

Some benefits of using Heterogeneous catalysts are that they;

- Simplify product purification.
- can be recovered by decantation or filtration or by the use of fixed bed arrangements
- show no decrease in reactivity even after several repeated usage
- can be easily disposed off in cement kilns

Some disadvantages however are that;

- they require high reaction temperatures and pressure and
- high volumes of alcohol which does not favour commercial application

### 2.9.3 Acid Catalysis

Acid catalysts are mainly used for transesterification of highly acidic fatty materials (such as palm oil and WVOs) to esterify the fatty acids. The process is a pretreatment of fats and oils with high FFA and is normally followed by alkaline transesterification. Acid catalysts also aid the formation of long and branched-chain esters, which are difficult to form with alkaline catalyst.

The disadvantages of this process are that;

- Acid catalyzed transesterifications are far slower than alkali-catalyzed reactions, and require higher temperatures, pressures and higher volumes of alcohol.

- These reactions also favour the formation of unwanted secondary products such as dialkyl ethers or glycerol ethers
- The presence of water in acid catalysis decreases the conversion significantly.

#### 2.9.4 Homogeneous Acid Catalysis

The most used acid catalyst is concentrated sulphuric acid (Conc.H<sub>2</sub>SO<sub>4</sub>), this is because it is of lower price and hygroscopic, which is necessary for the esterification of FFAs (removing released water from the reaction mixture). The disadvantages are, however, that it is corrosive, has the tendency to attack double bonds in unsaturated fatty acids and may cause darkening of ester product.

#### 2.9.5 Heterogeneous Acid Catalysis

Strong cation exchange resins are mostly used as heterogeneous acid catalysts for alcoholysis. These require high temperatures and longer time of reaction, hence, making them unattractive for commercial biodiesel production.

### **2.10 Homogenizing the Reaction Mixture**

A major problem associated with methanolysis is that the alcohol is a poor solvent for fatty acids. Thus transesterification does not proceed properly. The reaction mixture, therefore, has to be homogenized in some way at least during the initial stages of the reaction. The mixing intensity is very important in transesterification, vigorous mixing of reactants is one way of homogenization. This has been found to be successful in the batch and continuous processes of biodiesel production (Darnoko and Cheryan, 2000).

Other methods of achieving homogenization are by the application of low frequency ultrasonic irradiation and supercritical methanol. The advantage of these two methods which do not involve the use of an alkaline catalyst is that the product does not require washing if free of soaps. Also FFAs

present are converted directly to methyl esters thus there is no need for deacidification. The use of supercritical methanol is advantageous for feed stocks that contain water (like crude vegetable oils and waste oils) because water does not have a negative effect on conversion in transesterification with supercritical methanol ( Kusidiana and Saka, 2004).

However, high temperatures and pressures required, as well as alcohol to oil ratios of up 42:1 are major challenges for commercial application of this method in biodiesel production (Mittelbach and Rernschmidt, 2004).

### **2.11 Side Reaction of Transesterification**

For the purposes of biodiesel production, saponification is a very undesirable side-reaction inherent in the base-catalyzed transesterification reaction, and essentially all of the process and reaction optimizations for base-catalyzed biodiesel production must take it into consideration.

Soaps are very undesirable in biodiesel: they are gummy, leave sticky films which encourage bacteria, and directly increase corrosion. Entirely suppressing soap production in base-catalyzed transesterification processes is not possible, but the following reaction conditions reduce soap formation and must be insured for acceptable biodiesel production by base catalysis:

- Water greatly increases the saponification reaction rate. It is critical that water be eliminated from the feedstock for the reaction. The most common biodiesel production problem is wet oil feedstock or water contamination of the alcohol.
- Low free fatty acid concentration in the oil feedstock. The free fatty acids cannot be esterified by the base-catalyzed methods, but they can be converted to soaps. Thus the product should be cleansed of any soap.

- Substantial excess alcohol should be used to favour the desired transesterification reaction.
- Not too much alkali should be used; this will ensure a balance between achieving rapid and complete esterification, and not producing too much soap. (Saponification can occur with the free fatty-acid intermediate in the transesterification reaction too. This is why water increases saponification: it can interact with the intermediate to make the FFA, which is then saponified). At extreme alkali concentration, esters can be converted back to soaps.

From the above list the biggest operational problems to operators of base-catalyzed biodiesel conversion plants (which are by far the majority of plants in operation) are water and FFAs in feedstock. Many advertisements for base-catalyzed reactor systems make similar claims to the effect that whatever is being sold produces ASTM-quality biodiesel without washing or other subsequent steps to get rid of soaps and FFA in the output. This is the major problem with simple base-catalyzed conversion schemes. They are economical only with good feedstock, and there are unfortunate incentives to cutting corners which result in poor-quality product. Any consumer of Biodiesel must have an appropriately-cynical understanding of the difference between a process which is capable of producing a high-quality product given high-quality inputs and one which is not.

## **2.12 Product Purification**

Products of the reaction include not only biodiesel, but also byproducts, soap, glycerin, excess alcohol, and trace amounts of water. All of these byproducts must be removed, and the order of removal is process-dependent. The density of glycerin is greater than that of biodiesel, and this property difference is exploited to separate the bulk of the glycerin byproduct. Residual methanol is typically removed through distillation and reused, though it can be washed out (with water) as a waste as well. Soaps can be removed or converted into acids. Any residual water must be removed

from the fuel. After the separation has been accomplished, both the upper ester and the lower glycerol phase have to be purified to achieve maximum ester yields.

Methanol can be recovered by heating the ester phase and traces of glycerol can be removed by repeated washing steps with water or acid solutions; this, however, may reduce the ester yield due to hydrolysis (Mittelbach and Rernschmidt, 2004).

### **2.13 Quality Specifications of Biodiesel**

The assessment of fuel quality of biodiesel is usually determined by the ASTM standards. Quality standards are prerequisites for the commercial use of any fuel product. They serve as guide lines for the production process, guarantee costumers that they are buying high quality fuels, and provide authorities with approved tools for the assessment of safety risks and environmental pollution (Prankl, 2002). Manufacturers of engines and automobiles also rely on fuel standards for releasing warranties for their vehicles to be operated on biodiesel.

### **2.14 Benefits of Fatty Acid Methyl Esters (FAME) Fuels**

Air pollution is one of the most serious environmental problems all over the world. Since diesel engines of buses and trucks exhaust emit a huge amount of NO<sub>x</sub> and particulates, a clean alternative fuel is highly demanded. For the recent few decades, many efforts to develop a clean fuel have been under way in many countries. Biodiesel generates reduced amounts of NO<sub>x</sub> compared to petrodiesel.

Among many possible sources, biodiesel fuel derived from vegetable oil (VOs) attracts attention as a promising one to be substituted for conventional diesel fuels. Continuously increasing use of petroleum will intensify local air pollution and accelerate the global warming problems caused by CO<sub>2</sub>. If pure or blend biodiesel is used as fuel, the net production of CO<sub>2</sub> and sulphur can be highly

suppressed. Scharmer *et al.* ( 1995) have estimated that using the same volume of fossil fuel and biodiesel, the biodiesel will cause 3.2% reduction in the amount of CO<sub>2</sub> produced by fossil fuel

Biodiesel can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel not only has proper viscosity, boiling point, and high cetane number, but also is simple to use.

From research, it can be concluded that the world biofuels market has been growing at an accelerated pace in the last twenty years, and this trend is expected to continue in the future. This market can be divided into two broad categories: biodiesel and ethanol. Biodiesel is manufactured from natural oils, whether they are from animal or vegetable matter. Ethanol is produced from sugars, either harvested directly or broken down from starches. Both sectors of the industry have grown significantly, with the United States and Brazil focusing their production efforts largely on ethanol and the European Union, concentrating on biodiesel. According to Hodge (2008), the worlds energy consumption stands at 3Cubic Miles of Oil per year (CMO/yr) of which biomass contributed only 6.33% (it implies that biodiesel alone is even less than that).

### **2.15 Application of Fatty Acid Alkyl Esters**

Biodiesel is mainly used as renewable energy for diesel engines. There are also a wide range of industrial applications either directly or as starting material for the production of other compounds. Alkyl ester from soybean and rapeseed oil can be used in the cleanup of oil spills on polluted beaches as cited by Miller and Mudge (1997). They can also be used as biodegradable, non toxic paint-strippers (Menecy, *et al.*, 1999), graffiti removers and cleaning solvents for machinery (Dunn, 2003). They are suitable as solvents in the production of cutback asphalt, hence can replace the hydrocarbons (Lackey *et al.*, 2003). They can also serve as carrier fluids for the formulation of pesticides and insecticides (Engels *et al.*, 1999), as an inert medium for milling of aluminum

pigments (Barry and Chattopadhyay, 1999) and as emulsifiers for well- treatment fluids in the oil industry (Parris and Robinson, 2002).

The fatty acid alkyl esters are also used to fuel kerosene lamps (Reinecke and Kania, 1998), and fire lighters (Cox, 2003), when swallowed in small amounts will not have health hazards except for a laxative effect (Dunn, 2003). Work is still on going on the use of rape seed oil methyl esters as low-price absorbent for volatile organic pollutants in industry. From preliminary results of research, rape seed oil is suitable for the removal of chlorinated hydrocarbons, aromatic compounds and ethers from industrial exhaust gas streams (Bay *et al.*, 2004).

Fatty acid methyl esters have a number of indirect uses as studied by Schuchardt *et al.*, (1998); they usually serve as starting materials for the production of other compounds. They are used to produce alkanolamides, used as non-ionic surfactants and emulsifying, thickening and plastifying agents (Farris, 1979) and the transesterification with iso-propanol to yield iso-propyl esters; these find application in the cosmetic industry. They are also found indirect application in the pharmaceutical industry and for nutritional purposes (in alkali-catalyzed transesterification with carbohydrates to produce sucrose polyesters which are used as edible non-calorific oil). Some of the applications of fatty acid alkyl esters have been summarized in Figure 3.

## **2.16 National Enabling Environment for Biodiesel Production in Ghana**

The fuel sector in Ghana is currently controlled by the government. The country currently imports all the crude oil it utilizes, however, the refining of oil is carried out in the country, by the Tema Oil Refinery (TOR), and the storage and distribution to regional depots is carried out by the Bulk Oil Storage and Transport Limited ( BOST), a company solely owned by the government. Hence the capacity to transport and store biodiesel across the country currently exists in Ghana.

With regards to crops that can be used as feedstock for biodiesel, three plants have been identified as suitable; these are palm oil, Jatropha, and coconut (Caminiti *et al.*; 2007).

According to Caminiti *et al* (2007), despite limited access to finance, the government of Ghana is keen to support the industry.

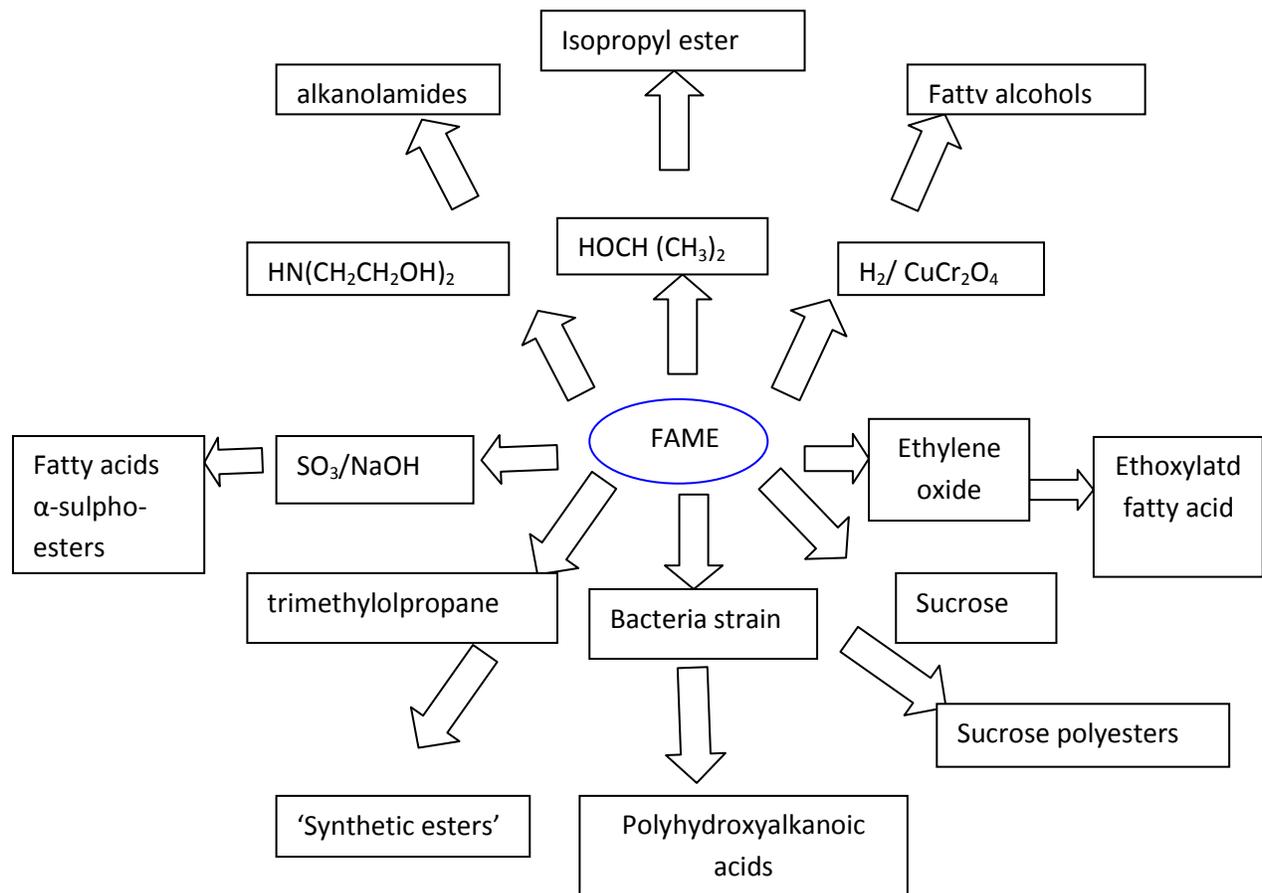


Figure 3: Potential indirect application of fatty acid methyl ester, Adapted from Schuchardt *et al.*, 1998.

Some larger banks, such as Merchant Bank of Ghana, have received sovereign guarantees to attract capital for the provision of loans to producers of biofuels. In regards to financing of feedstock production, the National Microfinance and Small Loan Center is willing to give smaller loans for the

cultivation of *Jatropha*, while the Agriculture Development Bank will continue providing financing for all crops produced in Ghana (including *Jatropha*), Caminiti *et al* (2007).

