

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

By

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DECLARATION

I hereby declare that this thesis is the result of my own original work undertaken under the supervision of the undersigned, that all works consulted have been referenced and that no part of the thesis has been presented for another degree in this University or elsewhere.

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DEDICATION

To my ultimate source of love, care and inspiration

My Lovely Mum Mrs. Harriet Boakye



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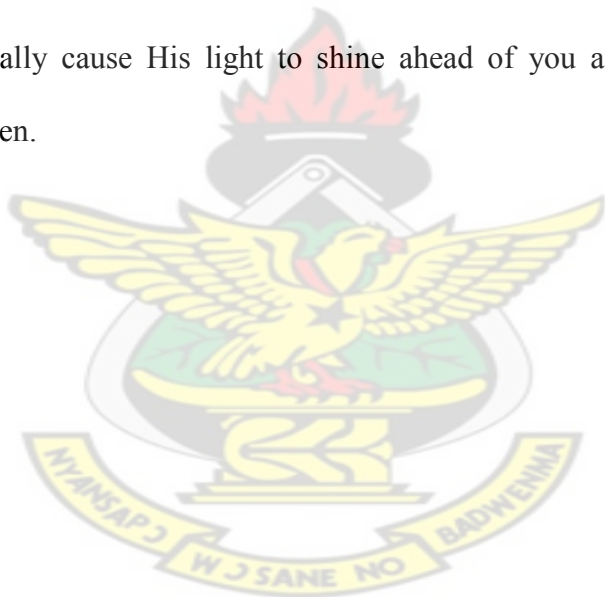
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May Jehovah continually cause His light to shine ahead of you all and bless you in all endeavours of life, Amen.



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ABSTRACT

The dwindling reserve of fossil fuel and their associated geo-political and environmental problems have increased the need to seek alternative renewable and sustainable sources for fuel production. Biodiesel, mostly produced from vegetable oils, is mono-alkyl ester and is perceived to replace/supplement fossil diesel fuel. Both edible and non-edible vegetable oils can be used as feedstock in the production of biodiesel. The use of edible oils for fuel production is a concern as the global food demand rises. There are also sustainability issues on deforestation and ecological imbalance with large scale biofuel production. The high supply cost of feedstocks which account for more than 80 % of the overall biodiesel production cost coupled with their competition as food sources have turned the attention to the exploitation of non-edible feedstocks such as *Jatropha*, Castor bean oil, Neem oil, Pongame oil and Sea mango oil.

In this study, biodiesel was produced from non-edible vegetable oil sources namely *Jatropha curcas* oil and waste vegetable oils (Soya bean and Cottonseed). Fresh Soya bean and Cottonseed oils were transesterified to serve as control. Unsupported potassium carbonate (K_2CO_3) was used as a catalyst to assess its technical feasibility and process conditions for transesterification of the oils.

Various qualitative and quantitative analytical techniques were employed for the characterization of the oil feedstocks prior to transesterification. Such techniques were also used to access the completeness of reactions based on the purity of FAME produced. They include gravimetric, volumetric, potentiometric, mass spectrometric and chromatographic techniques.

A single-step alkali transesterification process was used to convert four oil samples (fresh Soya bean oil, waste Soya bean oil, fresh Cottonseed oil and waste Cottonseed oil) to fatty

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acid methyl esters (FAME) because they contained relatively low percentage free fatty acid (% FFA < 1 %). The *Jatropha curcas* oil contained high free fatty acid (5.70 %) which was reduced to 1.31 % in an acid pre-treatment esterification process prior to transesterification; hence, a two-step transesterification process was employed.

The experimental results suggest that K_2CO_3 is a better alternative to other known alkali catalysts such as NaOH, KOH, $NaOCH_3$ and $KOCH_3$ since it provides practically complete alcoholysis with least amount of soap production.

It was observed that a catalyst amount of 4 wt. % K_2CO_3 with 60 °C reaction temperature and 600 rpm reaction speed was the optimum conditions for the transesterification of the non-edible vegetable oils. Also, the optimum oil to methanol molar ratio for the conversion of both Cottonseed waste vegetable oil (CWVO) and Soya bean waste vegetable oil (SWVO) to FAME was 1:6 whilst that for the *Jatropha curcas* oil (JCO) was 1:8. The optimum reaction periods were 40 min, 80 min and 120 min respectively for the conversion of CWVO, SWVO and JCO to FAME. The combination of the optimum parameters of catalyst amount, oil: methanol molar ratio, reaction temperature as well as reaction time gave a FAME yield of about 99.5 % for both CWVO and SWVO but 94.8 % for JCO.

K_2CO_3 as a catalyst has been shown to have great potential for transesterification in this work. Biomass such as cocoa pods and plantain peels contain this mineral compound in substantial amounts and readily abound in Ghana. K_2CO_3 can easily be extracted from such biomass ash using classical economic extraction technology. Given the viability of waste vegetable to produce biodiesel, research to assess the quantity of waste vegetable oil generated in Ghana should be encouraged in the match to realizing the actual production of biodiesel through such routes.

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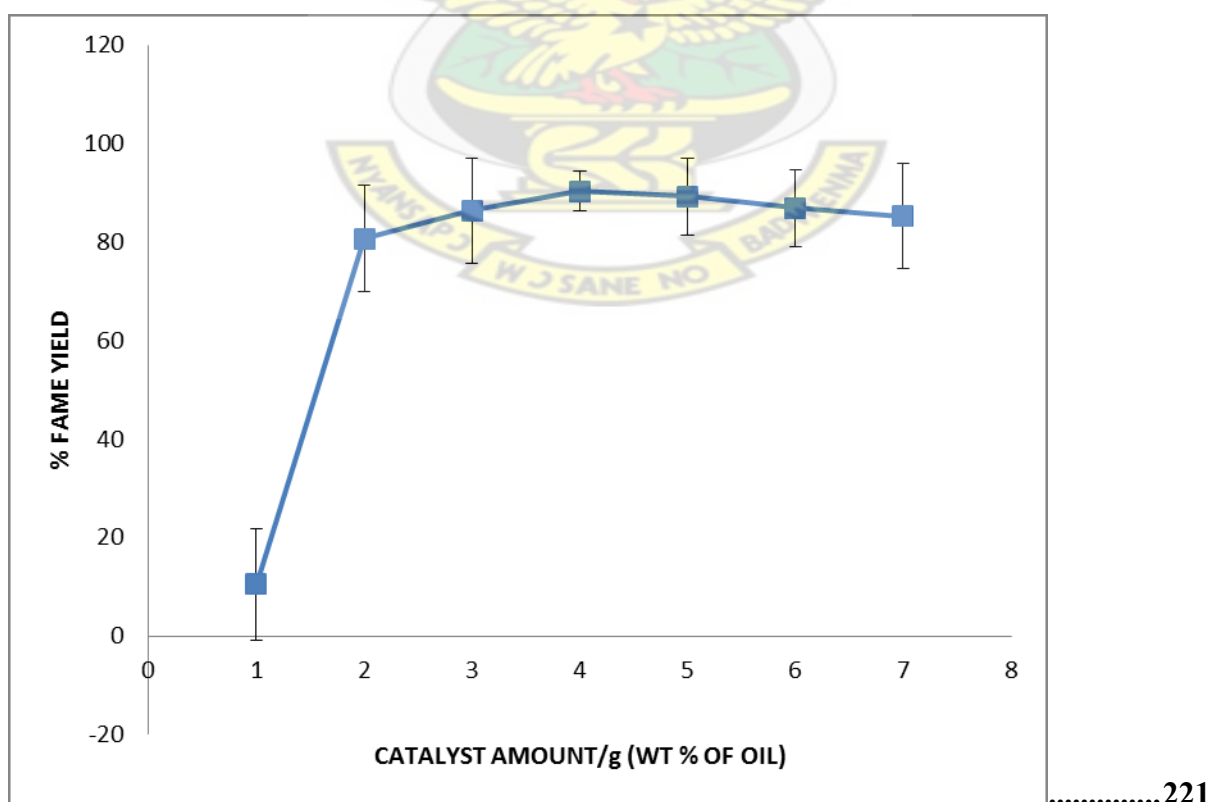


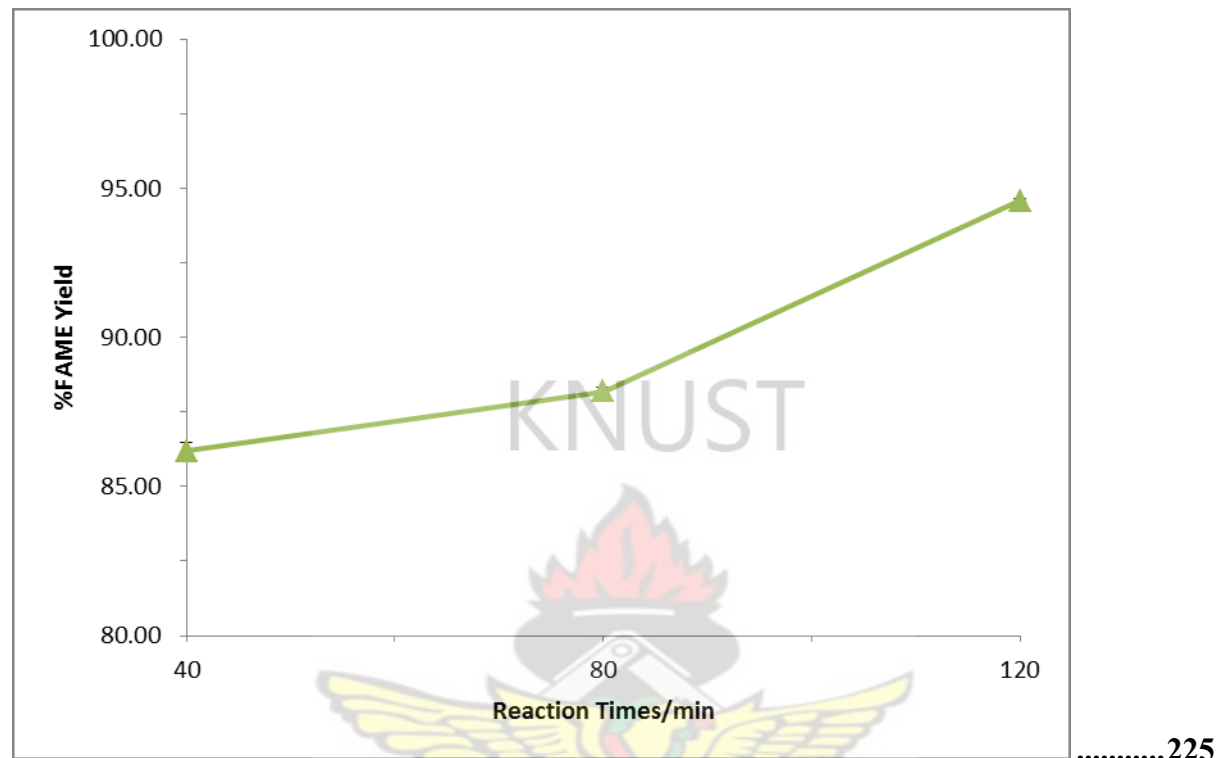
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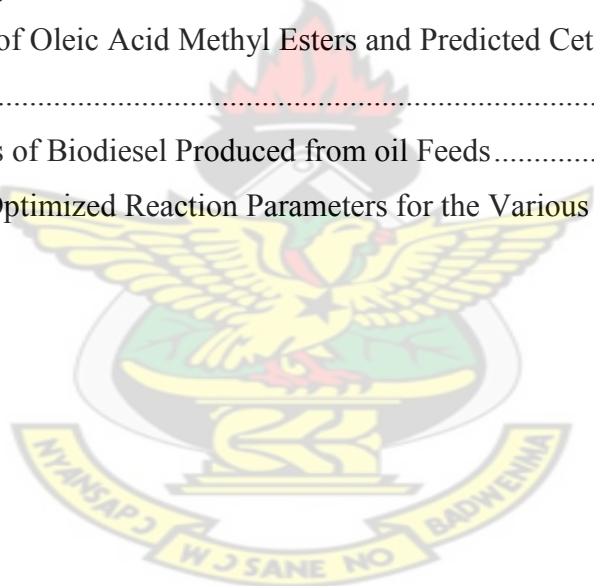
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1. Themes P. Biofuels and commodity markets—palm oil focus, FAO, Commodities and Trade Division (2006). (Online). Available at faorlc.cgnet.com/as/priorities/Bioenergy/pdfs/commodity.pdf [Accessed on 12, 07, 2011].....230

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ABBREVIATIONS AND NOMENCLATURE

ABE	Acetone Butanol Ethanol
ABNT	Associação Brasileira de Normas Técnicas (Brazilian Association for Technical Standards)
ACS	American Chemical Society
ANOVA	Analysis of Variance
ANP	Agência Nacional do Petróleo (National Petroleum Agency)
AOCS	American Oil Chemists' Society
AR	Analytical Reagent
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated Total Reflectance- Fourier Transform Infrared
AUCC	Association of Universities and Colleges of Canada
BFOB	Blend of Fresh Oil Biodiesel
BFVO	Blend of Fresh Cottonseed and Soya bean Vegetable Oil
BioDME	Biobased Dimethyl Ether
BSE	Bovine Spongiform Encephalopathy – Mad Cow Disease
BWOB	Blend of Waste Oil Biodiesel
BWVO	Blend of Waste Cottonseed and Soya bean Vegetable Oil
B2	2 % Biodiesel
B5	5 % Biodiesel
B100	Pure Biodiesel
CAREG	Canada- Africa Research Exchange Grants
CFPP	Cold Flow Plugging Point
CL	Confidence Level
CN	Cetane Number
cP	Centipoise
CSFO	Cottonseed Fresh Vegetable Oil
CSFOB	Cottonseed Fresh Oil Biodiesel
CSO	Cottonseed Oil
CWVO	Cottonseed Waste Vegetable Oil
CWVOB	Cottonseed Waste Vegetable Oil Biodiesel
DG	Di-Glyceride
DME	Dimethyl Ether
DMF	Dimethyl Furan

EN	European Norm
EPA	Environmental Protection Agency
EtOH	Ethanol
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FID	Flame Ionization Detector
GC-MS	Gas Chromatography- Mass Spectroscopy
GSB	Ghana Standard Board
HSD	Honestly Significant Difference
IDRC	International Development Research Centre
IEA	International Energy Agency
ISO	International Standard Organisation
JCO	<i>Jatropha curcas</i> oil
JCOB	<i>Jatropha curcas</i> oil Biodiesel
KNUST	Kwame Nkrumah University of Science and Technology
LSD	Least Significant Difference
MATLAB	Matrix Laboratory
ME	Methyl Ester
MeOH	Methanol
MG	Mono- Glyceride
MSTFA	N-Methyl- N-Trimethylsilyl Trifluoroacetamide
SBFO	Soya bean Fresh Vegetable Oil
SBFOB	Soya bean Fresh Oil Biodiesel
SC-CO ₂	Super Critical Carbon (II) Oxide
SCF	Super Critical Fluid
SPSS	Statistical Package for the Social Sciences
SWVO	Soya bean Waste Vegetable Oil
SWVOB	Soya bean Waste Vegetable Oil Biodiesel
TG	Tri-Glyceride
TOR	Tema Oil Refinery
USLD	Ultra-Low-Sulphur-Diesel
UWO	University of Western Ontario
WVO	Waste Vegetable Oil

CHAPTER ONE

1.0 BACKGROUND OF STUDY

1.1 Introduction

There is the need to develop suitable long-term strategies based on utilization of renewable and environmentally friendly fuels that would gradually substitute the declining fossil fuel production due to the depletion of the world's accessible oil reservoirs (Westermann *et al.*, 2007). Most of the energy consumed worldwide is derived from fossil sources such as petroleum, coal and natural gas. Today, 86 % of the world energy consumption and almost 100 % of the energy needed in the transportation sector is derived from fossil fuels (Dorian, Franssen, and Simbeck, 2006). However, these sources are limited and exhaustible, hence, getting totally depleted in the near future. Thus, looking for alternative sources of energy that is inexhaustible and renewable such as hydro, biomass, geothermal, hydrogen, nuclear, wind and solar is of vital importance. Renewable energy technologies can create significant employment opportunities and improve rural livelihoods. A substantial improvement in the potential for employment opportunities and income generation can be achieved when renewable energy projects are integrated with local commercial activities. The decentralised nature of renewable energy technologies makes them well suited to the rural context and the skills required to establish these technologies can be easily developed locally, thereby reducing the need for imported expertise. Thus, the benefits of renewable energy sources which include employment opportunities through the creation of income generating activities, environmental improvements and sustainability issues, reduced energy expenditures, etc. have the potential to solve many socio-economic and environmental problems (MacLeana and Laveb, 2003).

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According to the American Society for Testing and Materials (ASTM), biodiesel is defined as a fuel comprising monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. “Bio” represents its renewable and biological source in contrast to traditional petroleum-based diesel fuel. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Körbitz, 1999; Agarwal and Das, 2001). Biodiesel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996). It provides lubricating properties that can reduce engine wear and extend engine life (Wedel, 1999). It also gives a better engine performance due to its higher cetane number. Thus, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

Moreover, biodiesel can be produced economically across a variety of places and scales; from urban to rural, small to commercial, because it can be refined under normal atmospheric temperature and pressure. The ease of production also contributes to biodiesel's high net energy balance, for example, soybean-biodiesel produces a 93 % energy gain vs. 25 % for corn-ethanol (Kurki, Hill and Morris, 2006).

Despite its importance, more than 95 % of biodiesel is mainly prepared from conventionally grown edible oils (Gui, Lee and Bhatia, 2008) such as soybean, sunflower, rapeseed, palm, etc. This causes an imbalance between the utilization of energy resources and food

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consumption. In recent times, environmentalists have begun to debate on the negative impact of biodiesel production from edible oil (Butler, 2006). They claimed that there may be increase in deforestation in countries like Malaysia, Indonesia and Brazil due to large scale cultivation of oil crop plants for biodiesel production. The land use for production of edible oil as feedstock for biodiesel production competes with the use of land for food production. Arable land that would otherwise have been used to grow food would instead be used to grow fuel crops. In fact, this trend is already being observed in certain parts of this world.

In order to meet the increasing demand of biodiesel in the past few years there has been significant expansion in the plantation of oil crops. The ending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel even though there is continuous increase in the production of vegetable oil. Thus, the implementation of biodiesel as a substitute fuel for petro-diesel may lead to the reduction of edible-oil supply worldwide. Figure 1 shows the trend in global vegetable oil ending stocks due to the production of biodiesel in the years 1991–2005 (Gui, Lee and Bhatia, 2008).

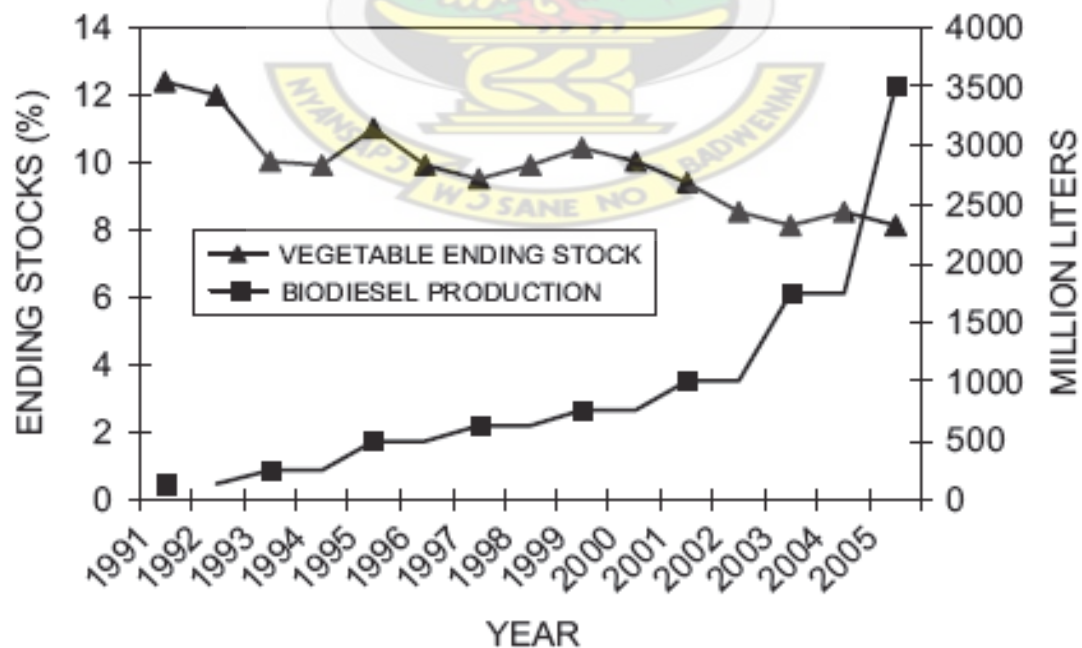


Figure 1 Global vegetable oil ending stock and biodiesel production (Source; Gui Lee and Bhatia, 2008)

Again, the overall biodiesel production process is more expensive than that of traditional fossil fuels because the raw materials cost usually covers more than 80 % of the total production costs (Haas *et al.*, 2006). The high cost of edible plant and vegetable oils as raw materials used for biodiesel production is the major bottleneck which greatly prohibits its widespread application. Thus, biodiesel production has currently not yet been commercialized all over the world (Thamsiriroj and Murphy, 2009; Yan and Lin, 2009; Hammond, Kallu and McManus, 2008). One way of reducing the cost of biodiesel is to employ low quality feedstocks such as waste or used vegetable oils, non-edible oils and soap stock (by-product of vegetable oil refinery), which are cheaply available and can be regarded as attractive feedstocks for biodiesel production (Canakci and Sanli, 2008; Felizardo, Correia and Raposo, 2006; Mohammad and Ali, 2002; Zhang and Jiang, 2008 and Altun and Oner, 2009).

Furthermore, management of waste cooking oils and fats pose a significant challenge because of their disposal problems and possible contamination of water and land resources. Even though some of the waste oil is used for soap production, a higher percentage is discharged into the environment. As large amounts of waste vegetable oils are illegally dumped into rivers and landfills, causing environmental pollution (Yang *et al.*, 2007), the use of waste vegetable oil to produce biodiesel as petro-diesel substitute offers significant advantages because of the reduction in environmental pollution.

Many types of methods have been developed to convert vegetable oils or triglycerides into biodiesel. The four main categories are the direct use of the triglycerides or vegetable oil,

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micro-emulsion, thermal cracking and transesterification. Direct use of triglycerides or vegetable oil is not applicable to most of diesel engines as the high viscosity would damage the engine by causing coking and trumpet formation (Agarwal and Agarwal, 2007). Biodiesel obtained from micro-emulsion and thermal cracking methods would likely lead to incomplete combustion due to a low cetane number and energy content (Leung, Wu and Leung, 2010). Transesterification is the most common method for biodiesel production due to its simplicity, thus this method has been widely used to convert vegetable oil into biodiesel (Helwani *et al.*, 2009 and Jain and Sharma, 2010a). The transesterification process or methanolysis (alcoholysis), which refers to a catalyzed chemical reaction involving vegetable oil and MeOH to yield fatty acid methyl ester as the main product and glycerol as a by-product (Huber, Iborra and Corma, 2006, Lotero *et al.*, 2005 and Marchetti, Miguel and Errazu, 2007), is shown in equation (1).



where TG, MeOH and ME denote triglyceride, methanol and methyl esters respectively.

Previously, many alkali or base catalysts have been used in transesterification reactions. K_2CO_3 provides practically complete alcoholysis with least amount of soap production as compared to other alkali or base catalyst such as NaOH, KOH, NaOCH_3 and KOCH_3 (Baroi, Yanful and Bergougnou, 2009; Hartman, 1956). According to US Patents 6890451 B2 (Sapienza, Johnson and Ricks, 2005) and 7138071 B2 (Sapienza, Johnson and Ricks, 2006), glycerol containing K_2CO_3 can be an excellent environmentally benign anti-icing or de-icing agent. Thus, it can be used on airport runways and also on the wings, fuselage, and tail of aircrafts for de-icing.

Unsupported K_2CO_3 is a better alternative for biodiesel production. Among traditional catalysts, KOH and its methylate are the most expensive. KOH is synthesized by electrolysis of KCl solution and the current method of producing K_2CO_3 is by reacting KOH with CO_2 .

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Thus, the price of K_2CO_3 is more expensive than KOH (Baroi, Yanful and Bergougnou, 2009). However, most biomass such as plantain peels, cocoa pods and *Jatropha curcas* seedcake contain potassium. Hence the production of K_2CO_3 from these biomass sources will help reduce its cost thereby reducing the overall cost of biodiesel production.

1.2 Problem Statement

Globally, conventionally grown edible oils are the major feedstocks used for biodiesel production. This causes an imbalance between the utilization of energy sources and food consumption and contributes to the higher cost of biodiesel feedstocks. Also, the use of alkali or base catalyst, which is expensive, for transesterification enhances the production of soap as side reaction which affects the quality of the biodiesel produced.

The current study is intended to investigate the feasibility of producing biodiesel from non-edible oil sources such as waste vegetable oil and *Jatropha curcas* as well as optimization of the transesterification process using potassium carbonate. The success of the research will prevent the competition between the use of edible oil as energy source and food. It will also help to reduce the overall cost of biodiesel production since non-edible oil feeds will be employed and potassium carbonate can be produced locally from some biomass sources such as plantain peels, cocoa pods and *Jatropha* cake.

1.3 Justification for Research

Increasing uncertainty about global energy production and supply, environmental concerns due to the use of fossil fuels, high price and unsustainable nature of petroleum products are the major reasons to search for alternatives to fossil diesel. Having regard to the rate of actual energy consumption, petroleum resources are getting depleted as well as causing environmental hazards of global warming; natural disasters etc. Thus, there is the need to

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focus on new energy sources that can replace fossil fuel and meet emission standards. Biodiesel is proven to be one of the best available sources to fulfil the energy demand and to meet the emission standards (MacLeana and Laveb, 2003; Agarwal and Das, 2001 and Körbitz, 1999).

However, the continual use of edible oil for biodiesel production will cause food insecurity. Thus, the need to focus on non-edible oil feeds such as waste vegetable oil and *Jatropha curcas*. The use of waste vegetable oil as biodiesel feedstock will help mitigate the environmental hazards posed by the improper handling of waste vegetable oil. Also, the use of waste and other non-edible oils as biodiesel feedstock will reduce the cost of biodiesel production since the feedstock costs constitutes approximately 70-95 % of the overall cost of biodiesel production. Hence, the use of waste cooking oils, generated as waste or by-product of meal preparation and other non-edible oils need to be given higher priority over the edible oils as biodiesel feedstock.

Potassium carbonate can be produced locally from some biomass such as cocoa pods, plantain peels and *Jatropha* cake. The use of potassium carbonate as catalyst for transesterification does not produce water as side reaction with alcohols as in the case of alkali or base catalyst and hence, reduces soap formation which could affect the quality of biodiesel produced (Baroi, Yanful and Bergougnou, 2009). Also, the local production of potassium carbonate may help to reduce its cost and contribute to the overall reduction in the cost of biodiesel production. This will significantly enhance the economic viability of biodiesel production in locations such as Ghana, where this biomass abound.

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1.4 Objectives

The main goal of this research is to produce biodiesel from non-edible oil feedstocks such as waste vegetable oil (cotton seed and Soya bean waste oils) and *Jatropha curcas* oil using unsupported potassium carbonate as a catalyst.

The specific objectives intended to be achieved are to:

- i) Investigate the technical feasibility of producing biodiesel from non-edible oil feedstocks such as waste vegetable oils (WVO) and *Jatropha curcas* oil (JCO) using unsupported potassium carbonate as catalyst at the laboratory scale.
- ii) Optimize the reaction parameters namely catalyst amount, oil to methanol molar ratio, reaction time and reaction temperature to produce biodiesel from WVO and JCO of reasonable quality.
- iii) Evaluate the effect of reaction parameters on the purity of biodiesel produced using Gas chromatography-mass spectrophotometry (GC-MS).

1.5 Scope of the Study

The research work involved the following:

- i) Production of biodiesel from waste vegetable oil and *Jatropha* oil using unsupported potassium carbonate as catalyst for the transesterification process.
- ii) Evaluation of the effect of reaction parameters on the yield and purity of biodiesel produced.
- iii) The use of statistical applications such as SPSS, Excel and MATLAB to analyse experimental results.

1.6 Experimental Strategy

- The experiment was started using 1:6 oil: methanol molar ratio at 60 °C reaction temperature and reaction speed of 600 rpm for 2 hours while varying the catalyst amount as weight percent of the oil feedstock for an amount sufficient to get a high conversion.
- The optimum catalyst amount was selected while the oil: methanol molar ratio was varied maintaining the 60 °C reaction temperature and reaction speed of 600 rpm for 2 hours.
- The reaction time was varied while maintaining the optimum catalyst amount and oil: methanol molar ratio at 60 °C reaction temperature and reaction speed of 600 rpm.
- The reaction temperature was varied while maintaining the optimum catalyst amount, oil: methanol molar ratio and reaction time at 600 rpm reaction speed.
- The best reaction parameter combination was chosen based on highest conversion and best phase purity of fatty acid methyl esters.
- Biodiesel quality parameters were determined for fatty acid methyl esters produced.

1.7 Originality and Contribution of the Thesis

In this study, transesterification of waste vegetable oil (WVO) and high % FFA *Jatropha curcas* oil (JCO) to produce biodiesel using unsupported potassium carbonate as catalyst was done for the first time.

The immense potential of potassium carbonate production in Ghana (OPC, 2012) from cocoa husks can speed up local biodiesel production, given the abundance of oil bearing seeds in the country

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1.8 Structure of the Thesis

The structure of the thesis is organized into five main chapters. Chapter one comprises the background of the study which is introduction, the problem statement, justification for research, objectives, scope of the study, experimental strategy and the originality and contribution of the thesis. Chapter two mainly covers the literature review of the study and chapter three describes the materials used and the research methodology employed in the study. In chapter four, all the results obtained in the study were analyzed and discussed. Finally, conclusions and recommendations based on the research are made in chapter five.



CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Overview of Biofuels

Fuels whose energy is derived from biological carbon fixation is termed biofuels. Biofuels comprise fuels derived from biomass conversion, as well as solid biomass, liquid fuels and various biogases (Demirbas, 2009a). Fossil fuels originated from ancient carbon fixation, yet, they are not considered biofuels by the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Globally, biofuels are gaining increased public and scientific attention, the driving forces are oil price hikes, the need for increased energy security, concern over greenhouse gas emissions from fossil fuels, and support from government subsidies.

The worldwide biofuel production reached 105 billion litres (28 billion gallons US) in 2010, which was 17 % increment from that produced in 2009. Biofuels accounted for 2.7 % of the world's fuels for road transport, a contribution largely made up of ethanol and biodiesel. Also, in 2010 the global ethanol fuel production reached 86 billion litres (23 billion gallons US), with the United States and Brazil as the world's top producers, accounting together for 90 % of global production. Mandates for blending biofuels exist in 46 countries at the national level and in 26 states and provinces as of early 2012 (REN21, 2012). According to the International Energy Agency (IEA), biofuels have the potential to meet up to 27 % of the world's demand for transportation fuels by 2050 (Tanaka, 2011).

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Generally, biofuels can be classified into ‘first – generation’ and ‘second – generation’ biofuels depending on the source of feedstock used for the production.

2.1.1 First Generation Biofuels

‘First-generation’ or conventional biofuels are biofuels made from sugar, starch, and vegetable oil. They include solid biofuels; liquid biofuels which comprise straight vegetable oil, biodiesel, bioalcohols, green diesel, bioethers, and gaseous biofuels which are biogas and syngas. Examples of solid biofuels include wood, sawdust, grass trimmings, domestic refuse, charcoal, agricultural waste, non-food energy crops, and dried manure. One of the advantages of solid biomass fuel is that it is often a by-product, residue or waste-product of other processes, such as farming, animal husbandry and forestry. In theory this means there is no competition between fuel and food production, although this is not always the case (Urban and Mitchell, 2011). Several studies have also shown that biomass fuels have significantly less impact on the environment than fossil based fuels. Bio-char, a derivative of solid biofuel made from agricultural waste through biomass pyrolysis can substitute for wood charcoal as wood stock becomes scarce. For example, in order to protect Virunga National Park from deforestation associated with charcoal production biomass briquettes are being promoted as an substitute to charcoal in eastern Democratic Republic of Congo (Ofor and Ndwufo, 2011).

Straight unmodified edible vegetable oil is not often used as fuel because of its basic use as food and viscosity problems associated with its use in engines. To ensure that the fuel injectors atomize the vegetable oil in the correct pattern for efficient combustion, vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers. This is easier in warm or temperate climates. Big corporations like MAN B&W Diesel, Wärtsilä, and Deutz AG as well as a number of smaller companies such as Elsbett

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offer engines that are compatible with straight vegetable oil, without the need for after-market modifications. Vegetable oil can also be used in many older diesel engines that do not use common rail or unit injection electronic diesel injection systems.

Due to the design of the combustion chambers in indirect injection engines, these are the best engines for use with vegetable oil. This system allows the relatively larger oil molecules more time to burn. Some older engines, especially Mercedes are driven experimentally by enthusiasts without any conversion, a handful of drivers have experienced limited success with earlier pre-"Pumpe Duse" VW TDI engines and other similar engines with direct injection. Several companies like Elsbett or Wolf have developed professional conversion kits and successfully installed hundreds of them over the last decades (Flannery, 2012).

Biodiesel is produced from oils or fats using transesterification and is a liquid similar in composition to fossil/mineral diesel. Chemically, it consists mostly of fatty acid methyl (or ethyl) esters (FAMES). Many current generation diesel engines are made so that they can run on B100 without altering the engine itself, although this depends on the fuel rail design. Pure biodiesel (B100) is the lowest emission diesel fuel. Although liquefied petroleum gas and hydrogen have cleaner combustion, they are used to fuel much less efficient petrol engines and are not as widely available. Biodiesel can be used in any diesel engine when mixed with mineral diesel. It also effectively cleans the engine combustion chamber of carbon deposits, helping to maintain efficiency. Biodiesel is also an oxygenated fuel, meaning that it contains a reduced amount of carbon and higher hydrogen and oxygen content than fossil diesel. This improves the combustion of biodiesel and reduces the particulate emissions from un-burnt carbon. Biodiesel is also safe to handle and transport because it is as biodegradable as sugar,

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10 times less toxic than table salt, and has a high flash point of about 148 °C (300 F)) compared to petroleum diesel fuel, which has a flash point of 52 °C (125 F) (Bevill, 2010).

Biologically produced alcohols, most commonly ethanol, and less commonly propanol and butanol, are produced by the action of microorganisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (which is more difficult). Biobutanol (also called biogasoline) is often claimed to provide a direct replacement for gasoline, because it can be used directly in a gasoline engine in a similar way to biodiesel in diesel engines. Ethanol fuel is the most common biofuel in Brazil. The ethanol production methods used are enzyme digestion (to release sugars from stored starches), fermentation of the sugars, distillation and drying.

An advantage of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is that it has a higher octane rating than ethanol-free gasoline available at roadside gas stations which allows an increase of an engine's compression ratio for increased thermal efficiency (Kojima and Johnson, 2005). In high altitude (thin air) locations, some states mandate a mix of gasoline and ethanol as a winter oxidizer to reduce atmospheric pollution emissions. Methanol is currently produced from natural gas, a non-renewable fossil fuel. It can also be produced from biomass as biomethanol. The methanol economy is an alternative to the hydrogen economy, compared to today's hydrogen production from natural gas. Butanol ($\text{C}_4\text{H}_9\text{OH}$) is formed by ABE (acetone, butanol, ethanol) fermentation and experimental modifications of the process show potentially high net energy gains with butanol as the only liquid product (Qureshi *et al.*, 2012).