## **2.17 Biodiesel Potential in Ghana**

There is potential for the biodiesel industry in Ghana that could be supported by the already explicit interest of the government and small entrepreneurs, who are already involved in the nascent industry. According to the research conducted by Technoserve in Ghana on the possibility of biodiesel production, three models were developed. The first model is based on the government's policy draft for the biodiesel industry and identifies all of Ghana as the potential market. Based on the analysis of this model, it can be concluded that if Ghana were to seek a biodiesel industry competitive with current diesel prices, it would have to increase productivity of *Jatropha* growers, reduce the seed price by 55 percent, and provide a tax break of 5 percent on the total blended fuel, Caminiti *et al* (2007).

The second model takes a sectoral approach, targeting the mining sector as the market for biodiesel. The most promising sector in Ghana would be that of mining since it consumes approximately 40 percent of the national production of diesel. The last model deviates from the production of biodiesel by identifying the potential for Ghana to participate in the world market of biofuels as a supplier of raw materials through the exportation of vegetable oils to Europe. This model can be used to increase the supply of feedstock until capacity for biodiesel production is built in Ghana.

## 2.18 Kinetic Study of Transesterification

The goal of kinetic experiments is to measure the concentration of a species at a particular time during a reaction so that a rate law can be determined. However, it is exceedingly difficult to get an accurate measurement of a concentration at a known time because the techniques used to measure concentrations do not work instantaneously, but rather take time to perform.

One of the earliest methods used to measure concentrations at specified times is to quench the reaction either by flash freezing it or by adding a substance that severely inhibits the reaction. Both of these techniques are problematic because one can't be sure that the reaction has completely stopped. The reaction may still be going on during the analysis. Additionally, the reaction mixture is destroyed for the purposes of kinetic experiments, so the chemist must make multiple trial runs and waste a large amount of reagents to observe the concentrations at multiple points in time.

Chemical kinetics is the study of the rates of chemical reactions. Such reaction rates range from the almost instantaneous, as in an explosion, to the almost unnoticeably slow, as in corrosion. The aim of chemical kinetics is to make predictions about the composition of reaction mixtures as a function of time, to understand the processes that occur during a reaction, and to identify what controls its rate.

A fundamental challenge in chemical kinetics is the determination of the reaction order (or, in general, the rate law) from experimental information. It is known that the rate law is closely related to the reaction mechanism, and the knowledge of the mechanism of a given reaction allows the control of the reaction. But how one actually determines a rate law is the problem.

The first step is to control the conditions under which a reaction occurs, and then determine the rate of that reaction. If the reaction rate is measured just after defining the reaction conditions, then this is a measurement of the initial rate of the reaction.

The rate of a chemical reaction is defined as the rate of change of the concentration of one of its components, either a reactant or a product. The experimental investigation of reaction rates, therefore, depends on being able to monitor the change of concentration with time. Classical procedures for reactions that take place in hours or minutes make use of a variety of techniques for determining concentration, such as spectroscopy and electro-chemistry. Very fast reactions are studied spectroscopically. Spectroscopic procedures are available for monitoring reactions that are initiated by a rapid pulse of electromagnetic radiation and are over in a few femtoseconds (1 fs =  $10^{-15}$  s).

The analysis of kinetic data commonly proceeds by establishing a rate law, a mathematical expression for the rate in terms of the concentrations of the reactants (and sometimes products) at each stage of the reaction. For instance, it may be found that the rate of consumption of a reactant is proportional to the concentration of the reactant, in which case the rate law is

$$\text{Rate} = k [\text{Reactant}]$$

where [Reactant] denotes the concentration of the reactant and  $k$  is called the rate constant. The rate constant is independent of the concentrations of any species in the reaction mixture but depends on the temperature. A reaction with a rate law of this form is classified as a first-order rate law. More generally, a reaction with a rate law of the form

$$\text{Rate} = k[\text{Reactant A}]^a[\text{Reactant B}]^b \dots$$

is said to be of order  $a$  in A, of order  $b$  in B, and to have an overall order of  $a + b + \dots$ . Some rate laws are far more complex than these two simple examples and many involve the concentrations of the products.

The advantage of identifying the reaction order is that all reactions with the same rate law (but different characteristic rate constants) behave similarly. For example, the concentration of a reactant in a first-order reaction decays exponentially with time at a rate determined by the rate constant

$$[\text{Reactant}] = [\text{Reactant}]_0 e^{-kt}$$

where  $[\text{Reactant}]_0$  is the initial concentration of the reactant.

The identification of a rate law provides valuable insight into the reaction mechanism, the sequence of elementary steps by which a reaction takes place. The aim is to identify the reaction mechanism by constructing the rate law that it implies. This procedure may be simplified by identifying the rate-determining step of a reaction, the slowest step in a sequence that determines the overall rate.

In general, for a mechanism of many steps (including their reverse), the construction of the overall rate law is quite difficult, requiring an approximation or a computer for a numerical analysis. A hazard of using kinetic information to identify a reaction mechanism, however, is that more than one mechanism might result in the same rate law, especially when approximate solutions are derived. For this reason, a proposed reaction mechanism must be supported by additional evidence.

Once a reaction mechanism has been identified, attention turns to the molecular properties that govern the values of the rate constants that occur in the individual elementary steps. A clue to the factors involved is provided by the experimental observation that the rate constants of many

reactions depend on temperature according to the Arrhenius expression where  $E_a$  is called the activation energy.

The simplest model that accounts for the Arrhenius expression is the collision theory of gas-phase reaction rates, in which it is supposed that reaction occurs when two reactant molecules collide with at least a minimum kinetic energy (which is identified with the activation energy). A more sophisticated theory is the activated complex theory (also known as the transition state theory), in which it is supposed that the reactants encounter each other, form a loosened cluster of atoms, then decompose into products. Reactions in solution require more detailed consideration than reactions in gases.

The rate of a reaction may also be increased by using a catalyst (a substance that takes part in a reaction by providing an alternative pathway with lower activation energy but is regenerated in the process and is therefore not consumed). Catalysis is the foundation of the chemical industry and a great effort is made to discover or fabricate efficient and economical catalysts for the production of biodiesel lately. It is also necessary to optimize all the parameters involved in the production of biodiesel to reduce cost and maximize profit.

## **2.19 Fuel Properties**

### **2.19.1 Flash Point (FP)**

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of diesel. Due to its higher flash point temperature, diesel fuel is inherently safer than many other fuels such as gasoline.

### 2.19.2 Viscosity

Viscosity refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions.

### 2.19.3 Cetane Number (CN)

This is a relative measure of the interval between the beginning of injection and autoignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater its combustibility. Fuels with low Cetane Numbers will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with Cetane Numbers above 50. Cetane tests provide information on the ignition quality of a diesel fuel. Research using cetane tests will provide information on potential tailoring of vegetable oil-derived compounds and additives to enhance their fuel properties.

### 2.19.4 Cetane Index (CI)

Cetane index is an approximation of fuel ignition quality through measurement of distillation range and specific gravity. It is not affected by the use of combustion improver additives; therefore, it produces an indication of the base cetane number of the fuel.

### 2.19.5 Density

Density is the weight per unit volume of a substance. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre.

The aspects listed above are the key aspects that determine the efficiency of a fuel for diesel engines. There are other aspects or characteristics which do not have a direct bearing on the performance, but are important for reasons such as environmental impact etc. These are:

### 2.19.6 Ash Percentage

Ash is a measure of the amount of metals contained in the fuel. High concentrations of these materials can cause injector tip plugging, combustion deposits and injection system wear. The ash content is important for the heating value, as heating value decreases with increasing ash content. Ash content for bio-fuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest.

### 2.19.7 Water and Sediment

Diesel fuel should be clear in appearance and free of water and sediment. The presence of these materials generally indicates poor fuel handling practices. Water and sediment can and will cause shortened filter life or plugged fuel filters which can in turn lead to fuel starvation in the engine. In

addition, water can have negative impact on fuel corrosion and on microbial growth. It is for that reason that it is recommended that separate analysis and maximum levels be assigned.

#### 2.19.8 Distillation

This property provides a measure of the temperature range over which a fuel volatilize or turns to a vapor. Volatility is one of the primary factors which distinguish #1 from #2 diesel fuel. No. 1 diesel typically has greater volatility than No. 2. The highest temperature recorded during distillation is called the end point. Ideally, one would specify an end point in the definition of fuel properties. However, because a fuel's end point is difficult to measure with good repeatability, the fuel's 90% or 95% distillation point is commonly used. The Engine Manufacturers Association (EMA) prefers the 95% distillation point since its reproducibility is acceptable and it is closer to the fuel's end point than the 90% point currently measured in D 975. In applications which operate at low loads and frequent idle periods, like bus engines, lower end point is desirable to reduce smoke and combustion deposits. Hence EMA recommends distillation temperature specifications lower than the current D 975 specification to cover those applications.



## CHAPTER THREE

### 3.1 MATERIALS AND METHODS

#### Materials

The Crude Jatropha seed oil was obtained from Busunu Bioenergy (Damongo, Ghana). By using the ASTM methods (2008); the free fatty acid content was found to be 3.23%, the acid value was 6.418 mg KOH/g of oil, and density of the oil was determined as  $0.909\text{g/cm}^3$ . Certified methanol of 99.8 % purity was obtained from BDH (England). The catalyst (potassium hydroxide) was of analytical grade from BDH (England).

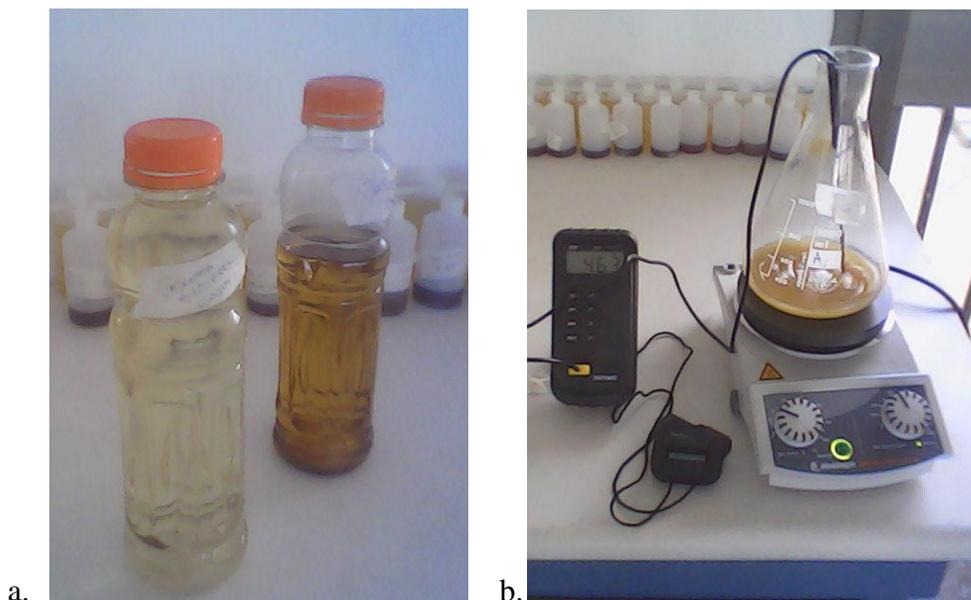


Figure 4: *a, Methyl ester and the triglycerides of Jatropha curcas seed oil. b, The setup used for the transesterification process. (KNUST-Kumasi, Physical Chemistry laboratory).*

Reaction raw materials:

1. Jatropha Oil
2. Methanol ( $\text{CH}_3\text{OH}$ ) (Analytical grade )
3. Potassium hydroxide (anhydrous dry) (Analytical grade - BDH,England)

Materials for Titration:

1. Isopropyl alcohol ( Analytical grade - BDH,England)
2. Distilled water
3. Phenolphthalein indicator

Materials for Washing:

1. Warm Water

Determination of density

A 10ml density bottle was used for density determination. The initial weight of the empty bottle was taken, then it was filled with water and the weight was recorded. The weight of the density bottle and Jatropha oil was taken. The actual weight was calculated by difference and divided by the volume of the density bottle to get the density.

Determination of Acid number and FFA

A mass of 1 gram KOH was dissolved in 1 liter of distilled water in a volumetric flask to make a 0.1% KOH solution. Phenolphthalein indicator was used to get the end point. In another beaker, 1 ml of oil was dissolved in 10 ml of pure isopropyl alcohol. The beaker was gently warmed by standing it on a hot water bath, it was stirred until all the oil dissolved in the alcohol and the mixture turned clear. 2 drops of phenolphthalein indicator was added. Using a burette, the 0.1% KOH solution was added drop wise to the oil alcohol phenolphthalein solution, ensuring that it was stirred all the time, until the solution stayed pink (magenta) for 10

seconds. The number of millilitres of 0.1% KOH solution used was considered as grams. This was assumed to be the number of grams of KOH that would be needed per liter of oil.

Production process of biodiesel

1. Jatropha oil was filtered to remove any solid particles and water.
2. Titration was done to determine the acid number and to estimate the amount of catalyst needed.
3. The catalyst (potassium hydroxide) was then thoroughly mixed in methanol till it dissolved completely to give potassium methoxide.
4. Jatropha oil was heated slightly and mixed with the potassium methoxide with a magnetic stirrer running.
5. The mixture was then allowed to settle overnight and glycerine was removed from bottom.
6. Biodiesel fraction was then washed and dried.
7. The percentage yield was taken.
8. The biodiesel was then checked for quality.

### **3.2 Equipment**

Reactions were carried out in a 1L conical flask, serving as the reactor. The reactor was equipped with a magnetic stirrer-bar and a temperature probe, (shown in Figure 4. b), the reactor was placed on a hot plate and the reaction temperature maintained within 5°C of that required for the reaction.

### **3.3 Experimental Procedure**

The reactor was initially filled with the desired amount of oil, then placed on a hot plate with its associated equipment and heated to a predetermined temperature. The catalyst was dissolved in the methanol and the resulting methoxide solution was added to the agitated reactor. The reaction was

timed as soon as the potassium methoxide solution was added to the reactor and the stirring continued for the recommended time. The mixture was transferred into a separating funnel, allowing glycerol to separate by gravity for 2 h (Figure 5), after removing the glycerol layer, the yield of the methyl ester layer was taken; taking the volume and mass where necessary.



*Figure 5: Some of the processes during the transesterification (KNUST-Kumasi, Physical Chemistry laboratory).*

### **3.4 Optimization of Reaction Conditions**

#### **3.4.1 Molar Ratio**

A volume of 50ml oil was preheated in a conical flask. The methoxide solution was prepared from about 0.5g of KOH and a volume of methanol (depending on the molar ratio of oil to methanol) in a separate flask. The methoxide solution was then added to the oil and the mixture was agitated using a magnetic stirrer, for one hour and then allowed to separate over night (in a separating funnel). The biodiesel and the glycerol separated by phase separation; the upper layer was the methyl ester and

the lower layer glycerol. The yield of the methyl ester was recorded. The process was repeated four other times for each molar ratio.