Green diesel, also known as renewable diesel, is a form of diesel fuel which is derived from renewable feedstock including canola, algae, *Jatropha* and *salicornia* in addition to tallow.

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Green diesel uses traditional fractional distillation to process the oils, not to be confused with biodiesel which is chemically quite different and processed using transesterification. “Green Diesel” as commonly known in Ireland should not be confused with dyed green diesel sold at a lower tax rate for agriculture purposes, using the dye allows custom officers to determine if a person is using the cheaper diesel in higher taxed applications such as commercial haulage or cars (BBC News, 2004).

Bioethers, also referred to as fuel ethers or oxygenated fuels are cost-effective compounds that act as octane rating enhancers. They also enhance engine performance, whilst significantly reducing engine wear and toxic exhaust emissions. Greatly reducing the amount of ground-level ozone, they contribute to the quality of the air we breathe. According to Polish Patent Application No. PL 382 733 (Sokol, 2008), it is possible to etherify glycerol which is a by-product of biodiesel production with either alcohols or alkenes for the production of oxygenated compounds, namely ethers of glycerol, which can be added to conventional diesel in vehicle engines as a second generation of biocarburants. The procedure of obtaining bio-ethers from glycerol production according to the invention consists in catalytic treatment of crude waste glycerol. In this liquid conversion process stable and quasi-stable glycerol wastes are converted into ethers of glycerol (heating fuel) and potassic fertilizer with 29,8% of K_2O (% weight in dry mass). The ethers of glycerol can be combusted (heat of combustion 29 185 kJ/ kg) to electrical energy. The offered technology of glyceric wastes utilisation to bioether (second generation of biocarburants) is safe for environment, with no liquid and solid wastes.

Biogas is methane produced by the process of anaerobic digestion of organic material by anaerobes (Redman, 2008). It can be produced either from biodegradable waste materials or

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by the use of energy crops fed into anaerobic digesters to supplement gas yields. Well-functioning biogas systems can provide a lot of benefits for their users, the society and the environment in general. Biogas can be used for the production of heat, light and electricity. The solid by-product, digestate, can be used as a biofuel or a fertilizer. Biogas production improves hygienic conditions through reduction of pathogens, worm eggs and flies and provides environmental advantages through protection of soil, water, air and woody vegetation. Also, the use of biogas reduces the workload, mainly for women, in firewood collection and cooking. The micro-economic benefits of biogas through energy and fertilizer substitution, provides additional income sources and increasing yields of animal husbandry and agriculture. At the macro-economic level it brings about decentralization of energy generation, import substitution and environmental protection (Xiaohua *et al.*, 2007). Thus, biogas technology can substantially contribute to conservation and development, if the concrete conditions are favourable. However, the required high investment capital and other limitations of biogas technology should be thoroughly considered.

Syngas, a mixture of carbon monoxide, hydrogen and other hydrocarbons is produced by partial combustion of biomass, that is, combustion with an amount of oxygen that is not sufficient to convert the biomass completely to carbon dioxide and water (Evans, 2008). Before partial combustion the biomass is dried, and sometimes pyrolysed. The resulting gas mixture, syngas, is more efficient than direct combustion of the original biofuel; more of the energy contained in the fuel is extracted. Syngas may be burned directly in internal combustion engines, turbines or high-temperature fuel cells (Nagel, 2008). The wood gas generator is a wood-fuelled gasification reactor mounted on an internal combustion engine. Syngas can be used to produce methanol, dimethyl ether (DME) and hydrogen (Hayer *et al.*,

2011), or converted via the Fischer-Tropsch process to produce a diesel substitute, or a mixture of alcohols that can be blended into gasoline.

2.1.2 Second Generation Biofuels (Advanced Biofuels)

Second generation biofuels are biofuels produced from sustainable feedstock. Sustainability of a feedstock is defined among others by availability of the feedstock, impact on greenhouse gas (GHG) emissions and impact on biodiversity and land use. Many second generation biofuels are under development such as Cellulosic ethanol, Algae fuel, biohydrogen, biomethanol, dimethyl furan (DMF), bio-dimethyl ether (BioDME), Fischer-Tropsch diesel, biohydrogen diesel, mixed alcohols and wood diesel. Cellulosic ethanol production uses non-food crops or inedible waste products and does not divert food away from the animal or human food chain. Lignocellulose is the "woody" structural material of plants. This feedstock is abundant and diverse, and in some cases (like citrus peels or sawdust) it is in itself a significant disposal problem.

Producing ethanol from cellulose is a difficult technical problem to solve. In nature, ruminant livestock (like cattle) eat grass and then use slow enzymatic digestive processes to break it into glucose (sugar). In cellulosic ethanol laboratories, various experimental processes are being developed to do the same thing, and then the sugars released can be fermented to make ethanol fuel. In 2009 scientists reported developing, using "synthetic biology", "15 new highly stable fungal enzyme catalysts that efficiently break down cellulose into sugars at high temperatures", adding to the 10 previously known (EurekAlert, 2009). The use of high temperatures has been identified as an important factor in improving the overall economic feasibility of the biofuel industry and the identification of enzymes that are stable and can

operate efficiently at extreme temperatures is an area of active research (Yeoman *et al.*, 2010).

Lanzatech has developed a technology to use industrial waste gases such as carbon monoxide (CO) from steel mills as a feedstock for a microbial fermentation process to produce ethanol (Voegelé, 2009).

2.2 Historical Background of Biodiesel

Transesterification of vegetable oils was conducted as early as 1853 by Scientists, E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf Diesel's (1858–1913) prime model, a single 3 m (10 ft) iron cylinder with a fly wheel at its base, run on its power for the first time in Augsburg, Germany, on August 10, 1893. In remembrance of this event, August 10 has been declared "International Biodiesel Day" (Lin *et al.*, 2011). Diesel later demonstrated his engine and received the *Grand Prix* (highest prize) at the World Fair in Paris, France in 1900.

This engine stood as an example of Diesel's vision because it was powered by peanut oil a biofuel, though not *biodiesel*, since it was not transesterified. He believed that the utilization of biomass fuel was the real future of his engine. In a 1912 speech Diesel said, "The use of vegetable oils for engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and coal-tar product of the present time." During the 1920s, diesel engine manufacturers altered their engines to utilize the lower viscosity of petrol diesel (a fossil fuel) which was much cheaper to produce, rather than vegetable oil.

Despite the widespread use of fossil petroleum-derived diesel fuels, interest in vegetable oils as fuels in internal combustion engines is reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal,

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Germany, Brazil, Argentina, Japan and China have been reported to have tested used vegetable oils as diesel fuels during this time.

On August 31, 1937, G. Chavanne of the University of Brussels (Belgium) was granted patent for a “Procedure for transformation of vegetable oils for their uses as fuels” (fr. ‘procede de Tranformation d’Huiles Vegetales en vue de Leur Utilisation comme Carburants’) Belgian Patent 422,877 which describe the alcoholysis (often referred to as transesterification) of vegetable oils (Knothe, 2001). In 1977, Brazilian scientist Expedito Patent produced biodiesel using transesterification with ethanol, and again filed a patent for the same process. This process is classified as biodiesel by international norms, conferring a “standardized identity and quality”.

Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979. By 1983, the process of producing fuel-quality, engine-tested biodiesel was completed and published internationally (SAE Technical Paper, 1983). An Austrian company, Gaskoks, obtained the technology from the South African Agricultural Engineers; the company erected the first biodiesel pilot plant in November 1987, and the first industrial-scale plant in April 1989 (with a capacity of 30,000 tonnes of rapeseed per annum). Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as *diester*) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of 30 %. Renault, Peugeot and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiment with 50 % biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up; by 1998, the Austrian Biofuel Institute had identified 21 countries with commercial biodiesel projects.

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In September 2005, Minnesota became the first U.S state to mandate that all diesel fuel sold in the state contain part biodiesel, requiring a content of at least 2% biodiesel (Ge *et al.*, 2012). For strengthening the quality control requirements of engine and equipment manufacturers, and allowing further companies to issue biodiesel engine warranties for the use of biodiesel fuels, a series of biodiesel standards were issued in succession, such as DIN 51606 (Germany), EN 14214 (Europe), ASTM D6751 (USA and Canada). In 2008, the current version of EN 14214 and ASTM D6751 were published, and superseded previous standards (Pahl, 2008). With the quick development of biodiesel industry, biodiesel is playing a more and more important role in global primary energy. A summary of the key milestones in the development of biodiesel industry is shown in Table 1.



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Table 1 Key Milestones in the Development of Biodiesel Industry (Lin *et al.*, 2011)

Date	Event
August 10,1893	Rudolf Diesel's prime diesel engine model, which was fuelled by peanut oil, ran on its own power for the first time in Augsburg, Germany
1900	Rudolf Diesel showed his engine at the world exhibition in Paris, his engine was running on 100 % peanut oil
August 31,1937	A Belgian scientist, G. Chavanne, was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels". The concept of what is known as "biodiesel" today was proposed for the first time
1977	A Brazilian scientist, Expedito Parente, applied for the first patent of the industrial process for biodiesel
1979	Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa
1983	The process for producing fuel-quality, engine-tested biodiesel was completed and published internationally
November,1987	An Austrian company, Gaskoks established the first biodiesel pilot plant
April, 1989	Gaskoks established the first industrial-scale plant
1991	Austria's first biodiesel standard was issued
1997	A German standard, DIN 51606, was formalized
2002	ASTM D6751 was first published
October, 2003	A new Europe-wide biodiesel standard, DIN EN14214 was published
September, 2005	Minnesota became the first US state to mandate that all diesel fuel sold in the state contain part biodiesel, requiring a content of at least 2 % biodiesel
October, 2008	ASTM published new Biodiesel Blend Specifications Standards
November, 2008	The current version of the European Standard EN 14214 was published and supersedes EN 14214:2003

2.3 Feedstocks for Biodiesel Production

Biodiesel can be produced from a variety of biolipids. The choice of feedstock for biodiesel production depends greatly on climate, local soil conditions and availability; consequently different regions are focusing their efforts on different types of oil. Mostly, the raw materials of biodiesel are soybean oil, sunflower oil, Cottonseed oil, palm oil, palm kernel oil, coconut oil (copra), groundnut oil, rapeseed oil and canola oil. Beef and sheep tallow and poultry oil from animal sources as well as waste cooking oil are also sources of raw materials. Other biodiesel feedstock sources include: neem seed, Jatropha, almond, barley, camelina (*Camelina sativa*), fish oil, karanja (*Pongamia glabra*), laurel, oat, poppy seed, okra seed, rice bran, sesame, sorghum and wheat (Pinto *et al.*, 2005; Montefri, Tai and Obbard, 2010; Anwar *et al.*, 2010 and Altun, 2011). The fatty acid composition of the triglyceride used for the production of biodiesel determines the physical and chemical properties of the fatty acid methyl or ethyl esters produced.

Most biodiesels are produced from food- grade oils and are referred to as ‘first generation’ biodiesel. With vegetable oil price soaring high in recent years, the cost of producing biodiesel will keep rising since the feedstock acquisition currently accounts for over 80 % of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry (Meng *et al.*, 2009). Biodiesel will lose its competitive advantage due to high price coupled with problems associated with the impacts on food security and land change. To mitigate these challenges, scientists are developing a new generation of biodiesel feedstocks of varying type, quality, and cost to help avoid such problems. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases,

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various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. Also, genetic modification is employed to obtain favourable traits of biodiesel crops, such as higher yields or the ability to grow on non-arable land (Ghage and Raheman, 2005; Veljkovic *et al.*, 2006; Ramadhas, Javarai and Muraleedharan, 2005; Achten *et al.*, 2008; Moser, 2009; Demirbas, 2009b; Li, Zhang and Sun, 2010 and Oner and Altum, 2009).

Microalgae use sunlight, carbon dioxide and water to produce oils like plants, but they do so more efficiently than crop plants. Different algae species produce different amounts of oil. The oil productivity of many microalgae has been found to greatly exceed the oil productivity of the best producing oil crops (Chisti, 2007; Becker, 1994; Riesing, 2005; Demirbas, 2010). According to Lin *et al.*, (2011), microalgae are the fastest-growing photosynthesizing organisms and can complete an entire growing cycle every few days. Thus, approximately 46 tons of oil/hectare/year can be produced from diatom algae. Some feasibility studies conducted reveal that specially bred mustard varieties can produce reasonably high oil yields and have the added benefit that the meal left over after the oil has been pressed out can act as an effective and biodegradable pesticide (Demirbas, 2008). Moreover, the production of algae can be achieved almost anywhere, even on sewage or salt water, and does not require fertile land or food crops, and processing requires less energy than the algae provides (Demirbas, 2010).

2.3.1 Potential Feedstocks for Biodiesel Production-Waste Vegetable Oil and Non-Edible Oilseeds

The production of biodiesel from different non-edible oilseed crops and waste vegetable oil has been extensively investigated over the last few years. Lists of some non-edible oilseed crops that have been used to produce biodiesel are shown in Table 2 below.

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Table 2 Some Non-edible Oilseeds Used for Biodiesel Production

Non-edible oilseed crop	Reference
<i>Jatropha curcas</i>	Patil and Deng, 2009; Ganapathy, Murugesan and Gakkhar, 2009; Tiwari, Kumar and Raheman, 2007
<i>Pongamia pinnata</i> (Karanja)	Naik <i>et al.</i> , 2008; Agarwal and Rajamanoharan, 2009
<i>Nicotiana tabacum</i> L. (tobacco seed)	Usta <i>et al.</i> , 2005; Veljkovic <i>et al.</i> , 2006
Rice bran	Lin <i>et al.</i> , 2009; Sinha, Agarwal and Garg, 2008
<i>Madhuca indica</i> (Mahua)	Ghadge and Raheman, 2005; Raheman and Ghadge, 2007
<i>Azadirachta indica</i> (Neem)	Rao, Rao and Reddy, 2008
<i>Hevea brasiliensis</i> (Rubber plant)	Ramadhas, Jayaraj and Muraleedharan, 2005
Castor	Sousa, Lucena and Fernandes, 2010
Linseed	Demirbas, 2009d
Sea mango	Kansedo, 2009
<i>Putranjiva roxburghii</i>	Kumar and Sharma, (2011)
<i>Schleichera triguga</i>	Kumar and Sharma, (2011)
<i>Thevatia peruviana</i>	Kumar and Sharma, (2011)
<i>Simmondsia chinensis</i>	Kumar and Sharma, (2011)
<i>Melia azedarach</i>	Kumar and Sharma, (2011)
<i>Cerbera odollam</i>	Kumar and Sharma, (2011)
<i>Calophyllum inophyllum</i>	Kumar and Sharma, (2011)
<i>Sapindus mukorossi</i>	Kumar and Sharma, (2011)
<i>Argemone Mexicana</i>	Kumar and Sharma, (2011)
<i>Ricinus communis</i>	Kumar and Sharma, (2011)

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Microalgae	Chisti, 2007; Demirbas, 2009c; Amin, 2009; Huang, 2010
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Figure 2 below show some pictures of non-edible fruit bearing plants that can be used for biodiesel production.



Figure 2 Some selected non-edible fruits bearing plants (Source: Kumar and Sharma, 2011).

Throughout the world, large amounts of these non-edible oil plants are available in nature and can be utilized for biodiesel production. Table 3 below shows the estimated amounts of waste vegetable oil (WVO) in some countries. Unfortunately, published data from Sub-Sahara Africa is not available. However, given current population sizes and the large number of restaurants, hotels, road side food providers and households in Sub-Sahara African cities and

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towns that use vegetable oils for cooking, it is conceivable that similar large quantities of waste oils exist in these countries. Thus, huge quantities of waste vegetable oils are available as potential biodiesel feedstock. The use of waste vegetable oil will eradicate the environmental problems posed by the improper disposal of such waste and in turn reduce the overall cost of biodiesel production.

Table 3 Quantities of Waste Vegetable Oil Generated in Some Countries

Country	Amount of WVO generated ,tones/year
United States of America	118,939,655 (Radich A, 2006)
Canada	135,000 (Statistics Canada, 2006)
United Kingdom	200,000 (Carter <i>et al</i> , 2005)
10 EU Countries	1,000,000 (Kulkarni and Dalai, 2006)

Therefore, to promote the global commercialization of biodiesel, low-cost non-edible oils and waste vegetable oils should be employed as feedstocks. In Graz, Austria used vegetable oil is utilized for production of biodiesel to fuel buses.

2.4 Biodiesel in Ghana

At a press conference in Accra on 8th August, 2003, Mr. Onuah Amoah, an Engineer and Executive Chairman of the Ghana Bio-energy Limited, said “Ghana is to earn about 240 million dollars in savings from a cut in diesel import from next year”. He explained that the country would save annually about US\$200 million used to import 700,000 tonnes of diesel and another US\$40 million worth for the thermal plant at Aboadze. According to him, the first phase of the US\$1.2 million factory that will produce the fuel was near completion at Pomadze in the Central Region. It will have an initial capacity of 360,000 tonnes but production of expected to expand over the years (Kakie, 2007).

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Physic nut (*Jatropha curcas*), known in Akan as (*Nkaneadua*) Ewe as (*Kpotsikpoti*) and Ga as (*Kutubletsuo*) is a multi-purpose and drought-resistance shrub which grows well in all parts of Ghana. It bears fruit throughout the year with normal rainfall and lasts for over 50 years. Its yield per hectare per annum, when matured, is about nine tonnes. It can be harvested from the fifth month after cultivation and can achieve maturity from the third year after planting. Biodiesel can be used in premium diesel substitute for vehicles, stationary engines, farming, construction and mining equipment, burners, marine engines and for electricity generation.

Onuah Amoah who is the brain behind the project, maintained that the biodiesel programme, when well implemented will produce 3.6 million tonnes of biodiesel, 6.8 million tonnes of organic fertilizer, 2.2 million of seed coat powder and 396 thousand tonnes of glycerine per annum, all from the physic plant. These, he added, could earn the country US\$3 million per annum. According to Onuah Amoah, a good implementation would also lower Ghana's reliance on imported goods by about US\$500 million, create wealth, simulate rural development, reduce rural urban drift and halt youth streetism. In addition, one million unskilled and 50,000 skilled jobs will be created. It will also enhance the productivity of agricultural crops in Ghana, making farming and forestry more profitable, he added.

But to achieve all that Onuah Amoah said the country needed to cultivate about one million hectares of physic nut trees. That, he added, would result in 2.2 billion natural physic nut trees. He encouraged farmers in the country to cultivate the plant and urged the citizens with huge tracts of land, which were not utilized to contact Ghana Bio-Energy Ltd, for the cultivation of crops.

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A farmer who cultivates a 10 acre farm will earn a gross revenue of about GH¢100 per month. Registered farmers will receive organic fertilizer from the company and payment spread over the period, he said. He intimated that the company would supply all farmers with seed for planting. According to The Ghanaian Times Newspaper published on 8th August, 2003., the then Deputy Minister of Information, Mr. Andrews Awuni, said test run of the biodiesel had already been conducted and approved by the Ghana Standard Board (GSB), Tema Oil Refinery (TOR) and the Environmental Protection Agency (EPA) (Kakie, 2007)).

2.5 Some Primary Reasons for the Growing Interest in Biodiesel Production

- i) It provides a market for excess production of vegetable oils and animal fats;

There is increasing demand around the world for soyabean meal to provide the protein for human and animal consumption. If new markets are not found for the soyabean oil, then the price will be low and farmers will have even more difficulty producing a profit. The animal by-products industry also has a problem with more supply than the current market can absorb. This is compounded by the potential for even greater restrictions on the use of animal fats in animal feeds because of concerns about the spread of BSE (Bovine Spongiform Encephalopathy – Mad Cow Disease) (Taylor and Woodgate, 2003).

- ii) It decreases the country's dependency on imported petroleum;

Petroleum markets tend to be sensitive to small fluctuations in supply so an additional source of fuel can have a surprising impact on keeping fuel prices stable.

- iii) Biodiesel is renewable and contributes less to global warming than fossil fuels due to its closed carbon cycle;

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The primary feedstock for biodiesel is a biologically-based oil or fat, which can be grown season after season, hence biodiesel is renewable. Also, since most of the carbon in the fuel was originally removed from the air by plants, there is very little net increase in carbon dioxide levels. However, some fossil carbon is contained in the methanol used to make methyl esters, and some fossil fuel is used during the production process. A life cycle study on biodiesel use in an urban bus conducted by the National Renewable Energy Laboratory found that CO₂ emission were reduced by 79 % for pure biodiesel compared with petroleum diesel fuel (Sheehan *et al.*,1998).

iv) The exhaust emissions from biodiesel are lower than with regular diesel fuels;

Biodiesel provides substantial reduction in carbon monoxide, unburned hydrocarbons, and particulate emissions from diesel engines. While the carbon monoxide and unburned hydrocarbons from diesels are already very low compared with gasoline engine, biodiesel reduces them further. Particulate emissions, especially the black soot portion, are greatly reduced with biodiesel.

v) Biodiesel has excellent lubricating properties;

Even when added to regular diesel fuel in an amount equal to 1 – 2 %, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulphur diesel fuel, into an acceptable fuel (Gerpen, 2005).

2.5.1 Environmental Benefits of Biodiesel

Environmental benefits of biodiesel in comparison to petroleum based fuels include:

- i) At the tailpipe, biodiesel emits 4.7 % more CO₂ than petroleum diesel”. However, if “biomass carbon is accounted for separately from fossil-derived carbon”, one can

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conclude that biodiesel reduces emissions of carbon monoxide (CO) by approximately 50 % emission and carbon dioxide by 78 % on a net lifecycle basis because the carbon in biodiesel emissions is recycled from carbon that was in the atmosphere, rather than the carbon introduced from petroleum that was sequestered in the earth's crust.

ii) Typically, emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Increases in NO_x can be effectively eliminated with the use of normal mechanical remediation techniques (e.g. catalysts or timing changes).

iii) Biodiesel contains fewer aromatic hydrocarbons: benzo(a)fluoranthene: 56 % reduction; Benzopyrenes: 71 % reduction.

iv) Biodiesel can reduce by as much as 20 % the direct (tailpipe) emission of particulates, small particles of solid combustion products, on vehicles with particulate filters, compared with low-sulphur (<50 ppm) diesel. Particulate emissions as the result of production are reduced by around 50 %, compared with fossil-sourced diesel. (Beer *et al*, 2004).

v) Biodiesel has a higher cetane rating than petro-diesel, which can improve performance and clean up emissions compared to crude petro-diesel (with cetane lower than 40).

vi) Biodiesel is considered readily biodegradable under ideal conditions and non-toxic. A University of Idaho study compared biodegradation rates of biodiesel, neat vegetable oils, biodiesel and petroleum diesel blends, and neat 2-D diesel fuel. Using low

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concentration of the product to be degraded (10 ppm) in nutrient and sewage sludge amended solutions, they demonstrated that biodiesel degraded at the same rate as a dextrose control and 5 times as quickly as petroleum diesel over a period of 28 days, and that biodiesel blends doubled the rate of petroleum diesel degradation through co-metabolism. The same study examined soil degradation using 10 000 ppm of biodiesel and petroleum diesel, and found biodiesel degraded at twice the rate of petroleum diesel in soil. In all cases, it was found that biodiesel also degraded more completely than petroleum diesel, which produced poorly degradable undetermined intermediates. Toxicity studies for the same project demonstrated no mortalities and few toxic effects on rats and rabbits with up to 500 mg/kg of biodiesel. Petroleum diesel showed no mortalities at the same concentration either, however toxic effects such as hair loss and urinary discolouring were noted with concentrations of >2000 mg/l in rabbits.

vii) In the United States, biodiesel is the only alternative fuel to have successfully completed the Health Effects Testing requirement (Tier I and Tier II) of the Clean Air Act (1990).

viii) Since biodiesel is more often used in a blend with petroleum diesel, there are fewer formal studies about the effects on pure biodiesel in unmodified engines and vehicles in day-to-day use. Fuel meeting the standards and engine parts that can withstand the greater solvent properties of biodiesel is expected to—and in reported cases does—run without any additional problems than the use of petroleum diesel.

ix) The flash point of biodiesel (>150°C) is significantly higher than that of petroleum diesel (64°C) or gasoline (-45°C) which makes it safer to handle. The gel point of

biodiesel varies depending on the proportion of different types of esters contained. However, most biodiesel, including that made from soyabean oil, has a somewhat higher gel and cloud point than petroleum diesel. In practice this often requires the heating of storage tanks, especially in cooler climates.

x) Pure biodiesel (B 100) can be used in any petroleum diesel engines, though it is more commonly used in lower concentrations. Some areas have mandated ultra-low sulphur petro-diesel (ULSD), which reduces the natural viscosity and lubricity of the fuel due to the removal of sulphur and certain other materials. Additives are required to make ULSD properly flow in engines, making biodiesel one popular alternative. Ranges as low as 2 % (B 2) have been shown to restore lubricity (Ge *et al.*, 2012).

2.6 Criticisms of Biodiesel

Some demerits in biodiesel production are the concerns of the environment.

i) Loss of habitats and endangerment of plant and animal species

The location where oil-producing plants are grown is of increasing concern to some environmentalists, one of the prime worries being that countries may clear large areas of topical forest in order to grow such oil rich crops such as oil palm. In the Philippines and Indonesia such forest clearing is already underway for the production of palm oil for food. Loss of habitat on such a scale could endanger numerous species of plants and animals. A particular concern which has received considerable attention is the threat to the already-shrinking population of orang-utans on the Indonesia islands of Borneo and Sumatra, which face possible extinction (Porteous, 2008).

ii) Replacement of Annual food crops with Non-food energy crops

Non-food energy crops and lipid rich algae with vastly greater oil yields may also replace low-yield annual food crops such Soya beans, skirting the deforestation risk associated with widespread uptake of biodiesel.

iii) Land Degradation

As non-food crops also facilitate the use of degraded lands, wastewater, processed sewage, and other waste streams, the benefits of such crops go well beyond their greater yields. Moreover, select non-foods crops such as Jatropha and castor bean can be grown in polycultures, in non-till agricultural applications, and they scale well from the standpoint of production, storage, and processing. As such, these crops have considerable promise for small-scale famers throughout tropical and temperate latitudes, providing a cash crop option which can also displace local demand for imported petroleum.

iv) Emissions of NO_x

If burned without additives, biodiesel (B100) is estimated to produce about 10 % more nitrogen oxide (NO_x) tailpipe-emissions than petro-diesel. As biodiesel has low sulphur content, NO_x emissions can be reduced through the use of catalytic converters to less than the NO_x emissions from conventional diesel engines. Moreover, as a transportation fuel, biodiesel is in its infancy in terms of additives which are capable of improving energy density, resistance to gelling, and NO_x emission. Recent advances in the use of cerium oxide, however, hold the potential to nearly eliminate NO_x emissions from both petro-diesel and biodiesel and diesel fuel additives based on cerium oxide can improve fuel consumption by 11 % in unmodified diesel engines

2.7 Processes for Biodiesel Preparation

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process.

2.7.1 Direct Use and Blending of Vegetable Oil

In August 1982, the first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota. The main issues raised were the cost of the fuel, the effects of vegetable oil fuels on engine performance and durability and fuel preparation, specifications and additives. Also, oil production, oilseed processing and extraction also were considered (Wanger and Petterson, 1982).

The advantages of vegetable oils as diesel fuel include: liquid nature-portability; heat content (80% of diesel fuel); ready availability and renewability. The disadvantages are: higher viscosity; lower volatility and the reactivity of unsaturated hydrocarbon chains (Pryde, 1983). Problems occur only after prolonged use of the vegetable oils in engines, especially with direct-injection engines. The problems include: coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices; carbon deposits; oil ring sticking and thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils. Two severe problems associated with direct use of vegetable oils as fuels were oil deterioration and incomplete combustion (Peterson, Auld and Korus, 1983).

Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Ma and Hanna, 1999). Several

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experiments have been run on the dilution of vegetable oils with petro-diesel. Most studies concluded that blending of vegetable oil with petro-diesel is not suitable for long term fuelling of direct injection diesel engines (Ma and Hanna, 1999). According to a study on the review of the direct use of vegetable oil as fuel by Ma and Hanna (1999), severe injector coking led to decreases in power output and thermal efficiency when 100 % of crude soybean oil was used. Because the more unsaturated vegetable oil will be used in the blend, the problem will be the tendency of the blend to oxidize and polymerize and cause injector coking and carbon deposition in the combustion chamber of the engine. A study showed that *Jatropha curcas* oil/petro-diesel blends increased fuel consumption and decreased thermal efficiency and exhaust temperature relative to straight petro-diesel (Dunn, 2005). However, another study shows that a blend of 97.4% diesel and 2.6 % *Jatropha* oil (by volume) gave the highest cetane number and even better engine performance with less fuel consumption than the diesel fuel (Forson, Oduro and Donkoh, 2004). The direct use of vegetable oils in diesel engine is not favourable and problematic because it has many inherent failings. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. The probable reasons for the problems and the potential solutions are shown in Table 4.

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Table 4 Known Problems, Probable Cause and Potential Solutions for Using Straight Vegetable Oil in Diesel Engines (Harwood, 1984)

Problem	Probable cause	Potential solution
Short-term		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Other ashes.	Partially refine the oil to remove gums. Filter to 4-microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long-term		
4. Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
6. Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerization	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.

2.7.2 Micro-Emulsification

Schwab, Bagby, and Freedman (1987), defined micro-emulsion as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1 ± 150 nm range formed spontaneously from two normally immiscible liquids and one or

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more ionic or non-ionic amphiphiles. Micro-emulsion with solvents such as methanol, ethanol and 1-butanol has been found to solve the problem of the high viscosity of vegetable oils. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984). Short term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel, in spite of the lower cetane number and energy content (Goering *et al.*, 1982b).

Micro-emulsions which are also called hybrid fuels are clear or translucent stable dispersion of oils, alcohol or ester and amphiphilic molecules. To remain in single-phase at constant temperature and pressure, micro-emulsions do not require agitation (Srivastava and Prasad, 200; Dunn 2005). Alcohols such as methanol or ethanol have limited solubility in nonpolar vegetable oils. Therefore amphiphilic molecules, which have one polar hydrophobic end and one nonpolar hydrophobic end in their structure, can bring them into one phase. Medium chain ($C_4 - C_{12}$) n – alcohol or long chain unsaturated fatty alcohols act as amphiphile compounds and can be used to prepare micro emulsion using lower alcohols ($C_1 - C_3$) and vegetable oils (Srivastava and Prasad, 200; Dunn, 2005). A micro- emulsion of methanol with vegetable oils can perform nearly as well as diesel fuels (Srivastava and Prasad, 2000).

Schwab *et al.* (1987) used the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsified fuel formulations. All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for No. 2 diesel.

The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. Methanol was often used due to its economic advantage over ethanol.

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Like blending of vegetable oils, micro emulsions also have problems of long term use in engines. A non- ionic emulsion which was made of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol had a viscosity of 6.31 cSt at 40°C, a cetane number of 25 and an ash content of less than 0.01% (Ziejewski *et al.*,1984)). Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. In a 200 h laboratory screening endurance test, no significant deterioration in performance was observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were reported

2.7.3 Thermal Cracking (Pyrolysis)

The conversion of one substance into another by means of heat or by heat with the aid of a catalyst is termed pyrolysis. It involves heating in the absence of air or oxygen (Sonntag, 1979b) and cleavage of chemical bonds to yield small molecules (Weisz *et al.*, 1979). According to Sonntag, (1979b) the pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many researchers have studied the pyrolysis of vegetable oils to obtain products suitable for fuel.

The variety of reaction paths and reaction products that may be obtained from the reactions that occur makes pyrolytic chemistry difficult. The pyrolysed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. Baroi, Yanful and Bergougrou (2007), revealed that the pyrolysis of vegetable oils demonstrate that with increase in the temperature, the liquid fraction products are decreased and the gaseous

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fraction products increase and the aromatics are increased in the liquid fraction products. Cracking or thermal decomposition of triglycerides or vegetable oils produces a class of compounds that includes alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil. The pyrolysed vegetable oils possess acceptable amounts of sulphur, water and sediment and give acceptable copper corrosion values but unacceptable ash, carbon residue amounts and pour point (Srivastava and Prasad, 2000). Carboxylic acids present in the pyrolysed vegetable oils are undesirable because they contain oxygen and are corrosive to metals. To reduce these undesirable carboxylic acids and increase the saturated alkanes in the product oil, catalytic cracking (cracking in the presence of catalyst) and catalytic hydrocracking (cracking in the presence of catalyst and hydrogen) are the suitable processes. Of these two processes catalytic hydrocracking is the most suitable process because it can produce a higher alkane content liquid fraction fuel than catalytic cracking with lower cyclic compounds (aromatics) and carboxylic acid content (Baroi, Yanful and Bergougnou, 2007). The detailed mechanism of the thermal decomposition of triglycerides as proposed by Schwab *et al.*, (1988) is shown in figure 3 below.

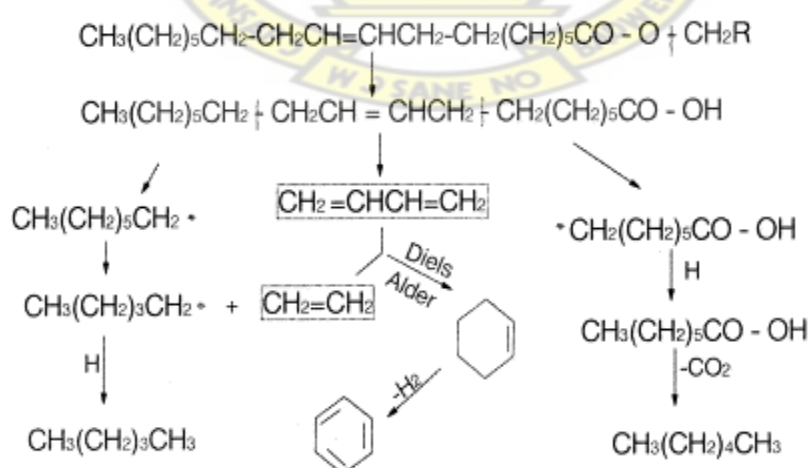


Figure 3 The mechanism of thermal decomposition of triglycerides (Schwab *et al.*, 1988)

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The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel.

2.7.4 Transesterification

Transesterification (also called alcoholysis) is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. This process is widely used to reduce the viscosity of triglycerides. The general overall reaction is shown in Figure 4.



Figure 4 General overall reaction of transesterification

When methanol is used as the lower alcohol to replace the glycerol of the triglycerides, the process is called methanolysis and fatty acid methyl esters (FAME) are formed. The overall process is a sequence of three, consecutive and reversible reactions, in which di and monoglycerides are formed as intermediates. The overall process and the three consecutive reaction steps of methanolysis are illustrated in Figures 5 and 6 respectively. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters according to Le Chatelier's principle and to allow its phase separation from the glycerol formed.