#### 3.4.2 Amount of Catalyst

A volume of 50ml oil was preheated in a conical flask. The methoxide solution was prepared from 12ml of methanol and a known amount of KOH (ranging from 0.2 - 1.2g) in a separate flask. The methoxide solution was then added to the oil and the mixture agitated using a magnetic stirrer, for one hour and then allowed to separate over night (in a separating funnel). The biodiesel and the glycerol separated by phase separation; the upper layer was methyl ester and the lower layer glycerol. The yield of the methyl ester was recorded. The process was repeated three other times for each amount of KOH used.

#### 3.4.3 Temperature

A volume of 50ml oil was preheated in a conical flask. The methoxide solution was prepared from 0.60g of KOH and 12ml of methanol in a separate flask (ie 1:6 oil to methanol molar ratio). The methoxide solution was then added to the oil and the mixture agitated using a magnetic stirrer, for one hour. The temperature of reaction was varied at 10°C interval from 45-85°C and the mixture then allowed to separate over night (in a separating funnel). The biodiesel and the glycerol separated by phase separation; the upper layer was the methyl ester and the lower layer glycerol. The yield of the methyl ester was recorded. The process was repeated three other times for each molar ratio.

#### 3.4.4 Time of Reaction

A volume of 50ml oil was preheated in a conical flask. The methoxide solution was prepared from 0.60g of KOH and 12ml of methanol in a separate flask. The methoxide solution was then added to the oil and the mixture agitated using a magnetic stirrer, with a given period of time (of 15-75mins at

15mins interval). The temperature of reaction was 55°C and the mixture was then allowed to separate over night (in a separating funnel). The biodiesel and the glycerol separated by phase separation; the upper layer was the methyl ester and the lower layer glycerol. The yield of the methyl ester was recorded. The process was repeated three other times for each molar ratio.

#### 3.4.5 Product Purification

The biodiesel was separated from the glycerol in the separating funnel. The biodiesel was washed with dilute acetic acid before washing with warm water. The acetic acid brings the pH of the solution closer to neutral because it neutralizes and drops out any KOH suspended in the biodiesel. The washing was repeated twice with warm water and the biodiesel – water mixture allowed to settle; the washing was done to get rid of any soap or glycerol that may have remained in the biodiesel layer. The biodiesel was then heated slightly to remove any residual water in it.

### 3.5 Determination of Fuel Properties

The ASTM - 08 methods were used for all the determinations. The determinations were carried out at the Tema Oil Refinery (TOR). Most of the properties analyzed determine the efficiency of a fuel for diesel engines. There are other aspects or characteristics which do not have a direct bearing on the performance, but are important for reasons such as environment impact etc.

#### 3.5.1 Kinematic Viscosity at 37.8°C

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity) was employed. An 861 viscosity tube was filled up to half the lower bulb with biodiesel. The tube was maintained at constant temperature (37.8°C) for 30min. The fluid was then drawn above the upper bulb and time of flow for the release of the fluid was taken. The time of flow was then multiplied by the constant of the tube used.

### 3.5.2 Sulphur Content

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry was used. About 5ml of biodiesel was kept in a transparent dish and inserted into the equipment. The results were generated automatically on a display interface.

### 3.5.3 Density

D4052 Test method for density determination of liquids was used. A hydrometer and a thermometer were used to determine the density of the Jatropha methyl ester. A 1000ml measuring cylinder was filled with biodiesel, a hydrometer (840 -900) and a thermometer were immersed. The readings were taken and used to calculate the density.

### 3.5.4 Pour Point

D97 Test method for pour point determination was used. The cloud point and pour point cabinet was used. A 10ml sample was kept in a glass tube and fitted with a cork and thermometer. The sample was placed in the cabinet until it became solid. The temperature readings were recorded and corrected by a factor of +3 (that is correction factor from calibration from the instrument).

### 3.5.5 Colour

D1500 Test method for the determination of colour was employed. About 10ml of the sample was placed in a glass tube and inserted into a photometer. The knobs were adjusted until the colour of the sample conformed to those of the standards.

### 3.5.6 Ash

D482 Test method for ash content determination was used. About 25ml of sample was charred and the mass taken after cooling in a desiccator. The weight of the charred sample was determined and calculated as a percentage mass of the sample used.

### 3.5.7 Evaporated at 360°C

This is the volume of sampled distilled (that is evaporated and condensed) at 360°C (the automatic distillatory is used for such analysis (Figure 6). It shows the purity of the sample being analyzed. When the sample contains a lot of water the 360°C distillation is not achieved.

### 3.5.8 Water by Distillation

D95 Test method for water by distillation was employed. A 100ml volume of toluene was added to 100ml Jatropha methyl ester and the mixture distilled at 300°C for 60mins. The volume of water condensed was taken.

### 3.5.9 **Cetane Index (CI)**

D4737 Test Method for Calculated Cetane Index by Four Variable Equation was employed. This is a calculated number based on the density and distillation range of the fuel. There are various versions of this, depending on whether the metric or imperial units are used, and how many distillation points are used. These days most oil companies use the '4-point method', ASTM D4737, based on density, 10%, 50% and 90% recovery temperatures.



*Figure 6: Automatic distillator at Quality Control Unit - Tema Oil Refinery (TOR), Ghana.*

#### 3.5.10 Metals

EN14538 Fat and oil derivatives-Fatty acid methyl esters (FAME): Determination of Ca, K, Mg, Na, Pb, Ni and V content were done using optical emission spectral analysis with inductively coupled plasma (ICP - OES) (Figure 7). In ICP-OES a special device is used that heats the sample to very high temperatures (6,000 to 10,000 K) in the presence of argon ions. The sample was ashed; the resulting ash was dissolved in dilute HCl, before injecting it into the instrument. The sample was heated to a temperature where it was atomized and a significant proportion of the atoms were in an excited state. Atomic emissions are produced when the electrons in an excited state fall back to lower energy levels. Since the allowed energy levels for each atom is different, they each have characteristic emission spectrum from which they were identified. The emitted radiation was therefore passed through a wavelength selector to isolate specific peaks in the spectra corresponding to the atom of interest, and the intensity of the peak was measured using a detector and displayed on a read-out device.

### 3.5.11 Total Acid Number (TAN)

D974 Test Method for Acid and Base Number determination by Color-Indicator Titration was used to determine TAN. A 100ml volume of isopropanol was added to about 20ml of Jatropha methyl ester and the mixture titrated against 0.001M KOH using methyl red as indicator.

### 3.5.12 Carbon Residue

D4530 Test Method for Determination of Carbon Residue (Micro Method) was used to analyze the carbon content. The micro carbon tester (ALCOR) was used.

### 3.5.13 Basic Water and Sediments (BSW)

D2709 Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge was used. A 50ml sample of toluene and 50ml Jatropha biodiesel were mixed, heated to about 115°C for 30mins and centrifuged for 30mins at 1800rpm.

### 3.5.14 Flash Point

D93 Test Methods for Flash Point by Pensky-Martens Closed Cup Tester (Figure 8).



*Figure 7: Flash point Tester at Quality control Unit -Tema Oil Refinery (TOR), Ghana*



*Figure 8 :Inductively Coupled Plasma-Optical Emission Spectrometer (ICP OES), for metal analyses at Tema Oil Refinery (TOR), Ghana.*

## CHAPTER FOUR

### 4.1 RESULTS AND DISCUSSIONS

#### The Effect of Molar Ratio

The amount of substance involved in a reaction determines how much product will be formed. This is because in order for any reaction to occur, the particles must first collide. This is true whether both particles are in solution, or whether one is in solution and the other a solid. If the concentration is higher, the chances of collision are greater.

The alcohol to oil molar ratio is one of the most important factors that can affect the yield of esters. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 moles of ester and 1 mole of glycerol, but most researchers have found that excess alcohol was required to drive the reaction close to completion. In this research, methanol was used as the preferred alcohol. The effect of methanol in the range of 3:1 to 9:1 (molar ratio) was investigated, keeping other process parameters fixed. The reaction temperature was kept approximately constant at  $55 \pm 5^{\circ}\text{C}$ , and reaction was performed for 60min. In order to study the effect of molar ratio on ester yield, trials were conducted with molar ratios of oil to methanol (in the range of 1:3–1:9), (Table 1). The catalyst concentration and reaction time were 1% w/v of oil and 60min respectively. The yields of methyl esters to the different molar ratio of oil/methanol, is shown in Figure 9. The maximum ester yield was obtained at a methanolysis of oil molar ratio of 1:6. The higher molar ratio than the stoichiometric value results in a higher rate of ester formation and could ensure complete reaction.

In the present work, when the ratio was increased from 1:3 to 1:6, the ester yield was found to be raised from 65 to about 85%. It could be assumed that, the reaction was incomplete for a molar ratio less than 6:1. Moreover, it was observed that at higher molar ratio, a longer time was required for the subsequent separation (to see significant difference between the biodiesel and glycerol layers) stage since separation of the ester layer from the glycerol was difficult. Thus, the separation process was left over night in the case of molar ratio. The excess methanol hinders the separation, so that the relative yield of esters decreases because part of the glycerol may remain in the biodiesel phase. This is due to the fact that methanol can work as an emulsifier with one polar hydroxyl group. Hence, the best results were obtained for a molar ratio of 1:6. From the results shown in Figure 9, it was found that the ester yield increased gradually with increase in molar ratio of methanol to vegetable oil, and decreased after a maximum yield of ester. The ester yield decreases with increase in the molar ratio from this point on; this could be attributed to the fact that the reverse reaction or saponification was favoured, while at lower molar ratios the yield decreased due to incomplete transesterification resulting from insufficient alcohol groups to replace all the acid groups in the triglyceride.

The results obtained are in line with the reports of earlier works of Zhang *et al.* (2003), Freedman *et al.* (1984) and Boocock *et al.* (1996). Meher *et al.* (1999) and Usta (2005) who observed high ester yields utilizing the molar relation of 1:6 during the methanolysis of *P. pinnata* and tobacco seed oils, respectively. The incremental gain in ester yield decreases with increase in the molar ratio. Similar results were reported by earlier researchers for other vegetable oils, soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversions (93 to 98%) at a 6:1 molar ratio. Tanaka *et al.* (1981), in their novel two-step

<b>MOLAR RATIO</b>												
<b>Molar Ratio</b>	<b>Vol Oil/ml</b>	<b>Vol Methanol/ ml</b>	<b>Amount Catalyst/g</b>	<b>Temp/°C</b>	<b>Time/s</b>	<b>Trial1/ ml</b>	<b>Trial2/ ml</b>	<b>Trial3/ ml</b>	<b>Trial4/ ml</b>	<b>Trial5/ ml</b>	<b>Average Yield/ml</b>	<b>% Yield</b>
<b>1:3</b>	<b>48</b>	<b>6</b>	<b>0.48</b>	<b>65</b>	<b>60</b>	<b>33.5</b>	<b>39.5</b>	<b>36</b>	<b>36</b>	<b>33</b>	<b>35.6</b>	<b>65.93</b>
<b>1:4</b>	<b>48</b>	<b>8</b>	<b>0.48</b>	<b>65</b>	<b>60</b>	<b>41</b>	<b>43</b>	<b>44</b>	<b>44</b>	<b>32</b>	<b>38</b>	<b>70.37</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.48</b>	<b>65</b>	<b>60</b>	<b>45.5</b>	<b>46.5</b>	<b>46</b>	<b>47</b>	<b>45</b>	<b>46</b>	<b>85.19</b>
<b>1:8</b>	<b>48</b>	<b>16</b>	<b>0.48</b>	<b>65</b>	<b>60</b>	<b>47</b>	<b>45</b>	<b>46.5</b>	<b>45</b>	<b>44</b>	<b>44.5</b>	<b>82.41</b>
<b>1:9</b>	<b>48</b>	<b>18</b>	<b>0.48</b>	<b>65</b>	<b>60</b>	<b>45.5</b>	<b>41</b>	<b>45</b>	<b>47</b>	<b>38</b>	<b>42.5</b>	<b>78.70</b>

*Table 1: Values for the optimization of the Molar Ratio for the transesterification of Jatropha curcas seed oil.*

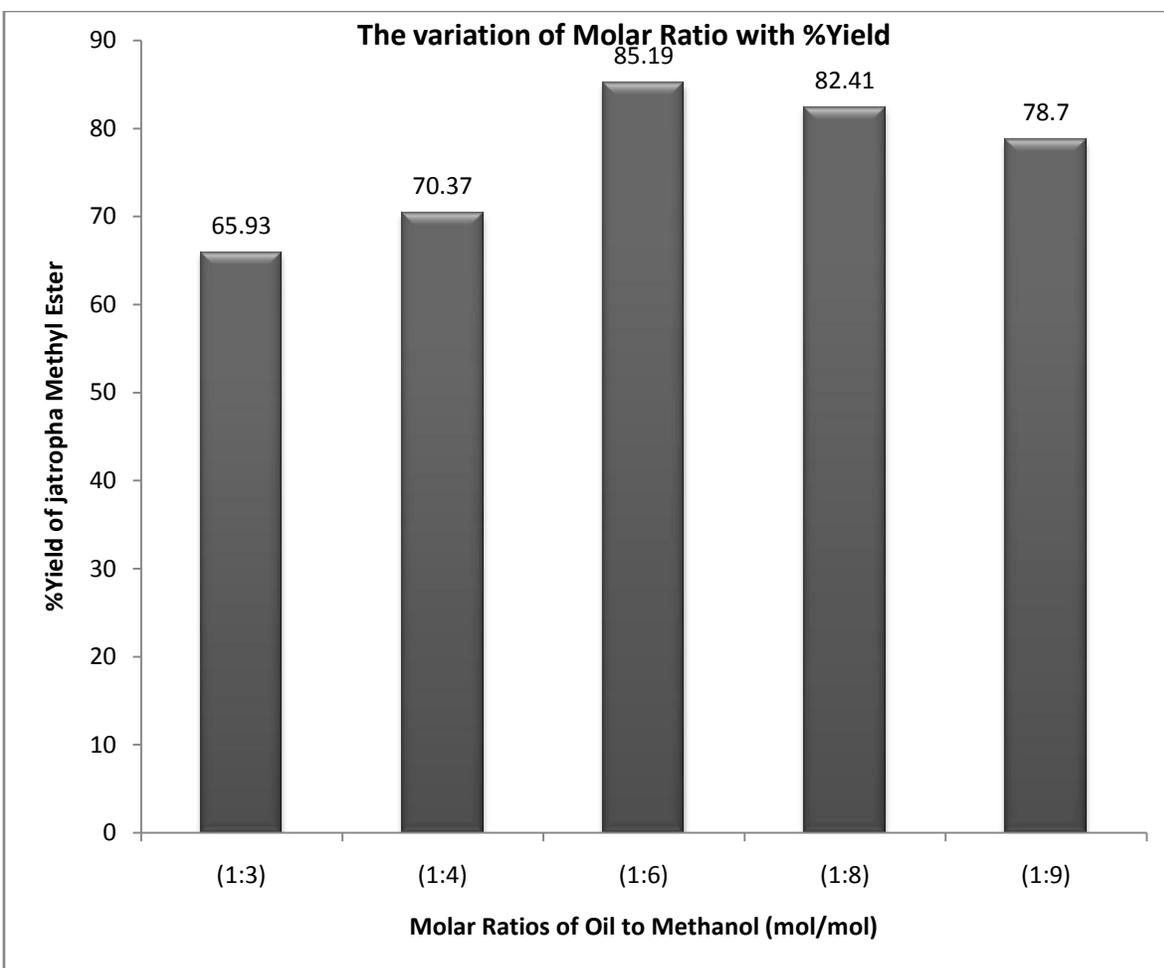


Figure 9: The variation of Molar Ratio with % Jatropha methyl ester yield. Reaction conditions: KOH; 1.2%w/v of oil, temperature;  $55 \pm 5^\circ\text{C}$ , Time of reaction; 60min.

transesterification of oils and fats such as tallow, coconut oil and palm oil, used 6:1 to 30:1 molar ratios with alkali catalysis to achieve a conversion of 99.5%.