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USING UNSUPPORTED POTASSIUM CARBONATE**

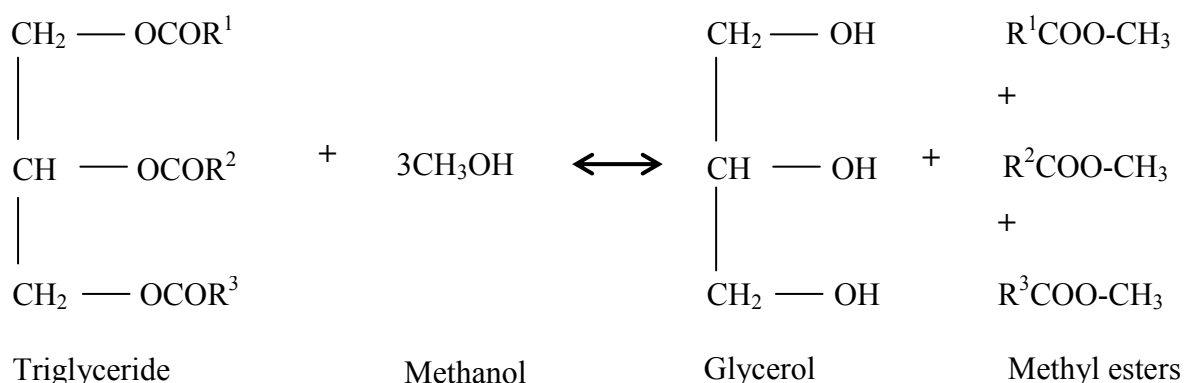


Figure 5 Overall transesterification reaction using methanol (Methanolysis)

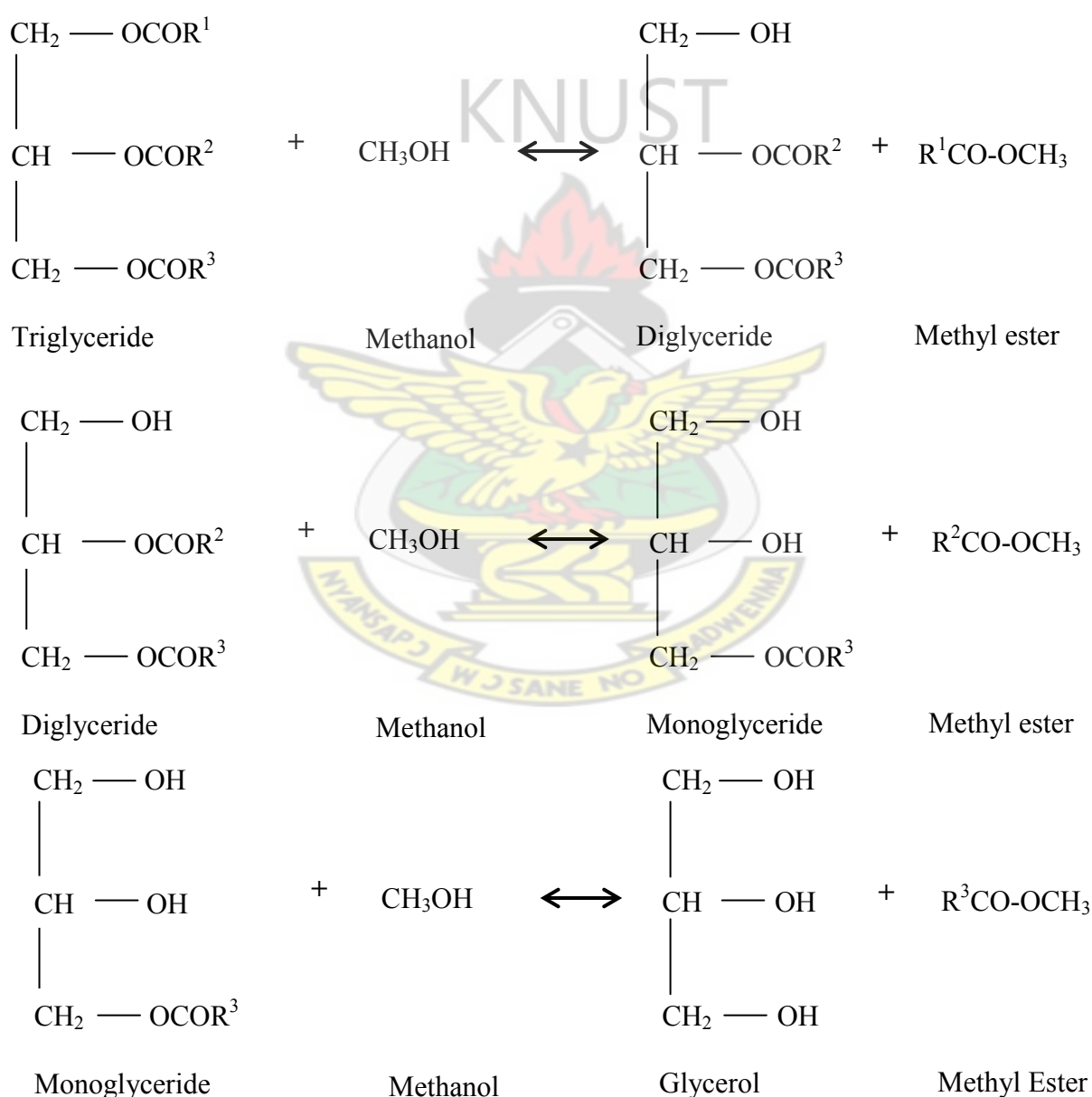


Figure 6 Detailed steps of the transesterification reaction (Methanolysis)

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According to Gerpen and Knothe (2005), when a larger molar excess (30:1) of alcohol to oil ratio is used the forward reaction is pseudo-first order; for a smaller molar excess (6:1) of alcohol the reaction is second-order and the reverse reaction is found to be second order. Transesterification is a reversible reaction, however in the final step when mono alkyl ester is formed; the back reaction does not take place or is very negligible because the glycerol formed is not miscible with the product, leading to a two-phase system (Gerpen and Knothe, 2005).

The transesterification reaction can take place using catalyst at lower temperatures, atmospheric pressure and lower molar excess of alcohol. For methanol base transesterification the most commonly used temperature is 60 °C and the methanol to oil molar ratio is 6:1 (Gerpen and Knothe, 2005). On the other hand, transesterification reactions can occur without any catalyst using a large excess of alcohol in such a temperature and pressure that the alcohol reaches its supercritical state. Demirbas (2007) revealed that in the case of methanolysis the minimum reaction temperature and pressure should be above 512.2K and 8.1 MPa, because these are the critical temperature and pressure of methanol. In this approach a very high conversion of triglyceride into fatty acid methyl esters can be obtained at the price of high temperature and pressure. Thus, this process solves the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of alcohol in the super critical state.

Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. 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). According to Pinto *et al.*, (2005), methyl, rather than ethyl, ester

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production are the predominant commercial products because methanol is considerably cheaper and more available than ethanol, and the downstream recovery of unreacted alcohol is much easier (Zhou and Boocock, 2006). Ethanol is renewable because it is produced from renewable agricultural resources, thereby attaining total independence from petroleum-based alcohols. The extra carbon atom in the ethanol molecule as compared to methanol slightly increases the heat content and the cetane number. Also, ethanol has a much higher dissolving potential for oils. Finally, another important advantage in the use of ethanol is that the ethyl esters have cloud and pour points that are lower than the methyl esters (Encinar *et al.*, 2007). However, the use of ethanol has the following demerits. The formation of methyl esters as a result of base catalysis is not as difficult as the formation of ethyl esters; reaction rate with ethanol is slightly slower than with methanol, and that accounts for the more difficult formation of the ethoxide anion (Om Tapanes *et al.*, 2008). Also, the formation of stable emulsion during ethanolysis is a problem. In ethanolysis, the emulsion from the alcohol and oil are more stable and tends to complicate the separation and purification of esters whiles that formed in methanolysis break down quickly and easily forms an upper methyl ester rich layer and lower glycerol rich layer (Zhou and Boocock, 2006; Encinar *et al.*, 2007).

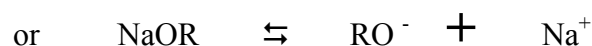
The main parameters that are critical in the transesterification process include the type and concentration of catalyst (alkaline or acid), alcohol to oil molar ratio, temperature, reaction time, rate of stirring, purity of the reactants (mainly water content) and free fatty acid content of the triglyceride. A catalyst is usually used to improve the reaction rate and yield. The reaction can be catalyzed by alkalis, acids, or enzymes.

2.7.4.1 Alkali or Base Catalyzed Transesterification

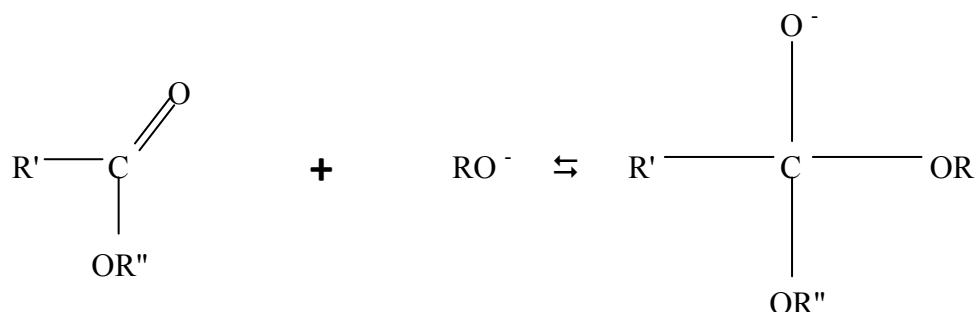
The alkali catalysts used for transesterification include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. The base catalysed transesterification reaction is 4000 times faster than the acid catalyzed processes and are less corrosive to industrial equipment compared to acidic catalyst, hence most commercial transesterifications are conducted with alkaline catalysts (Srivastava and Prasad, 2000). 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 (Leung and Guo, 2006). The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used or a two – step acid esterification followed by transesterification with an alkali can be utilized.

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps (Eckey, 1956). The first step of the base catalyzed reaction mechanism involves the attack of the alkoxide ion on the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol to regenerate the anion of the alcohol (alkoxide ion). In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride (Meher *et al.*, 2006a). This mechanism is shown in Figure 7.

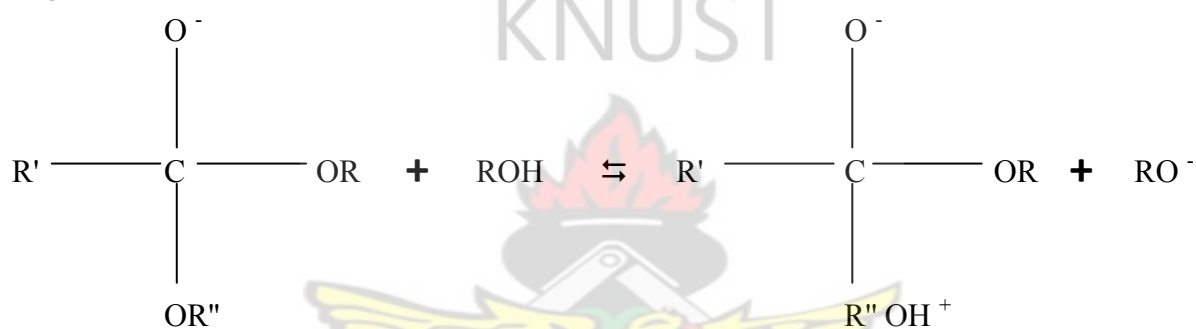
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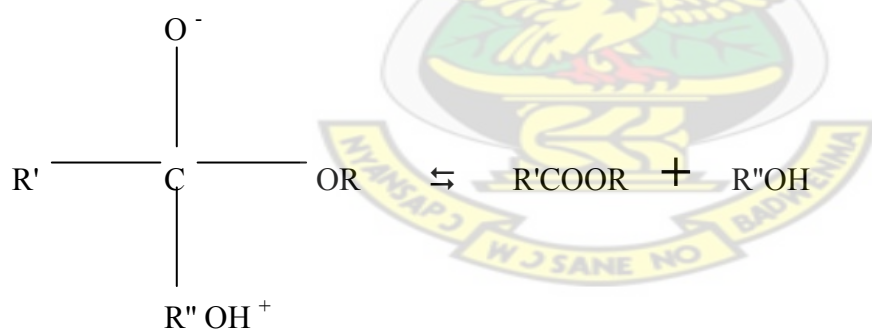
Step. 1.



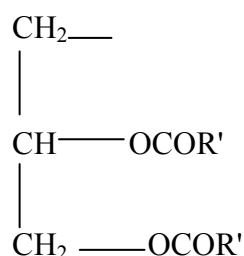
Step. 2.



Step. 3.



Where $\text{R}'' =$



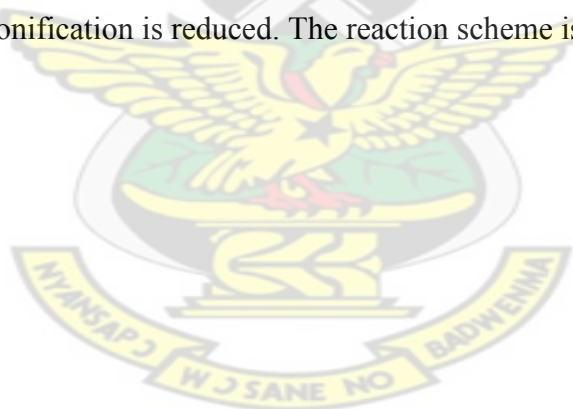
$\text{R}' =$ Carbon chain of fatty acid

$\text{R} =$ Alkyl group of alcohol

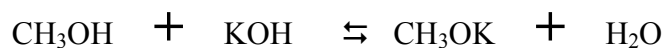
Figure 7 Mechanism of base catalyzed transesterification (Meher *et al.*, 2006a)

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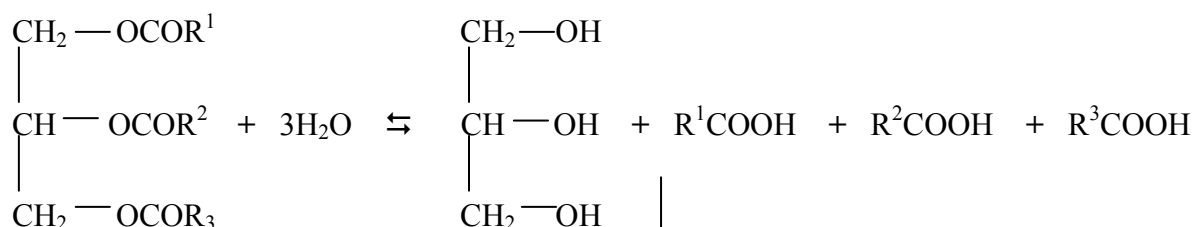
One of the major complications related with base catalyzed reaction is formation of soap as an undesired reaction between free fatty acids (FFA) and bases, which consumes some of the base. Thus the base available for catalyzing the reaction is reduced. Gerpen and Knothe (2005) showed that 3 % or less FFA content of the feedstock does not affect the transesterification significantly, but if the feedstock contains more than 5% FFA, the formation of soap inhibits separation of glycerol from the methyl esters. The hydroxide ion of sodium or potassium hydroxide catalysts reacts with the alcohol to produce water which hydrolyse the triglyceride to form diglyceride and free fatty acids irrespective of whether the alcohol is anhydrous or not. This FFA reacts with potassium or sodium ions and as result soap is formed and also reduces the formation of monoalkyl esters. This saponification reaction increases with the reaction temperature. However, the use of sodium or potassium alkoxide or methylate as a catalyst produces less water due to the absence of a hydroxide ion, hence; the extent of saponification is reduced. The reaction scheme is shown in Figure 8.



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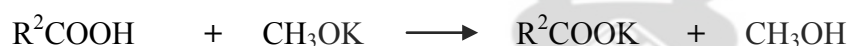
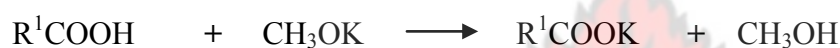
Methanol Potassium hydroxide Potassium methoxide



Triglyceride

Glycerol

Free Fatty Acids



Soap

Figure 8 Formation of soap

The comparative study conducted by Bondioli (2004) using sodium hydroxide, sodium methoxide; calcium oxide, barium oxide; strontium oxide and potassium carbonate revealed that potassium carbonate formed the least amount of soap when oxidized fat was used as the feedstock. The reason may be lack of formation of water by the reaction when potassium carbonate was used. The presence of little amount of soap formed might be due to the presence of moisture in the alcohol, air and in the triglyceride.

2.7.4.2 Acid- Catalysed Transesterification

Usually Bronzed acids like Hal, BF₃, H₃PO₄, H₂SO₄ and sulphonic acids are used in acid catalysed transesterification reactions (Lotero *et al.*, 2005). Preferably, sulphuric and sulphonic acids are mostly used. Although acid-catalysed transesterification reactions are much slower it is often preferred when the FFA content in the oils or feedstock is higher. The process involves simultaneously the esterification and transesterification reactions. Thus the FFA present in the oil in the presence of acid catalysts is esterified to form fatty acid alkyl esters followed by transesterification for maximum conversion of the feedstock into alkyl esters. The acid catalyzed esterification reaction is faster than the transesterification reaction. The presence of water or the formation of water during the esterification reaction of FFA affect the accessibility of the catalyst to the triglyceride molecules and inhibit the transesterification reaction as shown in figure 9 (Ataya, Dube and Ternan, 2007).



Figure 9 Esterification reaction

Due to the polarity that exists when FFA, alcohol and acid catalyst are combined, there is no phase difference in the reaction. In the first step of the acid catalyzed transesterification reaction mechanism, the carbonyl group is protonated by the acid catalyst; the compound formed in the intermediate steps by the nucleophilic attack of the alcohol produces a tetrahedral intermediate. The last step is the proton migration and breakdown of the intermediate (Lotero *et al.*, 2005). This mechanism is shown in the Figure 10. The adjoining carbon atom is made more electrophilic and more susceptible to nucleophilic attack due to the

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protonation of the carbonyl oxygen. However, the base catalysed transesterification takes on a more straight-forward route by firstly creating an alkoxide ion, which directly acts as a strong nucleophile, hence , giving rise to a different chemical pathway for the reaction . Thus, the formation of a more electrophile species in acid catalysis as opposed to a stronger nucleophile in base catalysis accounts for the different reaction rates.

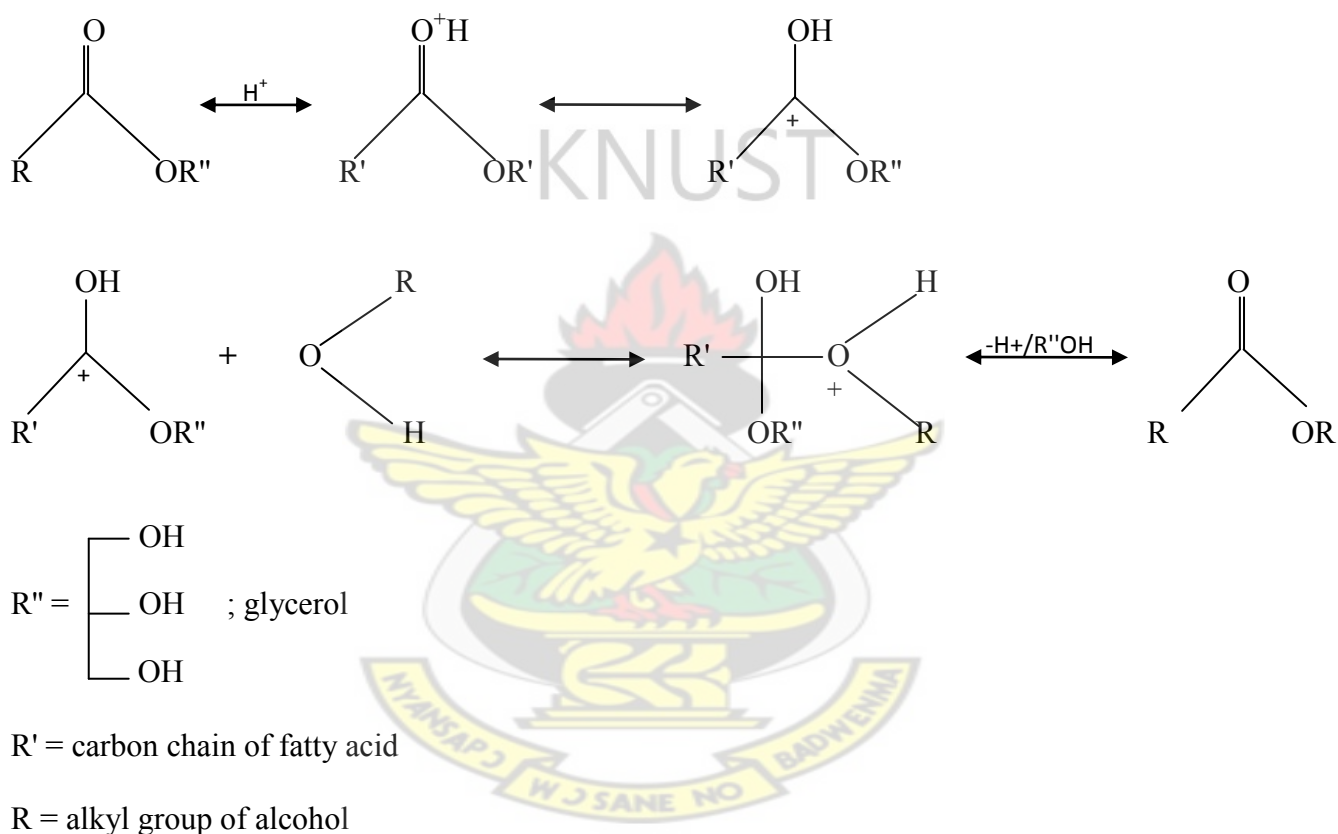


Figure 10 Acid catalyzed transesterification reaction (Meher *et al.*, 2006a)

2.7.4.3 Enzyme-Catalyzed Transesterification

The use of biocatalysts to catalyze triglyceride transformation to biodiesel has the following advantages: low temperature requirements of the reaction, easy separation of the enzymes and obtaining relatively pure glycerol without any treatment. The process is environmentally friendly and more sustainable. According to De Paola *et al.* (2009) and Kumar, Madras and

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Modak (2004), enzymatic transesterification can be carried out at 35 to 45°C. Unlike chemical catalysts, enzymes do not produce soaps in the conversion of lipids to biodiesel and catalyze the esterification of FFA and TG in one step without any need of the washing step. However, the major drawbacks of the use of biocatalysts for transesterification are: high cost of enzymes, slower reaction rate and possible enzyme inactivation by short chain alcohols like methanol (Noureddini, Gao, and Philkana, 2005 and Robles-Medina *et al.*, 2009). Lipase, a group of hydrolytic enzymes known as hydrolases are obtained from microorganisms such as bacteria and fungi and are capable of catalysing methanolysis reactions. The most commonly used Lipases are from *Mucor miehei*, *Rhizopus oryzae*, *Candida antarctica*, and *Pseudomonas cepacia* (Robles-Medina *et al.*, 2009). Lipase work in mild conditions and in biological systems they have the ability to convert triglycerides from different origin as well as FFAs to esters and glycerol (Marchetti, Miguel, and Errazu, 2007).

The major biocatalysts are extracellular lipases that refer to the recovered enzymes from the microorganism which is then purified and intracellular lipases where the enzyme remains inside the producing cell walls (Robles-Medina *et al.*, 2009). According to the proposed mechanism in Lipase catalyzed transesterification reaction, the enzyme at first catalyses the hydrolysis reaction in which FFA are liberated and then these FFA go through enzyme catalysed esterification reaction in which fatty acid alkyl ester/biodiesel are formed (Al-Zuhair, 2006). Lipases have been divided into three types in terms of regioselectivity which are:

- (i) SN-1,3-specific: hydrolyze ester bonds in positions R1 or R3 of TG,
- (ii) SN-2-specific: hydrolyze ester bond in position R2 of TG,
- (iii) nonspecific: do not distinguish between positions of ester (Taher *et al.*, 2011 cited in Antczak *et al.*, 2009).

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According to Fjerbaek, Christensen, and Norddahl (2009), biodiesel production from TG by lipases should be non-stereospecific where all TG, DG, and MG can be converted to fatty acids methyl esters (FAME).

Reusability of the enzyme by using it in an immobilized form is essential from economic point of view because of their high cost. Soluble enzyme acts as a solute in that they are dispersed in the solution and can move freely, but at the same time difficult to separate and to handle. Enzyme immobilization, a technique where free movement of the enzyme is restricted and localized to an inert support or carrier is an approach that helps to overcome the difficulty of separation of soluble enzymes which usually act as solute and are dispersed in solution. In addition to the fact that immobilized enzymes can be reused, the operating temperature of the process can be increased (Fjerbaek, Christensen, and Norddahl, 2009). Enzyme immobilization can be carried out in different ways. It can be classified into chemical and physical methods as shown in Figure 11.

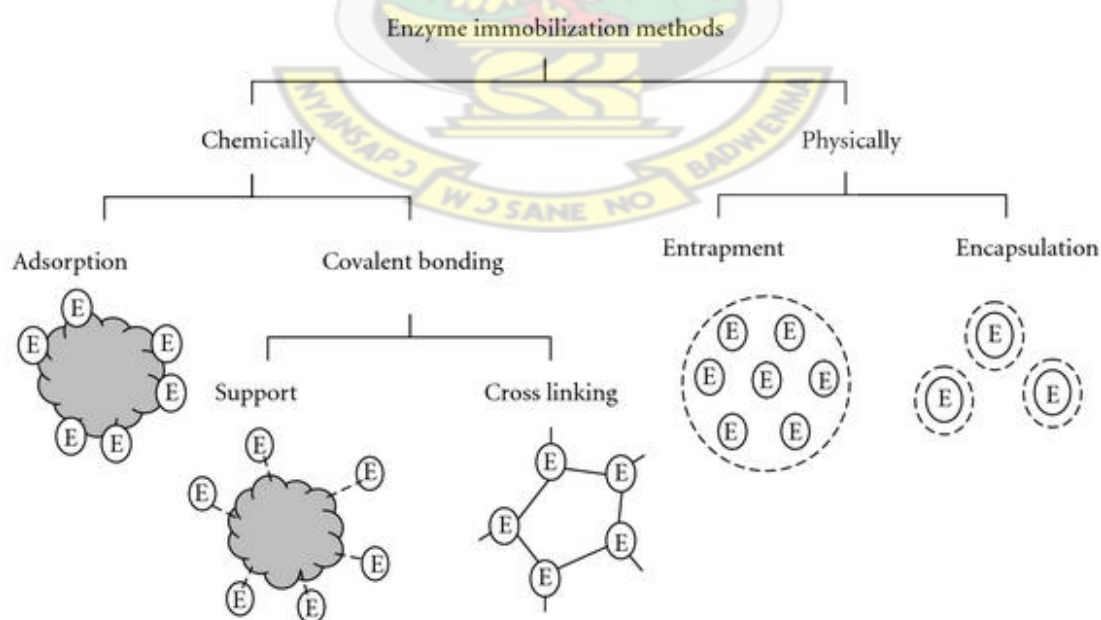


Figure 11 Enzyme immobilization methods (Source: Taher *et al.*, 2011)

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As a result of its ease of use, the absence of expensive and toxic chemicals, ability to retain the activity and feasibility of regeneration, physical adsorption has been clearly selected by most researchers (Al-Zuhair, Ling, and Jun 2007). But, immobilized enzymes are also subjected to diffusion limitation (internal and external) and inactivation (mostly by methanol). The addition of an inert solvent has been suggested to overcome immobilized lipase inactivation. However, solvents can be toxic, flammable, and have to be separated from the ester for reuse. Thus, solvent addition is not highly recommended since this will require using solvent recovery units, which will increase production cost. Hence, efforts have been made to produce alternative solvents that are non-toxic and environmentally friendly, have same advantages of dissolving both substrates and reduce excess alcohol inhibition and at the same time avoid the drawbacks of difficult separation of the solvent. Hence, supercritical fluids (SCF), for example SC-CO₂ (supercritical carbon dioxide), have been suggested as alternative solvents (Romero, *et al.*, 2005). Without using an organic solvent the alternative approaches for mitigating the deactivation of enzymes are either using longer chain length of the alcohols as miscibility of triglycerides increase with the increase of the chain length of the alcohols or step by step addition of short chain alcohols (Modi *et al.*, 2006; Shimada, 2002). Glycerol, one of the products of transesterification, also negatively affects the rate and extent of the conversion, because it is easily absorbed on the surface of the enzyme (Xu *et al.*, 2003; Belafi-Bako *et al.*, 2002). Removal of glycerol from the reaction mixture is also necessary to obtain a high conversion and a rate of the reaction.

2.7.4.4 Heterogeneous Catalysts

Chouhan and Sarma (2011), mentioned that different heterogeneous catalysts might be used for biodiesel production, including basic, acidic, mixed materials and materials generated from bio-waste. The most currently studied heterogeneous catalysts include calcium oxide,

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both pure, derived or supported in different materials (silica and alumina, amongst others), supported sodium, potassium, and their hydroxides, catalysts containing zirconia (ZrO), hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$), catalysts based on dolomite ($\text{CaMg}(\text{CO}_3)_2$), several other oxides such as the ones of zinc, manganese, aluminium, iron and titanium, silica/silicates based materials and zeolites. Calcium oxide, both alone or supported, seems to be the most promising catalyst, presenting higher basicity, lower solubility, acceptable reaction conditions and also lower price (Dias *et al.*, 2011). Heterogeneous base/acid catalysts are thought to be very attractive for biodiesel production as a result of easy separation of reaction products and for minimizing waste formation due to neutralization of homogeneous base/acid catalysts. They could be classified as Bronsted or Lewis catalysts, though in many cases both types of the sites could be present and it is difficult to evaluate the relative importance of the two types of sites in the reaction.

According to Di Serio *et al.*, (2008), the reaction mechanisms of both Bronsted and Lewis catalysts are similar to homogeneous Bronsted basic homogeneous catalysts (i.e. NaOH , KOH) unlike the case of acid catalyst. Moreover, both homogeneous (i.e. H_2SO_4 , *p*-toluene sulphonic acid) and heterogeneous Bronsted acid catalysts are active mainly in the esterification reaction whereas both homogeneous (i.e. metal acetate, metal complex) and heterogeneous Lewis acid catalysts are more active in the transesterification reaction. The formation of water in the esterification reaction can deactivate these Lewis catalysts. The reaction temperature is usually increased to produce a sufficient reaction rate in the transesterification reaction due to the low activity of the acid catalyst.

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D'Cruz *et al.*, (2007) and Di Serio *et al.*, (2008) revealed that, even though it is claimed that the heterogeneous catalysts are insoluble, in many experiments, leaching of catalysts was observed which could be due to the presence of glycerol in the reaction.

Also, Di Serio *et al.*, (2008), revealed that both basic (anion exchange) and acidic (cation exchange) ion exchange resins have been tried as heterogeneous catalysts. In case of basic ion exchange resins (i.e. PA308, PA 306, PA 306s, HPA 25) the catalytic activity diminishes during the reactions because of the resin's hydroxyl ion exchange reactions with triglycerides and as a result of the formation of fatty acids. In case of acidic resins (i.e. Amberlyst – 15) the catalytic deactivation is due to the blockage of the sites by adsorbed intermediates or product species.

To be economically viable and to compete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve continuous processing in a flow system, should have as few reaction steps as possible and limit the number of separation processes through the use of the robust heterogeneous (solid) catalyst. The appropriate solid catalysts can be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. Unlike homogenous catalyst, heterogeneous catalyst neither dissolves in the polar alcohol or the non-polar triglyceride and so the transesterification process starts with three phases. Thus in most cases it is observed that for getting higher reaction rates and conversions, one need higher temperature, pressure, higher molar ratio of alcohol to triglycerides or other means to overcome the mass transfer limitations (Di Serio *et al.*, 2008). Use of co-solvent can improve the mass transfer limitation arising from phase difference. Cyclic ethers especially THF are preferred to use as the co-solvent as they can dissolve both alcohol and the oil phase. The

boiling point of THF is close to the one of methanol (most commonly used in biodiesel production), so it can be easily removed and recovered along with excess methanol (Boocock *et al.*, 1996).

2.7.5 Other Methods of Transesterification

The other methods that could be employed in transesterification are: ultra- and high-shear in-line and batch processes; ultrasonic method and microwave irradiation technique.

2.7.5.1 Ultra- and High-Shear in-line and Batch Processes

Ultra- and High Shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This drastically reduces production time and increases production volume. The reaction takes place in the high-energetic shear zone of the Ultra- and High Shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size the larger the surface area the faster the catalyst can react.

2.7.5.2 Ultrasonic Cavitation Method

In the ultrasonic reactor method, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This cavitation provides simultaneously the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Hence the process of transesterification can run inline rather than using the time consuming batch processing (Thanh *et al.*, 2010). Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

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Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. Ultrasound frequencies range from approximately 20 kHz to 10 MHz, with associated acoustic wavelengths in liquids of roughly 100-0.15 mm. The application of ultrasound to chemical reactions and processes is called sonochemistry. The chemical effects of ultrasound (sonochemical) in liquids derive from several nonlinear acoustic phenomena, of which cavitation is the most important (Stavarache, Vinatoru and Maeda, 2007). Acoustic cavitation is the formation, growth, and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound. Acoustic cavitation can lead to implosive compression if treated under proper conditions which will produce intense local heating, high pressures, enormous heating and cooling rates, and liquid jet streams. Ultrasonication provides the mechanical energy for mixing and the required activation energy for initiating the transesterification reaction. Ultrasonication can help to reduce the separation time from 5 to 10 hours required with conventional agitation, to less than 15 minutes. The ultrasonication also helps to decrease the amount of catalyst required by 50 to 60 % due to the increased chemical activity in the presence of cavitation. Another benefit is the increase in purity of the glycerol.

2.7.5.3 Hydrodynamic Cavitation Method

Generally, hydrodynamic cavitation can simply be generated by the passage of the liquid through a constriction such as throttling valve, orifice plate, venturi etc. When the liquid passes through the constriction, the kinetic energy/velocity of the liquid increases at the expense of the pressure. If the throttling is sufficient to cause the pressure around the point of vena contracta to fall below the threshold pressure for cavitation (usually vapour pressure of the medium at the operating temperature), millions of cavities are generated. Subsequently as the liquid jet expands and the pressure recovers, the cavities collapse. During the passage of the liquid through the constriction, boundary layer separation occurs and substantial amount

of energy is lost in the form of permanent pressure drop. Very high intensity fluid turbulence is thus present downstream of the constriction; its intensity depends on the magnitude of the pressure drop, which, in turn, depends on the geometry of the constriction and the flow conditions of the liquid i.e., the scale of turbulence. A careful design of the system allows generating cavity collapse conditions similar to acoustic cavitation thereby enabling different applications requiring different cavitation intensities, which have been successfully carried out using acoustic cavitation phenomena but at much lower energy inputs as compared to sonochemical reactors.

Ji *et al.*, (2006) revealed that among mechanical stirring, ultrasonic cavitations and hydrodynamic cavitations, ultrasonic cavitation gives the highest conversion within the shortest time. On the other hand hydrodynamic cavitations are the most cost effective on the basis of the power consumption though they gave a little slower conversion than ultrasonic cavitations. Mechanical stirring performance is the worst among these three methods both in cost and conversions. Temperature has a positive impact on the increasing miscibility of the alcohol and of the oil phase.

2.7.5.4 Microwave Method

Current research is being directed into using commercial microwave ovens to provide the heat needed in the transesterification process (Leadbeater *et al.*, 2006 and Leadbeater *et al.*, 2007). The microwaves provide intense localized heating that may be higher than the recorded temperature of the reaction vessel. A continuous flow process producing 6 litres/minute at a 99% conversion rate has been developed and shown to consume only one-quarter of the energy required in the batch process (Leadbeater *et al.*, 2007). Although it is

still in the lab-scale, development stage, the microwave method holds great potential to be an efficient and cost-competitive method for commercial-scale biodiesel production.