#### 4.2 The Effect of Catalyst

In a chemical reaction, the bonds holding the reactants together must first be broken before the reaction can begin. Breaking bonds requires energy, and the minimum energy needed to start a reaction is referred to as the activation energy. Catalysts work by providing an alternative reaction pathway for the breaking and remaking of bonds. The activation energy for this new pathway is often less than the activation energy of the normal pathway. When a homogeneous

catalyst is present, one of the reactants (substrate) reacts with the catalyst forming an intermediate product. The intermediate product then reacts with the other reactant to form the final product.

The effect of KOH concentration was studied in the range of 0.5–1.10g (1.0 – 2.2% w/v of oil) of KOH (Table 2). The reaction temperature and time were kept constant at 55°C and 1 h, respectively. The results for different amounts of catalyst are shown in Figure 10.

It was found that the ester yield decreased as the amount of catalyst increased from 0.5 to 1.10g. Ester yield decreased as the KOH concentration increased above 0.6g. This lesser yield at high KOH concentration may possibly be due to high soap formation. Excess KOH reduces the yield and quality, and also leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end.

The effects of KOH concentrations on the transesterification of the Jatropha seed oil were investigated with their concentrations varying from 1-2.2% w/v or a mass in the range of 0.50 to 1.10g. The reaction conditions during the whole process were fixed at reaction time of 60 min, 65°C and a molar ratio of 1:6.

Ester yield for 6:1 ratio with 1.2% potassium hydroxide after 60 min gave the best yield.

<b>AMOUNT OF CATALYST (g)</b>											
<b>Molar ratio</b>	<b>Vol of /ml</b>	<b>Vol of Methanol /ml</b>	<b>Amount of Catalyst</b>	<b>Temp /</b>	<b>Time /</b>	<b>Trial1 /ml</b>	<b>Trial2 /ml</b>	<b>Trial3 /ml</b>	<b>Trial4 /ml</b>	<b>Average Yield/ml</b>	<b>% Yield</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.5</b>	<b>65</b>	<b>60</b>	<b>43.5</b>	<b>43</b>	<b>45</b>	<b>44.5</b>	<b>44</b>	<b>81.48</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>60</b>	<b>46.5</b>	<b>45.5</b>	<b>47.5</b>	<b>46.5</b>	<b>46.5</b>	<b>86.11</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.7</b>	<b>65</b>	<b>60</b>	<b>44.5</b>	<b>44</b>	<b>46</b>	<b>45.5</b>	<b>45</b>	<b>83.33</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.8</b>	<b>65</b>	<b>60</b>	<b>42</b>	<b>43.5</b>	<b>45</b>	<b>45.5</b>	<b>44</b>	<b>81.48</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.9</b>	<b>65</b>	<b>60</b>	<b>43.5</b>	<b>44</b>	<b>45.5</b>	<b>43</b>	<b>44</b>	<b>81.48</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>1</b>	<b>65</b>	<b>60</b>	<b>42</b>	<b>43.5</b>	<b>44</b>	<b>42.5</b>	<b>43</b>	<b>79.63</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>1.1</b>	<b>65</b>	<b>60</b>	<b>39</b>	<b>36.5</b>	<b>37.5</b>	<b>35</b>	<b>37</b>	<b>68.52</b>

*Table 2: Values for the optimization of the Amount of Catalyst for the transesterification of Jatropha curcas seed oil.*



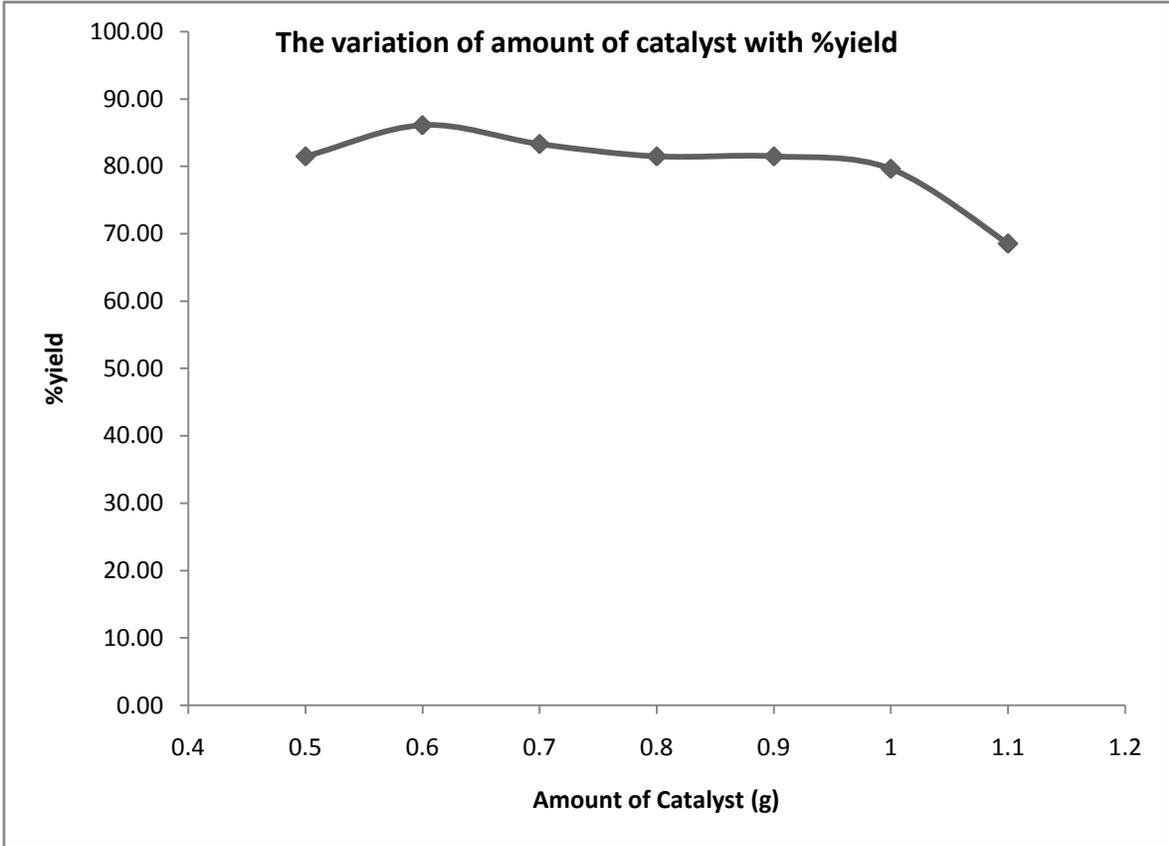


Figure 10: The variation of amount of KOH with % yield. Reaction conditions: Molar ratio; 1:6, Temperature; 65°C, Time; 60min.

**4.3 The Effect of Reaction Temperature**

The temperature is necessary in the collision and kinetics of a reaction. Entropy increases with increasing temperature, causing the reacting species to collide more frequently or faster with sufficient energy, thus shifting the equilibrium position towards the favoured direction. For studying the effect of temperature on the yield of the transesterification reaction, the reaction temperature was varied as 45, 55, 65, 75 and 85°C, while the other parameters such as molar ratio of methanol to oil (6:1), reaction time (60min) and amount of catalyst (1.2%) were kept constant. The effect of reaction temperature on the ester yield is shown in Figure 11. It is found

that ester yield decreases as the reaction temperature increases above 65°C, it may have probably favoured the side reaction; this is saponification. High process temperatures tend to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification.

Transesterification can occur at different temperatures, depending on the oil used. In methanolysis of *Jatropha* oil, the reaction proceeded with appreciable yield at a temperature range of 25°C - 85°C with a molar ratio of 6:1 and 1.2% w/v (by weight of oil) of KOH catalyst. Five different temperatures were used. After 60min of reaction, ester yields were approximately 81.5, 87, 86, 85 and 84% for 45, 55, 65, 75 and 85 °C, respectively, as shown in Table 3. After 60 min, ester formation was observed to increase from 45 - 55°C and decreased gradually from 65 - 85°C. Temperature clearly influenced the reaction rate and yield of ester. High temperature will burn the alcohol and will result in much lesser yield, this could have accounted for the fall in yield after 55°C (as shown in Figure 11).

A study by Leung and Guo (2006) showed that temperatures higher than 323 K had negative impact on the product yield for neat oil. Alkaline alcoholysis of vegetable oils is normally performed near the boiling point of the alcohol. The reaction temperature above boiling point of alcohol is ignored as high temperatures turn to accelerate the saponification of glycerides by the base catalyst before completion of the alcoholysis.

<b>TEMPERATURE(°C)</b>										
<b>Molar Ratio</b>	<b>Vol of oil/</b>	<b>Vol of methanol/ml</b>	<b>Amount of Catalyst/g</b>	<b>Temp/°C</b>	<b>Time/s</b>	<b>Trial1 /ml</b>	<b>Trial2/ml</b>	<b>Trial 3 /ml</b>	<b>Average Yield/ ml</b>	<b>% Yield</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>45</b>	<b>60</b>	<b>43.5</b>	<b>44</b>	<b>44.5</b>	<b>44</b>	<b>81.48</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>55</b>	<b>60</b>	<b>46.5</b>	<b>47</b>	<b>47.5</b>	<b>47</b>	<b>87.04</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>60</b>	<b>46.5</b>	<b>47</b>	<b>46</b>	<b>46.5</b>	<b>86.11</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>75</b>	<b>60</b>	<b>45</b>	<b>46</b>	<b>47</b>	<b>46</b>	<b>85.19</b>
<b>1:6</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>85</b>	<b>60</b>	<b>46</b>	<b>45</b>	<b>45.5</b>	<b>45.5</b>	<b>84.26</b>

*Table 3: Values for the optimization of the Reaction Temperature for the transesterification of Jatropha curcas seed oil.*

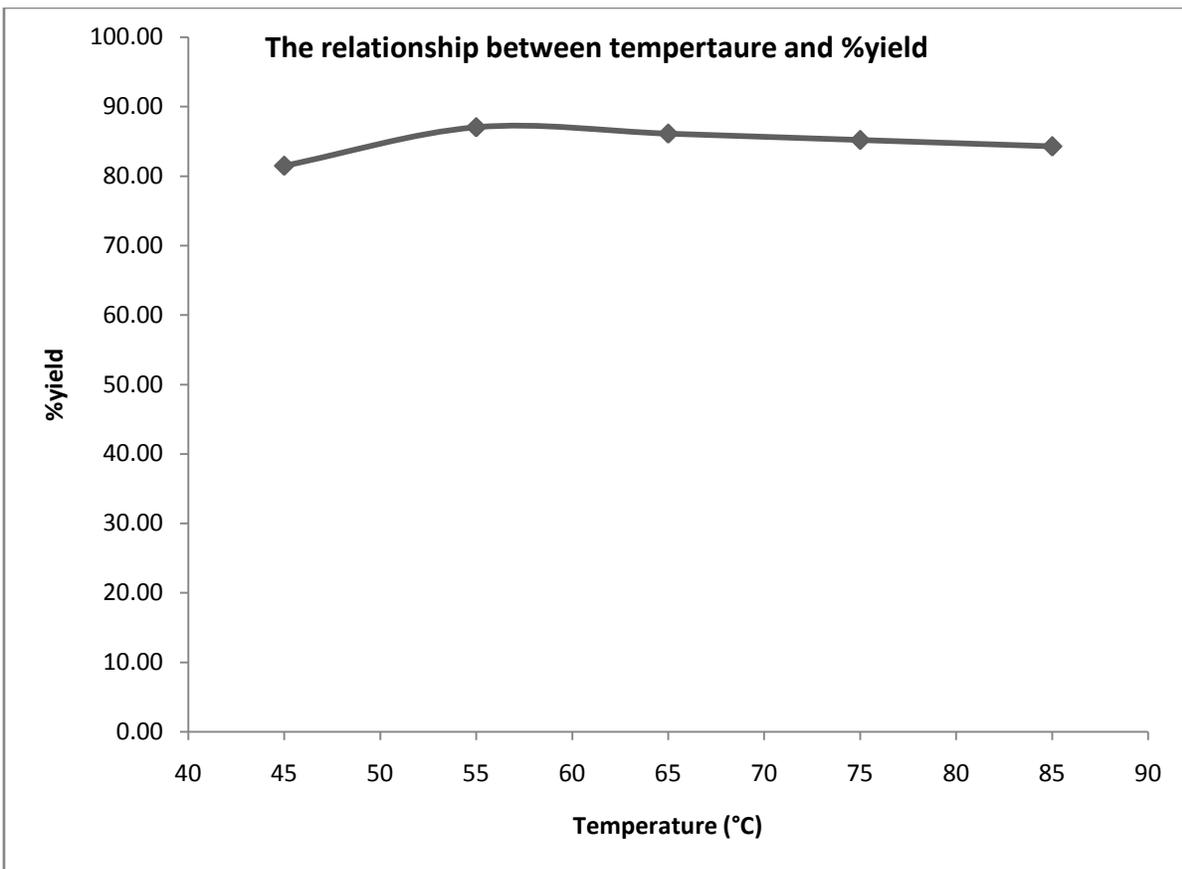


Figure 11: The variation of % yield with Temperature.

#### 4.4 The Effect of Reaction Time

The conversion rate increases with reaction time. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into Jatropha oil. In this work, the effect of reaction time from 10 min to 60 min on the reaction yield was investigated. It was found that as the reaction time was increased beyond 45 min, the ester yield decreased slightly (as shown in Figure 12). Several investigators found that the reaction starts very fast and almost 80% of the conversion takes place in the first 5 min, and after 1 h, almost 93–98% conversion of the triglycerides into ester takes place (Fukuda *et al.*, 2001 and Furuta *et al.*, 2006).

TIME OF REACTION										
Molar Ratio	Vol Oil/ml	Vol Methanol/ml	Amount Catalyst/g	Temp/°C	Time/min	Trial1/ml	Trial2/ml	Trial3/ml	Average Yield/ml	% Yield
1:6	48	12	0.6	55	15	44	43.5	44.5	44	81.48
1:6	48	12	0.6	55	30	46	45	44	45	83.33
1:6	48	12	0.6	55	45	46.5	47	47.5	47	87.04
1:6	48	12	0.6	55	60	44	44.5	43.5	44	81.48
1:6	48	12	0.6	55	75	46.5	45.5	46	44	81.48

Table 4: Values for the optimization of the Time of Reaction for the transesterification of *Jatropha curcas* seed oil.

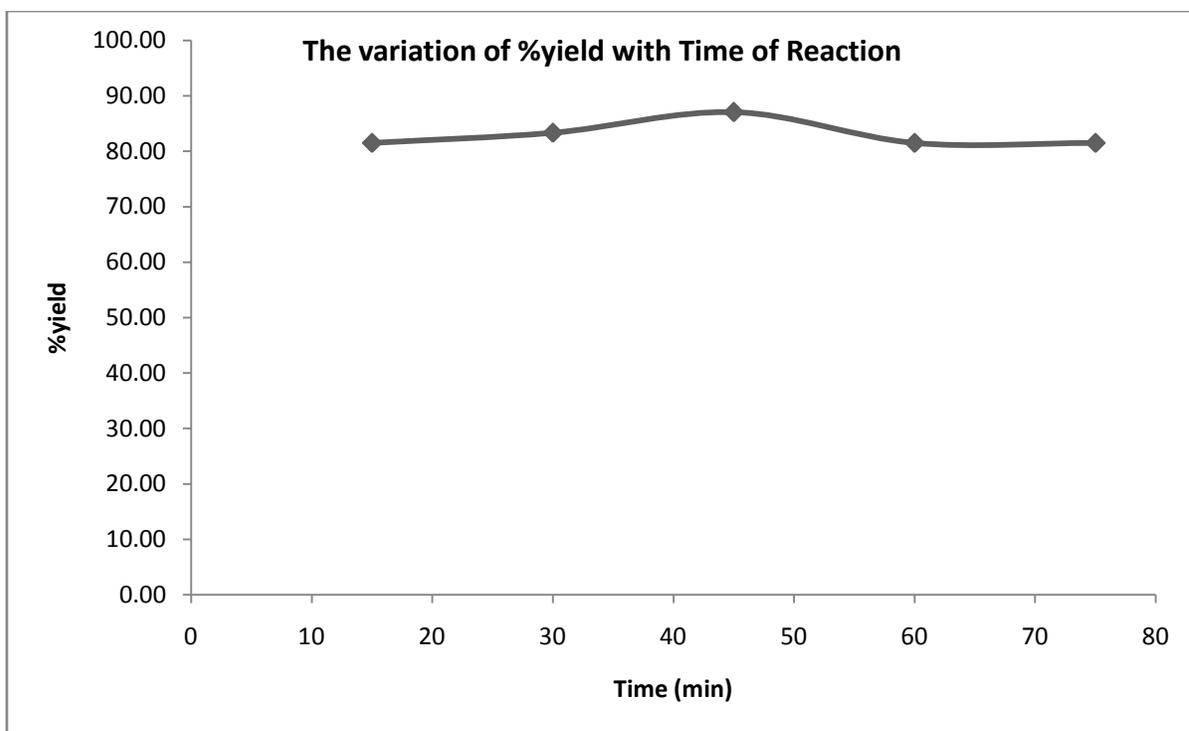


Figure 12: The Effect of Reaction Time on the % Yield of *Jatropha methyl ester*.

#### 4.5 Effect of stirring

The mixing (or the effect of stirring) appears to be of particular importance for the transesterification process; it ensures homogeneity within the reaction mixture. It increases the contact area between oils and potassium hydroxide or methanol solution. Mixing facilitates the initiation of the reaction. Without mixing, the reaction occurred only at the interface of the two layers and considered too slow to be feasible. In this study, methanolysis was conducted with different rate of stirring such as 100, 250, 500, 600 and 1000 revolutions per minute (rpm). The yield of methyl esters versus time at different rates of mixing is shown in Figure 13. It was observed that the reaction of methanolysis was practically incomplete at 100 rpm and only

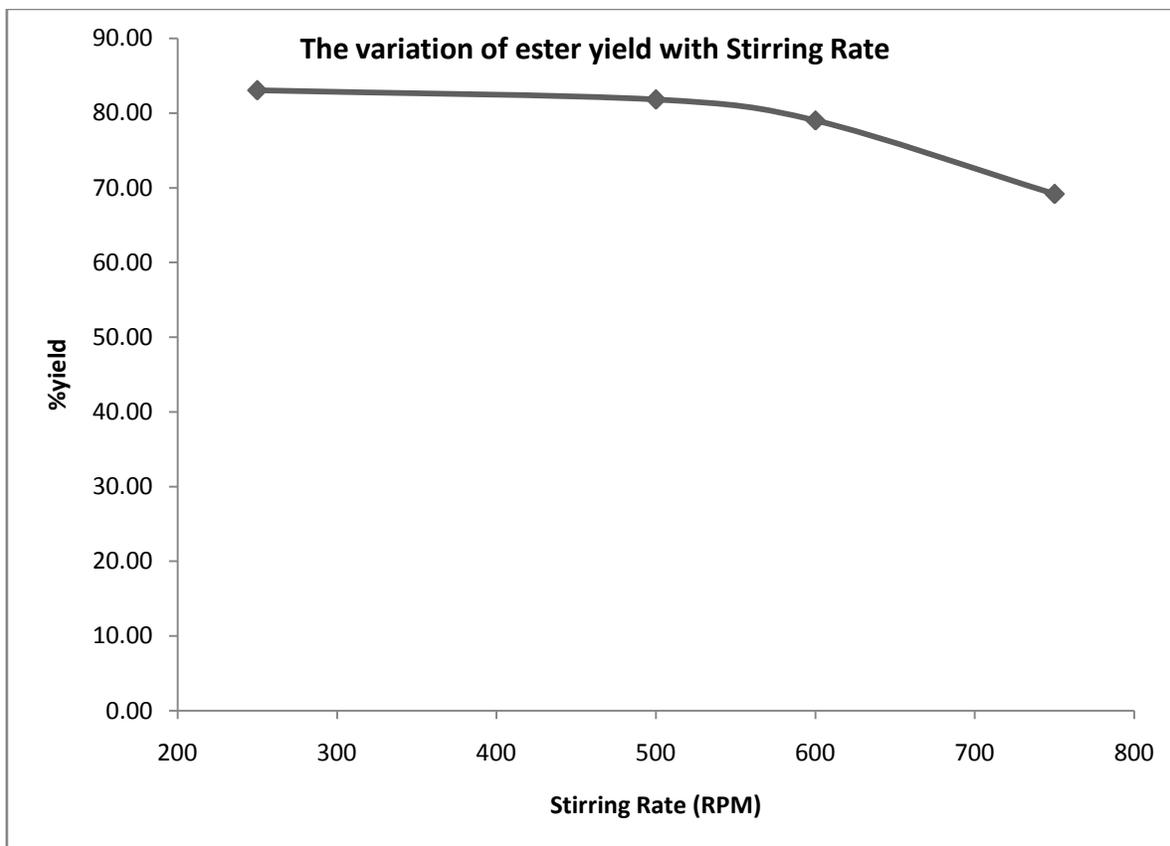
<b>STIRRING RATE</b>											
<b>Molar Ratio</b>	<b>Vol of oil(ml)</b>	<b>Vol of methanol (ml)</b>	<b>Amount of Catalyst (g)</b>	<b>Temp(°C)</b>	<b>Time (min)</b>	<b>RPM</b>	<b>Trial I</b>	<b>Trial II</b>	<b>Trial III</b>	<b>Vol of Yield</b>	<b>% Yield</b>
<b>(1:6)</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>45</b>	<b>250</b>	<b>44.5</b>	<b>46</b>	<b>44</b>	<b>44.83</b>	<b>83.02</b>
<b>(1:6)</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>45</b>	<b>500</b>	<b>43.5</b>	<b>44.5</b>	<b>44.5</b>	<b>44.17</b>	<b>81.79</b>
<b>(1:6)</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>45</b>	<b>600</b>	<b>43</b>	<b>40.5</b>	<b>44.5</b>	<b>42.67</b>	<b>79.01</b>
<b>(1:6)</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>45</b>	<b>750</b>	<b>38.5</b>	<b>35.5</b>	<b>38</b>	<b>37.33</b>	<b>69.14</b>
<b>(1:6)</b>	<b>48</b>	<b>12</b>	<b>0.6</b>	<b>65</b>	<b>45</b>	<b>1000</b>	<b>*</b>	<b>*</b>	<b>*</b>	<b>*</b>	<b>*</b>

*Table 5: Values for the optimization of the Stirring Rate for the transesterification of Jatropha curcas seed oil.*

*\*\_ Could not be measured due to difficulty in separation between ester and glycerol layers.*

exhibited a yield which was difficult to separate. The yield was observed to decrease as the stirring rate went above 500rpm; the backward reaction may have been favoured when mixing intensity was accelerated. The yield of methyl esters at 250 rpm and 500 rpm were approximately 83 and 82% respectively after 45min of reaction (Table 5).

Stirring can play an important role in the yield of biodiesel production.



**Figure 13: The variation of ester yield with Stirring Rate. Conditions of reaction: molar ratio; 1:6, KOH 1.2%, Temperature; 65°C, and time; 45min.**

These results are in conformity with observations made by Ma *et al.* (1999) and Peterson *et al.* (1992), who studied the effect of agitation on the transesterification of vegetable oil and concluded that higher agitation promoted the homogenization of the reactants and thus lead to higher yields.

Stirring can play an important role in the yield of biodiesel production. Meher *et al.* (2006) conducted the transesterification reaction with 180, 360 and 600 revolutions per minute (rpm) and reported incomplete reaction with 180 rpm. The yield of methyl ester was the same with 360 and 600 rpm. Sharma and Singh (2007) reported that the mode of stirring too plays a vital role in the transesterification reaction. The yield of biodiesel increased from 85% to 89.5% when magnetic stirrer (1000 rpm) was replaced with mechanical stirrer (1100 rpm). A possible explanation may be a thorough mixing of the reactants with the mechanical stirrer.

#### **4.6 Process Parameter Selection**

The optimum reaction time and reaction temperature were selected as 45min and 55°C. It is clear that as the catalyst concentration is increased, the ester yield decreases for all molar ratios of methanol to oil. Ester yield is found to be a maximum for 6:1 molar ratio of methanol to oil and 0.60g (1.2% w/v of oil). The gain in yield with 6:1 molar ratio was not enough to justify the increase in the quantity of the additional alcohol used in the reaction, as the catalyst amount increases, the ester yield decreases. In this study, a mass of 0.60g (1.2% w/v) KOH was found to be optimum as it gave the best ester yield. In summary, for the transesterification of crude *Jatropha* seed oil, optimum reaction conditions were found to be 55°C reaction temperature, 6:1 molar ratio of methanol to oil, 1.2% catalyst and 45min reaction time. These conditions gave an ester yield of 90.18% weight of oil used.

#### **4.7 Rate and Order of Reaction**

Rate of reaction can be defined as the decrease in the concentration of reactants per unit time or the increase in the concentration of product per unit time. The rate of chemical reactions can only be found by experimentation. There are no theoretical or mathematical ways to calculate the rate of a reaction. The graphical approach was used to determine the order of reaction (Figures 14a, b, c, d, e

and 15a, b, c, d, e show those for second order and first order respectively). The power of the concentration in the rate law expression is called the order with respect to the reactant or product.

The order of reaction for the transesterification of *Jatropha curcas* to biodiesel was deduced by plotting graphs for; zero order (Conc against time), first order (ln(Conc) against time) and for second order (1/Conc against time). The  $r^2$  values obtained in Table 6 were then used to deduce the order of the reaction. The reaction was observed to be a first order reaction considering the  $r^2$  value for the first order, they were mostly higher (at 65, 75 and 85°C) than those of zero order and second order reactions.

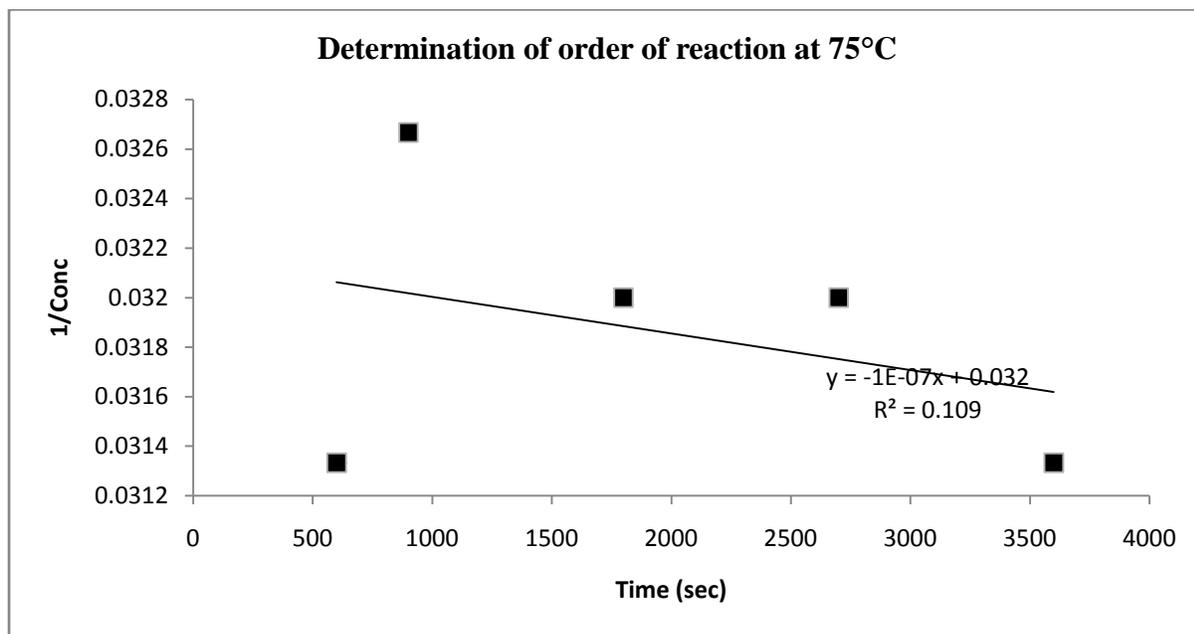


Figure 14a: Verification of Second order behavior for preparation of the *Jatropha methyl ester* at 75°C.