The use of the microwave method has some major drawbacks. This method of synthesis is not easily scalable from laboratory small-scale synthesis to industrial multi kilogram production. The most significant limitation of the scale up of this technology is the penetration depth of microwave radiation into the absorbing materials, which is only a few centimetres, depending on their dielectric properties. The safety implication aspect is another reason for not allowing microwave reactors in the biodiesel industry (Groisman and Gedanken, 2008).

2.8 Biodiesel Quality and Specifications

The standards that are developed to determine the quality of biodiesel depends on variety of factors which vary from region to region. The factors may include: availability of feedstocks for production of biodiesel; characteristics of the diesel fuel standards existing in each region, which are different and the predominance of the types of diesel engines most common in the region and the emissions regulations governing those engines. United States and Brazilian markets are mainly comprised of heavier duty diesel engines whiles Europe has a much larger diesel passenger car market. Consequently, it is not surprising that there are some significant differences among the three standards. The current standards for biodiesel in Brazil and the United States of America are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European Union biodiesel standard is only applicable for fatty acid methyl esters (FAME).

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In Brazil and the United States of America, biodiesel is perceived primarily as a blend stock for fossil diesel fuel, and so some parameters are set on the understanding of a certain percentage of biodiesel being present in the finished fuel. In the European Union, the standard for biodiesel describes a product that may be used as a stand-alone fuel or as a blending component in conventional hydrocarbon based diesel fuel, therefore some EU limit values are set to different levels to those of Brazil and USA, and the specification is more extensive. This difference in usage of biodiesel represents in some cases a considerable difficulty in achieving the eventual establishment of a common specification. Biodiesel specifications according to the United States of America, European Union and Brazilian standards are shown in Table 5.



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Table 5 Biodiesel Specifications Compilation

Property	Test Methods			Limits			
	USA	EU	Brazil	Units	USA	EU	Brazil
	ASTM D6751	EN 14241	ANP 42		ASTM D6751	EN 14241	ANP 42
Sulphated Ash	D874	ISO 3987	ABNT NBR 6294/ ISO 3987/ASTM D874	% mass	0.020 max	0.02 max	0.02 max
Group I Metals (Na + K)	UOP 391	EN 14108/ EN 14109	EN 14108/ EN 14109	mg/kg	5 max	5 max	10 max
Group II Metals (Ca + Mg)	UOP 389	EN 14538	EN 14538	mg/kg	5 max	5 max	Report
Methanol or Ethanol Content	-	EN 14110	ABNT NBR 15343/EN 14110	% mass		0.20 max	0.50 max
Acid Number	D664	EN 14104	ABNT NBR 14448/EN 14104/ASTM D664	mgKOH/g	0.50 max	0.50 max	0.80 max
Free Glycerol	D6584	EN 14105/ EN 14106	ABNT NBR 15341/EN 14105/EN 14106	% mass	0.02 max	0.02 max	0.02 max
Total Glycerol	D6584	EN 14105	ABNT NBR 15344/EN 14105/ASTM D6584	% mass	0.24 max	0.25 max	0.38 max
Copper Strip Corrosion	D130	EN 2160	ABNT NBR 14359/EN 2160/ASTM D130	Rating	Class 3	Class 1	Class 1
Phosphorus Content	D4951	EN 14107	EN 14107/ASTM D4951	% mass	0.001 max	0.0010 max	Report

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Table 5 Biodiesel Specifications Compilation (continued)

Carbon Residue(on 100% Sample)	D4530	EN 10370	EN 10370/ASTM D4530	% mass	0.050 max		0.10 max
Ester Content	-	EN 14103	ABNT NBR 15342/EN 14103	% mass	-	96.5 min	Report
Distillation Temperature, 90% Recovered	D1160	-	D1160	°C	360 max		360 max
Flash Point	D93	EN 3679	ABNT NBR 14598/EN 3679/ASTM D93	°C	130.0 min	120 min	100 min
Total Contamination	-	EN 12662	EN 12662	mg/kg	-	24 max	Report
Water and Sediment	D2709	-	D2709	% volume	0.050 max		0.050 max
Water Content		EN 12937		mg/kg	-	500 max	
Oxidation Stability, 110°C	EN 14112	EN 14112	EN 14112	hours	3.0 min	6.0 min	6.0 min
Monoacylglycerol Content	-	EN 14105	ABNT NBR 15342/EN 14105	% mass		0.80 max	-
Diacylglycerol Content	-	EN 14105	EN 14105	% mass		0.20 max	-
Triacylglycerol Content	-	EN 14105	ABNT NBR 15344/EN 14105	% mass		0.20 max	-
Sulphur Content	D5453	EN 20846/ EN 20884	EN 20846/EN 20884/ ASTM D5453	mg/kg	15/500	10	500 (note 3)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Table 5 Biodiesel Specifications Compilation (continued)

Cloud Point	D2500	EN 23015		°C	Report		
Cold Filter Plugging Point	D6371	EN 116	ABNT NBR14747/ ASTM D6371	°C		(5 max (Grade A) (0 max (Grade B) (-5 max (Grade C) (-10 max (Grade D) (-15 max (Grade E) (-20 max (Grade F)	
Density @ 15°C		EN 3675/ EN 12185		kg/m ³		860 - 900	
Density @ 20°C			ABNT NBR 7148/ABNT NBR14065/ASTM D1298/ ASTM D4052	kg/m ³			Report
Linolenic Acid Methyl Ester	-	EN 14103	-	% mass	-	12.0 max	-
Polyunsaturated (≥ 4 double bonds) Methyl Esters				% mass	-	1 max	-
Cetane Number	D 613	EN 5165	EN 5165 / D613		47 min	51.0 min	Report
Iodine Value	-	EN 14111	EN ISO14111	g iodine/100g	-	120 max	-
Kinematic viscosity	D455	EN ISO 3104	ABNT NBR 10441/ EN ISO 3104/D445	mm ² /s	3.5-5.0	1.9-6.0	Report

2.8.1 Sulphated Ash

Ash-forming materials may be present in fuels in the following forms: abrasive solids, soluble metallic soaps, and un-removed catalysts. These compounds are oxidized during the combustion process to form ash, which is connected with engine deposits and filter plugging (Mittelbach, 1996). For these reasons sulphated ash is limited in the fuel specifications.

Abrasive solids and un-removed catalysts contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but can contribute to filter plugging and engine deposits.

2.8.2 Alkali and Alkaline Earth Metals

Metal ions are introduced into the biodiesel fuel during the production process. Whereas alkali metals stem from catalyst residues, alkaline-earth metals may originate from hard washing water. Sodium and potassium are associated with the formation of ash within the engine, calcium soaps are responsible for injection pump sticking. These compounds are partially limited by the sulphated ash, however tighter controls are needed for vehicles with particulate traps. For this reason these substances are limited in the fuel specifications.

2.8.3 Free Glycerol

The content of free glycerol in fatty acid methyl ester is dependent on the production process, and high values may stem from insufficient separation or washing of the ester product. The glycerol may separate in storage once its solvent methanol has evaporated. Free glycerol separates from the biodiesel and falls to the bottom of the storage or vehicle fuel tank (Gerpen, 2008), attracting other polar components such as water, monoglycerides and soaps. High levels of free glycerol can cause injector deposits, as well as clogged fueling systems,

and result in a build-up of free glycerol in the bottom of storage and fueling systems. These can lodge in the vehicle fuel filter and can result in damage to the vehicle fuel injection system (Mittelbach, 1996). High free glycerol levels can also cause injector coking. For these reasons free glycerol is limited in the fuel specifications.

2.8.4 Total Glycerol

Total glycerol is the sum of the concentrations of free glycerol and glycerol bound in the form of mono-, di- and triglycerides. The concentration depends on the production process. Fuels out of specifications with respect to these parameters are prone to coking and may thus cause the formation of deposits on injector nozzles, pistons and valves (Mittelbach *et al.* 1983). For this reason total glycerol is limited in fuel specifications.

2.8.5 Copper Strip Corrosion

This corrosion resulting from biodiesel might be induced by some sulphur compounds and by acids, so this parameter is correlated with acid number. The parameter characterizes the tendency of a fuel to cause corrosion to copper, zinc and bronze parts of the engine and the storage tank. A copper strip is heated to 50°C in a fuel bath for three hours, and then compared to standard strips to determine the degree of corrosion. For biodiesel, the copper strip corrosion test value should be as low as 1. High copper strip corrosion indicates a severely degraded or acid-contaminated fuel. Some experts consider that this parameter does not provide a useful description of the quality of the fuel, as the results are unlikely to give ratings higher than class 1.

2.8.6 Methanol or Ethanol Content

Both methanol and ethanol affect the flash point of esters. Methanol (MeOH) or ethanol (EtOH) can cause fuel system corrosion, low lubricity, adverse effects on injectors due to its high volatility, and is harmful to some materials in fuel distribution and vehicle fuel systems. For these reasons, methanol and ethanol are controlled in the fuel specification.

2.8.7 Acid Number

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

2.8.8 Phosphorus Content

Phosphorus in FAME stems from phospholipids (animal and vegetable material) and inorganic salts (used frying oil) contained in the feedstock. Phosphorus has a strongly

negative impact on the long term activity of exhaust emission catalytic systems and for this reason its presence in biodiesel is limited by specification. Because phosphorus can damage catalytic converters used in emissions control systems, its level must be kept low. Catalytic converters are becoming more common on diesel-powered equipment as emissions standards are tightened, so low phosphorus levels will be of increasing importance. This specification was added to ensure that all biodiesel, regardless of the source, has low phosphorus content (ASTM, 2009).

2.8.9 Carbon Residue

Carbon residue is defined as the amount of carbonaceous matter left after evaporation and pyrolysis of a fuel sample under specific conditions. Although this residue is not solely composed of carbon, the term “carbon residue” is found in all biodiesel standards depending on the region because it has long been commonly used. The parameter serves as a measure for the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber when used as automotive fuel. It is considered as one of the most important biodiesel quality criteria, as it is linked with many other parameters. Mittelbach (1996), showed that for FAME, carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst or contaminants. Moreover, the parameter is influenced by high concentrations of polyunsaturated FAME and polymers (Mittelbach and Enzelsberger, 1999). For these reasons, carbon residue is limited in the biodiesel specifications.

2.8.10 Ester Content

This parameter is an important tool, like distillation temperature, for determining the presence of other substances and in some cases meeting the legal definition of biodiesel (i.e. mono-

alkyl esters). Low values of pure biodiesel samples may originate from inappropriate reaction conditions or from various minor components within the original fat or oil source. A high concentration of unsaponifiable matter such as sterols, residual alcohols, partial glycerides and unseparated glycerol can lead to values below the limit. As most of these compounds are removed during distillation of the final product, distilled methyl esters generally display higher ester content than undistilled ones. (Mittelbach and Enelsberger, 1999).

2.8.11 Distillation Temperature, 90% Recovered, Maximum

This parameter is an important tool, like ester content, for determining the presence of other substances and in some cases meeting the legal definition of biodiesel (i.e. monoalkyl esters).

2.8.12 Flash Point

Flash point is a measure of flammability of fuels and thus an important safety criterion in transport and storage. The flash point of petro-diesel fuels are only about half the value of those for biodiesels, which therefore represents an important safety asset for biodiesel. The flash point of pure biodiesels is considerably higher than the prescribed limits, but can decrease rapidly with increasing amount of residual alcohol. As these two aspects are strictly correlated, the flash point can be used as an indicator of the presence of methanol in the biodiesel. Flash point is used as a regulation for categorizing the transport and storage of fuels, with different thresholds from region to region, so aligning the standards would possibly require a corresponding alignment of regulations.

2.8.13 Total Contamination (Solids)

Total contamination is defined as the quota of insoluble material retained after filtration of a fuel sample under standardized conditions. It is limited to ≤ 24 mg/kg in the European

specification for both biodiesel and fossil diesel fuels. The Brazilian and American biodiesel standards do not contain this parameter, as it is argued that fuels meeting the specifications regarding ash content will show sufficiently low values of total contamination as well. The total contamination has turned out to be an important quality criterion, as biodiesel with high concentration of insoluble impurities tend to cause blockage of fuel filters and injection pumps. High concentrations of soaps and sediments are mainly associated with these phenomena.

2.8.14 Water Content and Sediment

The Brazilian and American standards combine water content and sediment in a single parameter, whereas the European standard treats water as a separate parameter with the sediment being treated by the Total Contamination property. Water is introduced into biodiesel during the final washing step of the production process and has to be reduced by drying. However, even very low water contents achieved directly after production do not guarantee that biodiesel fuels will still meet the specifications during combustion. As biodiesel is hygroscopic, it can absorb water in a concentration of up to 1000 ppm during storage. Once the solubility limit is exceeded (at about 1500 ppm of water in fuels containing 0.2% of methanol), water separates inside the storage tank and collects at the bottom (Mittelbach 1996). Free water promotes biological growth, so that sludge and slime formation thus induced may cause blockage of fuel filters and fuel lines. Moreover, high water contents are also associated with hydrolysis reactions, partly converting biodiesel to free fatty acids, also linked to fuel filter blocking. Finally, corrosion of chromium and zinc parts within the engine and injection systems have been reported (Kossmehl and Heinrich, 1997). Lower water concentrations, which pose no difficulties in pure biodiesel fuels, may become

problematic in blends with fossil diesel, as here phase separation is likely to occur. For these reasons, maximum water content is contained in the standard specifications.

2.8.15 Sulphur Content

Higher sulphur contents in fuels affect human health because their emissions are associated with higher mutagenic potentials when exposed to the environment. This is why strict measures are being introduced in all regions to ensure low sulphur contents in fuels. Low sulphur fuels are an important enabler for the introduction of advanced emissions control systems. Also, fuels rich in sulphur cause engine wear and reduce the efficiency and life-span of catalytic systems. Biodiesel fuels have traditionally been found to be virtually sulphur-free. The national standards for biodiesel reflect the regulatory requirements for maximum sulphur content in fossil diesel for the region in question.

2.8.16 Cold Climate Operability

The behaviour of automotive diesel fuel at low ambient temperatures is an important quality criterion, as partial or full solidification of the fuel may cause blockage of the fuel lines and filters, leading to fuel starvation and problems of starting, driving and engine damage due to inadequate lubrication. The melting point of biodiesel products depend on chain length and degrees of unsaturation, with long chain saturated fatty acid esters displaying particularly unfavourable cold temperature behaviour. The Cold Filter Plugging Point (CFPP) of a fuel reflects its cold weather characteristics (Meher *et al.*, 2006a). At low temperatures below 0°C biodiesel (commonly fatty acid methyl esters) will crystallize. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation (Azam *et al.*, 2005). CFPP defines the fuels limit of filterability. Normally either pour point or CFPP are specified (Meher, *et al.*, 2006). One of the solutions for this problem is using branched chain alcohols

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to prepare fatty acid branched chain alcohol esters (Srivastava and Prasad, 2000). Crystallization involves the arrangement of molecules in an orderly pattern. When branched chain alcohols are introduced into linear long-chain ester structures, intramolecular associations should be attended and the crystallization temperature reduced. But highly branched and heavy molecular weight alcohols are not as effective for the transesterification reaction for biodiesel production. In this method, so far, use of isopropanol as a branched chain alcohol is feasible though isopropanol is more expensive than methanol or ethanol. Other higher branched chain alcohols are very expensive and their transesterification give lower yield and more impurities than isopropanol (Lee *et al.*, 1995). Thus the use of other branched alcohols is not economically feasible. Another method to improve the cold flow properties of biodiesel is to remove high-melting saturated esters by inducing crystallization with cooling. This method is known as winterization. This process depresses the cloud point of esters by equilibrating them at temperatures below their cloud point and above their pour point over an extended period of time, then filtering away the solids and as a result the cloud point of the biodiesel is reduced to a lower temperature. The other method is to use a cold flow additive in the biodiesel, which can improve the pour point but doesn't greatly affect the cloud point, whereas both CFPP and low temperature flow tests are nearly a linear function of cloud point (Srivastava and Prasad, 2000).

2.8.17 Cetane Number

The cetane number of a fuel describes its propensity to combust under certain conditions of pressure and temperature. The higher the cetane value the better the ignition properties. The cetane number affects a number of engine performance parameters like combustion, stability, white smoke, noise and emissions of CO and hydrocarbons. Biodiesel has higher cetane value than conventional diesel fuel, which results in higher combustion efficiency (Meher *et al.*,

2006a). But with the increase of cetane number the iodine value decreases which means that the degree of unsaturation decreases. This situation leads to solidification at higher temperature. It means that biodiesel with a very high cetane number may have higher melting point, cloud point and pour point and that it can solidify at or above 0°C depending on the value of the cetane number or the iodine number of the biodiesel. The cetane number of diesel fuel in the EU is regulated at ≥ 51 . The cetane number of diesel fuel in the USA is specified at ≥ 40 . The cetane number of diesel fuel in Brazil is regulated and specified at ≥ 42 . The upper limit of the cetane number/value is very important especially for cold climate countries where the Cold Filter Plugging Point (CFPP) of the fuel is very important.

2.8.18 Oxidation Stability

Oxidation stability is the measure of the oxidative degradation which also inhibits long term storage of biodiesel. Due to their chemical composition, biodiesel fuels are more sensitive to oxidative degradation than fossil diesel fuel. Oxidative degradation develops when unsaturated molecules present in the biodiesel react with atmospheric oxygen and are converted to peroxides. This is especially true for fuels with a high content of di -and higher unsaturated esters, as the methylene groups adjacent to double bonds have turned out to be particularly susceptible to radical attack as the first step of fuel oxidation (Dijkstra *et al.* 1995). The hydro peroxides so formed may polymerize with other free radicals to form insoluble sediments and gums, which are associated with fuel filter plugging and deposits within the injection system and the combustion chamber (Mittelbach and Gangl, 2001). Cross-linking at the unsaturation site can occur and the material may get polymerized into a plastic-like body. At high temperature, commonly found in an internal combustion engine, the process can get accelerated and the engine can quickly become gummed up or clogged with the polymerized biodiesel (Azam *et al.*, 2005). Where the oxidative stability of biodiesel

is considered insufficient, antioxidant additives might have to be added to ensure the fuel will still meet the specification.

2.8.19 Mono-, Di- and Tri-acylglycerols

The standards for Brazil and the USA do not provide explicit limits for the contents of partial acylglycerides. However, the EU standard specifies individual limit values for mono-, di- and tri-acylglycerides as well as a maximum value for total glycerol. In common with the concentration of free glycerol, the amount of glycerides depends on the production process. According to Mittelbach *et al.* (1983), fuels out of specification with respect to these parameters are prone to deposit formation on injection nozzles, pistons and valves.

2.8.20 Density

The values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds, or can be decreased by the presence of low density contaminants such as methanol. The densities of biodiesels are generally higher than those of fossil diesel fuel.

2.8.21 Kinematic Viscosity

The kinematic viscosity of biodiesel is an important factor as it controls the characteristics of the injection from the diesel injector. Meher *et al.*, (2006a), revealed that it is important to control the viscosity within an acceptable limit to avoid problems with the fuel injector system performance since the viscosity of fatty acid methyl esters go to very high levels. The kinematic viscosity of biodiesel is higher than that of fossil diesel, and in some cases at low temperatures becomes very viscous or even solid. High viscosity affects the volume flow and injection spray characteristics in the engine, and at low temperatures may compromise the

mechanical integrity of injection pump drive systems (when used as stand-alone B100 diesel fuel).

2.8.22 Iodine Number, Linolenic Acid Methyl Ester and Polyunsaturated Biodiesel

The iodine number is an index of the number of double bonds in biodiesel, and therefore is a parameter that quantifies the degree of unsaturation of biodiesel. The iodine number is reported in terms of the grams of iodine that will react with 100 g of fat or oil under specified conditions. Engine manufacturers have argued that fuels with higher iodine number tend to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves when heated (Kosmehl and Heinrich, 1997). Unsaturated esters introduced into the engine oil are thought to form high-molecular compounds which adversely affect the lubricating quality, resulting in engine damage. However, the results of various engine tests reveal that polymerization reactions occur to a significant extent only in fatty acid esters containing three or more double bonds (Prankl and Worgetter, 1996). Three or more-fold unsaturated esters only form a minor share in the fatty acid pattern of various potential seed oils, which are excluded as feedstock according to some regional standards due to their high iodine value. Some biodiesel experts have suggested limiting the content of linolenic acid methyl esters and polyunsaturated biodiesel rather than the total degree of unsaturation as it is expressed by the iodine value.

The indirect consequence of higher iodine value brings about the degradation of biodiesel. High iodine value biodiesel, due to the increased content of unsaturated fatty acid esters is susceptible to thermal as well as oxidative degradation processes. These degradation products lead to significant changes of the chemical composition of the fuel e. g. formation of polymerized products, acids, aldehydes, ketones, and others. Indicators of such products are

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measurable by changes of acid value, viscosity, ester content, linolenic acid ester content, stability, carbon residue, and contamination of the biodiesel. Therefore, a comparison of the different indicators will demonstrate that iodine value itself is not always the most suitable parameter to predict biodiesel behaviour.



CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Reagents

Anhydrous grade (99.95 %) methanol, Karl Fischer titrant (1 component reagent 2 mg/ml), 34813 HYDRANAL[®]-Standard 5.0, ACS grade (99 %) K₂CO₃, H₂SO₄ (99 %), AR grade Isopropyl alcohol, toluene, triolein (≈ 99 %), methyl oleate (≈ 99 %), 0.1N KOH, 0.1N NaOH, anhydrous Na₂SO₄, anhydrous CaSO₄, n-heptane and MSTFA (N-Methyl- N-Trimethylsilyl Trifluoroacetamide) were obtained from the Civil and Environmental Engineering and the Chemical and Biochemical Engineering Laboratories at Western University, London, Canada where the research was conducted. All laboratory reagents used were manufactured by Sigma – Aldrich Co. LLC.

3.1.2 Oil Feedstocks

The oil feedstocks comprise fresh Soya bean (SBFO) and Cottonseed (CSFO) vegetable oils, blend of the fresh Soya bean and Cottonseed vegetable oils (BFVO), waste Soya bean (SWVO) and waste Cottonseed (CWVO) vegetable oils, blend of the waste Soya bean and waste Cottonseed vegetable oils (BWVO) and *Jatropha curcas* oil (JCO).

3.1.2.1 Fresh Oils

i) Individual Fresh Oils

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Fresh Soya bean and Cottonseed vegetable oils were purchased from Poku Trading Enterprise Ltd, Kumasi, Ghana. The fresh Soya bean and Cottonseed oil samples were analyzed to determine optimum oil to methanol molar ratio for the transesterification reaction. These were used as control experiments, thus the fatty acid methyl ester yields were compared to the yields obtained from using the waste Soya bean and Cottonseed vegetable oils. Double press virgin *Jatropha curcas* oil was purchased from Medors Biotech Pvt Ltd, New Delhi, India.

ii) Blend of Fresh Vegetable Oils (BFVO)

A blend of fresh vegetable oil sample was prepared by adding 500 ml each of the fresh Soya bean and Cottonseed vegetable oils. The blend obtained served as the feed for the optimization of catalyst amount for the transesterification of the fresh vegetable oils.

3.1.2.2 Waste Vegetable Oils (WVO)

i) Individual WVO

Some of the fresh Soya bean and Cottonseed oils were given to food vendors at Kwame Nkrumah University of Science and Technology, Kumasi, Ghana to fry fish and chicken before they were sent to the University of Western Ontario in simulation of actual process.

ii) Blend of Waste Vegetable Oils (BWVO)

A blend of waste vegetable oil sample was prepared by adding equal portions of the fresh Soya bean and Cottonseed vegetable oils. The blend obtained served as the oil stock for the catalyst amount experiments.

3.1.3 Sample Pre-treatment

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The WVO samples were filtered under vacuum through a hydrophobic and oleophilic 56 1b Cellulose filter paper to remove moisture due to the introduction of water from the fried foods into the oil. The filtration process also ensured the removal of traces of food that might have carried over in the process of collecting the oil samples. The oil samples were kept in tightly covered 1 litre gallon containers and stored in a cold and dark room at 5 °C under argon to prevent oxidation.

3.2 Determination of Characteristics of Feedstocks and Fatty Acid Methyl Esters

The properties required for the characterization of biodiesel feedstocks include: acid value; % FFA; iodine value; saponification value; viscosity; fatty acid composition; flash point; density; molecular weight and water content. Also, the properties used for the characterization of fatty acid methyl esters according to biodiesel standards and specifications include: sulphated ash; Group I metals (Na + K); Group II metals (Ca + Mg); methanol or ethanol content; acid number; free and total glycerol; copper strip corrosion test; phosphorus content; carbon residue (on 100% Sample); ester content; distillation temperature (90 % recovered); flash point; total contamination; water and sediment; water Content; oxidation stability (110 °C); monoacylglycerol, diacylglycerol, triacylglycerol content; sulphur content; cloud point; cold filter; plugging point; density @ 15 °C; linolenic acid methyl ester; polyunsaturated (≥ 4 double bonds) methyl esters; cetane number; iodine value and kinematic viscosity. Five out of the various properties including viscosity were determined for the feedstocks and the fatty acid methyl esters (FAME) produced. This is because, the research intended to investigate the feasibility of using unsupported potassium carbonate as catalyst for transesterification. The extent or completeness of the reaction was determined by the reduction in viscosity after transesterification. This was confirmed by determining the purity

of FAME produced with the GC – MS. The five properties and their determination are discussed herein:

3.2.1 Density

A 25 ml density bottle with an FA2004N digital precision electronic analytical balance was used for density determination at 15 °C according to ASTM D4052.

3.2.2 Viscosity

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

3.2.3 Acid Number

The acid number and percentage free fatty acid contents of feedstocks and fatty acid methyl esters were determined according to the following procedure which conforms to ASTM D664. Five grams (5 g) of sample was dissolved in 125 ml of solvent which was prepared by mixing 50 % isopropyl alcohol with 50 % toluene (v/v). Then, 2 ml of 1 % alcoholic phenolphthalein was added and titrated with 0.1 M KOH (same as the original 0.1 N KOH) solution. The procedure was repeated three times for repeatability of results. A blank titration was also done. The acid number/value was calculated using AOCS Cd 3d-63 equation:

Acid value, mg KOH/g of sample = $[(A-B) \times N \times 56.1] / W$ (2)

The % FFA which is approximately half of the value of acid number was calculated as:

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$$\% \text{ FFA} = [(A-B) \times N \times 28.2] / W \dots\dots\dots (3)$$

where;

A = volume, ml of KOH used in titration,

B = volume, ml of KOH used in titrating the blank,

N = 0.1 N,

W = 5 g (weight of sample).

3.2.4 Water Content

The water content in feedstocks and the fatty acid methyl esters were analyzed using the Mettler Toledo Karl Fischer DL 31 Titrator. The titrant used was a 1 component reagent 2 mg/ml KF titrant while anhydrous grade (99.95 %) methanol was used as solvent. A 34813 HYDRANAL[®]-Standard 5.0 standard for volumetric Karl Fischer titration (5.00 ± 0.02 mg/ml water, corresponds 5.91 ± 0.02 mg/g) was used for calibration before the analysis of samples were done according to EN ISO 12937 (results are shown in Appendix A.1).

3.3 Experimental Setup

The setup for the transesterification is shown in Figure 12 below.

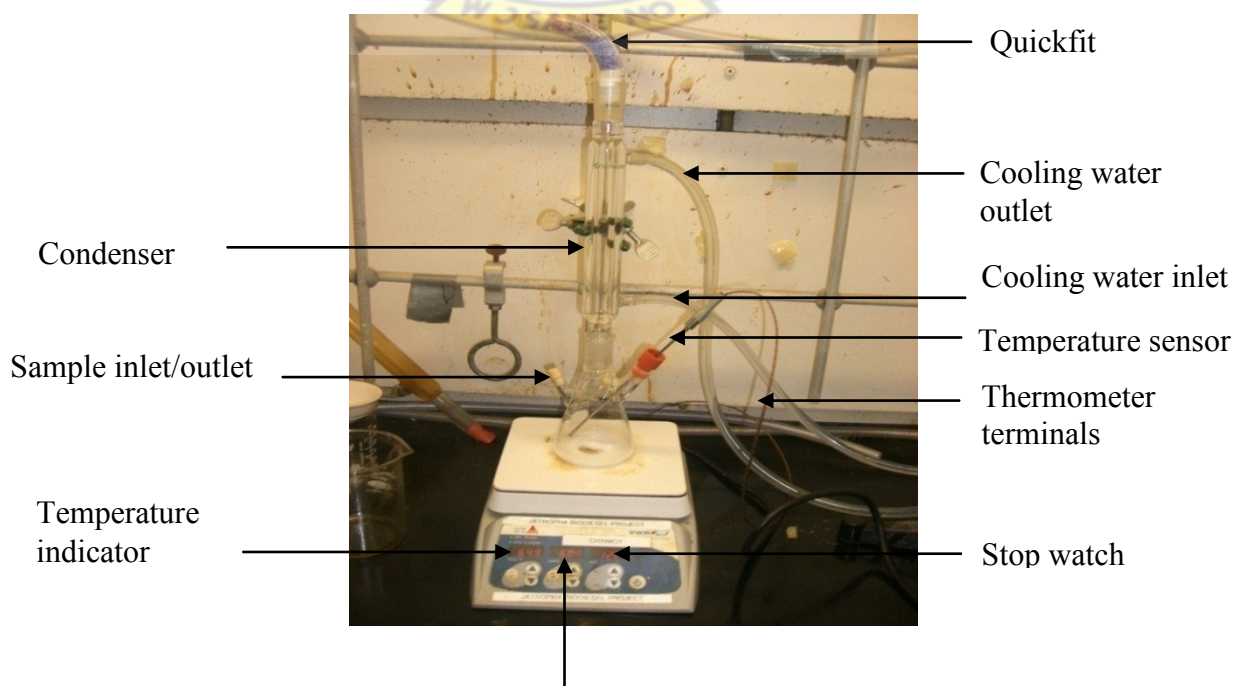


Figure 12 Experimental setup

The reactor was made by modifying a 250 ml Erlenmeyer flask which was fitted to a Liebig condenser. The size of the part of the fitting of the condenser to the flask was 24/40. The Liebig condenser was used for the condensation of methanol back into the reactor. Two more openings which were covered with rubber septum were made at the side of the Erlenmeyer flask by connecting 14/23 glass tubing to the flask. The dimensions of the reactor are shown in Figure 13 below. A temperature sensing probe connected to the hot plate was inserted through one of the openings into the reactor to help regulate the reaction at the set temperature. Addition of potassium carbonate - methanol mixture and oil feed into the reactor as well as withdrawal of samples from the reactor content was done through the other opening. A bent glass tube (Quickfit of 19/26 size) filled with anhydrous calcium sulphate and blocked at both ends with cotton wool was connected to the top of the condenser to ensure the entrance of moisture free air into the system. An advanced hot plate with stirrer (VWR 800 series) was used to provide controlled heating and stirring. The integrated stopwatch automatically stopped the heating and stirring at the set reaction time.

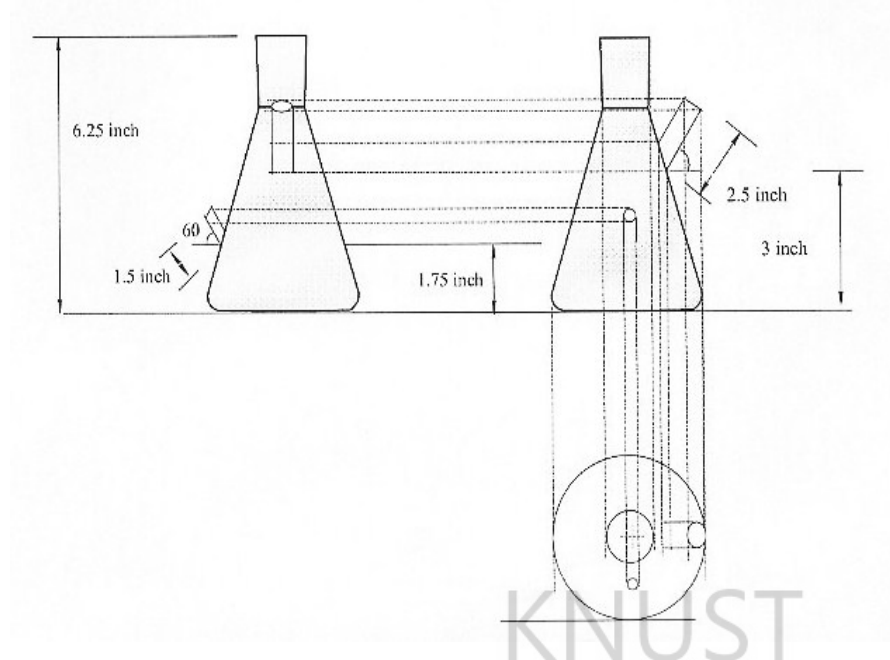


Figure 13 Dimensions of the Reactor

3.4 Equipment Calibration

All reagent dispensers were calibrated to give the exact volume of solutions or reagents needed. The sensitivity of the FA2004N digital precision electronic analytical balance was verified with reference weights and the readings were accurate up to 4-decimal places. A traceable ISO 17025 calibrated lollipop digital thermometer was used to check the sensitivity of the temperature sensing probe of the digital controller of the hot plate and the difference was $\pm 2\text{ }^{\circ}\text{C}$. The stirring sensitivity of the vendor specified magnetic stirrer as defined by the vendor was verified to be $\pm 2\%$. A 34813 HYDRANAL[®]-Standard 5.0 standard for volumetric Karl Fischer titration ($5.00 \pm 0.02\text{ mg/mL}$ water, corresponds $5.91 \pm 0.02\text{ mg/g}$) was used to calibrate the Karl Fischer Titrator before the analysis of the samples were done according to ISO 9001.

3.5 Procedure for Biodiesel Synthesis from the Various Feedstocks

3.5.1 Esterification

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This procedure was carried out to reduce the high % FFA of the Jatropha oil feed since that could enhance saponification and cause a reduction in the yield of the FAME. For every amount of percentage free fatty acid per gram of oil 0.05 g H_2SO_4 and 2.25 g of anhydrous CH_3OH were used. The sulphuric acid-methanol solution was added to the oil and heated at 60 °C while stirring at 600 rpm for 1 hour. After that, the reaction mixture was allowed to settle. The acid-methanol-water mixture which settled on top was separated from the esterified oil and the latter tested for a new percentage free fatty acid level. The procedure was repeated three times to ensure the percentage free fatty acid reduced from 5.70 % to 1.31 % for the transesterification reaction.



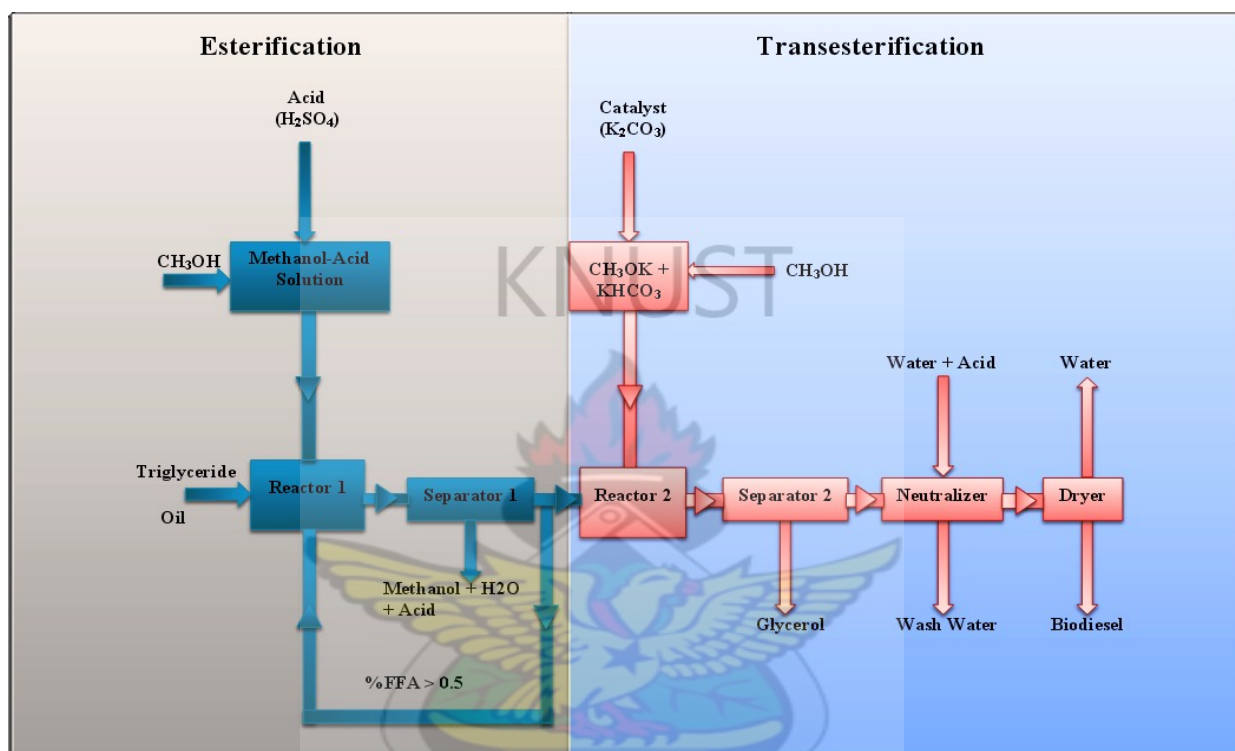
3.5.2 Transesterification

An amount of catalyst ranging from 1 g to 7 g wt. % of oil was added in separate experiments to 30 ml of methanol to dissolve to produce a carbonate solution. The catalyst was added to the methanol and heated to dissolve at 60 °C whilst condensing the methanol into the mixture. Exactly 100 g of oil feed was heated to 60 °C and charged into the reactor containing the carbonate alcohol mixture to aid in an increase of reaction. The mixture was stirred continuously while maintaining the temperature between 60-65 °C for 2 hours. The mixture was left for 8 hours undisturbed in a separating funnel to allow separation of glycerol from the fatty acid methyl ester phase. After separation, the crude biodiesel was washed 3-4 times with warm distilled water followed by 0.1 % H₂SO₄ to remove trace amounts of catalyst in the methyl ester. The washing was repeated until a clear water layer of neutral pH was obtained. The washed biodiesel was first dried using a 56 1b Cellulose filter paper and anhydrous sodium sulphate. A rotary evaporator was used to remove excess methanol that might have carried over during the washing process. The above procedure was repeated to determine an optimum catalyst amount for transesterification of the blend of fresh Soya bean and cotton seed oils and a blend of waste Soya bean and waste Cottonseed oil samples.

Once the optimum catalyst amount resulting in a higher yield was obtained, the second part of the experiment followed by maintaining the catalyst at the optimum amount at 60-65 °C reaction temperature for 2 hours whilst the methanol to oil molar ratios was varied in three experiments. These were 1:4, 1:6, 1:8 oil to methanol molar ratios for the amount with the higher yield to be chosen. Next, the optimized catalyst weight and oil to methanol molar ratio were maintained whilst the reactions were carried at different times namely, 40 min, 80 min and 120 min, to determine an optimum FAME yield. Lastly, the optimized catalyst amount,

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oil to methanol molar ratio and reaction time were maintained whilst the reaction temperature was varied from 55 °C, 60 °C and 65 °C to obtain the best yield. It was ensured that all the reaction contents were preheated to the desired temperature. The 8 hour reaction time was selected based on the preliminary experimental run with 1:6 oil to methanol molar ratio with a fixed amount of catalyst. The figure below shows the flow diagram of the experimental



procedure.

Figure 14 Schematic of the batch reaction processes of esterification and transesterification

3.6 Determination of Percentage Yield of FAME

The percentage yield of fatty acid methyl esters were estimated by mole concept and mass balance approach.

Assumptions:

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- i) After the transesterification reaction, if the reaction mixture settles, all the catalyst, methanol and glycerol would be in the lower glycerol phase and the upper biodiesel phase would be pure.
- ii) There would be no side reactions thus no soap production is expected.

Molecular weight of reactants, g/mol are: Cottonseed oil (848.3), Soya bean oil (874), Jatropha oil (870), Methanol (32.04), Glycerol (92.09)

Four grams (4 g) of catalyst (K_2CO_3) were used in all experiments.

Calculations:

For a 100 g of Cottonseed oil (CSO) used:

Number of moles, n (CSO) = $100/848.3 = 0.118$ moles,

So for a 1:4 oil/methanol molar ratio n (MeOH) = $4 \times 0.118 = 0.472$ moles.

Thus mass, m (MeOH) = $0.472 \times 32.04 = 15.123$ g, but actual MeOH used according to the stoichiometry = $3 \times 0.118 \times 32.04 = 11.342$ g

Unused MeOH = $15.123 - 11.342 = 3.781$ g

n (Glycerol) = n (CSO) = 0.118 moles, m (Glycerol) = $0.118 \times 92.09 = 10.867$ g

The process is depicted by the mass balance in the block diagram below.

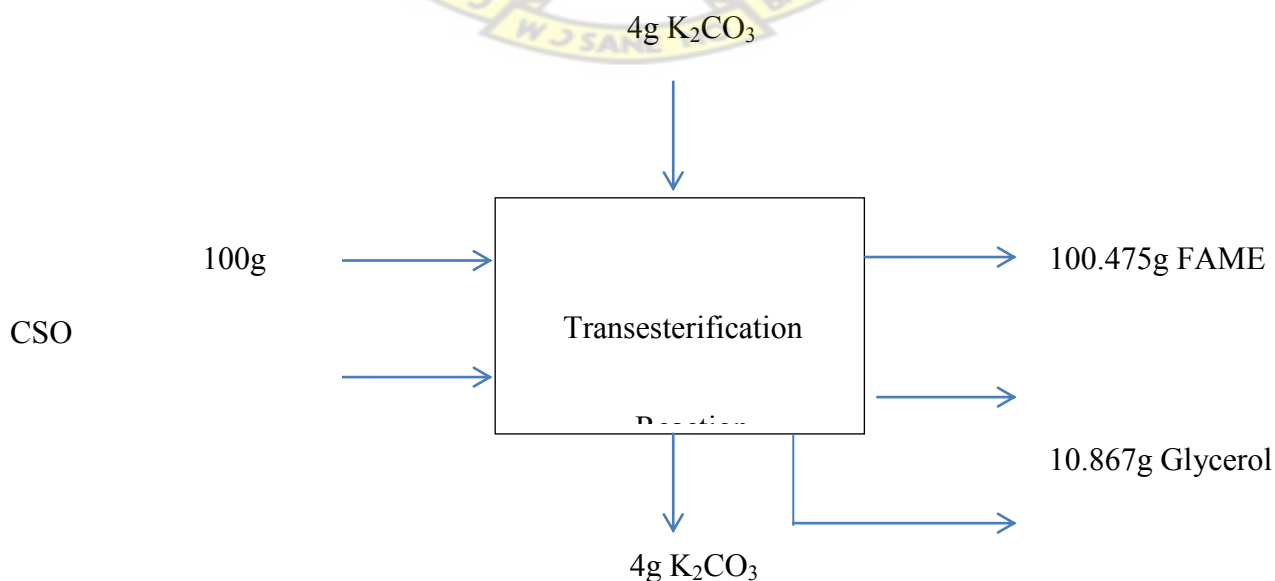


Figure 15 Schematic of mass balance of transesterification of Cottonseed oil with 1:4 oil/methanol ratio

Thus, the theoretical yield of FAME is 100.48g. The same procedure was used to determine the theoretical yield of FAME for the different oil/methanol molar ratios and different triglyceride samples as shown in the results.

The actual yield of FAME was determined after washing by weighing. The percentage yield is estimated as:

$$\% \text{ FAME YIELD} = (\text{actual yield/theoretical yield}) \times 100 \dots\dots\dots (4)$$

3.7 Determination of Percentage Composition of Oleic Acid Methyl Ester and the Prediction of Cetane Numbers of FAME

The percentage oleic acid methyl ester composition produced from the various oil feed stocks which were reported of a relative percentage of the total area were analyzed with an Agilent 7890A GC – MS. The instrument which was fitted with a DB-S Column 30m x 0.25mm I.D and film thickness of 0.25µm) was equipped with a flame ionization detector (FID).

The initial oven temperature was 50 °C. The oven was then heated: 50 °C for 1 min, 15 °C/min to 180 °C: hold for 0 min, 7 °C/min to 230 °C: hold for 0 min, 30 °C/min to 325 °C: hold for 40 min. The total run time was 1 hour. The detector make up gas used was helium. It was served at an inlet pressure of 26.708 psi. Hydrogen was used as a carrier gas for the FID which had a temperature of 380 °C.

Standard solutions of 12.5, 25, 50, 75, 90 and 100 % were prepared by diluting methyl oleate standard in different molar concentrations. The standard solutions were injected into the GC-

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MS to determine their area counts with their respective abundances. A graph of the area counts versus concentrations was plotted to obtain calibration curve which followed a second order polynomial. A 100 5 sample was silylated with 100 μ L MSTFA (N-Methyl-N-Trimethyl Trifluoroacetamide). After 20 min at room temperature, the silylated mixture was diluted with 8 mL of n-heptane and 1 μ L of this mixture was injected into the GC-MS. The molar concentration of oleic acid methyl ester in each biodiesel sample was obtained by using the calibration curve (Figure 20). The oleic acid methyl ester compositions were used to predict the cetane numbers of the produced biodiesel samples. According to Gerpen (1996), the following correlations (equations 5 and 6) can be used to predict cetane number (CN) of biodiesel samples.

$$\text{CN} = 45.954 + 0.279 * (\% \text{ Methyl Palmitate}) \dots\dots\dots (5)$$

$$\text{CN} = 43.194 + 0.193 * (\% \text{ Methyl Oleate}) \dots\dots\dots (6)$$

Hence, equation (6) was used in predicting cetane numbers of produced biodiesel samples.

3.8 Statistical Analysis

In all experiments the average of the percent mole conversions for three repetitive reactions has been calculated as the percent mole conversion of each oil feed to FAME. The errors were calculated on the basis of the 95 % confidence level. Analysis of variance (ANOVA) was performed to test for the effect of the various reaction conditions (i.e. catalyst amount, oil: methanol molar, reaction time and temperature) on the percent conversion of oil feed to FAME. This was followed by a multiple comparison test using the Tukey Honestly Significance test (Tukey HSD) or the Fisher Least Significance test (Fisher LSD) to do a pairwise comparison of the mean yields in all experiments.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Characteristics of Oil Feedstocks

Some properties of the oil feedstocks determined are represented in Table 6 below. The analyses were done in conformity with ASTM D 6751.

Table 6 Some Characteristics of Oil Samples

Property	Units	CSFO	SBFO	BFVO	CWVO	SWVO	BWVO	JCO
Density @ 15°C	g/ml	0.915	0.913	0.914	0.915	0.913	0.914	0.907
Kinematic viscosity	cP	34.3	30.7	32.5	34.7	32.4	33.6	32.1
Acid value	mg KOH/g oil	0.452	0.396	0.441	0.920	1.088	1.017	11.298
% FFA	%	0.227	0.199	0.222	0.462	0.547	0.511	5.679
Water content	%	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

The data show that CSFO, SBFO, BFVO, CWVO, SWVO and BWVO samples contained lower percentage free fatty acid of 0.227 %, 0.199 %, 0.222 %, 0.462 %, 0.547 % and 0.511 % respectively, so a single-step alkali transesterification was employed. However, the *Jatropha curcas* oil sample contained a higher percentage free fatty acid of 5.679 %. Alkali or base-catalyzed transesterification reaction requires low % FFA value (< 1 %) raw materials for biodiesel production. If the oil samples have high % FFA content (> 1 %) then the reaction requires more alkali catalyst to neutralize the FFA. The oil samples which had water content of less than 0.05 % were dried prior to transesterification to remove moisture. This was achieved by filtration as explained in section 3.1.3. The presence of water in oil feeds for biodiesel production normally cause soap formation and frothing which usually

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results in increase in viscosity. According to Demirbas (2009b and 2005), foam and gel formation caused by water hinders the separation of glycerol from biodiesel. Similarly, oil feeds containing high FFA also enhance soap formation as side reaction which could cause difficulty in the phase separation of the biodiesel from the glycerol phase and affect the yield and the purity of the alkyl esters produced. Thus, high free fatty acid and water always affect transesterification negatively by consuming the catalyst which leads to reduction of catalyst effect and subsequent reduction of methyl ester yield. High % FFA samples are therefore pre-treated to convert the FFA to methyl esters before transesterification. Hence, the *Jatropha* oil was esterified with sulphuric acid to reduce its high % FFA from 5.679 % to 1.31 %, followed by transesterification with unsupported K_2CO_3 . Thus, a two-step transesterification reaction was employed. The yields of the fatty acid methyl esters (FAME) produced were estimated using a mass balance approach and the purity of FAME (oleic acid methyl ester) confirmed with the GC-MS.

4.2 Effect of Catalyst Amount on Yield of FAME

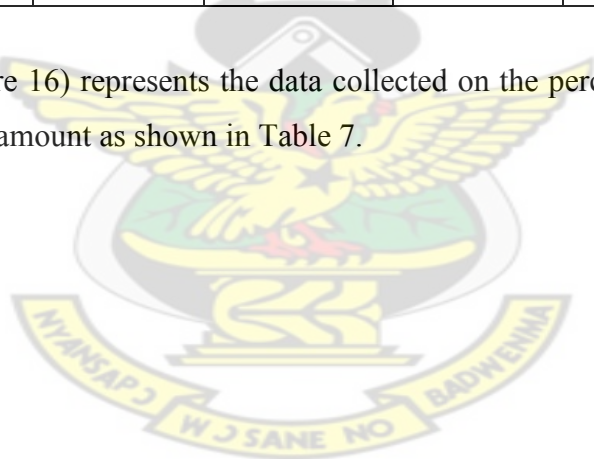
Different amounts of catalyst ranging from 1 g to 7 g (wt % of oil) were used for the transesterification reaction to determine an optimum yield of FAME and the results are presented in Table 7 below. The results showed that 4 g of K_2CO_3 (wt % of oil) gave the highest conversion of 100 g of each oil feed to FAME when 1:6 oil to methanol molar ratio was used with a reaction temperature of 60 °C while stirring was done at 600 rpm for 2 hours. The optimum yield of FAME under the above stated reaction conditions with the 4 g catalyst weight were 97.01 %, 95.35 % and 90.30 % for blend of fresh vegetable oil biodiesel (BFOB), blend of waste vegetable oil biodiesel (BWOB) and *Jatropha curcas* oil biodiesel (JCOB) respectively.

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Table 7 Effect of Catalyst Amount on Yield of FAME

Catalyst Amount/g (wt. % of oil)	SAMPL ID					
	BFOB		BWOB		JCOB	
	Avg. % FAME Yield	Error % @ 95 % C.L	Avg. % FAME Yield	Error % @ 95 % C.L	Avg. % FAME Yield	Error % @ 95 % C.L
1	14.32	0.85	11.09	0.04	10.47	0.04
2	90.09	0.05	82.12	1.17	80.67	0.15
3	93.27	0.14	92.10	1.14	86.33	0.04
4	97.01	0.12	95.35	0.20	90.30	0.02
5	94.47	0.02	93.41	0.15	89.22	0.04
6	93.47	0.20	93.13	0.09	86.94	0.04
7	93.03	0.05	92.46	0.78	85.19	0.02

The graph below (Figure 16) represents the data collected on the percentage yield of FAME with respect to catalyst amount as shown in Table 7.



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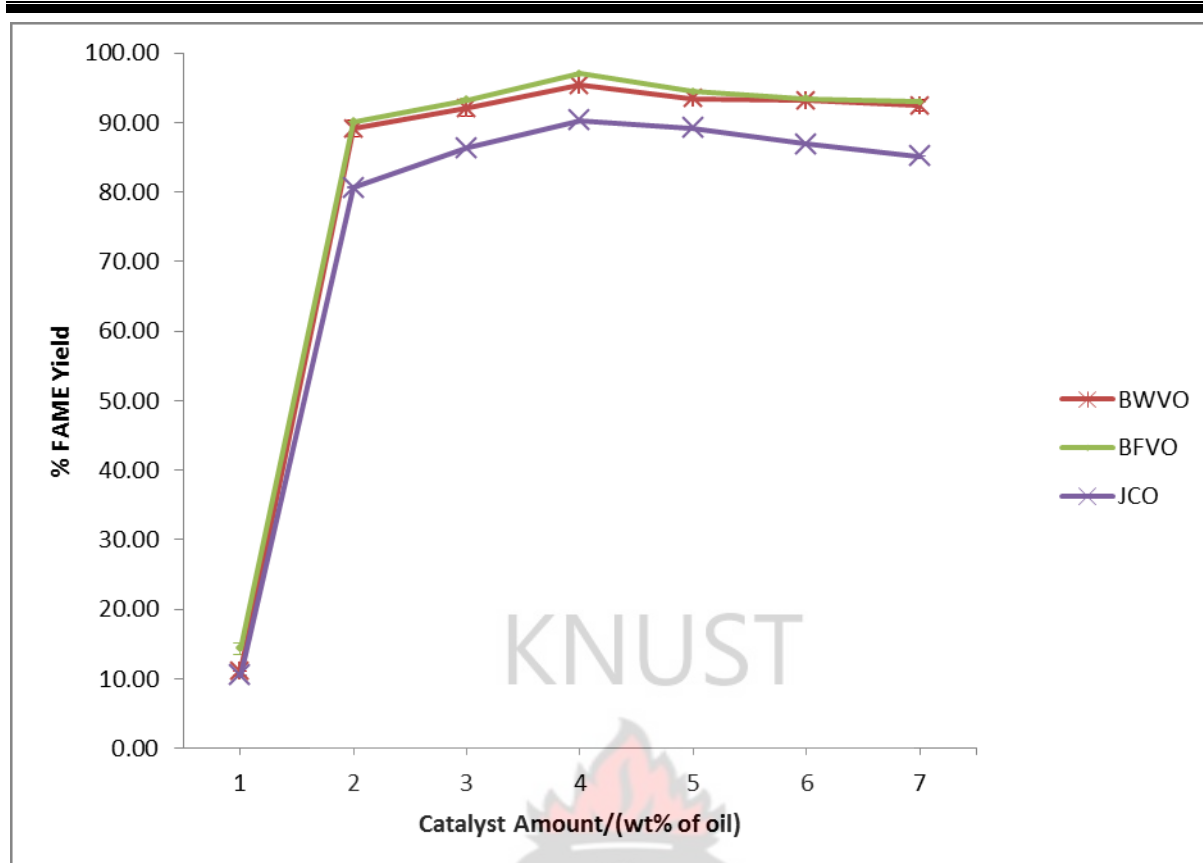


Figure 16 Effect of catalyst amount on yield of FAME

The 1 g of catalyst gave a lower yield because the reaction intermediates were unstable. This indicates that 1 g of K_2CO_3 was not sufficient to catalyze the transesterification reaction. An increase in the conversion of oil feeds to FAME (fatty acid methyl ester) occurred with a corresponding increase in catalyst amount to 4 g (wt % of oil). The conversion reduced when the weight of catalyst was increased from 4 g to 7 g in all cases.

Early studies conducted by Dorado *et al.*, (2004) and Baroi, Yanful and Bergounou, (2009) indicated that saponification of triglycerides causing the formation of soap and an increase in viscosity that results in reduced FAME conversion is as a result of excess alkali catalyst. Also, the mole concentration of FAME in the biodiesel phase was reduced due to the solubilization of soap at catalyst amount above the optimum weight of 4 g. Thus, the cause for significantly lower conversion of oil to biodiesel (FAME) when the catalyst amount was

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increased from an optimum weight of 4 g to 7 g might be due to secondary saponification. The multiple (pairwise) comparison test done for pairs of catalyst weight showed that the FAME yield for each catalyst amount in a pair did not yield statistically different results. Hence, for the blend of fresh vegetable oil the FAME yields for catalyst amount between 3 and 6 as well as between 3 and 7 (wt. % of oil) were not statistically different. The same effect was found between catalyst amount of 3 and 7, 5 and 6 as well as 6 and 7 (wt. % of oil) for the blend of waste vegetable oil biodiesel (see Appendix C.3). The qualitative soap presence analysis by Baroi, Yanful and Bergougnou (2009), using FTIR-ATR confirmed the increased solubilization of soap into the biodiesel phase at catalyst amount above the optimum weight. Platonov *et al.* (2002) revealed that more than 99% of KHCO_3 produced from the solubility reaction between anhydrous K_2CO_3 and methanol remain in the solid phase along with unreacted K_2CO_3 at room temperature (25°C). This is illustrated in equation (6) below.



The equilibrium of the above reaction is shifted towards product formation as a result of the phase distribution of KHCO_3 between the solid and liquid phase. KHCO_3 dissolves when the temperature is increased, thus the rate of backward reaction is favoured causing the concentration of CH_3OK to decrease while that of KHCO_3 increases. Also, Arzamendi *et al.*, (2008) showed that KHCO_3 was a weak catalyst with insignificant catalytic activity when compared to K_2CO_3 . Hence CH_3OK formed as shown in equation (6) is the main catalyst compound and therefore the transesterification reaction is dependent on it.

The BFVO feed was refined and contained no waxes and other contaminants with low % FFA of 0.222 % and gave the highest yield of 97.01 %. The BWVO feed contained some amount of waxes and gums with relatively high % FFA of 0.511 % and hence, resulted in a

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FAME yield of 95.35 %. The yield of FAME from Jatropha oil was 90.30 %. This was slightly lower as compared to the other feeds due to its % FFA value of 1.31 %.

Baroi, Yanful and Bergougnou, (2009) indicated that 6 g K_2CO_3 (wt % of Jatropha oil) gave the highest conversion (98.214 %), when 100 g of Jatropha oil was reacted with methanol at a temperature of 60 °C with stirring at 600 rpm for 10 hours using 1:6 oil/methanol molar ratio. The FAME yield of 98.214 % is higher than the 90.30 % obtained in the present study where 1:6 oil/methanol molar ratio was shown to be the best parameter for the transesterification of 100 g of Jatropha oil at 60 °C reaction temperature, 2 hours reaction time and stirring speed of 600 rpm using 4 g of K_2CO_3 as catalyst. Some of the Jatropha oil used by Baroi, Yanful and Bergougnou. (2009) was stored since year 2009 and used for the current research in 2011. The long storage of the Jatropha oil promoted rancidity which resulted in the high % FFA of 5.679 % as compared to the 1.47 % recorded by Baroi, Yanful and Bergougnou (2009). The possible formation of waxes and other contaminants due to the long storage of the Jatropha oil sample could also affect the yield in the present study. Acid esterification was employed as a pre-treatment step to reduce the high % FFA to 1.31 % prior to transesterification to give a maximum yield of 90.30 %. Based on the results obtained as shown in Table 3 and Fig 2, 4 g of K_2CO_3 was considered to be an optimum catalyst amount for the transesterification of CSFO, SBFO, CWVO SWVO and JCO. Hence, this catalyst amount was maintained throughout the experimentations to investigate the effects of other process parameters.

4.3 Effect of Oil: Methanol Molar Ratio on Yield of FAME

A fixed amount of 4 g catalyst was selected whilst the oil to methanol molar ratio was varied as 1:4, 1:6, and 1:8. A 60 °C reaction temperature was maintained whilst stirring was done at 600 rpm for 2 hours. The results are presented in Table 8 below.

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Table 8 Effect of Oil: Methanol Molar Ratio on Yield of FAME

Sample ID	Oil : Methanol Molar Ratio	Washed samples (after 6 hours of settling)	
		Avg. % FAME Yield	Error % @ 95 % C.L.
CSFO	1:4	88.08	0.45
	1:6	97.75	0.11
	1:8	95.29	0.68
SBFO	1:4	90.41	0.22
	1:6	96.41	0.17
	1:8	94.23	0.31
CWVO	1:4	82.32	0.43
	1:6	93.09	0.63
	1:8	92.14	0.61
SWVO	1:4	88.03	0.21
	1:6	95.72	0.89
	1:8	92.84	0.53
JCO	1:4	68.55	0.85
	1:6	86.72	0.68
	1:8	94.56	0.29

Figure 17 below is a graphical representation of the yield of fresh Cottonseed vegetable oil biodiesel (CSFOB), fresh Soya bean vegetable oil biodiesel (SBFOB), Cottonseed waste oil biodiesel (CWVOB) , Soya bean waste oil biodiesel (SWVOB) and *Jatropha curcas* oil biodiesel (JCOB) produced at the various oil to methanol molar ratios.

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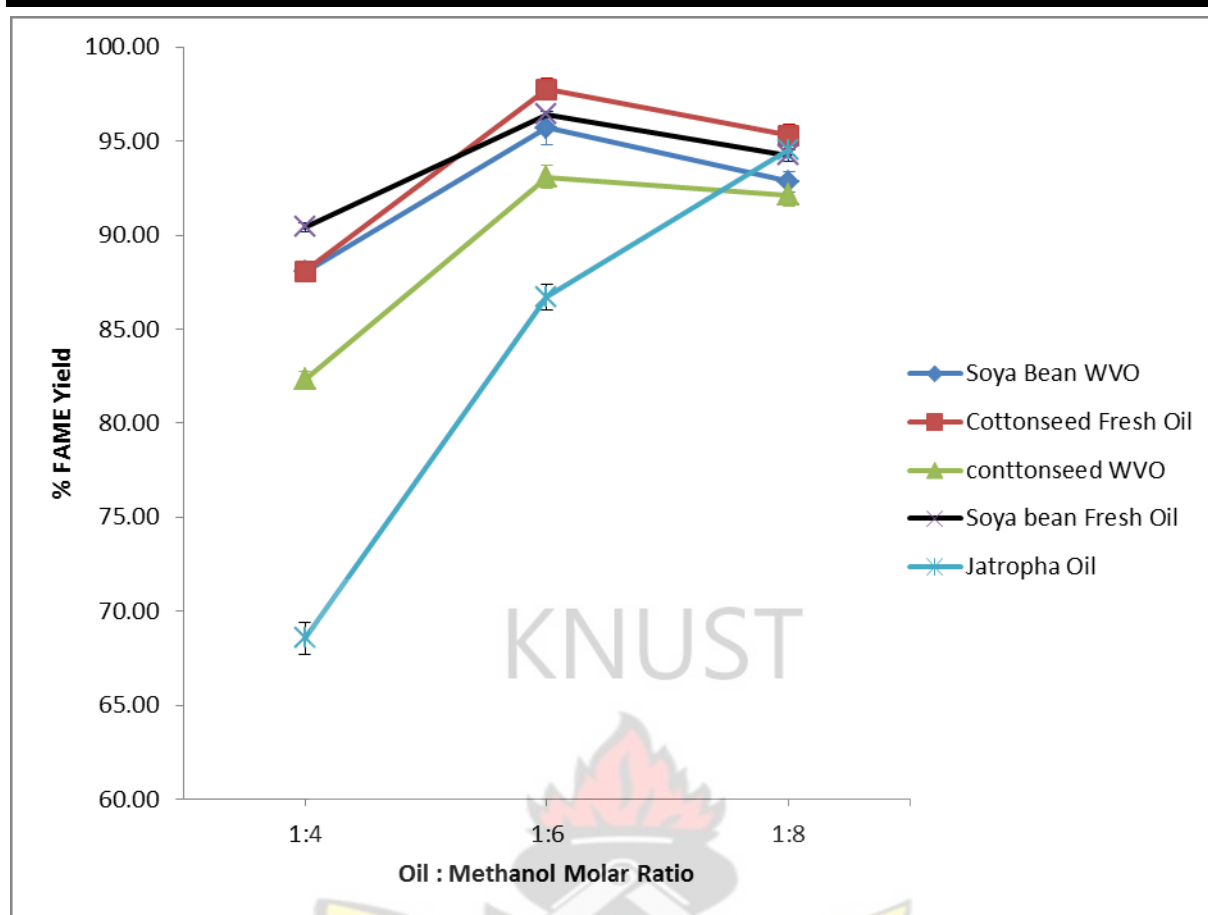


Figure 17 Effect of oil: methanol molar ratio on yield of FAME

The results show that when 1:4 oil to methanol molar ratio was used the FAME yield was lower as compared to when 1:6 and 1:8 oil to methanol molar ratio was used for the various oil samples. The yields obtained with the 1:4 oil/methanol molar ratio were 88.08 %, 90.41 %, 82.32 %, 88.03 % and 68.55 % respectively for Cottonseed fresh oil biodiesel (CSFOB), Soya bean fresh oil biodiesel (SBFOB), Cottonseed waste vegetable oil biodiesel (CWVOB), Soya bean waste vegetable oil biodiesel (SWVOB) and *Jatropha curcas* oil biodiesel (JCOB). This indicates that the amount of methanol was insufficient and hence, resulted in incomplete conversion of triglycerides to methyl esters. The oil/methanol molar ratio is considered to be one of the most important factors affecting the yield of biodiesel. Although the required stoichiometric ratio is 1:3 oil/methanol molar ratio, the transesterification process is usually carried out with an extra amount of alcohol in order to

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shift the equilibrium to the expected product, methyl ester side. It can be inferred from Table 8 that the optimum oil to methanol molar ratio for the transesterification of CSFO, SBFO, CWVO and SWVO was 1:6. At 1:6 oil/methanol molar ratio, the FAME yields obtained were 97.75 %, 96.41 %, 93.09 %, 95.72 % and 86.72 % respectively for CSFOB, SBFOB, CWVOB, SWVOB and JCOB.

According to Hoque *et al.* (2011), the optimum oil/methanol molar ratio for the transesterification of beef fat, chicken fat and used cooking oil was 1:6 with 1.25 % (wt % of oil) catalyst concentration, 65 °C reaction temperature, 2 hours reaction period and stirring speed of 150 rpm. The maximum yield at the optimum conditions with the 1:6 oil/methanol molar ratio were 87.4 %, 89 % and 88.3 % for beef fat, chicken fat and used cooking oil respectively. These results and those obtained in the current study are in agreement with many other studies which suggest the optimum molar ratio to be in between 4.8:1 and 6.5:1 for the maximum yield of biodiesel from used cooking oil and animal fat (Hoque, Singh and Chuan, 2011).

Also, when the oil/methanol molar ratio was 1:8 the FAME yields for CSFO, SBFO, CWVO, SWVO and JCO feeds were 95.29 %, 94.23 %, 92.14 %, 92.84 % and 94.56 % respectively. The FAME yields for CSFO, SBFO, CWVO and SWVO were low as compared to the those obtained at 1:6 oil/methanol molar ratio. This indicates that excess methanol dilute the catalyst concentration, leading to a reduction in oil conversion. Alamu (2007), observed that biodiesel yield increases as the oil to methanol ratio increases only up to a threshold mix. However, the best oil/methanol molar ratio that resulted in the highest yield for the transesterification of the *Jatropha curcas* oil feed was 1:8. The variation in optimum oil/methanol molar ratio for biodiesel yield for *Jatropha curcas* oil and the other oil sources could be mainly due to the variation of FFA. This difference in FFA content causes the

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catalyst to react differently towards the oils. The results of the experiments conducted by Baroi, Yanful and Bergounou (2009) indicated that 1:10 oil/methanol molar ratio gave the highest conversion (98.79 %), when 100 g of Jatropha oil was reacted with methanol at a temperature of 60 °C with stirring at 600 rpm for 10 hours using 6 g of K_2CO_3 as catalyst. The FAME yield of 98.79 % is higher as compared to 94.56 % in the present study where 1:8 oil/methanol molar ratio was shown to be the best condition for the transesterification of 100 g of Jatropha oil at 60 °C reaction temperature, 2 hours reaction time and stirring speed of 600 rpm using 4 g of K_2CO_3 as catalyst. Although Baroi, Yanful and Bergounou (2009), observed a higher FAME yield, the excess methanol used would increase the separation and purification cost of the methanol in the process. Based on the results obtained as shown in Table 8 and Figure 17, the oil/methanol molar ratio of 1:6 was considered to be an optimum condition for the transesterification of CSFO, SBFO, CWVO and SWVO while that of JCO was 1:8. Thus, these ratios were maintained throughout the experimentations to investigate the effects of other process parameters.

4.4 Effect of Reaction Time on Yield of FAME

Using the optimum catalyst amount and oil to methanol molar ratio, separate experiments were conducted at different reaction times of 40, 80 and 120 mins for CWVO, SWVO and JCO feedstocks. The optimum reaction time for the transesterification processes are 40 mins, 80 mins and 120 mins for CWVO, SWVO and JCO respectively as shown in Table 9 and represented graphically in Figure 18 below.

Table 9 Effect of Reaction Time on Yield of FAME

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Sample ID	Reaction Time, mins	Washed samples (after 6 hours of settling)	
		Avg. % FAME Yield	Error % @ 95 % C.L.
CWVO	40	98.27	0.62
	80	97.68	0.31
	120	93.09	0.63
SWVO	40	97.51	0.55
	80	98.48	0.10
	120	95.72	0.89
JCO	40	86.19	0.30
	80	88.19	0.14
	120	94.57	0.07

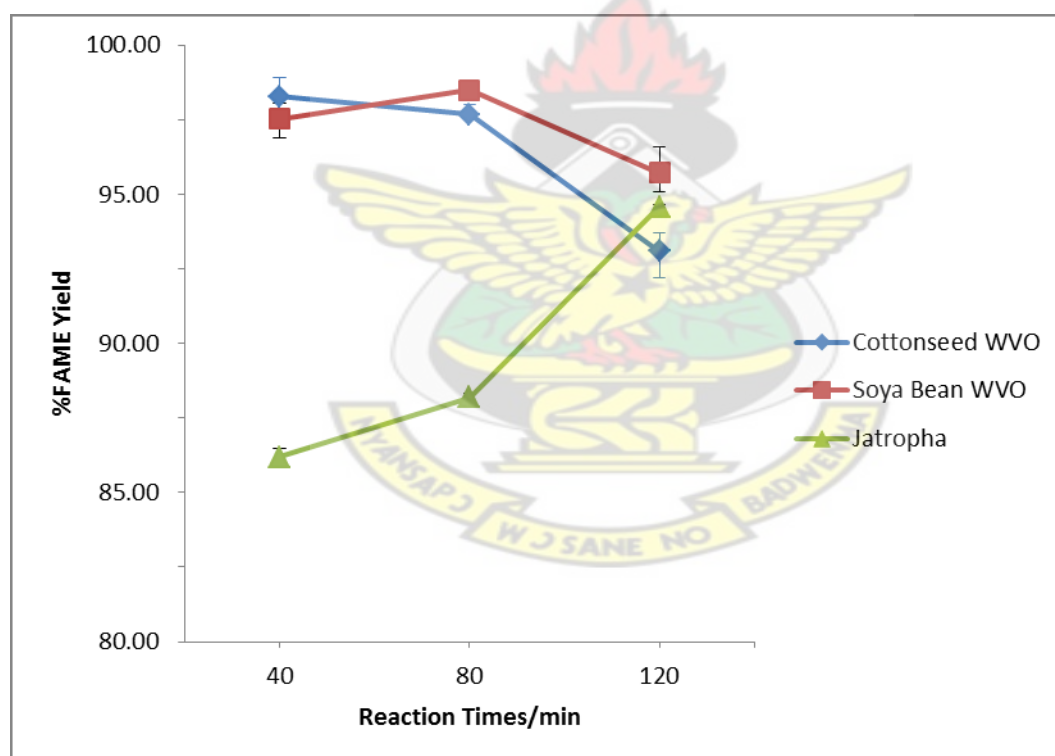


Figure 18 Effect of reaction time on yied of FAME

The results indicate that 40 mins of reaction time gave an optimum yield of 98.09 % for Cottonseed waste vegetable oil biodiesel (CWVOB). After 40 mins of reaction time, the methyl ester concentration reduced. This could be due to a possible conversion of some of

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the methyl esters into soap (saponification which usually occurs in the reverse direction). For the Soya bean waste vegetable oil feedstock the FAME yield increased till 80 mins of reaction time when an optimum yield of 98.48 % was obtained. Below the 80 mins of reaction time, the reaction was incomplete so the concentration of Soya bean FAME was low. After 80 mins of reaction time there could also be possible conversion of methyl esters into soap. The results show that 120 min of reaction time gave the highest yield of 94.57 % of FAME for the JCO. Below 120 min of reaction time, the methyl ester concentration was low. This could be due to incomplete conversion of some of the oil into FAME at reaction times below the optimum period of 120 min. The different reaction times observed for the various feedstocks could be associated with the different molecular structure of the oil feeds that contain different saturated fatty acids. While some fatty acids have lower activation energy, other types have higher activation energy thus require longer period of heating and stirring to react.