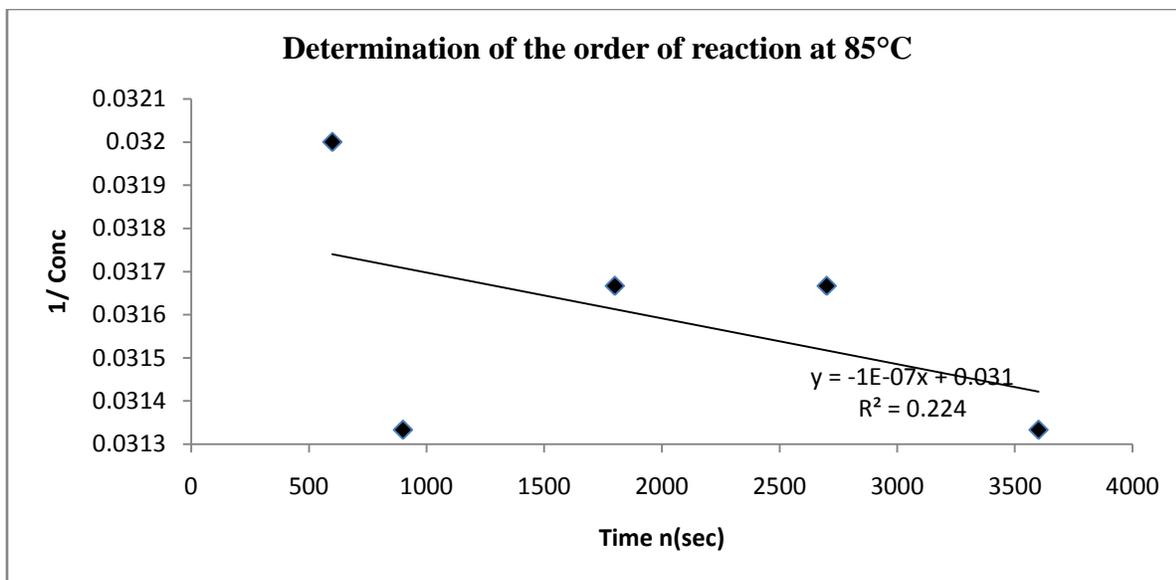


Figure 14b: Verification of Second order behavior for preparation of the Jatropha methyl ester at 85°C, MolarRatio (1:6), KOH (1.2%w/v),RPM (500),

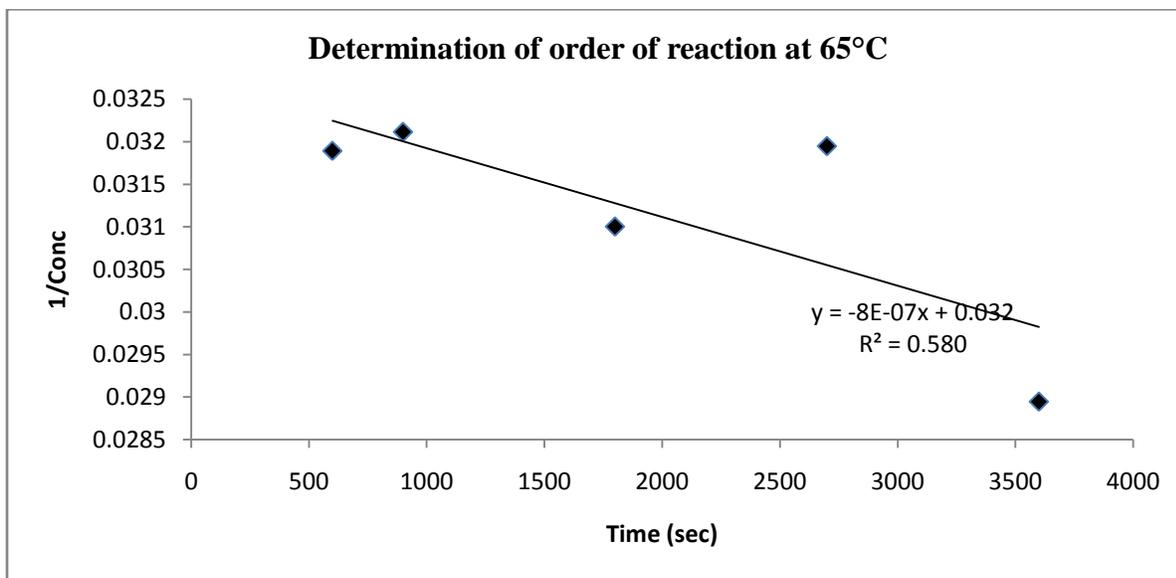


Figure 14c: Verification of Second order behavior for preparation of the Jatropha methyl ester at 65°C, MolarRatio (1:6), KOH (1.2%w/v),RPM (500),

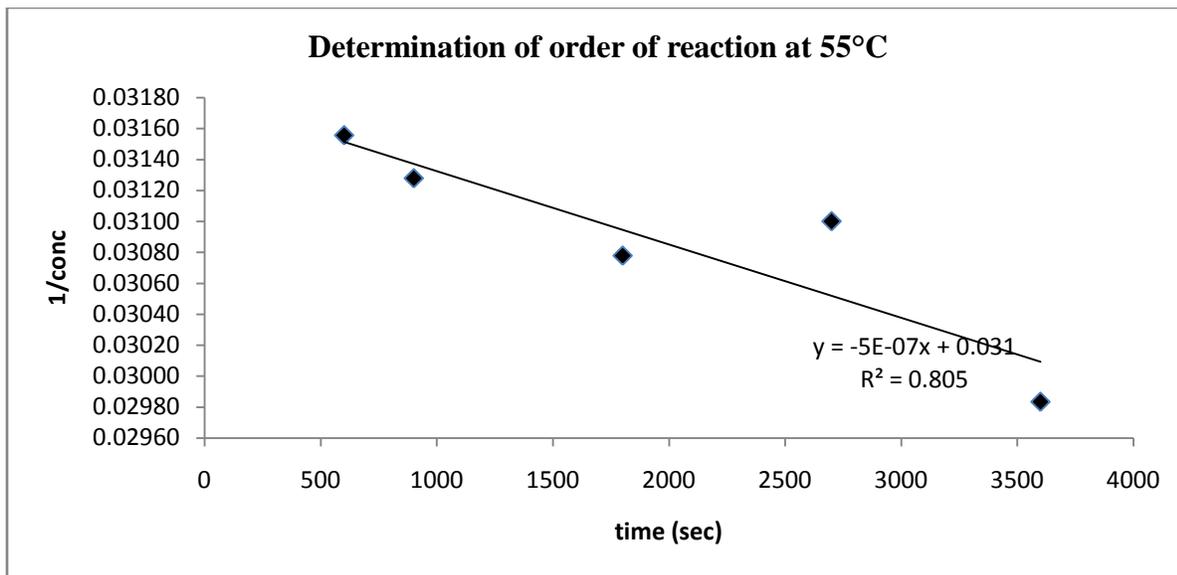


Figure 14d: Verification of Second order behavior for preparation of the Jatropha methyl ester at 55°C, MolarRatio (1:6), KOH (1.2%w/v),RPM (500),

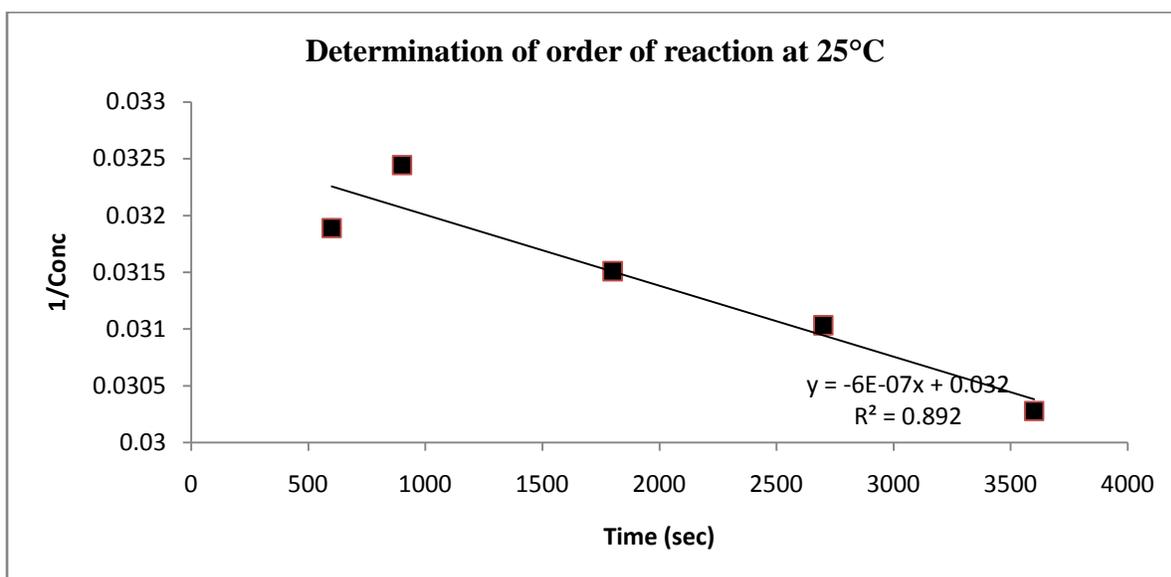
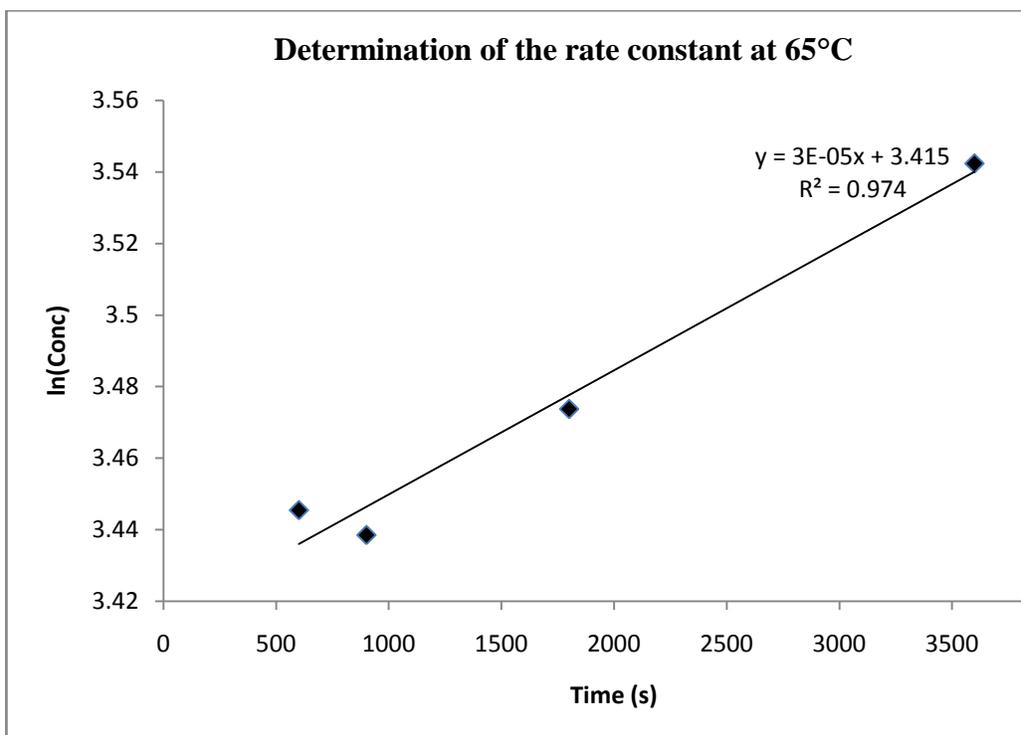


Figure 14e: Verification of Second order behavior for preparation of the Jatropha methyl ester at 25°C, MolarRatio (1:6), KOH (1.2%w/v),RPM (500).

Temp(°C)	r <sup>2</sup> values		
	Zero order (Conc vrsTime)	First order (Conc) vrs Time)	Second order (1/Conc vrs Time)
25	0.8969	0.8946	0.8920
55	0.8008	0.8032	0.8056
65	0.5831	0.9745	0.5801
75	0.1064	0.9000	0.1092
85	0.2226	0.9128	0.2248

**Table 6:** Verification of the order of reaction for the transesterification of *Jatropha curcas* seed oil.



**Figure 15a:** Determination of rate constant and order of reaction at optimized conditions; Molar Ratio (1:6), KOH (1.2%w/v), R PM (500), Temp. (65°C). The Rate Constant (k) = slope of straight line ( $3 \times 10^{-5}$ )

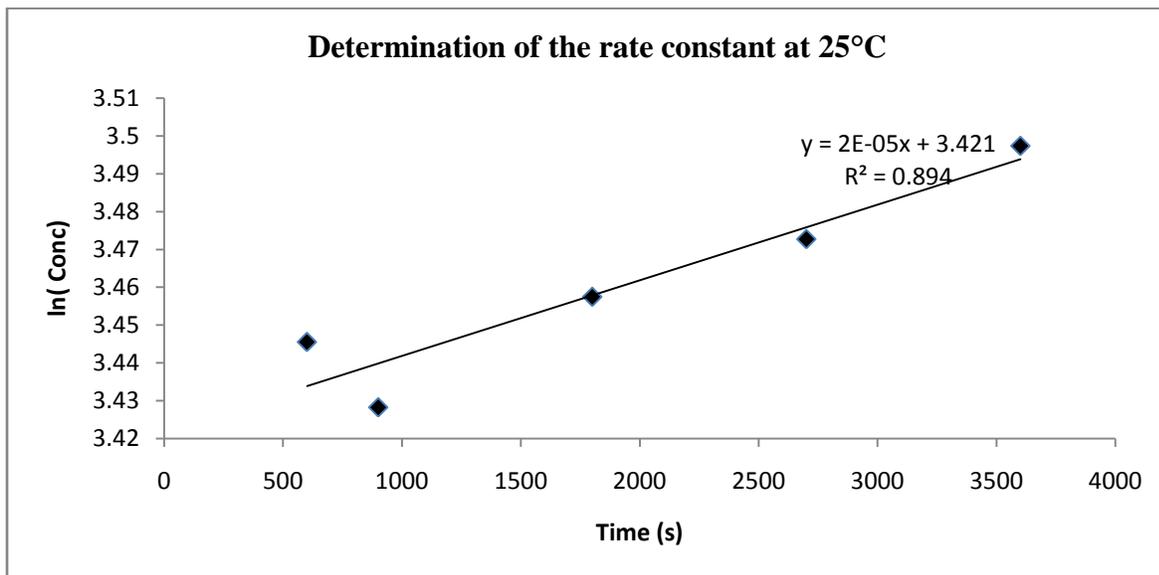


Figure 15b: Determination of rate constant at optimized conditions; Molar Ratio (1:6), KOH (1.2%w/v), RPM (500), Temp. (25°C). The Rate Constant ( $k$ ) = slope of straight line ( $2 \times 10^{-5}$ )