The maximum reaction time for most transesterification processes is 120 min. The optimum reaction time of 120 min for the complete formation of *Jatropha curcas* FAME in the current study agrees with the optimum recorded reaction time in many experiments. According to Hoque, Singh and Chuan (2011), the maximum biodiesel yields (87.4 %, 89 % and 88.3 % for beef fat, chicken fat and used cooking oil respectively) were obtained at reaction periods of 120 min with catalyst concentration of 1.25 wt % of oil, 65 °C and 150 rpm stirring speed. They observed that between 2- 3 hours of reaction time the process reached equilibrium. Also, they reported a declination in yield after 3 hours which could be due to the reversible nature of the transesterification reaction. The studies conducted on the optimization of biodiesel production from *Jatropha curcas* oil gave a maximum yield of about 90-95 % at 120 min reaction time, 60 °C reaction temperature with an oil/methanol molar ratio of 1:9 and

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0.5 % (w/w) of KOH as catalyst. The yield of FAME reduced beyond 120 min of reaction time as a result of degradation of FAME produced at prolonged reaction times (Patil and Deng, 2009). Moreover, a two-step acid-base catalyzed transesterification of JCO gave a maximum yield of 90.1 % at 6 hours reaction time with 1 % (w/w) catalyst concentration for H_2SO_4 and NaOH, 400 rpm of stirring speed and 3:7 oil/methanol molar ratio. Therefore a maximum reaction time of 120 min was selected for the current study. This is because prolonged heating might cause the produced FAME to revert back to its original state, thereby reducing the overall biodiesel yield and affecting the economics of production.

4.5 Effect of Reaction Temperature on Yield of FAME

For the determined optimum catalyst amount, oil to methanol molar ratio and reaction time, the temperature effects on the transesterification reaction were studied at 55 °C, 60 °C and 65 °C in separate experimental runs. Generally, transesterification can occur at reaction temperatures ranging from ambient to temperatures closer to the boiling point of the alcohol used. A high reaction temperature usually speeds up the reaction and shortens the reaction period. In this work, the maximum temperature level was limited to 65 °C as temperatures higher than that might cause the methanol to evaporate excessively. Even though the methanol could be condensed back into the reactor, the extent of evaporation would affect the kinetics of the reaction and that could result in lower yield and affect the purity of the FAME produced. Moreover, the minimum temperature was selected as 55 °C because at lower reaction temperatures, the completion of the transesterification reaction tends to be too long and that might not be suitable or practical for mass production. The results are presented in Table 10 and shown graphically in Figure 19 below.

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Table 10 Effect of Reaction Temperature on Yield of FAME

Sample ID	Reaction Temperature, °C	Washed samples (after 6 hours of settling)	
		Avg. % FAME Yield	Error % @ 95 % C.L,
CWVO	55	99.09	0.15
	60	99.46	0.06
	65	93.09	0.63
SWVO	55	98.15	0.36
	60	99.51	0.02
	65	95.72	0.89
JCO	55	87.51	0.47
	60	94.57	0.09
	65	90.00	0.37

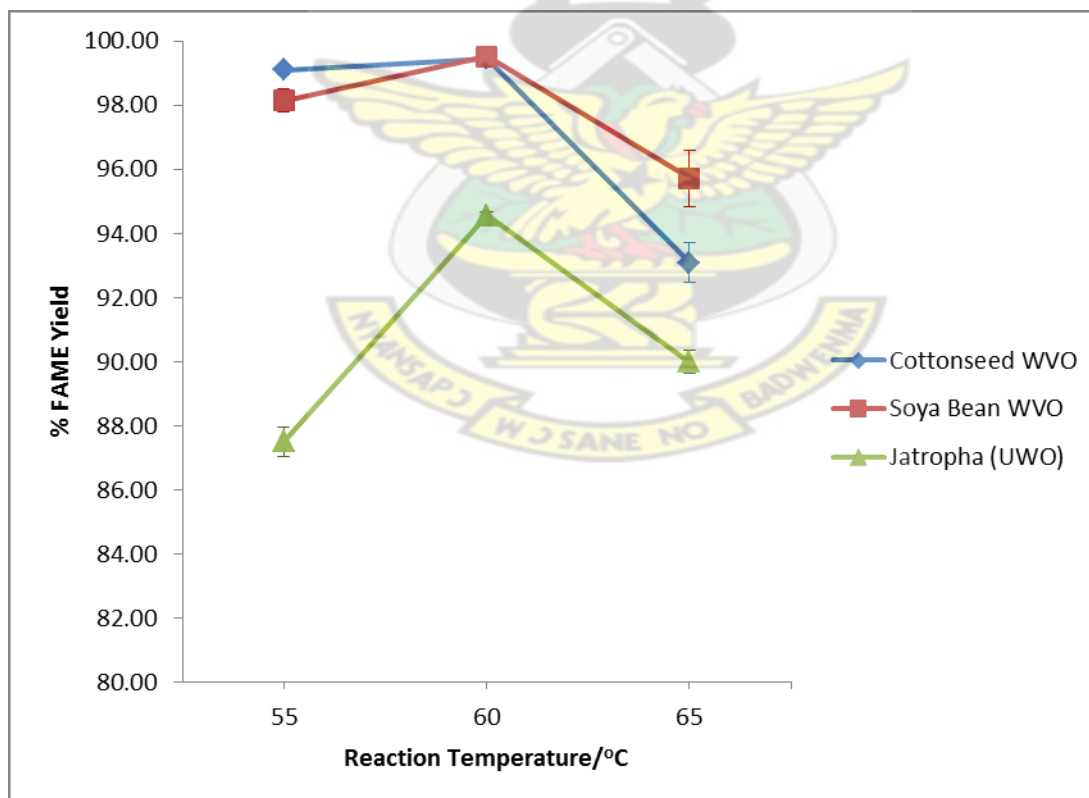


Figure 19 Effect of reaction temperature on yield of FAME

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It was observed that the optimum reaction temperature for all the oil feedstocks was 60 °C with corresponding FAME yield of 99.45 %, 99.51 % and 94.57 % for CWVOB, SWVOB and JCOB respectively. The yields at 55 °C were slightly lower with relatively higher standard deviations as compared to the yields at 60 °C. At 65 °C which was above the optimum temperature of 60 °C the FAME yield decreased. According to Patil and Deng (2009), the 2 % KOH alkali catalyzed transesterification of Jatropha oil was favoured at a reaction temperature of 60 °C with a maximum FAME yield of 90-95 % and this agrees with the yield of 94.57 % for JCOB in the present study. Some studies have shown that the saponification of triglycerides by alkali catalyst is much faster than alcoholysis at temperatures above 60 °C (Patil and Deng, 2009; Eevera *et al.*, 2009). Furthermore, transesterification above 60 °C reaction temperature causes excessive methanol loss due to evaporation and significantly reduce the yield of biodiesel. Hoque, Singh and Chuan (2011) showed that the optimum reaction temperature for the transesterification of used cooking oil that gave a maximum FAME yield of 87.6 % was achieved at 65 °C. This yield is lower as compared to those obtained in the current study. Also, the study conducted by Baroi, Yanful and Bergougrou, (2009) revealed that 65 °C reaction temperature was optimum for the production of 98.77 % yield of JCOB. This yield is lower as compared to 99.45 % and 99.51 % for CWVOB and SWVOB and higher than 94.57 % FAME yield obtained for JCOB in the present study. This might be due to the presence of waxes and phospholipids in the Jatropha oil sample used in the present study due to prolonged storage. Hence, 60 °C reaction temperature was optimized for the transesterification of both WVOs and JCO.

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4.6 Percentage Composition of Oleic Acid Methyl Ester and Predicted Cetane Numbers of FAME

GC-MS was used to determine the area counts of the methyl oleate standard and the biodiesel samples according to ASTM D6584-10A. The mass spectra for the blank, the standards and the biodiesel samples are shown in Appendix E. The results in Table 11 (deduced from Appendices E.2-E.4) were used to obtain a calibration curve (as shown in Figure 20) which was used to estimate the mole percent of oleic acid methyl ester in each biodiesel sample.

Table 11 Data for Methyl Oleate Calibration Curve

Mole % of Methyl Oleate (representative of FAME)	Area/count of peak (O-CH3) FAME indication
12.5	700445417
25	2850870613
50	5668426803
75	6097331592
90	6467844571
100	6504469547

Figure 20 below is the calibration curve of the methyl oleate standard.

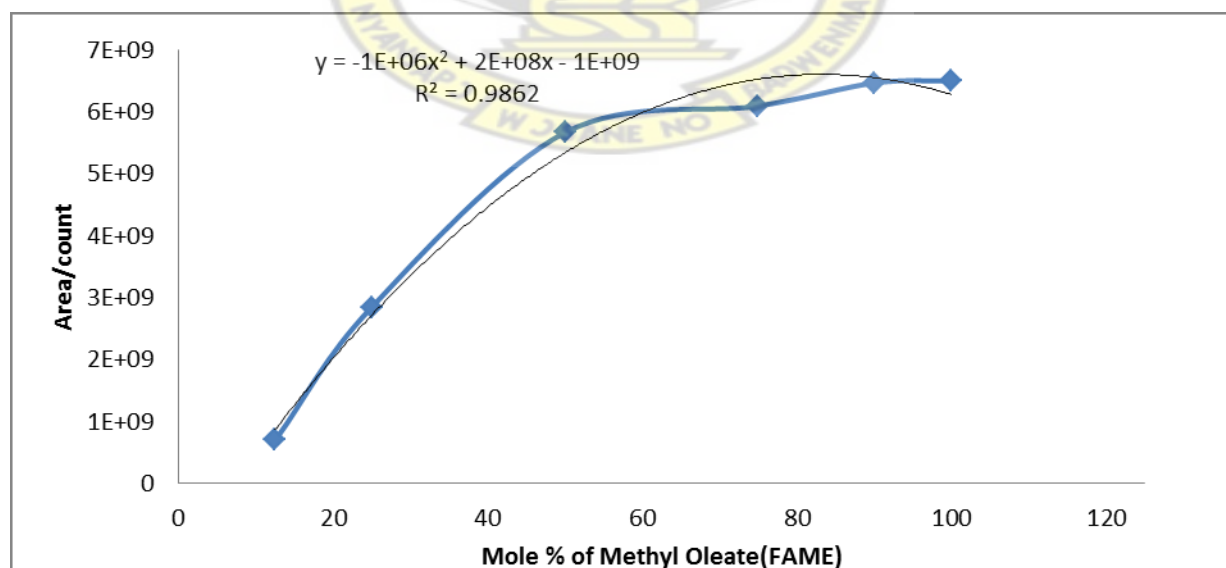


Figure 20 Methyl oleate standard calibration curve

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The oleic acid methyl ester composition and the corresponding predicted cetane numbers are shown in Table 12. The predicted cetane numbers for Soya bean fresh oil biodiesel (SBFOB) and Cottonseed fresh oil biodiesel (CSFOB) were 51.7 and 51.1 respectively. For the blend of fresh Soya bean oil and fresh Cottonseed oil biodiesel (BFOB) and blend of waste Soya bean oil and waste Cottonseed oil biodiesel (BWOB) the predicted cetane numbers were 52.1 and 52.2 respectively. Also, the predicted cetane number for Soya bean waste oil biodiesel (SWVOB*) and Cottonseed waste oil biodiesel (CWVOB*) were each found to be 51.3. The SBFOB, CSFOB, BFOB, BWOB, SWVOB* and CWVOB* samples were produced under reaction conditions of 1:6 oil: methanol molar ratio, 60 °C reaction temperature, 120 min of reaction time at 600 rpm of stirring speed with 4 wt % K₂CO₃ (wt % of oil) during the preliminary experimental run. At the optimum reaction conditions, the predicted cetane numbers for Soya bean waste oil biodiesel (SWVOB), Cottonseed waste oil biodiesel (CWVOB) and *Jatropha curcas* oil biodiesel (JCOB) were 51.6, 51.5 and 52.4 respectively.

Bamgboye and Hansen (2008) showed that the predicted cetane number for Soya bean methyl ester and Cottonseed methyl ester were 50.3 and 52.8 respectively. According to Kywe and Mya Oo (2009) the predicted cetane number for *Jatropha* oil methyl ester and *Jatropha* oil ethyl ester were 48 and 50 respectively. These values are similar to those predicted in the present study. The predicted cetane number for all biodiesel samples in the present study are within the acceptable range of 48-65 according to ASTM D6751.

Table 12 Mole Percent of Oleic Acid Methyl Esters and Predicted Cetane Numbers of FAME

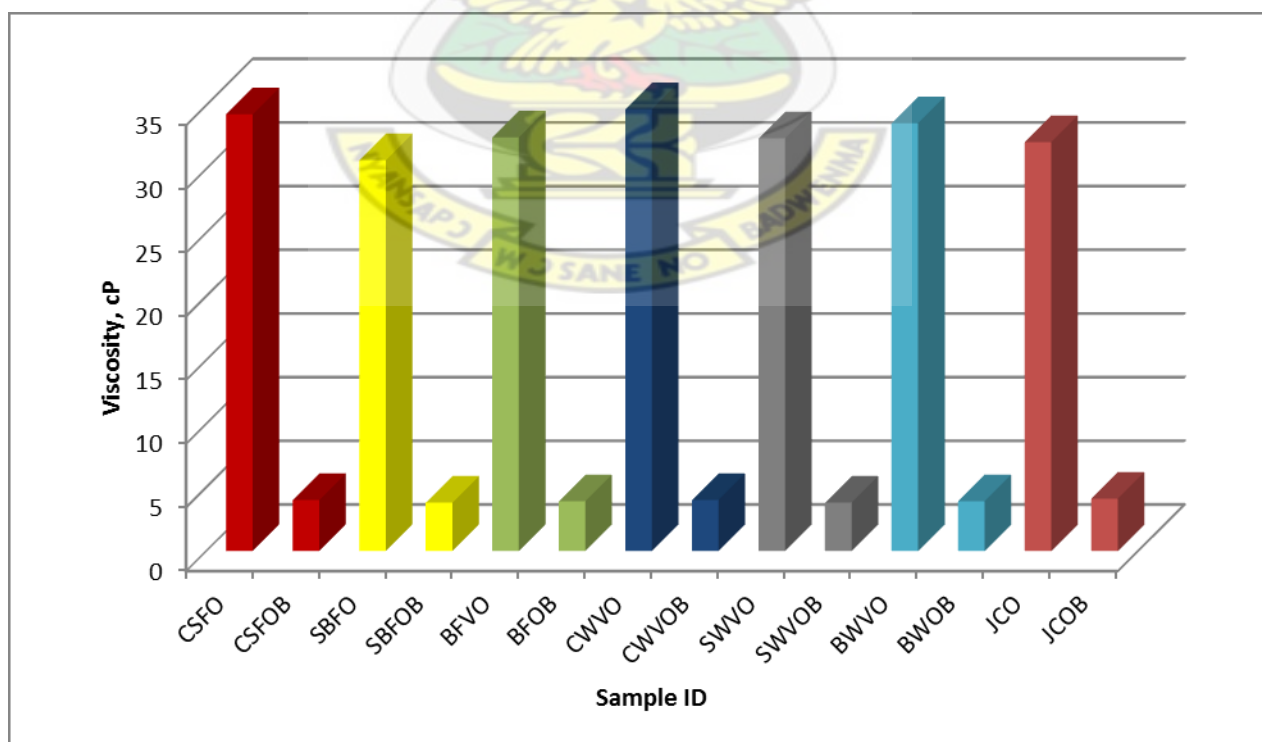
Sample ID	Area/count of peak (O-CH ₃) FAME indication	Mole % of FAME	Predicted Cetane Number
SBFOB	5856293536	43.93	51.7
CSFOB	5493011567	40.78	51.1
BFOB	6117588286	46.31	52.1
BWOB	6179448244	46.89	52.2

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SWVOB*	5624418965	41.90	51.3
SWVOB	5824149684	43.65	51.6
CWVOB*	5639490799	42.03	51.3
CWVOB	5728443890	42.80	51.5
JCOB	6254418812	47.60	52.4

4.7 Characteristics of Biodiesel

Some characteristics of the biodiesel produced from the various feedstocks are shown in Table 13. The results indicate that the viscosity of the oil feeds reduced from 34.3, 30.7, 32.5, 34.7, 32.4, 33.6 and 32.1 cP to 4.0, 3.8, 3.9, 4.0, 3.8, 3.9 and 4.1 cP respectively for CSFOB, SBFOB, BFOB, CWVOB, SWVOB, BWOB, and JCOB after transesterification. The viscosities of the biodiesel produced from the different feedstocks are within the acceptable range of 1.9-6.0 according to ASTM D6751-02. Figure 21 below compares the viscosity of oil feeds before transesterification to their respective biodiesel samples after transesterification.



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Figure 21 A graph of viscosity of each oil feed with their respective biodiesel samples

Hence, there would be no problem with a particular fuel injection system that runs on any of the biodiesel samples produced.

Acid values of 0.06, 0.10, 0.08, 0.12, 0.28, 0.20, 0.50 mgKOH/g oil for the various biodiesels produced in the order as above are lower than the maximum permissible level of 0.8 mg KOH/g oil. The predicted cetane numbers (51.1, 51.7, 52.1, 51.5, 51.6, 52.2 and 52.4) for biodiesel samples in the same order as above are within the acceptable range of 48-65 according to ASTM D6751-02. The water content of each biodiesel sample is lower than 0.05 % which are below the maximum permissible limit of 0.05 %.

Table 13 Characteristics of Biodiesel Produced from oil Feeds

Property	Units	CSFOB	SBFOB	BFOB	CSWOB	SBWOB	BWOB	JCOB	ASTM D6751-02
Density @ 15°C	g/ml	0.880	0.885	0.883	0.880	0.885	0.883	0.790	N/A
Kinematic viscosity	cP	4.0	3.8	3.9	4.0	3.8	3.9	4.1	1.9-6.0
Acid value	mgKOH/g oil	0.06	0.10	0.08	0.12	0.28	0.20	0.50	Max 0.80
Water content	%	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	Max 0.05
Predicted cetane number	-	51.1	51.7	52.1	51.5	51.6	52.2	52.4	48-65

The optimized reaction conditions for the transesterification of Cottonseed and Soya bean waste oils with their corresponding FAME yields are shown in Table 14.

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Table 14 Summary of Optimized Reaction Parameters for the Various Feedstocks

Sample ID	Catalyst amount (wt. % of oil)	Molar ratio oil: methanol	Reaction time/min	Reaction temperature/°C	Avg. % FAME Yield
CSWO	4	1:6	40	60	99.46
SBWO	4	1:6	80	60	99.51
JCO	4	1:8	120	60	94.57

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CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Waste vegetable oils and *Jatropha curcas* oil which are types of non-edible oil, can be alternative feedstocks for biodiesel production and can reduce the demand on food sources for renewable fuel production. In the present study, K_2CO_3 was used as an unsupported catalyst to understand its catalytic activity in transesterification of Cottonseed and Soya bean waste vegetable oils and *Jatropha curcas* oil. Based on the results from the study, the following conclusions are made:

- ❖ The optimum reaction conditions for the transesterification of the various oil feeds are: CWVOB [4 wt. % K_2CO_3 , 1:6 oil: methanol ratio, 40 min reaction time and 60 °C reaction temperature at 600 rpm reaction speed]; SWVOB [4 wt. % K_2CO_3 , 1:6 oil: methanol ratio, 80 min reaction time and 60 °C reaction temperature at 600 rpm reaction speed]; JCOB [4 wt. % K_2CO_3 , 1:8 oil: methanol ratio, 120 min reaction time and 60 °C reaction temperature at 600 rpm reaction speed].
- ❖ The FAME yield that resulted from the optimum reaction conditions were 99.46 %, 99.51 %, 94.57 % for CWVOB, SWVOB and JCOB respectively.
- ❖ The predicted cetane numbers of fatty acid methyl esters produced using the Gerpen correlation are 51.5, 51.6 and 52.4 for CWVOB, SWVOB and JCOB respectively.
- ❖ Transesterification reduced the viscosity, acid value and water content of the FAME produced thereby improving the quality of biodiesel and enhancing energy efficiency of the engine running on such fuel.

5.2 Recommendations

The present study has identified some important areas that should be further investigated including:

- ❖ Extensive research to estimate the amount of waste oil generated in Sub-Saharan Africa and particularly Ghana as a country should be done as it proves to be an alternate feedstock for biodiesel production.
- ❖ Reaction and solubility behaviour of K_2CO_3 in alcohols is not well known. Also, in the presence of glycerol the effect of the solubility and reaction behaviour of K_2CO_3 in alcohols is unknown. Therefore, there is the need to research the model study of the reaction and solubility of K_2CO_3 in alcohols in the presence and absence of glycerol as such study would give an understanding of the catalytic activity of K_2CO_3 for transesterification.
- ❖ The glycerol containing K_2CO_3 as by-product from the transesterification should be investigated to ascertain other useful applications aside the literature revelation of it use as anti-icing/ deicing agent; for example, possibility of being a raw material for fertilizer production.
- ❖ Potassium carbonate has great potential as a catalyst for the transesterification of biodiesel feedstock. Most biomass such as plantain peels and cocoa pods contains this mineral in significant amount. Potassium carbonate can easily be extracted from biomass ash using inexpensive extraction classical technology. This should be investigated.

REFERENCES

- Acaroglu M, and Demirbas A. (2007). Relationships between viscosity and density measurements of biodiesel fuels. *Energy Sources*; 29: pp. 705–12.
- Achten W.M.J., Verchot L., Franken Y.J., Mathijs E., Singh V.P., and Aerts R. (2008). *Jatropha bio-diesel production and use*. *Biomass Bioenergy*; 32: pp. 1063–84.
- Agarwal A.K., and Rajamanoharan K. (2009). Experimental investigations of performance and emissions of Karanja oil and its blends in a single cylinder agricultural diesel engine. *Appl Energy*; 86: pp. 106–12.
- Agarwal D. and Agarwal A.K. (2007). Performance and emissions characteristics of *Jatropha* oil (preheated and blends) in a direct injection compression ignition engine. *Appl. Therm. Eng.*, 27, pp. 2314–2323.
- Agarwal, A.K. and Das, L.M. (2001). Biodiesel development and characterization for use as a fuel in compression ignition engines. *J. Eng. Gas Turbines Power* 123, pp. 440–447.
- Alamu O.J. (2007). Effect of ethanol-palm kernel oil ratio on alkali-catalyzed biodiesel yield. *Fuel*, 08.011.
- Alcantara R., Amores J., Canoria L., Fidalgo E., Franco M.J., and Navarro A. (2000) Catalytic production of biodiesel from soybean oil, used frying oil and tallow. *Biomass Bioenergy*; 18: pp. 517–27.
- Ali Y., Hanna M.A., and Cuppett S.L. (1995). Fuel properties of tallow and soybean oil esters. *JAm Oil Chem Soc* 1995; 72: pp.1557–64.
- Altun S. (2011). Fuel properties of biodiesels produced from different feedstocks. *Energy Educ Sci Technol Part A* ; 26: pp.165–74.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Altun S., and Oner C. (2009). Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. *Appl Energy*; 86: pp. 2114–20.

Al-Zuhair S., Ling F .W, and Jun L.S. (2007). “Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase,” *Process Biochemistry*, vol. 42, no. 6, pp. 951–960.

Al-Zuhair S. (2006). The effect of substrate concentrations on the production of biodiesel by lipase-catalyzed transesterification of vegetable oils. *Journal of Chemical Technology and Biotechnology*, 81, pp. 299-305.

Amin S. (2009). Review on biofuel oil and gas production processes from microalgae. *Energy Convers Manage*; 50: pp. 1834–40.

Antczak M.S., Kubiak A., Antczak T., and Bielecki S. (2009). “Enzymatic biodiesel synthesis—key factors affecting efficiency of the process,” *Renewable Energy*, vol. 34, no. 5, pp. 1185–1194.

Anwar F., Rashid U., Ashraf M., and Nadeem M. (2010). Okra (*Hibiscus esculentus*) seed oil for biodiesel production. *Appl Energy* ; 87: pp.779–85

AOCS (American Oil Chemist’s Society) (2012). Official Method Cd. 3d- 63: Acid value determination. *Official Methods and Recommended Practices of the AOCS*, 6th Edition, USA.

Arzamendi G., Arguinarena, E., Campo I., Zabala S., and Gandia L.M. (2008). “Alkaline and alkaline- earth metals compounds as catalysts for the methanolysis of sunflower oil”, “Catalysis Today”, pp. 305-313 in Baroi C., Yanful E.K., and Bergougnou M.A. (2009). Biodiesel production from *Jatropha curcas* oil using potassium carbonate as unsupported catalyst. *International Journal of Chemical Reactor Engineering*, vol. 7, article A72.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Ataya F., Dubé M.A., and Ternan M. (2007). Acid-Catalyzed Transesterification of Canola Oil to Biodiesel under Single- and Two-Phase Reaction Conditions. *Energy and Fuels*, 2007, 21 (4), pp. 2450–2459.

Bamgboye A.I. and Hansen A.C. (2008). Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. *Int. Agrophysics*, Vol. (22), pp. 21-29.

Baroi C., Yanful E.K., and Bergounou M.A. (2009). Biodiesel production from *Jatropha curcas* oil using potassium carbonate as unsupported catalyst. *International Journal of Chemical Reactor Engineering*, vol. 7, Article A72.

BBC News (2004). "Customs seize illegal fuel". Available at: http://news.bbc.co.uk/2/hi/uk_news/northern_ireland/4083017.stm [Accessed on 25/07/2010].

Becker E.W. (1994). *Microalgae: biotechnology and microbiology*. Cambridge (New York): Cambridge Univ. Press.

Benjumea P., Agudelo J. and Agudelo A. (2008). Basic properties of palm oil biodiesel–diesel blends. *Fuel*; 87: pp. 2069–75.

Bevill K. (2010). New York City biodiesel supplier signs contract. *Energy Technology and Research*. Available at: http://energytechpages.blogspot.com/2010_09_01_archive.html [Accessed on 24/07/12].

Bounds A. (2007). "OECD warns against biofuels subsidies". *Financial Times Report*. [Accessed on 07/03/2008].

Brinkman N., Wang M., Weber T., and Darlington T. (2005). "Well-to-Wheels Analysis of Advanced/Vehicle Systems-A North American Study of Energy Use, Greenhouse Gas Emissions, and Criteria Pollutant Emissions" pp. 17-23, 25-88.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Belafi-Bako K., Kovacs F., Gubicza L., and Hancsok J. (2002). Enzymatic biodiesel production from sunflower oil by *Candida antarctica* Lipase in a solvent- free system. *Biocatalysis and Biotransformation*, 20 (6), pp. 437-439.

Boocock D.G.B., Konar S.K., Mao V., and Sidi H.(1996). Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. *Biomass and Bioenergy*, 11(1), pp. 43-50.

Briens C., Piskorz J. and Berruti F. (2008). "Biomass Valorization for Fuel and Chemicals Production -- A Review,". *International Journal of Chemical Reactor Engineering*, 6, R2. pp 2-51.

Butler R. A. (2006). Why is oil palm replacing tropical rainforests? Why are biofuels fueling deforestation? April 25, 2006. Available at: http://news.mongabay.com/2006/0425_oil_palm.html [Accessed on 03/03/2011].

Canakci M. (2007). The Potential of Restaurant Waste Lipids as Biodiesel Feedstocks. *Bioresource Technology* 98, pp. 183–190.

Canakci M., and Sanli H. (2008). Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Industrial Microbiology and Biotechnology*; 35: pp. 431–41.

Carter D., Darby D., Halle J., and Hunt P. (2005). *How To Make Biodiesel; Low-Impact Living Initiative*, Redfield Community, Winslow, Bucks, ISSN 0-9649171-0-3.

Chisti Y. (2007). Biodiesel from microalgae. *Biotechnol Adv*; 25: pp. 294–306.

Connemann J., and Fischer J. (1998). Biodiesel in Europe: biodiesel processing technologies. Paper presented at the International Liquid Biofuels Congress, Brazil. pp. 1-16.

Chen J., Jin H.L., and Li J.W. (2003). *Oleochemistry*. China: Chemical Industry Press Publishing; 2003.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Chouhan A.P.S., and Sarma A.K. (2011). Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renew Sustain Energy Reviews* 15(9). PP. 4378-4399.

Canakci M., and Sanli H. (2008). Biodiesel production from various feedstocks and their effects on the fuel properties. *J Ind Microbiol Biotechnol*; 35: pp. 431–41.

Canakci M., and Gerpen J.V. (2001). Biodiesel production from oils and fats with high free fatty acids. *Trans ASAE* 2001; 44: pp. 1429–36.

Cvengros J. (1998). Acidity and corrosiveness of methyl esters of vegetable oils. *Fett/Lipid*, Vol. 100, No 2, pp. 41-44, ISSN 1521-4133.

D'Cruz A., Kulkarni M.G., Meher L.C., and Dalai A.K. (2007). Synthesis of biodiesel from canola oil using heterogeneous base catalyst. *Journal of American Oil Chemist's Society*, 84, pp. 937-943.

Demirbas A. (2007). Biodiesel from sunflower oil in supercritical methanol with calcium oxide. *Energ. Convers. Manage.*, 48 (3), 937-941. pp. 1-5.

Demirbas A. (2008). *Biodiesel: a realistic fuel alternative for diesel engines*. London: Springer.

Demirbas A. (2009a). "Political, economic and environmental impacts of biofuels: A review". *Applied Energy* 86: S108–S117.

Demirbas A.H. (2009b). Inexpensive oil and fats feedstocks for production of biodiesel. *Energy Educ Sci Technol Part A*; 23: pp. 1–13.

Demirbas A. (2009c). Production of biodiesel from algae oils. *Energy Source Part A*; 31: pp.163–8.

Demirbas A. (2009d). Production of biodiesel fuels from linseed oil using methanol and ethanol in non-catalytic SCF conditions. *Biomass Bioenergy*; 33: pp.113–8.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Demirbas M.F. (2010). Microalgae as a feedstock for biodiesel. *Energy Educ Sci Technol Part A*; 25: pp.31–43.

Demirbas A. and Demirbas M.F. (2010). Importance of algae oil as a source of biodiesel. *Energy Convers Manage*. doi:10.1016/j.enconman.2010.06.05

De Paola M.G., Ricca E., Calabrò V., Curcio S., and Iorio G. (2009). “Factor analysis of transesterification reaction of waste oil for biodiesel production,” *Bioresource Technology*, vol. 100, no. 21, pp. 5126–5131.

Dias J. M., Alvim-Ferraz M.C.M., Almeida M. F., Díaz J.D.M., Polo M.S., and Utrilla J.R. (2011). Selection of heterogeneous catalysts for biodiesel production from animal fat. *Fuel* 94 , pp. 418–425.

Di Serio M., Tesser R., Pengmi L., and Santacesaria E., (2008). Heterogeneous catalysts for biodiesel production. *Energy and Fuels*, 22(1), pp. 207-217.

Dijkstra A. J., Maes P. J., Meert D., and Meeussen W. (1995). Interpreting the oxygen stability index. *Oils-Fats-Lipids 1995 Proceedings of the World Congress of the International Society for Fat Research*, pp. 629-637, The Hague, Netherland: P. J. Barnes & Associates, 1995.

Dorado M. P., Ballesteros E., Lopez F. J., and Mittelbach M. (2004). Optimization of alkali catalyzed transesterification of brassica oil for biodiesel production. *Energy and Fuels*, Vol. 18 Issue 1, pp. 77-83.

Dorian J. P., Franssen H.T., and Simbeck D.R. (2006). Global challenges in energy. *Energy Policy*. 34: pp. 1984– 1991.

Dunn R.O. (2005). Chapter 10: Other Alternative Diesel Fuels from vegetable oils. *Biodiesel Handbook*. AOCS Press.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Evera T., Rajendran K., and Saradha S. (2009). "Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions", "Renewable Energy", Vol. 34, Issue 3, pp. 762 – 765.

Encinar J. M., Juan F., Gonzalez J. F., and Rodriguez-Reinares, A. (2007). Ethanolysis of used frying oils: Biodiesel preparation and Characterization. *Fuel Process. Tech.*, 88 (5), 513-522 pp. 1-10.

Erdener H., Arinan A., and Orman S. (2011). Future Fossil Fuel Alternative; Di-methyl Ether (DME). A review. *International Journal of Renewable Energy Research, IJRER*, Vol. 1, No.4, pp.252-258.

EurekaAlert (2009). 15 new highly stable fungal enzyme catalysts that efficiently break down cellulose into sugars at high temperatures. Available at: www.eurekaalert.org [Accessed on 06/03/2010].

Evans G. (2008). "Liquid Transport Biofuels - Technology Status Report", National Non-Food Crops Centre. Biocentre, York Science Park, Innovation Way, Heslington York YO10 5DG, UK.

Evans J. (2008). "Biofuels aim higher". *Biofuels, Bioproducts and Biorefining (BioFPR)*. Available at: http://www.biofpr.com/details/feature/102347/Biofuels_aim_higher.html [Accessed on 03/03/2011].

Farrell A.E., Plevin R.J., Turner B.T., Jones A.D., O'Hare M., and Kammen D.M. (2006) "Ethanol can Contribute to Energy and Environmental Goals", *Science*, 311, 506-8.pp 5-31.

Felizardo P., Correia M.J.N., and Raposo I. (2006). Production of biodiesel from waste frying oils. *Waste Manage*; 26: pp. 487–94.

Fisher, Lawrence M. April 24th 2007. "Carbon gas is explored as a source of ethanol" *New York Times*.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Fjerbaek L., Christensen K.V., and Norddahl B. (2009). "A review of the current state of biodiesel production using enzymatic transesterification," *Biotechnology and Bioengineering*, Vol. 102, no. 5, pp. 1298–1315.

Flannery T. (2012). "Biochar may represent the single most important initiative for humanity's environmental future". Fish Lake Valley Biochar Initiative. BIORENEWAL.

Forson F.K., Oduro E.K., and Donkoh E.H. (2004). Performance of Jatropha oil blends in a diesel engine. *Renewable Energy*, 29, pp. 1135-1145.