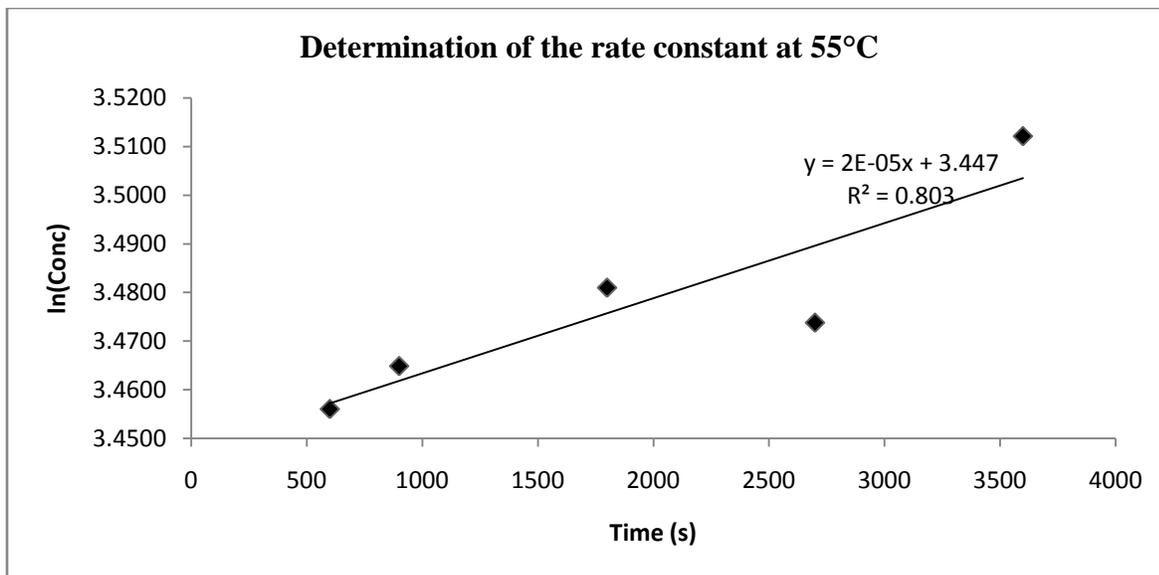


Figure 15c: Determination of rate constant at optimized conditions; Molar Ratio (1:6), KOH (1.2%w/v), RPM (500), Temp. (55°C). The Rate Constant ( $k$ ) = slope of straight line ( $2 \times 10^{-5}$ )

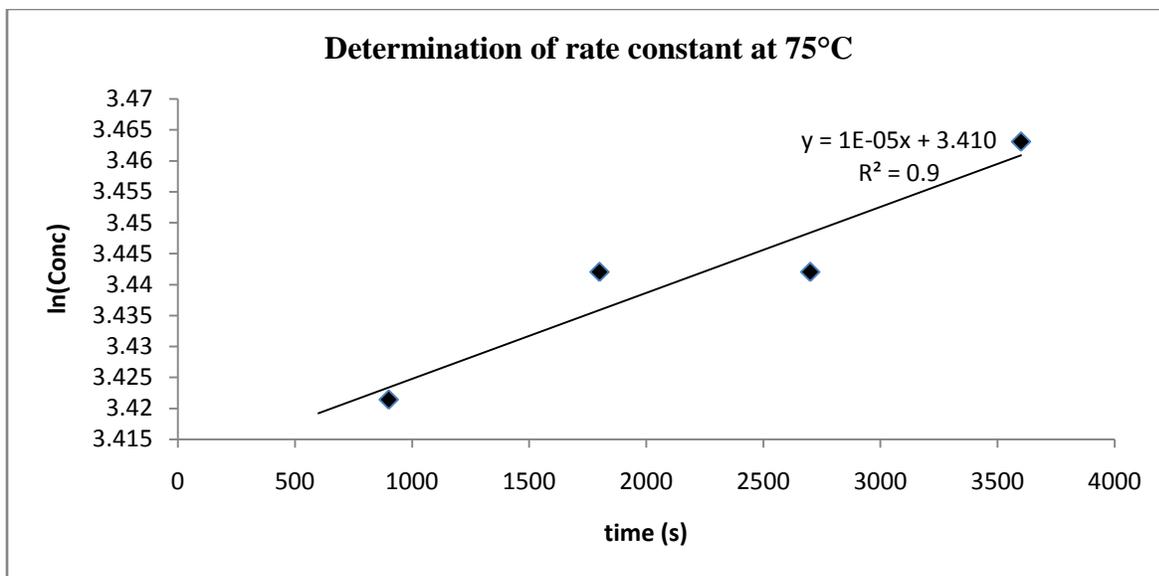


Figure 15d: Determination of rate constant at optimized conditions; Molar Ratio (1:6), KOH (1.2%w/v), RPM (500), Temp. (75°C). The Rate Constant ( $k$ ) = slope of straight line ( $1 \times 10^{-5}$ )

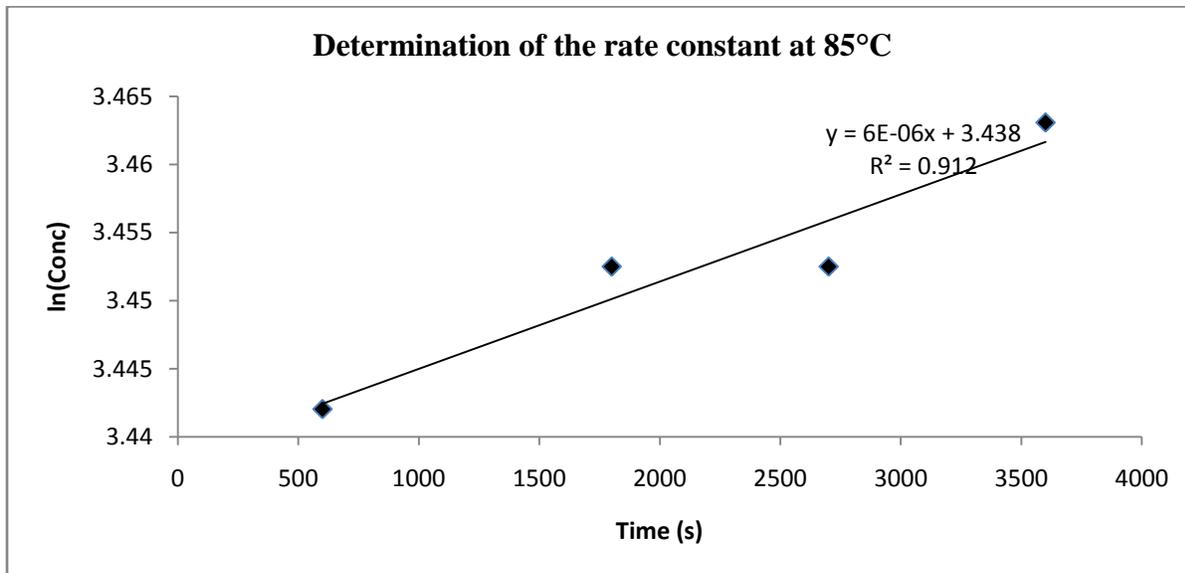


Figure 15e: Determination of rate constant at optimized conditions; Molar Ratio (1:6), KOH (1.2%w/v), RPM (500), Temp. (85°C). The Rate Constant ( $k$ ) = slope of straight line ( $6 \times 10^{-6}$ )

## 4.8 Rate Constant

Considering the optimized conditions, the rate constant was determined from the slope of a plot of  $\ln(\text{Conc})$  of ester against the time of reaction (for first order reaction), the rate constant is not actually a true constant. It varies, for example, if there is a change in the temperature of the reaction, addition of a catalyst, or change in type of catalyst. The rate constant is constant for a given reaction in which the concentration of the reactants changes over time; thus at every temperature range used a different rate constant was observed as shown in the plots in Figures 15a, b, c, d and e. The rate constants calculated over the five different temperature ranges (25, 55, 65, 75 and 85°C) gave  $k$  values as  $2 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $3 \times 10^{-5}$ ,  $1 \times 10^{-5}$  and  $6 \times 10^{-6}$  respectively.

## 4.9 Arrhenius Parameters

The collision theory shows that for a reaction to occur the reactants should collide with the proper orientation and sufficient energy; Arrhenius believed that for molecules to react upon collision, they must become "activated," and the parameter  $E_a$  has become known as the activation energy; only some collisions occur with enough energy to overcome the activation barrier to form products. Experimentally from a plot of  $\ln k$  against  $1/T$  (where  $T$ =absolute temperature) for temperatures of 25, 55, 65, 75 and 85°C, was used to determine  $E_a$  and  $A$  (Table 7). This gave a straight line with a slope of  $-E_a/R$  and the frequency factor or pre-exponential factor ( $A$ ) was calculated from natural log of the intercept ( $\ln A$ ). From Figure 16, the minimum energy required for the conversion of Jatropha oil to biodiesel is  $53,814 \text{ J mol}^{-1}$  and the pre-exponential factor  $A$  was  $1.162 \times 10^{13}$  per second ( $\text{s}^{-1}$ ).

The activation energy was found to be;  $E_a = 53,814 \text{ J per mol.}$ ,  
and the pre-exponential factor ( $A$ );  $A = 1.162 \times 10^{13} \text{ s}^{-1}$ .

From the results the process of transesterification of *Jatropha curcus* seed oil required about

<b>Determination of the Arrhenius Parameters ( Activation Energy (Ea) and Pre-exponential Factor)</b>				
<b>Temp ( °C)</b>	<b>Temp (K)</b>	<b>1/Temp (per K)</b>	<b>k</b>	<b>lnk</b>
<b>25</b>	<b>298</b>	<b>0.003355705</b>	<b>0.00002</b>	<b>-10.81978</b>
<b>55</b>	<b>328</b>	<b>0.00304878</b>	<b>0.00002</b>	<b>-10.81978</b>
<b>65</b>	<b>338</b>	<b>0.00295858</b>	<b>0.00003</b>	<b>-10.41431</b>
<b>75</b>	<b>348</b>	<b>0.002873563</b>	<b>0.00001</b>	<b>-11.51293</b>
<b>85</b>	<b>358</b>	<b>0.002793296</b>	<b>0.000006</b>	<b>-12.02375</b>

**Table 7: Data for the determination of Arrhenius Parameters**

54KJ or greater of energy per mol of oil for the reaction to occur; ie to overcome the activation barrier to form Jatropha methyl esters (biodiesel). Huayang *et al* (2007) in their work for the activation energy for transesterification of soybean oil using supercritical methanol, got a value of about 56KJ mol<sup>-1</sup>. Yun Liu and colleagues (2009) in their work for the preparation of biodiesel from waste cooking oil catalyzed by combined lipases in *tert*-butanol medium also deduced the reaction to be a pseudo-first-order reaction, and the calculated activation energy was 51.71 kJmol<sup>-1</sup>.

#### 4.10 Fuel Properties

**Table 8 gives a summary of all the fuel properties analyzed and the limits that they were compared with (ASTM standards).**

#### 4.10.1 Density

Biodiesel generally has a higher density than mineral diesel (EN 590 820-845 kg/m<sup>3</sup> at 15°C). Density increases with a decrease in chain length and with unsaturation. This can impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. The density was evaluated to be 886.4g/cm<sup>3</sup> at 31°C which is within the EN limits for biodiesel. The biodiesel had a lower density compared to the crude Jatropha oil (909 Kg/m<sup>3</sup>).

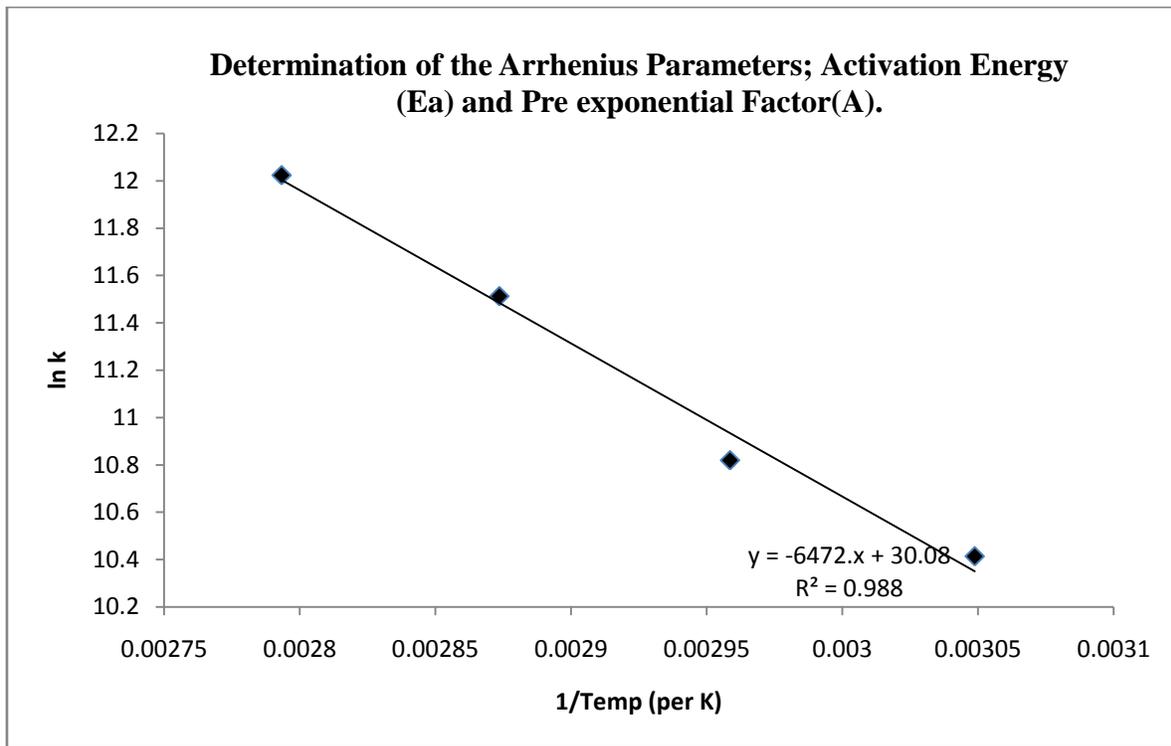


Figure 16: The variation of rate constant with temperature. From the equation of the line the value  $E_a$  and  $A$  can be determined.

#### 4.10.1 Viscosity

Viscosities of neat vegetable oils are many times higher which leads to serious problems in unmodified engines. The increase in viscosity results in poor atomization and incomplete

combustion which leads to coking of injector tips. This results in engine power loss. Biodiesel still has higher viscosity than mineral diesel (3.50-5.00 mm<sup>2</sup>/s at 40°C vs 2.00-4.50 mm<sup>2</sup>/s). Viscosity decreases with unsaturation but increases markedly with contamination by mono, di or triglycerides. The viscosity was 7.9, this value falls outside the ASTM limits (1.6 -6.0 Cst) for biodiesel. It should, however, be noted that density has a direct effect on viscosity. At 15°C the density would be lesser than the value at 31°C, and this could reduce the viscosity obtained. Incomplete transesterification could have also contributed to this factor

#### 4.10.2 **Flash Point**

Pure rapeseed methyl ester has a flash point value of up to 170°C. This test is used to determine the residual components within the fuel that are combustible. Especially methanol, which is a particular hazard due to its invisible flame. The flash point of the biodiesel could not be determined because the equipment was faulty, this property is very important for safe handling of biodiesel.

#### 4.10.3 **Sulphur Content**

Sulphur emissions are harmful to human health and high sulphur fuels cause greater engine wear. Biodiesel derived from pure Rapeseed oil will contain virtually no Sulphur, however FAME derived from animal sources may contain significant quantities. The biodiesel contained about 0.01 %wt, this value is acceptable because it is less than the 1.0max ASTM limits given.

#### 4.10.4 **Carbon Residue**

The Carbon Residue is the material left after evaporation of a sample fuel. This is a measure of the tendency of a fuel to produce deposits on injector tips and the combustion chamber. For FAME

samples it is an indication of the amount of glycerides, free fatty acids, soaps and catalyst residues remaining within the sample. The carbon residue was found to be approximately 0.16%wt which is within the ASTM limits of 0.2max.

#### **4.10.5 Cetane Number**

This serves as a measure of ignition quality. This is the most pronounced change from vegetable oil to the transesterified product. Fuels with low cetane numbers show an increase in emissions due to incomplete combustion. Palm Oil and Tallow derived biodiesels have the best cetane numbers. The lower limit for cetane index is 47 by ASTM standards. That of the sample gave 54.55, which is above the lower limit for cetane number. Thus the results obtained are acceptable.

#### **4.10.6 Water Content**

As FAME is hygroscopic it can pick up water during storage and as such there can be problems meeting the specification. Free water promotes biological growth and the reverse reaction turning biodiesel into free fatty acids. The Basic Water and Sediments content gave a value of about 0.01% volume, which is acceptable according to the ASTM limits of 0.05%.

#### **4.10.7 Acid Value**

Acid value is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in mg KOH required to neutralize 1g of FAME. High fuel acidity is linked with corrosion and engine deposits. The sample contained 0.14mgKOH/g of Total Acid; this value was also significantly lower than the crude Jatropha oil (6.4mg/g). The ASTM value for TAN is 0.5mgKOH/g; this implies that that of the sample is acceptable.

#### 4.10.8 Group I Metals

Sodium and Potassium are limited to a combined level of 5ppm. These arise from the addition of catalyst, and result in high ash levels in the engine. The Na and K content was 1.125ppm which did not exceed the ASTM standard of 5ppm, thus the Na and K levels are acceptable and not harmful.

#### 4.10.9 Group II Metals

Calcium and Magnesium are limited to a combined level of 5ppm. These may arise from the addition of hard water in the washing process. Calcium and Magnesium soaps have been related to injector pump sticking. Ca and Mg were also found to be 0.05ppm, which is less than the ASTM standard of 5ppm. This indicates that the levels are not harmful for usage of the biodiesel.

PROPERTY	UNITS	ASTM METHODS	JATROPHA (CRUDE)	ASTM LIMITS	JATROPHA BIODIESEL
METALS		EN - 14538			
Ca & Mg	Ppm			5max	0.05
Na & K	ppm			5max	1.125
Ni	Ppm			5max	0.45
Pb	Ppm	EN - 14538		5max	<0.025
V	Ppm	EN - 14538		5max	<0.025

Table 8: Fuel properties of *Jatropha methyl ester* compared with ASTM limits.

PROPERTY	UNITS	ASTM METHODS	JATROPHA (CRUDE)	ASTM LIMITS	JATROPHA BIODIESEL
Density	Kg/m <sup>3</sup>	ASTM D-1298	909	830 -880	886.4 (@ 31°C)
Kinematic Viscosity	Cst	ASTM D-445		1.6 – 6.0	7.9
Colour		ASTM D-1500		3max	0.5
Total-Acid Number	mgKOH/g	ASTM D-974	6.4	0.5	0.14
Pour Point	°C	ASTM D-97		+15	0
Water By Distillation	%Vol	ASTM D-95		0.05	<0.05
Basic Water And Sediments	%Vol	ASTM D-2709		1.0max	0.01
Ash Content	%wt	ASTM D-482		0.1max	0.001
Conradson Carbon Residue	%wt	ASTM D-4530		0.2max	0.16
Total Sulphur	%wt	ASTM D-2622		1.0max	0.01
Flash Point	°C	ASTM D-93		55min	
Evaporated @ 360°C	%VOL			85min	97
Cetane Index		ASTM D-130		47min	54.55

Conti. Table 8: Fuel properties of Jatropha methyl ester compared with ASTM limits.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The results of the present study showed that, the optimum reaction conditions for methanolysis of Jatropha oil was achieved at 1.2% KOH as catalyst, methanol to oil molar ratio 6:1, reaction temperature of 55°C, rate of mixing 250 rpm – 500rpm and a reaction time of 45min, provided the best yield. The reaction tends to be incomplete with a low rate of stirring i.e., at 100 rpm, whereas stirring at high rpm seems to favour the reverse reaction process.

The rate parameters showed that the transesterification of Jatropha curcas seed oil is first order with respect to the ester formation, this implies that the reaction will follow a similar mechanism like any other first order reaction. The density, viscosity, cetane index and higher heating values of biodiesel produced under optimized protocol in the present work meet the ASTM and EN standards.

An analysis of the variables affecting the biodiesel yield indicated that, within the experimental range considered, the most important factor is initial catalyst concentration. Besides, the molar ratio also has a significant effect on this response. Both factors have an influence on biodiesel yield and, therefore, an increase in the values of these variables produces a decrease in biodiesel yield for catalyst concentration but an increase in yield for molar ratio. The cause of yield losses at high catalyst concentration is due to triglyceride saponification and the subsequent dissolution of methyl ester in glycerol due to emulsification.

The temperature and time of reaction did not have a great impact on the percentage yield of the Jatropha methyl ester; these were seen in the graphical representation for the various reaction conditions studied.

All the fuel properties analyzed were within either the ASTM or the EN standard; the quality parameters were all within the acceptable limits. The cetane number of about 55 is acceptable; the properties for environmental impact assessment were also within the limits. These results imply that it is very possible to produce biodiesel from *Jatropha curcas* which is suitable for use in diesel engines.

## **5.2 Recommendations**

The economic viability of *Jatropha* biodiesel should be critically assessed, in terms of feedstock production, equipment for processing and cost of production. Research institution and individuals should take up measures to produce biodiesel to run their equipment to reduce dependence on petrodiesel.

Further research should be carried out with the appropriate experimental design to optimize the process conditions for large scale production. The economic viability and environmental impact of production of biodiesel from *Jatropha* should be critically assessed.

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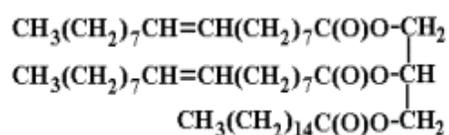
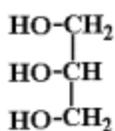
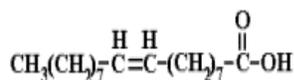
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## APPENDICES

### Initial Calculations for Required Amounts for Analyses

Triglycerides are the main constituents of vegetable oils and animal fats. Understanding of the chemical structure will help calculate the average molar mass of oil. It is a chemical compound formed by one glycerol molecule and three fatty acids.



Oleic acid

glycerol

Triglyceride

Fatty acid groups present in triglycerides

Fatty Acid	Formula	Molar Mass(g/mol)
Palmitic	C16:0	256.42
Stearic	C18:0	284.00
Oleic	C18:1	282.34
Linoleic	C18:2	280.45
Linolenic	C18:3	278.43

*Average Molar mass (fatty acid) = Dominant fatty acid in oil (Oleic) = 282.34g/mol*

*Molar Mass of oil = (12x3) + (1x5) + (282.34x3) = 888.02g/mol*

NB: The triglyceride molecule is made up of three carbon atoms chain, five hydrogen atoms and three fatty acid molecules

### **Volume of methanol corresponding to molar ratio**

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

V=Volume, n= number of moles, M=molar mass,  $\rho$ =density/ specific gravity

n=6mols, M (methanol) =32.04g/mol,  $\rho$ (methanol) = 0.7918g/ml

$$\text{Volume of methanol} = \frac{6\text{mol} \times 32.04\text{g/mol}}{0.7918\text{g/ml}} = 242.789\text{ml}$$

### **Volume of Oil corresponding to molar ratio**

n=1.0mol, M (Jatropha oil) = 888.02g/mol,  $\rho$ (Jatropha oil) =0.909g/ml

$$\text{Volume of Jatropha oil} = \frac{1.0\text{mol} \times 888.02\text{g/mol}}{0.909\text{g/ml}} = 976.92\text{ml}$$

For 6:1 methanol-oil molar ratio, you require about 243ml of methanol and 977ml of the Jatropha oil for transesterification.

### **Amount of catalyst required**

From literature 1%w/v of catalyst (KOH) to oil is usually used per 100ml of oil.

$$\begin{aligned} &= \frac{1}{100} \times 977 \\ &= 9.77\%w/v \end{aligned}$$

### Exact amounts of oil, methanol and KOH used

	Methanol (ml)	oil (ml)	KOH( g)
Calculated amount	242.79	976.92	9.77
Reduced amount (divided by 20)	12.00	48.00	0.50

### Determination of Order of Reaction and Arrhenius Parameters

The concentration (Conc.) was calculated as;

Moles of ester (3 from stoichiometric equation)/the average volume (Litres) of ester produced over four trials.

The graphical method was used to determine the order of reaction. A plot of  $\ln(\text{Conc.})$  against time (t) gave a straight line; ie first order reaction and the slope gave the rate constant k.

The Rate;  $R = \text{volume of Ester produced (Litres)} / \text{time taken (min)}$ .

A plot of  $\ln k$  against  $1/\text{temp}$  gave a straight line for the reaction for temp of 65, 75 and 85°C. The slope of this graph was  $-E_a / R$ ; and the intercept gave the pre-exponential factor A.

Calculation of average yield (Litres):  $\frac{\text{sum of all trials}}{\text{no. of trials}}$

Calculation of % yield:  $\frac{\text{moles of methyl ester}}{\text{stoichiometric moles of (oil + methanol)}} \times 100$

*stoichiometric moles of (oil + methanol)*

Calculation of rate:  $\frac{\text{yield of methyl ester}}{\text{time taken}}$

*time taken*

### **Determination of Density of Jatropha Oil and Jatropha Methyl Ester**

A 10ml density bottle at 25°C was used for density and relative density analyses. The initial weight of the empty bottle was taken, then it was filled with water and the weight was recorded. The weight of the density bottle and methyl ester of Jatropha oil was taken. The densities of water and Oil were recorded by difference; as shown below,

Volume of density bottle = 10.00cm<sup>3</sup>

Mass of empty density bottle = 10.69g

Mass of density bottle and water =20.64g

Mass of density bottle and oil = 19.78g

Mass of water = 9.95g

Mass of oil = 9.09g

Mass of biodiesel = 8.77g

$$\text{Density} = \frac{\text{mass of substance (g)}}{\text{volume of substance (cm}^3\text{)}}$$

Density of water =0.995g/cm<sup>3</sup>

Density of oil = 0.909g/cm<sup>3</sup>

### **Determination of Acid Value (AV) and Free Fatty Acids (FFA)**

A 0.02M KOH solution was titrated against 1.0 ml of Jatropha oil dissolved in 10.0ml of methanol. Phenolphthalein indicator was used to develop the colour. The titre values were recorded at a point

where the pink colour persist for at least 15sec. the process was repeated four other times and the average titre taken. A blank was performed correct for the actual titre value.

### Blank

Reading(ml)	I	II	III
Final	<b>30.20</b>	<b>31.10</b>	<b>31.90</b>
Initial	<b>29.40</b>	<b>29.40</b>	<b>31.10</b>
Titre	<b>0.80</b>	<b>0.90</b>	<b>0.80</b>

Titre = 0.80 ml

### Jatropha oil

Reading(ml)	I	II	III	IV
Final	<b>7.40</b>	<b>13.70</b>	<b>19.60</b>	<b>29.30</b>
Initial	<b>1.40</b>	<b>7.40</b>	<b>13.70</b>	<b>23.60</b>
Titre	<b>6.00</b>	<b>6.30</b>	<b>5.90</b>	<b>5.80</b>

Titre = 6.00 ml

Where;

$M$  (oleic acid) =  $282\text{gmol}^{-1}$

Conc (KOH) = Concentration of KOH used

$v(\text{KOH})$  = Volume of KOH used

$m(\text{oil})$  = mass of oil used

### Calculation for FFA

$$FFA(\%) = \frac{concKOH \times M \text{ Oliec acid} \times vKOH \times 100}{m \text{ oil} \times 1000}$$

$$FFA \text{ of oil} = \frac{0.02M \times 282 \times (6.00 - 0.80) \times 100}{0.909 \times 1000} = 3.23\%$$

### Calculation of Acid Value

Acid value is the amount of KOH in mg per g of oil required to neutralize the acid present. It is given as;

$$AV \left( \frac{mg}{g} \right) = \frac{concKOH \times MKOH \times vKOH}{m \text{ oil} \times 1000}$$

$$AV \text{ of oil} = \frac{0.02M \times 56.1 \times (6.00 - 0.80)}{0.909 \times 1000}$$

$$= 6.418 \text{ mg/g of oil}$$

### Units of some Parameters as used in the analyses

Parameter	units
Concentration	Mol/litre
Rate	Litre /min or Litre/s
Rate Constant	Litre mol <sup>-2</sup> s <sup>-2</sup>
Order of Reaction (2 <sup>nd</sup> )	-----
Activation Energy	J mol <sup>-1</sup>
Pre-exponential Factor	s <sup>-1</sup>

\*\*One cubic mile of oil (CMO) is equal to 1.1 trillion gallons (that is 26 billion barrels of oil).