Freedman B., Pryde E.H., and Mounts T.L.(1984).Variables affecting the yields of fatty esters from transesterified vegetable oils. *J Am Oil Chem Soc*; Vol. 61, pp. 1638-43 in Hoque M.E., Singh A., and Chuan Y.L. (2011). Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield. *Biomass and Bioenergy*, Vol. 35, pp. 1582-1587.

Furniss B.S., Hannaford A.J., Smith P.W.A., and Tatchell A.R. (1989). *Vogel's Textbook of practical organic chemistry*, 5th Ed. pp 164,165,168 and 236.

Gallagher B.J. (2011) The economics of producing biodiesel from algae. *Journal of Renew Energy* 36 (1), pp 158-162.

Ganapathy T., Murugesan K., and Gakkhar R.P.(2009). Performance optimization of Jatropha biodiesel engine model using Taguchi approach. *Appl Energy*; 86: pp. 2476–86.

Ge H., Scharffbillig J., Ahlberg C. and Clark E. (2012). Minnesota Biodiesel Cold Weather Issues. A Biodiesel Blend Handling Guide. Minnesota Department of Agriculture, USA.

Gerpen J.V. (2008). Biodiesel production technology, a workshop for the 2008 biodiesel conference and expo. Moscow, ID: University of Idaho.

Gerpen J.V. (2005). Biodiesel processing and production. *Fuel Processing Technology*, 86, pp. 1097– 1107.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Ghadge S.V., and Raheman H. (2005). Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass Bioenergy*; 28: pp. 601–5.

Graille J. (1986). “Vegetable oil alcoholysis pilot trials using natural catalysis to produce diesel fuels”, “*Oleagineux*”, Vol. 41, Issue 10, pp. 457 – 464.

Graille J., Lozano P., Pioch D., and Geneste P. (1985). “Alcoholysis tests of vegetable oils with natural catalyzers for the production of diesel fuels”, “*Oleagineux*”, Vol. 50, Issue 5, pp. 271 – 276.

Gui M.M., Lee K.T., and Bhatia, S. (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy* 33, pp. 1646–1653.

Goering C.E., Schwab A., Daugherty M., Pryde M., and Heakin A. (1982). Fuel properties of eleven vegetable oils. *Trans ASAE* 1982; 25: pp.1472–7.

Groisman Y., and Gedanken A. (2008). Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. *J Phys Chem C*, 112, pp. 8802–8808.

Granados M.L., Poves M.D.Z., Alonso D.M., Mariscal R., Galisteo F.C., and Moreno-Tost R. (2007). Biodiesel from sunflower oil by using activated calcium oxide. *Appl Catal B-Environ* 2007; 73: pp. 317–26.

Gogate P.R., and Pandit A.B.(2005). A review and assessment of hydrodynamic cavitation as a technology for the future. *Ultrasonics Sonochemistry*, 12, pp. 21–27.

Graboski M.S., and McCormick R.L.(1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog Energy Combust Sci* ;24: pp. 125–64.

Ghadge S.V., and Raheman H. (2005). Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass Bioenergy*;28: pp. 601–5.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Goering C.E., Campion R.N., Schwab, A.W., and Pryde E.H. (1982b). In vegetable oil fuels, proceedings of the international conference on plant and vegetable oils as fuels, Fargo, North Dakota. American Society of Agricultural Engineers, St Joseph, MI 4, pp. 279 - 286.

Haas M.J. (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: vegetable oil soapstock. *Fuel Process Technol*; 86: pp.1087–96.

Haas M.J., McAloon A.J., Yee W.C., and Foglia, T.A. (2006). A process model to estimate biodiesel production costs. *Bioresour. Technol.* 97, pp. 671–678.

Hammerschlag R. (2006). "Ethanol's Energy Return on Investment: A Survey of the Literature 1999-Present", *Environ. Sci. Technol.*, 40, pp. 1744-50.

Hammond G.P., Kallu S., and McManus M.C. (2008). Development of biofuels for the UK automotive market. *Appl Energy*; 85: pp. 506–15.

Hartman L. (1956). "Methanolysis of triglycerides", "Journal of the American Oil Chemist's Society", 33, pp. 129.

Harwood H.J. (1984). Oleochemicals as a fuel: Mechanical and economic feasibility. *JAOCS* 61, pp. 315-324.

Hayer F., Bakhtiary-Davijany H., Myrstad R., Holmen A., Pfeifer P., and Venvik H.J. (2011). Synthesis of dimethyl ether from syngas in a micro-channel reactor—Simulation and experimental study. *Chemical Engineering Journal*, Vol. 167, Issues 2–3, pp. 610-615.

Helwani Z., Othman M.R., Aziz N., Fernando W.J.N., and Kim J. (2009). Technologies for production of biodiesel focusing on green catalytic techniques. *Fuel Process. Technol.*, 90, pp. 1502–1514.

Helwani Z., Othman M.R., Aziz N., Kim J., and Fernando W.J.N. (2009). Solid heterogeneous catalyst for transesterification of triglycerides with methanol: a review. *Appl. Catal. A: Gen.*, 363, pp. 1–10.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Huang G., Chen F., Wei D., Zhang X., Chen G. (2010). Biodiesel production by microalgal biotechnology. *Appl Energy*;87: pp.38–46.

Huber G. W., Iborra S.. and Corma A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.*, 106, pp. 4044–4048.

Hoque M.E., Singh A., and Chuan Y.L. (2011). Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield. *Biomass and Bioenergy*, Vol. 35, pp. 1582-1587.

Jain S., and Sharma M.P. (2010). Biodiesel production from *Jatropha curcas* oil. *Renewable and Sustainable Energy Reviews*, Volume 14, Issue 9, December 2010, pp. 3140–3147.

Jain S., and Sharma M. P. (2010). Prospects of biodiesel from *Jatropha* in India: A Review. *Renew. Sust. Energ. Rev.*,14, Pp. 763–771.

Ji J., Wang J., Li Y., Yu Y., and Xu Z. (2006). Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. *Ultrasonics*, 44, pp. 411-414.

Kakie C.K. (2007). Production of biodiesel from copra. A Process Engineering Project Report presented to Department of Chemical Engineering, Faculty of Chemical and Materials Engineering, The College of Engineering, Kwame Nkrumah University of Science and Technology, Kumasi. November, 2007. pp. 1-43.

Kansedo B. J. (2009). Synthesis of Biodiesel from Palm Oil and Sea Mango Oil Using Sulfated Zirconia Catalyst. MSc. Thesis, Universiti Sains, Malaysia. pp. 1 – 46.

Knothe G. (2001). "Historical Perspectives on Vegetable Oil-Based Diesel Fuels" (PDF). *INFORM*, Vol. 12(11), pp. 1103-1107.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Kojima M., and Johnson T. (2005). Potential for Biofuels for Transport in Developing Countries. Energy Sector Management Assistance Programme (ESMAP) Report. The International Bank for Reconstruction and Development/THE WORLD BANK. 1818 H Street, N.W. Washington, D.C. 20433, U.S.A. pp.1-182.

Korbitz W. (1999). Biodiesel production in Europe and North American, an encouraging prospect. *Renew. Energy* 16, pp. 1078–1083.

Kosmehl S. O. and Heinrich H. (1997). The Automotive Industry's View on the Standards for Plant Oil-Based Fuels, In: *Plant Oils as Fuels. Present State of Science and Future Developments*, N. Martini and J. Schell (Eds.), 18-28, ISBN 3540647546 9783540647546, Berlin, Germany.

Krawczyk T. (1996). Biodiesel. *INFORM* 7 (8), pp. 801–822.

Kulkarni M.G., and Dalai, A.K. (2006). Waste Cooking Oils an Economical Source for Biodiesel: A Review. *Ind. Eng. Chem. Res.* 45, pp. 2901-2913.

Kumar R., Madras G., and Modak J. (2004). “Enzymatic synthesis of ethyl palmitate in supercritical carbon dioxide,” *Industrial and Engineering Chemistry Research*, vol. 43, no. 7, pp. 1568–1573.

Kumar A., and Sharma S. (2011). Potential of non-edible oil resources as biodiesel feedstock: an Indian perspective. *Renewable and Sustainable Energy Reviews* 15:1791–1800. pp. 1-10.

Kywe T.T., and Mya Oo M. (2009). Production of Biodiesel from *Jatropha* Oil (*Jatropha curcas*) in Pilot Plant. *World Academy of Science, Engineering and Technology*, (50). pp. 1-7.

Leadbeater N.E., Boucher B.M., Barnard T.M., Stencel L.M., and Wilhite B.A. (2006). “Fast, Easy Preparation of Biodiesel Using Microwave Heating”. *Energy & Fuels* 20: pp. 2281-2283.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Leadbeater N.E., Boucher B.M., Barnard T.M., Stencel L.M., and Wilhite B.A. (2007). "Continuous-Flow Preparation of Biodiesel Using Microwave Heating". *Energy & Fuels* 21: Pp. 1777-1781.

Lee S., Tanaka D., Kusaka J., and Daisho Y.(2002). Effects of diesel fuel characteristics on spray and combustion in a diesel engine. *JSAE*; 23: pp. 407–14.

Leung D. Y. C. and Guo Y. (2006). Transesterification of neat and used frying oil: Optimization for biodiesel production. *Fuel Process Tech.*, 87 (10), 883–890. pp. 1-8.

Lin L., Ying D., Chaitep S., and Vittayapadung S. (2009). Biodiesel production from crude rice bran oil and properties as fuel. *Appl Energy*; 86: pp. 681–8.

Lin L., Cunshan Z., Vittayapadung S., Xiangqian S., and Mingdong D. (2011). Opportunities and challenges for biodiesel fuel. *Applied Energy* 88: 1020–1031. pp. 1-12

Linstromberg W.W., and Baumgarten H.E.(1978). *Organic Chemistry: A Brief Course*. Lexington, MA: D.C. Heath and Company.

Li Y., Zhang X.D., and Sun L. (2010). Fatty acid methyl esters from soap stocks with potential use as biodiesel. *Energy Convers Manage*; 51: pp. 2307–11.

Lotero E., Liu Y., Lopez D.E., Suwannakarn K., Bruce D.A., and Goodwin J.G. (2005). Synthesis of Biodiesel via Acid Catalysis. *Industrial & Engineering Chemistry Research Vol* (44), 14, American Chemical Society, Columbus, OH 43210-3337, United States, pp. 5353-5363.

Lotero E., Liu Y., Lopez D. E., Suwannakarn K., Bruce D. A., and Goodwin J.G. (2005). Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.*, 44, pp. 5353–5363.

MacLeana H.L. and Laveb L.B. (2003). Evaluating automobile fuel/propulsion system technologies. *Prog Energy Combust Sci*; 29: pp.1–69.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Ma F., and Hanna M.A. (1999). Biodiesel production: a review. *Bioresource Technology* 70. pp. 1-15.

Marchetti J. M., Miguel V.U., and Errazu A. F. (2007). Possible methods for biodiesel production. *Renew. Sustain. Energy Rev.*, 11, pp. 1300–1311.

Meng X., Yang J., Xu X., Zhang L., Nie Q.J., Xian M. (2009). Biodiesel production from oleaginous microorganism. *Renew Energy*; 34: pp. 1–5.

Mitchell D. (2008). A Note on Rising Food Prices. World Bank policy research working paper no.4682, World Bank – Development Economics Group (DEC), Washington, DC; August 27, 2008.

Mittelbach M. (1996). Diesel fuel derived from vegetable oils, VI: specifications and quality control of biodiesel, *Bioresource Technology*, Vol. 56, pp. 7-11, ISSN 0960-8524.

Mittelbach, M. (2000) Chemische und motortechnische Untersuchungen der Ursachen der Einspritzpumpenverklebung bei Biodieselbetrieb; Bund-Bundesländerkooperations-projekt.

Mittelbach M., and Enzelsberger H. (1999). Transesterification of heated rapeseed oil for extending diesel fuel, *Journal of the American Oil Chemists Society*, Vol. 76, pp. 545–550, ISSN 1558-9331.

Mittelbach M., and Gangl S. (2001). Long storage stability of biodiesel made from rapeseed and used frying oil. *Journal of the American Oil Chemists Society*, Vol. 78, No 6 , pp. 573-577, ISSN 1558-9331.

Mittelbach M., Worgetter M., Pernkopf J., and Junek H. (1983). Diesel fuel derived from vegetable oils: preparation and use of rape oil methyl ester. *Energy in Agriculture*, Vol. 2, pp. 369-384, ISSN 0167-5826.

Modi M.K., Reddy J.R.C., Rao B.V.S.K., and Prasad R.B.N. (2006). Lipase-mediated transformation of vegetable oils into biodiesel using propan-2-ol as acyl acceptor. *Biotechnology Letters*, 28, pp. 637-640.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Mohammad I. and Ali O. (2002). Experimental evaluation of the transesterification of waste palm oil into biodiesel. *Bioresour Technol*; 85: pp. 253–6.

Montefri M.J., Tai X.W., and Obbard J.P. (2010). Recovery and pre-treatment of fats, oil and grease from grease interceptors for biodiesel production. *Appl Energy*; 87: pp. 3155–61.

Moser B.R. (2009). Biodiesel production, properties, and feedstocks. *In Vitro Cell Dev Biol-Plant*; 45: pp. 229–66.

Nagel F.(2008).’’Electricity from wood through the combination of gasification and solid oxide fuel cells’’, Ph.D. Thesis, Swiss Federal Institute of Technology, Zurich.

Naik M., Meher L.C., Naik S.N., and Das L.M.(2008). Production of biodiesel from high free fatty acid Karanja (*Pongamia pinnata*) oil. *Biomass Bioenergy*; 32: pp. 354–7.

Noureddini H., Gao X., and Philkana R.S. (2005). “Immobilized *Pseudomonas cepacia* lipase for biodiesel fuel production from soybean oil,” *Bioresource Technology*, Vol. 96, no. 7, pp. 769–777.

Ofor M.O., and Nwufu M. I. (2011). The search for alternative energy sources: *Jatropha* and moringa seeds for biofuel production. *Journal of Agriculture and Social Research (JASR)*. Vol. 11, no. 2, pp. 87-94.

Om Tapanes N. C., Gomes Aranda, D. A., de Mesquita Carneiro J. W., and Ceva Antunes O. A. (2008). Transesterification of *Jatropha curcas* oil glycerides: Theoretical and experimental studies of biodiesel reaction. *Fuel*, 87 (10-11), 2286–2295 pp. 1-10.

Organic Potash Corporation (OPC), (2012). Available at: www.organicpotash.com/opc/home/ [Accessed on 05/09/12].

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Pahl G. (2008). Biodiesel: growing a new energy economy. Vermont, USA: Chelsea Green Publishing Company.

Patil P.D., and Deng S. (2009). Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel Vol. 88, pp.1302–1306.

Peterson C.L., Auld D.L., and Korus R.A. (1983). Winter rape oil fuel for diesel engines: Recovery and utilization. JAOCS 60, pp.1579-1587.

Pinto A. C., Guarieiro L. N., Rezende M. J., Ribeiro N. M., Torres E. A., Lopes W. A., Pereira P. A., and Andrade J. B. (2005). Biodiesel: An overview. J. Brazil. Chem. Soc., 16 (6B), 1313-1330. pp. 2-18.

Pioch D., Lozano P., Rasoanantoandro M.C., Graille J., Geneste P., and Guida A., (1993). Biofuels from catalytic cracking of tropical vegetable oils. Oleagineux- 48, pp. 289-291.

Platonov A. Y., Evdokimov A. N., Kurzin A. V., and Maiygorova H. D. (2002). “Solubility of Potassium carbonate and Potassium Hydrocarbonate in Methanol”, “J. Chem. Eng. Data.”, 47, pp. 1175–1176.

Porteous A. (2008). Dictionary of Environmental Science and Technology. Fourth Edition Published by John Wiley & Sons Ltd, Baffins Lane, Chichester, West Sussex PO19 1UD, England. Pp. 63. ISBN 978-0-470-06195. British Library.

Prankl H., and Worgetter M.(1996). Influence of the iodine number of biodiesel to the engine performance, Liquid Fuels and Industrial Products from Renewable Resources. Proceedings of the 3rd Liquid Fuel Conference, pp. 191-196, Nashville, Tennessee, USA, September 15-17, 1996.

Pryde E.H. (1983). Vegetable oil as diesel fuel: Overview. JAOCS 60, pp. 1557 - 1558.

Pryde E.H. (1984). Vegetable oils as fuel alternatives – symposium overview. JAOCS 61, pp. 1609 -1610.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

- Qureshi N., Bowman M.J., Saha B.C., Hector R., Berhow M.A., and Cotta M.A. (2012). Effect of cellulosic sugar degradation products (furfural and hydroxymethyl furfural) on acetone–butanol–ethanol (ABE) fermentation using *Clostridium beijerinckii* P260. *Food and Bioproducts Processing*, Vol 90, Issue 3, pp. 533-540.
- Radich A. (2006). Biodiesel performance, costs, and use. US Energy Information Administration. Available at: <http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/index.html>. [Accessed on 18/08/2011].
- Raheman H., and Ghadge S.V. (2007). Performance of compression ignition engine with mahua (*Madhuca indica*) biodiesel. *Fuel*; 86: pp. 2568–73.
- Ramadhas A.S., Jayaraj S., and Muraleedharan C. (2005). Biodiesel production from high FFA rubber seed oil. *Fuel*; 84: pp. 335–40.
- Rao T.V., Rao G.P., and Reddy K.H.C. (2008). Experimental investigation of pongamia, *Jatropha* and neem methyl esters as biodiesel on CI engine. *JJMIE*; 2: pp. 117–22.
- Redman G. (2008). The Andersons Centre. "Assessment of on-farm AD in the UK", National Non-Food Crops Centre, 2008-06-09.
- REN21 (2012). "Renewables 2012: Global Status Report". pp. 75. [Accessed on 27/08/2012].
- Riesing T.F. (2005). Cultivating algae for liquid fuel production. Available at: <http://oakhavenpc.org/> [Accessed on 03/03/2012].
- Robles-Medina A., González-Moreno P.A., Esteban-Cerdán L., and Molina-Grima E. (2009), "Biocatalysis: towards ever greener biodiesel production," *Biotechnology Advances*, Vol. 27, no. 4, pp. 398–408.
- Romero M.D., Calvo L., Alba C., Habulin M., Primožic M., and Knez Z. (2005). "Enzymatic synthesis of isoamyl acetate with immobilized *Candida antarctica* lipase in supercritical carbon dioxide," *Journal of Supercritical Fluids*, Vol. 33, no. 1, pp. 77–84.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

SAE Technical Paper (1983). SAE International Off Highway Meeting, Milwaukee, Wisconsin, USA, Paper series no. 831356.

Sapienza R., Johnson A., and Ricks W. (2006). "Environmentally benign anti – icing or de-icing fluids", "US Patent 7138071 B2", Date issued: 21 Nov, 2006.

Sapienza R., Johnson A., and Ricks W. (2005). "Environmentally benign anti – icing or de-icing fluids employing triglyceride processing by-products", "US Patent 6890451 B2", Date issued: 10 May, 2005.

Sarin R., Sharma M., Sinharay S., Malhotra R.K. (2007). Jatropha–palm biodiesel blends: an optimum mix for Asia. *Fuel*; 86: pp. 1365–1371.

Schwab A.W., Dykstra G.J., Selke E., Sorenson S.C., and Pryde E.H., (1988). Diesel fuel from thermal decomposition of soybean oil. *JAOCS* 65, pp. 1781-1786.

Schwab A. W., Bagby M.O., and Freedman B. (1987). Preparation and properties of diesel fuels from vegetable oils. *Fuel* 66 (10): pp. 1372-1378.

Semwal S., Arora A.K., Badoni R.P., and Tuli D.K. (2011). Biodiesel production using heterogeneous catalysts. *Bioresource Technol* 2011; 102: pp. 2151–61.

Sharma Y.C., Singh B., and Korstad J. (2011). Latest developments on application of heterogenous basic catalysts for an efficient and eco-friendly synthesis of biodiesel: a review. *Fuel* 2011; 90: pp. 1309–24.

Sheehan J., Camobreco V., Duffield J., Graboski M., and Shapouri H.(1998). Life Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus," Report from the National Renewable Energy Laboratory for the U.S. Department of Energy's Office of Fuels Development and for the U.S. Department of Agriculture's Office of Energy, NREL/SR-580-24089, May 1998.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Shimada Y., Watanabe Y., Sugihara A., and Tominaga Y., (2002). Enzymatic alcoholysis for biodiesel fuel production and application to oil processing. *Journal of Molecular Catalysis B: Enzymatic*, 17, pp. 133-142.

Sinha S., Agarwal A.K., Garg S.(2008). Biodiesel development from rice bran oil: transesterification process optimization and fuel characterization. *Energy Convers Manage*; 49: pp. 1248–57.

Sokol W.A. (2008).’’ New process of bioethers (Second Generation of Biocarburants) production from waste glycerol utilisation’’.’’ Polish Patent Application No. PL 382 733’’, Polish Science and Innovation for the Environment. Institute of Natural Fires, ul. Wojska Polskiego 71 B, 60-630 Poznań, Poland.

Sonntag N.O.V. (1979b). Reactions of fats and fatty acids. *Bailey's industrial oil and fat products*, Vol. 1, 4th edition, ed. Swern, D., John Wiley & Sons, New York, pp. 99.

Sousa L.L., Lucena I.L., and Fernandes F.A.N.(2010). Transesterification of castor oil: effect of the acid value and neutralization of the oil with glycerol. *Fuel Process Technol*; 91: pp. 194–6.

Statistics Canada (2006) *Canada's Population Clock*. Statistics Canada, Demography Division, 2006. Updated in 27 October 2006.

Stavarache C., Vinatoru M. and Maeda Y. (2007). Aspects of ultrasonically assisted transesterification of various vegetable oils with methanol. *Ultrasonics Sonochemistry*, 14, pp 380-386.

Taher H., Al-Zuhair S.1., Al-Marzouqi A.H., Haik Y., and Farid M.M. (2011). Review of Enzymatic Transesterification of Microalgal Oil-Based Biodiesel Using Supercritical Technology. *Enzyme Research*, Volume 2011, Article ID 468292, pp. 25. Available at: <http://www.hindawi.com/journals/er/2011/468292/> [Accessed on 03/04/2012].

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Tanaka N. (2011). Technology Roadmaps: Biofuels for Transport. International Energy Agency (IEA) Report, 20th April, 2011. pp. 3. Available at: <http://iea.org/publications/freepublications/publication/name,3979,en.html> [Accessed on 29/08/12].

Taylor D.M. and Woodgate S.L. (2003). Rendering practices and inactivation of transmissible spongiform encephalopathy agents. *Rev. sci. tech. Off. int. Epiz.*, 22 (1), pp 297-310.

Thamsiriroj T., and Murphy J.D. (2009). Is it better to import palm oil from Thailand to produce biodiesel in Ireland than to produce biodiesel from indigenous Irish rape seed. *Appl Energy*; 86: pp. 595–604.

Thanh T.L., Okitsu K., Sadanga Y., Takenaka N., Maeda Y. and Bandow H. (2010). Ultrasonic assisted production of biodiesel from vegetable oils in a small scale circulation process. *Bioresource Technology*, 101, pp. 639-645.

The American Oil Chemists' Society. The lipid library report; 2010. Available at: <http://lipidlibrary.aocs.org/> [Accessed on 03/04/2012].

Thurmond W. (2007). 'THE FUTURIST'. Available at: <http://www.wfs.org/futcontja07.htm>. [Accessed on 17/08/2011].

Tiwari A.K., Kumar A., and Raheman H. (2007). Biodiesel production from *Jatropha* oil (*Jatropha curcas*) with high free fatty acids: an optimized process. *Biomass Bioenergy*; 31: pp. 569–75.

Urban F., and Mitchell T.(2011). Climate change, disasters and electricity generation. London: Overseas Development Institute and Institute for Development Studies. pp. 9-35.

Usta N.(2005). An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. *Energy Convers Manage*; 46: pp. 2373–86.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Veljkovic' V.B., Lakic'evic' S.H., Stamenkovic' O.S., Todorovic' Z.B., and Lazic' M.L. (2006). Biodiesel production from tobacco (*Nicotiana tabacum L.*) seed oil with a high content of free fatty acids. *Fuel*; 85: pp. 2671–5.

Voegelé E. (2009). "LanzaTech develops waste gas to ethanol technology", *Ethanol Producer Magazine*. Available at: <http://www.ethanolproducer.com/articles/5933/lanzatech-develops-waste-gas-to-ethanol-technology>. [Accessed on 29/10/2009].

Wanger G.L. and Petterson C.L. (1982). Vegetable oil fuels. Proceedings of the international conference on plant and vegetable oils as fuels. Leslie Backers, Ed. St Joseph, MI: ASAE. pp 279-286.

Wedel R.V. (1999). Technical handbook for marine biodiesel in recreational boats. Prepared for National Renewable Energy Laboratory, US Department of Energy, Subcontract No. ACG-7-16688-01 under Prime Contract No. DE-AC36-83CH10093, pp. 32.

Weisz P.B., Haag W.O., and Rodeweld P.G. (1979). Catalytic production of high-grade fuel (gasoline) from biomass compounds by shaped selective catalysis. *Science* 206, pp. 57-58.

Westermann P., Jorgensen B., Lange L., Ahring B.K., and Christensen C. H. (2007). Maximizing renewable hydrogen production from biomass in a bio/catalytic refinery. *Int. J. Hydrogen Energy* 32: pp. 4135– 4141.

Worldwatch Institute report, (2011). "Biofuels Make a Comeback Despite Tough Economy". [Accessed on 31/08/2011].

Wyatt V.T., Hess M.A., Dunn R.O. (2005). Fuel properties and nitrogen oxide emission levels of biodiesel produced from animal fats. *J Am Oil Chem Soc*; 82: pp.585–91.

Xiaohua W., Chonglan D., Xiaoyan H., Weiming W., Xiaoping J., and Shangyun J. (2007). The influence of using biogas digesters on family energy consumption and its economic benefit in rural areas—comparative study between Lianshui and Guichi in China. *Renewable and Sustainable Energy Reviews*, Vol. 11, Issue 5, pp. 1018–1024.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Xu Y., Du W., Liu D., and Zeng J.(2003). A novel of enzymatic route for biodiesel production from renewable oils in a solvent-free medium. *Biotechnology Letters*, 25, pp. 1239-1241.

Yan J., and Lin T. (2009). *Biofuels in Asia*. *Appl Energy*; 86:S1–S10.

Yang, H-H., Chien S-M., Lo M.Y., Lan J.C.W., Lu W.C., and Ku Y.Y. (2007). Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. *Atmospheric Environment*, 41, pp. 7232–7240.

Yeoman C.J., Han Y., Dodd D., Schroeder C.M., Mackie R.I., and Cant I.K. (2010). Thermostable enzymes as biocatalysts in the biofuel industry. PMID 20359453. *Advances in Applied Microbiology* 70: pp.1 – 55.

Zhang J.J., and Jiang L.F. (2008). Acid-catalyzed esterification of *Zanthoxylum bungeanum* seed oil with high free fatty acids for biodiesel production. *Bioresour Technol*; 99: pp. 8995–8998.

Zheng S., Kates M., Dube M.A., and McLean D.D. (2006). Acid-catalyzed production of biodiesel from waste frying oil. *Biomass and Bioenergy*, 30, pp. 267-272.

Zhou W., and Boocock D. G. B. (2006). Phase behaviour of the base-catalyzed transesterification of soybean oil. *J. Am. Oil Chem. Soc.*, 83 (12), 1041-1045: pp. 1-5.

Ziejewski M., Kaufman K.R., Schwab A.W., and Pryde, E.H. (1984). Diesel engine evaluation of a non-ionic sunflower oil-aqueous ethanol micro-emulsion. *JAOCS* 61, pp. 1620-1626.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

APPENDICES

APPENDIX A: Characterization of Oil Feedstocks

A.1 Preliminary Experimental Results

Table A.1.1 Result for Acid Number and % FFA Determination

Sample ID	Run No.	Burette Reading, mL		Titre (A) mL	Blank (B) mL	Results Acid No.	Results % FFA
		Initial	Final				
CSWVO	1	0.40	1.40	1.00	0.20	0.920	0.462
	2	1.50	2.50	1.00	0.20		
	3	2.50	3.55	1.05	0.19		
			Avg.	1.02	0.197		
CSFVO	1	6.00	6.60	0.60	0.20	0.452	0.227
	2	6.60	7.20	0.60	0.20		
	3	7.25	7.85	0.60	0.19		
			Avg.	0.60	0.197		
SBWVO	1	3.55	4.70	1.15	0.20	1.088	0.547
	2	4.70	5.90	1.20	0.20		
	3	5.90	7.05	1.15	0.19		
			Avg.	1.17	0.197		
SBFVO	1	1.75	2.30	0.55	0.20	0.396	0.199
	2	2.30	2.85	0.55	0.20		
	3	2.85	3.40	0.55	0.19		
			Avg.	0.55	0.197		
JCO	1	0.05	10.30	10.25	0.20	11.298	5.679
	2	0.10	10.40	10.30	0.20		
	3	0.10	10.35	10.25	0.19		
			Avg.	10.27	0.197		
BFVO	1	6.00	6.59	0.59	0.20	0.441	0.222
	2	6.60	7.19	0.59	0.20		
	3	7.25	7.84	0.59	0.19		
			Avg.	0.59	0.197		
BWVO	1	3.55	4.65	1.10	0.20	1.017	0.511
	2	4.70	5.80	1.10	0.20		
	3	5.80	6.91	1.11	0.19		
			Avg.	1.10	0.197		

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table A.1.2 Results for Density Determination

Sample ID	Flask no.	Mass of empty flask (A),g	Mass of flask + Oil (B),g	Mass of Oil (C),g	Density, g/cm ³
CSWVO	1	21.1406	43.9983	22.8577	0.914308
	2	20.7013	43.6001	22.8988	0.915952
	3	20.8075	43.6630	22.8555	0.914220
	4	21.0623	43.9493	22.8870	0.915480
				Avg.	0.915
CSFVO	1	21.1406	43.9529	22.8123	0.912492
	2	20.7013	43.6246	22.9233	0.916932
	3	20.8075	43.6701	22.8626	0.914504
	4	21.0623	43.9172	22.8549	0.914196
				Avg.	0.915
SBWVO	1	21.1406	43.9609	22.8203	0.912812
	2	20.7013	43.5026	22.8013	0.912052
	3	20.8075	43.6337	22.8262	0.913048
	4	21.0623	43.8752	22.8129	0.912516
				Avg.	0.913
SBFVO	1	21.1406	43.9749	22.8343	0.913372
	2	20.7013	43.5223	22.821	0.912840
	3	20.8075	43.5974	22.7899	0.911596
	4	21.0623	43.8979	22.8356	0.913424
				Avg.	0.913
JCO	1	21.1406	43.8146	22.674	0.906960
	2	20.7013	43.3732	22.6719	0.906876
	3	20.8075	43.4903	22.6828	0.907312
	4	21.0623	43.7694	22.7071	0.908284
				Avg.	0.907
BFVO	1	21.1406	43.9525	22.8119	0.912476
	2	20.7013	43.6211	22.9198	0.916792
	3	20.8075	43.6698	22.8623	0.914492
	4	21.0623	43.9168	22.8545	0.914180
				Avg.	0.914
BWVO	1	21.1406	43.997	22.8564	0.914256
	2	20.7013	43.555	22.8537	0.914148
	3	20.8075	43.6617	22.8542	0.914168
	4	21.0623	43.9471	22.8848	0.915392
				Avg.	0.914

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**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table A.1.3 Results for Viscosity Determination

Sample ID	Rpm	% Torque	Shear stress	Shear rate	Viscosity, cP
CSWVO	25	13.6	10.6	30.6	34.6
	50	27.1	21.2	61.2	34.7
	75	40.7	31.9	91.7	34.7
	100	54.2	42.2	122	34.7
	120	65.0	51.0	147	34.7
	150	81.3	63.6	183	34.7
	180	97.4	76.2	220	34.6
				Avg.	34.7
CSFVO	25	13.4	10.5	30.6	34.3
	50	26.8	21.0	61.2	34.3
	75	40.2	31.5	91.7	34.3
	100	53.5	41.9	122	34.3
	120	64.3	50.3	147	34.3
	150	80.3	62.9	183	34.3
	180	96.3	75.4	220	34.2
				Avg.	34.3
SBWVO	25	12.6	9.9	30.6	32.3
	50	25.3	19.8	61.2	32.4
	75	37.9	29.7	91.7	32.3
	100	50.6	39.6	122	32.4
	120	60.7	47.5	147	32.4
	150	75.9	59.4	183	32.4
	180	90.9	71.1	220	32.3
				Avg.	32.4
SBFVO	25	11.9	9.3	30.6	30.5
	50	24.0	18.8	61.2	30.7
	75	35.9	28.2	91.7	30.7
	100	48.0	37.6	122	30.7
	120	57.6	45.1	147	30.7
	150	72.0	56.4	183	30.7
	180	86.3	67.5	220	30.7
	200	95.8	75.1	245	30.7
				Avg.	30.7

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table A.1.3 Results for Viscosity Determination (Continued)

Sample ID	Rpm	% Torque	Shear stress	Shear rate	Viscosity, cP
JCO	25	12.5	9.9	30.6	32.0
	50	25.1	19.6	61.2	32.1
	75	37.6	29.4	91.7	32.1
	100	50.1	39.2	122	32.1
	120	60.1	47.0	147	32.1
	150	75.1	58.8	183	32.0
	180	90.0	70.4	220	32.0
	200	99.9	78.2	245	32.0
				Avg.	32.1
BFVO	25	12.7	9.9	30.6	32.4
	50	25.4	19.9	61.2	32.5
	75	38.1	29.9	91.7	32.5
	100	50.8	39.8	122	32.5
	120	61.0	47.7	147	32.5
	150	76.2	59.7	183	32.5
	180	91.3	71.5	220	32.5
				Avg.	32.5
BWVO	25	13.1	10.3	30.6	33.5
	50	26.2	20.5	61.2	33.6
	75	39.3	30.8	91.7	33.5
	100	52.4	40.9	122	33.6
	120	62.9	49.3	147	33.6
	150	78.6	61.5	183	33.6
	180	94.2	73.7	220	33.5
				Avg.	33.6

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BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

APPENDIX B: Reaction Parameters Effect on Yield of FAME

B.1 Effect of Catalyst Amount on Yield of FAME

Table B.1.1 Effect of Catalyst Amount on Conversion of FAME from Blend of Fresh Vegetable Oil (Table 7)

Experimental Run	Catalyst Amount (wt. % of Oil)/g	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Level
1	1	14.56	100.46	14.49	14.32 ± 0.85
2		13.99		13.93	
3		14.61		14.54	
1	2	90.52	100.46	90.11	90.09 ± 0.05
2		90.50		90.09	
3		90.48		90.07	
1	3	93.64	100.46	93.21	93.27 ± 0.14
2		93.71		93.28	
3		93.75		93.32	
1	4	97.44	100.46	96.99	97.01 ± 0.12
2		97.42		96.97	
3		97.51		97.06	
1	5	94.91	100.46	94.48	94.47 ± 0.02
2		94.89		94.46	
3		94.90		94.47	
1	6	93.99	100.46	93.56	93.47 ± 0.20
2		93.87		93.44	
3		93.84		93.41	
1	7	93.43	100.46	93.00	93.03 ± 0.05
2		93.46		93.03	
3		93.47		93.04	

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table B.1.2 Effect of Catalyst Amount Conversion of FAME from Blend of Waste Vegetable Oil (Table 7)

Experimental Run	Catalyst Amount (wt% of Oil)/g	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Level
1 2 3	1	11.16 11.13 11.14	100.46	11.11 11.08 11.09	11.09 ± 0.04
1 2 3	2	89.86 89.74 88.99	100.46	89.45 89.33 88.58	89.12 ± 1.17
1 2 3	3	92.84 91.99 92.73	100.46	92.41 91.57 92.31	92.10 ± 1.14
1 2 3	4	95.75 95.88 95.73	100.46	95.31 95.44 95.29	95.35 ± 0.20
1 2 3	5	93.85 93.90 93.78	100.46	93.42 93.47 93.35	93.41 ± 0.15
1 2 3	6	93.60 93.55 93.53	100.46	93.17 93.12 93.10	93.13 ± 0.09
1 2 3	7	93.13 92.99 92.53	100.46	92.70 92.56 92.11	92.46 ± 0.78

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table B.1.3 Effect of Catalyst Amount on Conversion of FAME from *Jatropha curcas* oil (Table 7)

Experimental Run	Catalyst Amount (wt.% of Oil)/g	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Level
1	1	10.50	100.46	10.45	10.47 ± 0.04
2		10.51		10.46	
3		10.53		10.48	
1	2	81.11	100.46	80.74	80.67 ± 0.15
2		81.01		80.64	
3		81.00		80.63	
1	3	86.74	100.46	86.34	86.33 ± 0.04
2		86.72		86.32	
3		86.71		86.31	
1	4	90.71	100.46	90.29	90.30 ± 0.02
2		90.72		90.30	
3		90.73		90.31	
1	5	89.62	100.46	89.21	89.22 ± 0.04
2		89.62		89.21	
3		89.65		89.24	
1	6	87.35	100.46	86.95	86.94 ± 0.04
2		87.34		86.94	
3		87.32		86.92	
1	7	85.57	100.46	85.18	85.19 ± 0.02
2		85.59		85.20	
3		85.58		85.19	

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

B.2 Effect of Oil: Methanol Molar Ratio on Yield of FAME

Table B.2 Effect of Oil: Methanol Molar Ratio on Yield of FAME from Various Oil Feeds (Table 8)

Name of TG	Experimental Run	Molar Ratio/ Oil:Methanol	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Level
CSWVO	1		82.71		82.32	
	2	1:4	82.53	100.48	82.14	82.32 $\pm$ 0.43
	3		82.88		82.49	
	1		93.74		93.30	
	2	1:6	93.25	100.48	92.81	93.09 $\pm$ 0.63
	3		93.62		93.18	
	1		92.35		91.91	
	2	1:8	92.53	100.48	92.09	92.14 $\pm$ 0.61
	3		92.84		92.40	
CSFVO	1		88.38		87.96	
	2	1:4	88.71	100.48	88.29	88.08 $\pm$ 0.45
	3		88.42		88.00	
	1		98.25		97.79	
	2	1:6	98.22	100.48	97.76	97.75 $\pm$ 0.11
	3		98.16		97.70	
	1		95.71		95.26	
	2	1:8	95.49	100.48	95.04	95.29 $\pm$ 0.68
	3		96.04		95.59	
SBWVO	1		88.52		88.11	
	2	1:4	88.35	100.46	87.95	88.03 $\pm$ 0.21
	3		88.43		88.03	
	1		96.32		95.88	
	2	1:6	96.41	100.46	95.97	95.72 $\pm$ 0.89
	3		95.75		95.31	
	1		93.36		92.93	
	2	1:8	93.02	100.46	92.59	92.84 $\pm$ 0.53
	3		93.42		92.99	

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**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Table B.2 Effect of Oil: Methanol Molar Ratio on Yield of FAME from Various Oil Feeds
(Continued) (Table 8)

Name of TG	Experimental Run	Molar Ratio/ oil: methanol	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Level
SBFVO	1		90.86		90.44	
	2	1:4	90.73	100.46	90.31	90.41 ± 0.22
	3		90.90		90.48	
	1		96.93		96.49	
	2	1:6	96.79	100.46	96.35	96.41 ± 0.17
	3		96.85		96.41	
	1		94.78		94.35	
	2	1:8	94.53	100.46	94.10	94.23 ± 0.31
	3		94.69		94.26	
JCO	1		69.25		68.93	
	2	1:4	68.76	100.46	68.45	68.55 ± 0.85
	3		68.59		68.28	
	1		86.90		86.50	
	2	1:6	87.43	100.46	87.03	86.72 ± 0.68
	3		87.03		86.63	
	1		94.88		94.45	
	2	1:8	95.11	100.46	94.67	94.56 ± 0.29
	3		94.98		94.55	

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BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

B.3 Effect of Reaction Time on Yield of FAME

Table B.3 Effect of Reaction Time on Yield of FAME from Various Oil Feeds (Table 9)

Name of TG	Experimental Run	Reaction Time/min	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Interval
CSWVO	1		98.56		98.09	
	2	40	99.03	100.48	98.56	98.27 ± 0.62
	3		98.64		98.17	
	1		98.00		97.53	
	2	80	98.21	100.48	97.74	97.68 ± 0.31
	3		98.23		97.76	
	1		93.74		93.29	
	2	120	93.25	100.48	92.80	93.09 ± 0.63
	3		93.62		93.17	
SBWVO	1		98.19		97.74	
	2	40	97.94	100.46	97.49	97.51 ± 0.55
	3		97.75		97.30	
	1		98.95		98.50	
	2	80	98.89	100.46	98.44	98.48 ± 0.10
	3		98.97		98.52	
	1		96.32		95.88	
	2	120	96.41	100.46	95.97	95.72 ± 0.89
	3		95.75		95.31	
JCO	1		86.72		86.32	
	2	40	86.49	100.46	86.09	86.19 ± 0.30
	3		86.54		86.14	
	1		88.64		88.23	
	2	80	88.53	100.46	88.12	88.19 ± 0.14
	3		88.61		88.20	
	1		94.99		94.56	
	2	120	94.99	100.46	94.56	94.57 ± 0.07
	3		95.04		94.60	

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BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

B.3 Effect of Reaction Temperature on Yield of FAME

Table B.3 Effect of Reaction Temperature on Yield of FAME from Various Oil Feeds (Table 10)

Name of TG	Experimental Run	Reaction Temperature/oC	Actual Yield of FAME/g	Theoretical Yield of FAME/g	% FAME (Biodiesel) Yield	95% Confidence Interval
CSWVO	1		99.51		99.03	
	2	55	99.63	100.48	99.15	99.09 ± 0.15
	3		99.55		99.07	
	1		99.96		99.48	
	2	60	99.94	100.48	99.46	99.46 ± 0.06
	3		99.91		99.43	
	1		93.74		93.29	
	2	65	93.25	100.48	92.80	93.09 ± 0.63
	3		93.62		93.17	
SBWVO	1		98.71		98.26	
	2	55	98.65	100.46	98.20	98.15 ± 0.36
	3		98.43		97.98	
	1		99.96		99.50	
	2	60	99.98	100.46	99.52	99.51 ± 0.02
	3		99.97		99.51	
	1		96.32		95.88	
	2	65	96.41	100.46	95.97	95.72 ± 0.89
	3		95.75		95.31	
JCO	1		87.72		87.32	
	2	55	87.91	100.46	87.51	87.51 ± 0.47
	3		88.1		87.70	
	1		94.98		94.55	
	2	60	95.05	100.46	94.61	94.57 ± 0.09
	3		94.99		94.56	
	1		90.26		89.85	
	2	65	90.56	100.46	90.15	90.00 ± 0.37
	3		90.42		90.01	

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BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

APPENDIX C: Supplementary Material for Statistical Analysis

C.1 Report on Catalyst Amount for Blend of Fresh Vegetable Oil Biodiesel

ANOVA

% FAME (Biodiesel) Yield

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	16219.291	6	2703.215	1.487E5	.000
Within Groups	.255	14	.018		
Total	16219.545	20			

Multiple Comparisons

Dependent Variable: % FAME (Biodiesel) Yield

	(I) Catalyst Weight	(J) Catalyst Weight	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
LSD	1	2	-75.77000*	.11009	.000	-76.0061	-75.5339
		3	-78.95000*	.11009	.000	-79.1861	-78.7139
		4	-82.68667*	.11009	.000	-82.9228	-82.4505
		5	-80.15000*	.11009	.000	-80.3861	-79.9139
		6	-79.15000*	.11009	.000	-79.3861	-78.9139
		7	-78.70333*	.11009	.000	-78.9395	-78.4672
	2	1	75.77000*	.11009	.000	75.5339	76.0061
		3	-3.18000*	.11009	.000	-3.4161	-2.9439
		4	-6.91667*	.11009	.000	-7.1528	-6.6805
		5	-4.38000*	.11009	.000	-4.6161	-4.1439
		6	-3.38000*	.11009	.000	-3.6161	-3.1439
		7	-2.93333*	.11009	.000	-3.1695	-2.6972
	3	1	78.95000*	.11009	.000	78.7139	79.1861
		2	3.18000*	.11009	.000	2.9439	3.4161
		4	-3.73667*	.11009	.000	-3.9728	-3.5005

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

	5	-1.20000*	.11009	.000	-1.4361	-.9639
	6	-.20000	.11009	.091	-.4361	.0361
	7	.24667*	.11009	.042	.0105	.4828
4	1	82.68667*	.11009	.000	82.4505	82.9228
	2	6.91667*	.11009	.000	6.6805	7.1528
	3	3.73667*	.11009	.000	3.5005	3.9728
	5	2.53667*	.11009	.000	2.3005	2.7728
	6	3.53667*	.11009	.000	3.3005	3.7728
	7	3.98333*	.11009	.000	3.7472	4.2195
5	1	80.15000*	.11009	.000	79.9139	80.3861
	2	4.38000*	.11009	.000	4.1439	4.6161
	3	1.20000*	.11009	.000	.9639	1.4361
	4	-2.53667*	.11009	.000	-2.7728	-2.3005
	6	1.00000*	.11009	.000	.7639	1.2361
	7	1.44667*	.11009	.000	1.2105	1.6828
6	1	79.15000*	.11009	.000	78.9139	79.3861
	2	3.38000*	.11009	.000	3.1439	3.6161
	3	.20000	.11009	.091	-.0361	.4361
	4	-3.53667*	.11009	.000	-3.7728	-3.3005
	5	-1.00000*	.11009	.000	-1.2361	-.7639
	7	.44667*	.11009	.001	.2105	.6828
7	1	78.70333*	.11009	.000	78.4672	78.9395
	2	2.93333*	.11009	.000	2.6972	3.1695
	3	-.24667*	.11009	.042	-.4828	-.0105
	4	-3.98333*	.11009	.000	-4.2195	-3.7472
	5	-1.44667*	.11009	.000	-1.6828	-1.2105
	6	-.44667*	.11009	.001	-.6828	-.2105

*. The mean difference is significant at the 0.05 level.

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

% FAME (Biodiesel) Yield

Tukey B

Catalyst Weight	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
1	3	14.3200					
2	3		90.0900				
7	3			93.0233			
3	3			93.2700	93.2700		
6	3				93.4700		
5	3					94.4700	
4	3						97.0067

Means for groups in homogeneous subsets are displayed.

C.2 Report on Catalyst amount for Blend of Waste Oil Biodiesel

ANOVA

% FAME (Biodiesel) Yield

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	17142.916	6	2857.153	3.706E4	.000
Within Groups	1.079	14	.077		
Total	17143.996	20			

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Multiple Comparisons

% FAME (Biodiesel) Yield

Tukey HSD

(I) Catalyst Weight	(J) Catalyst Weight	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-78.02667 [*]	.22671	.000	-78.8008	-77.2526
	3	-81.00333 [*]	.22671	.000	-81.7774	-80.2292
	4	-84.25333 [*]	.22671	.000	-85.0274	-83.4792
	5	-82.32000 [*]	.22671	.000	-83.0941	-81.5459
	6	-82.03667 [*]	.22671	.000	-82.8108	-81.2626
	7	-81.36333 [*]	.22671	.000	-82.1374	-80.5892
2	1	78.02667 [*]	.22671	.000	77.2526	78.8008
	3	-2.97667 [*]	.22671	.000	-3.7508	-2.2026
	4	-6.22667 [*]	.22671	.000	-7.0008	-5.4526
	5	-4.29333 [*]	.22671	.000	-5.0674	-3.5192
	6	-4.01000 [*]	.22671	.000	-4.7841	-3.2359
	7	-3.33667 [*]	.22671	.000	-4.1108	-2.5626
3	1	81.00333 [*]	.22671	.000	80.2292	81.7774
	2	2.97667 [*]	.22671	.000	2.2026	3.7508
	4	-3.25000 [*]	.22671	.000	-4.0241	-2.4759
	5	-1.31667 [*]	.22671	.001	-2.0908	-.5426
	6	-1.03333 [*]	.22671	.006	-1.8074	-.2592
	7	-.36000	.22671	.692	-1.1341	.4141
4	1	84.25333 [*]	.22671	.000	83.4792	85.0274
	2	6.22667 [*]	.22671	.000	5.4526	7.0008
	3	3.25000 [*]	.22671	.000	2.4759	4.0241
	5	1.93333 [*]	.22671	.000	1.1592	2.7074
	6	2.21667 [*]	.22671	.000	1.4426	2.9908
	7	2.89000 [*]	.22671	.000	2.1159	3.6641
5	1	82.32000 [*]	.22671	.000	81.5459	83.0941
	2	4.29333 [*]	.22671	.000	3.5192	5.0674
	3	1.31667 [*]	.22671	.001	.5426	2.0908

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

	4	-1.93333*	.22671	.000	-2.7074	-1.1592
	6	.28333	.22671	.863	-.4908	1.0574
	7	.95667*	.22671	.012	.1826	1.7308
6	1	82.03667*	.22671	.000	81.2626	82.8108
	2	4.01000*	.22671	.000	3.2359	4.7841
	3	1.03333*	.22671	.006	.2592	1.8074
	4	-2.21667*	.22671	.000	-2.9908	-1.4426
	5	-.28333	.22671	.863	-1.0574	.4908
	7	.67333	.22671	.108	-.1008	1.4474
7	1	81.36333*	.22671	.000	80.5892	82.1374
	2	3.33667*	.22671	.000	2.5626	4.1108
	3	.36000	.22671	.692	-.4141	1.1341
	4	-2.89000*	.22671	.000	-3.6641	-2.1159
	5	-.95667*	.22671	.012	-1.7308	-.1826
	6	-.67333	.22671	.108	-1.4474	.1008

*. The mean difference is significant at the 0.05 level.



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

% FAME (Biodiesel) Yield

Tukey HSD

Catalyst Weight	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
1	3	11.0933					
2	3		89.1200				
3	3			92.0967			
7	3			92.4567	92.4567		
6	3				93.1300	93.1300	
5	3					93.4133	
4	3						95.3467
Sig.		1.000	1.000	.692	.108	.863	1.000

Means for groups in homogeneous subsets are displayed.

C.3 Report on Catalyst Amount for *Jatropha curcas* oil Biodiesel

ANOVA

% FAME (Biodiesel) Yield

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	15016.684	6	2502.781	3.575E6	.000
Within Groups	.010	14	.001		
Total	15016.694	20			

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Multiple Comparisons

Dependent Variable: % FAME (Biodiesel) Yield

(I) Catalyst Weight	(J) Catalyst Weight	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
LSD 1	2	-70.20667 [*]	.02160	.000	-70.2530	-70.1603
	3	-75.86000 [*]	.02160	.000	-75.9063	-75.8137
	4	-79.83667 [*]	.02160	.000	-79.8830	-79.7903
	5	-78.75667 [*]	.02160	.000	-78.8030	-78.7103
	6	-76.47333 [*]	.02160	.000	-76.5197	-76.4270
	7	-74.72667 [*]	.02160	.000	-74.7730	-74.6803
2	1	70.20667 [*]	.02160	.000	70.1603	70.2530
	3	-5.65333 [*]	.02160	.000	-5.6997	-5.6070
	4	-9.63000 [*]	.02160	.000	-9.6763	-9.5837
	5	-8.55000 [*]	.02160	.000	-8.5963	-8.5037
	6	-6.26667 [*]	.02160	.000	-6.3130	-6.2203
	7	-4.52000 [*]	.02160	.000	-4.5663	-4.4737
3	1	75.86000 [*]	.02160	.000	75.8137	75.9063
	2	5.65333 [*]	.02160	.000	5.6070	5.6997
	4	-3.97667 [*]	.02160	.000	-4.0230	-3.9303

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

	5	-2.89667 [*]	.02160	.000	-2.9430	-2.8503
	6	-.61333 [*]	.02160	.000	-.6597	-.5670
	7	1.13333 [*]	.02160	.000	1.0870	1.1797
4	1	79.83667 [*]	.02160	.000	79.7903	79.8830
	2	9.63000 [*]	.02160	.000	9.5837	9.6763
	3	3.97667 [*]	.02160	.000	3.9303	4.0230
	5	1.08000 [*]	.02160	.000	1.0337	1.1263
	6	3.36333 [*]	.02160	.000	3.3170	3.4097
	7	5.11000 [*]	.02160	.000	5.0637	5.1563
5	1	78.75667 [*]	.02160	.000	78.7103	78.8030
	2	8.55000 [*]	.02160	.000	8.5037	8.5963
	3	2.89667 [*]	.02160	.000	2.8503	2.9430
	4	-1.08000 [*]	.02160	.000	-1.1263	-1.0337
	6	2.28333 [*]	.02160	.000	2.2370	2.3297
	7	4.03000 [*]	.02160	.000	3.9837	4.0763
6	1	76.47333 [*]	.02160	.000	76.4270	76.5197
	2	6.26667 [*]	.02160	.000	6.2203	6.3130
	3	.61333 [*]	.02160	.000	.5670	.6597
	4	-3.36333 [*]	.02160	.000	-3.4097	-3.3170
	5	-2.28333 [*]	.02160	.000	-2.3297	-2.2370
	7	1.74667 [*]	.02160	.000	1.7003	1.7930

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

7	1	74.72667 [*]	.02160	.000	74.6803	74.7730
	2	4.52000 [*]	.02160	.000	4.4737	4.5663
	3	-1.13333 [*]	.02160	.000	-1.1797	-1.0870
	4	-5.11000 [*]	.02160	.000	-5.1563	-5.0637
	5	-4.03000 [*]	.02160	.000	-4.0763	-3.9837
	6	-1.74667 [*]	.02160	.000	-1.7930	-1.7003

*. The mean difference is significant at the 0.05 level.

KNUST

% FAME (Biodiesel) Yield

Catalyst Weight	N	Subset for alpha = 0.05						
		1	2	3	4	5	6	7
Tukey B ^a 1	3	10.4633						
2	3		80.6700					
7	3			85.1900				
3	3				86.3233			
6	3					86.9367		
5	3						89.2200	
4	3							90.3000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

C.4 Report for Oil: Methanol Molar Ratio

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Cottonseed	Between Groups	213.503	2	106.752	2.036E3	.000

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

WVO	Within Groups	.315	6	.052		
	Total	213.818	8			
Cottonseed FVO	Between Groups	151.495	2	75.748	2.044E3	.000
	Within Groups	.222	6	.037		
	Total	151.718	8			
Soya bean WVO	Between Groups	90.554	2	45.277	750.307	.000
	Within Groups	.362	6	.060		
	Total	90.916	8			
Soya bean FVO	Between Groups	55.476	2	27.738	2.883E3	.000
	Within Groups	.058	6	.010		
	Total	55.534	8			
Jatropha (UWO)	Between Groups	1067.614	2	533.807	7.925E3	.000
	Within Groups	.404	6	.067		
	Total	1068.019	8			



**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Multiple Comparisons

Dependent Variable		(I) Molar Ratio	(J) Molar Ratio	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
Cottonseed WVO	LSD	1:4	1:6	-10.78000*	.18696	.000	-11.2375	-10.3225
			1:8	-9.81667*	.18696	.000	-10.2742	-9.3592
		1:6	1:4	10.78000*	.18696	.000	10.3225	11.2375
			1:8	.96333*	.18696	.002	.5058	1.4208
		1:8	1:4	9.81667*	.18696	.000	9.3592	10.2742
			1:6	-.96333*	.18696	.002	-1.4208	-.5058
Cottonseed FVO	LSD	1:4	1:6	-9.66667*	.15717	.000	-10.0513	-9.2821
			1:8	-7.21333*	.15717	.000	-7.5979	-6.8287
		1:6	1:4	9.66667*	.15717	.000	9.2821	10.0513
			1:8	2.45333*	.15717	.000	2.0687	2.8379
		1:8	1:4	7.21333*	.15717	.000	6.8287	7.5979
			1:6	-2.45333*	.15717	.000	-2.8379	-2.0687
Soya bean WVO	LSD	1:4	1:6	-7.69000*	.20057	.000	-8.1808	-7.1992
			1:8	-4.80667*	.20057	.000	-5.2975	-4.3159
		1:6	1:4	7.69000*	.20057	.000	7.1992	8.1808
			1:8	2.88333*	.20057	.000	2.3925	3.3741
		1:8	1:4	4.80667*	.20057	.000	4.3159	5.2975
			1:6	-2.88333*	.20057	.000	-3.3741	-2.3925
Soya bean FVO	LSD	1:4	1:6	-6.00667*	.08009	.000	-6.2026	-5.8107
			1:8	-3.82667*	.08009	.000	-4.0226	-3.6307
		1:6	1:4	6.00667*	.08009	.000	5.8107	6.2026
			1:8	2.18000*	.08009	.000	1.9840	2.3760
		1:8	1:4	3.82667*	.08009	.000	3.6307	4.0226
			1:6	-2.18000*	.08009	.000	-2.3760	-1.9840
Jatropha (UWO)	LSD	1:4	1:6	-18.16667*	.21190	.000	-18.6852	-17.6482
			1:8	-26.00333*	.21190	.000	-26.5218	-25.4848
		1:6	1:4	18.16667*	.21190	.000	17.6482	18.6852
			1:8	-7.83667*	.21190	.000	-8.3552	-7.3182
		1:8	1:4	26.00333*	.21190	.000	25.4848	26.5218
			1:6	7.83667*	.21190	.000	7.3182	8.3552

*. The mean difference is significant at the 0.05 level.

KNUST



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Homogeneous Subsets

Cottonseed WVO

Molar Ratio	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 1:4	3	82.3167		
1:8	3		92.1333	
1:6	3			93.0967

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Cottonseed FVO

Molar Ratio	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 1:4	3	88.0833		
1:8	3		95.2967	
1:6	3			97.7500

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Soya bean WVO

Molar Ratio	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 1:4	3	88.0300		
1:8	3		92.8367	
1:6	3			95.7200

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Soya bean FVO

Molar Ratio	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 1:4	3	90.4100		
1:8	3		94.2367	
1:6	3			96.4167

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Jatropha (UWO)

Molar Ratio	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 1:4	3	68.5533		
1:6	3		86.7200	
1:8	3			94.5567

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

C.5 Report for Reaction Time

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Cottonseed WVO	Between Groups	48.326	2	24.163	500.957	.000
	Within Groups	.289	6	.048		
	Total	48.615	8			
Soya bean WVO	Between Groups	11.812	2	5.906	99.246	.000
	Within Groups	.357	6	.060		
	Total	12.169	8			
Jatropha (UWO)	Between Groups	115.224	2	57.612	9.393E3	.000
	Within Groups	.037	6	.006		
	Total	115.261	8			

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

Multiple Comparisons

Dependent Variable		(I)	(J)	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
		Reacti on Time	Reacti on Time				Lower Bound	Upper Bound
Cottonseed WVO	LSD	40	80	.59667*	.17932	.016	.1579	1.0354
			120	5.18667*	.17932	.000	4.7479	5.6254
		80	40	-.59667*	.17932	.016	-1.0354	-.1579
			120	4.59000*	.17932	.000	4.1512	5.0288
		120	40	-5.18667*	.17932	.000	-5.6254	-4.7479
			80	-4.59000*	.17932	.000	-5.0288	-4.1512
Soya bean WVO	LSD	40	80	-.97667*	.19918	.003	-1.4641	-.4893
			120	1.79000*	.19918	.000	1.3026	2.2774
		80	40	.97667*	.19918	.003	.4893	1.4641
			120	2.76667*	.19918	.000	2.2793	3.2541
		120	40	-1.79000*	.19918	.000	-2.2774	-1.3026
			80	-2.76667*	.19918	.000	-3.2541	-2.2793
Jatropha (UWO)	LSD	40	80	-2.00000*	.06394	.000	-2.1565	-1.8435
			120	-8.39000*	.06394	.000	-8.5465	-8.2335
		80	40	2.00000*	.06394	.000	1.8435	2.1565
			120	-6.39000*	.06394	.000	-6.5465	-6.2335
		120	40	8.39000*	.06394	.000	8.2335	8.5465
			80	6.39000*	.06394	.000	6.2335	6.5465

*. The mean difference is significant at the 0.05 level.

Homogeneous Subsets

Cottonseed WVO

Reacti on Time	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 120	3	93.0867		
80	3		97.6767	
40	3			98.2733

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Soya bean WVO

Reaction Time	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 120	3	95.7200		
40	3		97.5100	
80	3			98.4867

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Jatropha (UWO)

Reaction Time	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 40	3	86.1833		
80	3		88.1833	
120	3			94.5733

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

C.6 Report for Reaction Temperature

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Cottonseed WVO	Between Groups	76.676	2	38.338	1.653E3	.000
	Within Groups	.139	6	.023		
	Total	76.815	8			
Soya bean WVO	Between Groups	22.111	2	11.056	221.213	.000
	Within Groups	.300	6	.050		
	Total	22.411	8			
Jatropha (UWO)	Between Groups	76.992	2	38.496	1.936E3	.000
	Within Groups	.119	6	.020		
	Total	77.112	8			

Multiple Comparisons

Dependent Variable		(I) Reaction Temperature	(J) Reaction Temperature	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
							Lower Bound	Upper Bound
Cottonseed WVO	LSD	55	60	-.37333*	.12437	.024	-.6776	-.0690
			65	5.99667*	.12437	.000	5.6924	6.3010
		60	55	.37333*	.12437	.024	.0690	.6776
			65	6.37000*	.12437	.000	6.0657	6.6743
		65	55	-5.99667*	.12437	.000	-6.3010	-5.6924
			60	-6.37000*	.12437	.000	-6.6743	-6.0657
Soya bean WVO	LSD	55	60	-1.36333*	.18253	.000	-1.8100	-.9167
			65	2.42667*	.18253	.000	1.9800	2.8733
		60	55	1.36333*	.18253	.000	.9167	1.8100
			65	3.79000*	.18253	.000	3.3434	4.2366
		65	55	-2.42667*	.18253	.000	-2.8733	-1.9800
			60	-3.79000*	.18253	.000	-4.2366	-3.3434
Jatropha (UWO)	LSD	55	60	-7.06333*	.11515	.000	-7.3451	-6.7816
			65	-2.49333*	.11515	.000	-2.7751	-2.2116
		60	55	7.06333*	.11515	.000	6.7816	7.3451
			65	4.57000*	.11515	.000	4.2882	4.8518

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
USING UNSUPPORTED POTASSIUM CARBONATE**

65	55	2.49333*	.11515	.000	2.2116	2.7751
	60	-4.57000*	.11515	.000	-4.8518	-4.2882

*. The mean difference is significant at the 0.05 level.

Cottonseed WVO

Reaction Temperature	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 65	3	93.0867		
55	3		99.0833	
60	3			99.4567

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Soya bean WVO

Reaction Temperature	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 65	3	95.7200		
55	3		98.1467	
60	3			99.5100

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

Jatropha (UWO)

Reaction Temperature	N	Subset for alpha = 0.05		
		1	2	3
Tukey B ^a 55	3	87.5100		
65	3		90.0033	
60	3			94.5733

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

APPENDIX D. Supplementary material for chapter 3

D.1 Biodiesel production pictures

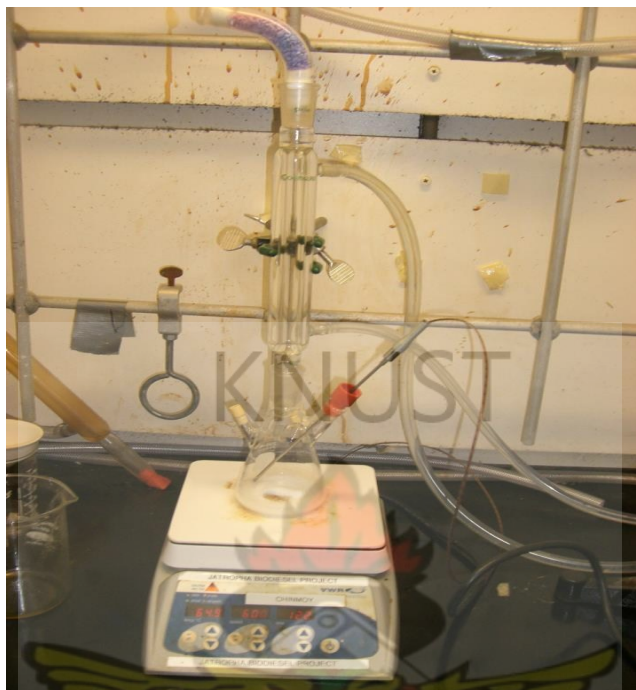
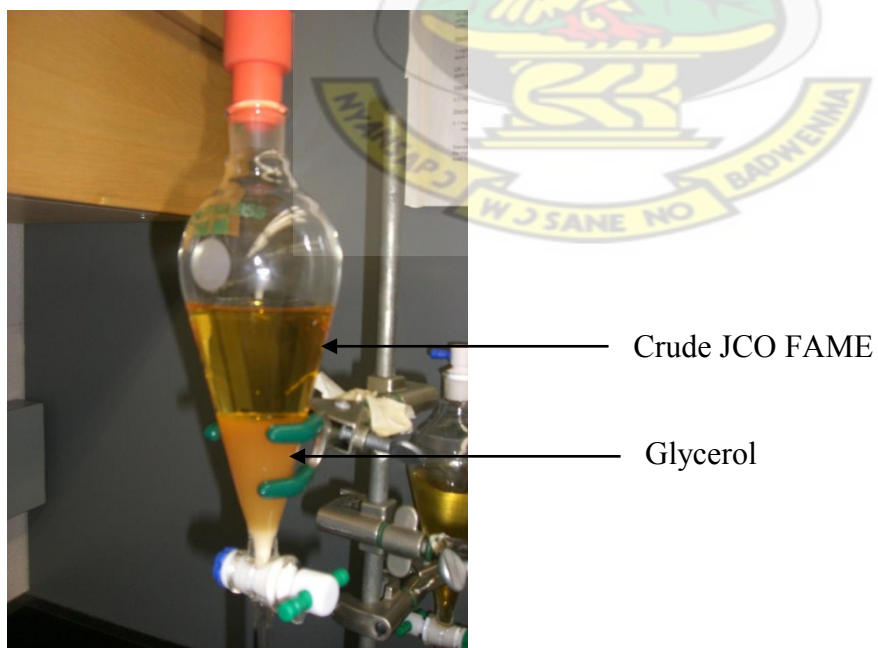


Figure D.1.1 Dissolution of K_2CO_3 in methanol prior to transesterification



JCO FAME and glycerol

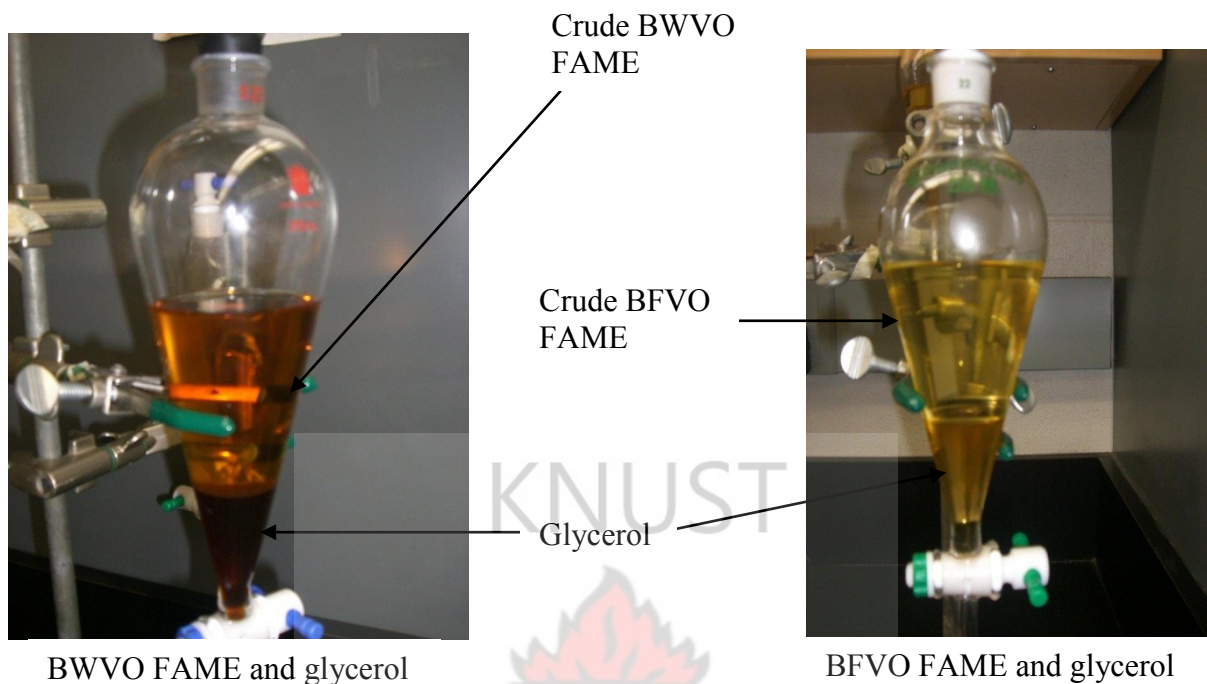


Figure D.1.2 Settling of FAME and glycerol phases

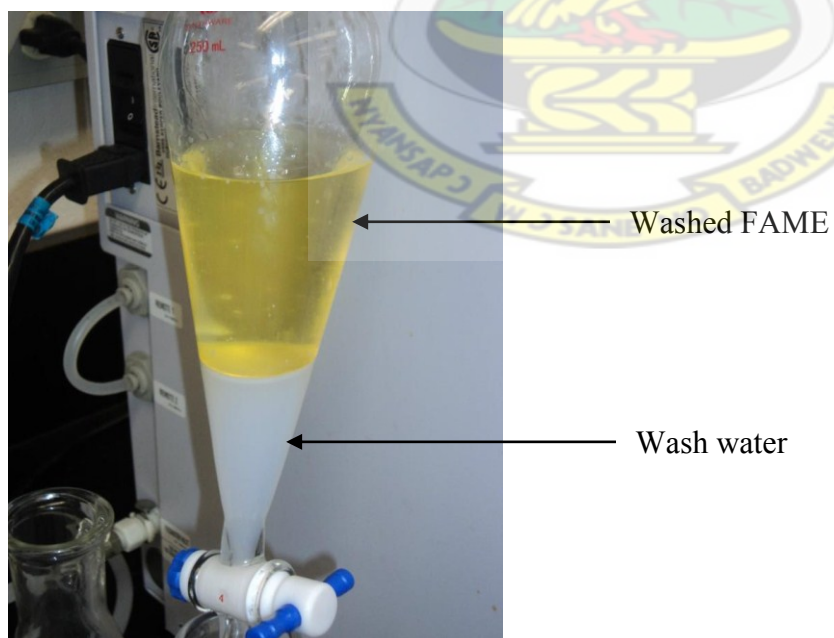


Figure D 1.3 Washing of crude FAME



Figure D 1.4 Biodiesel samples

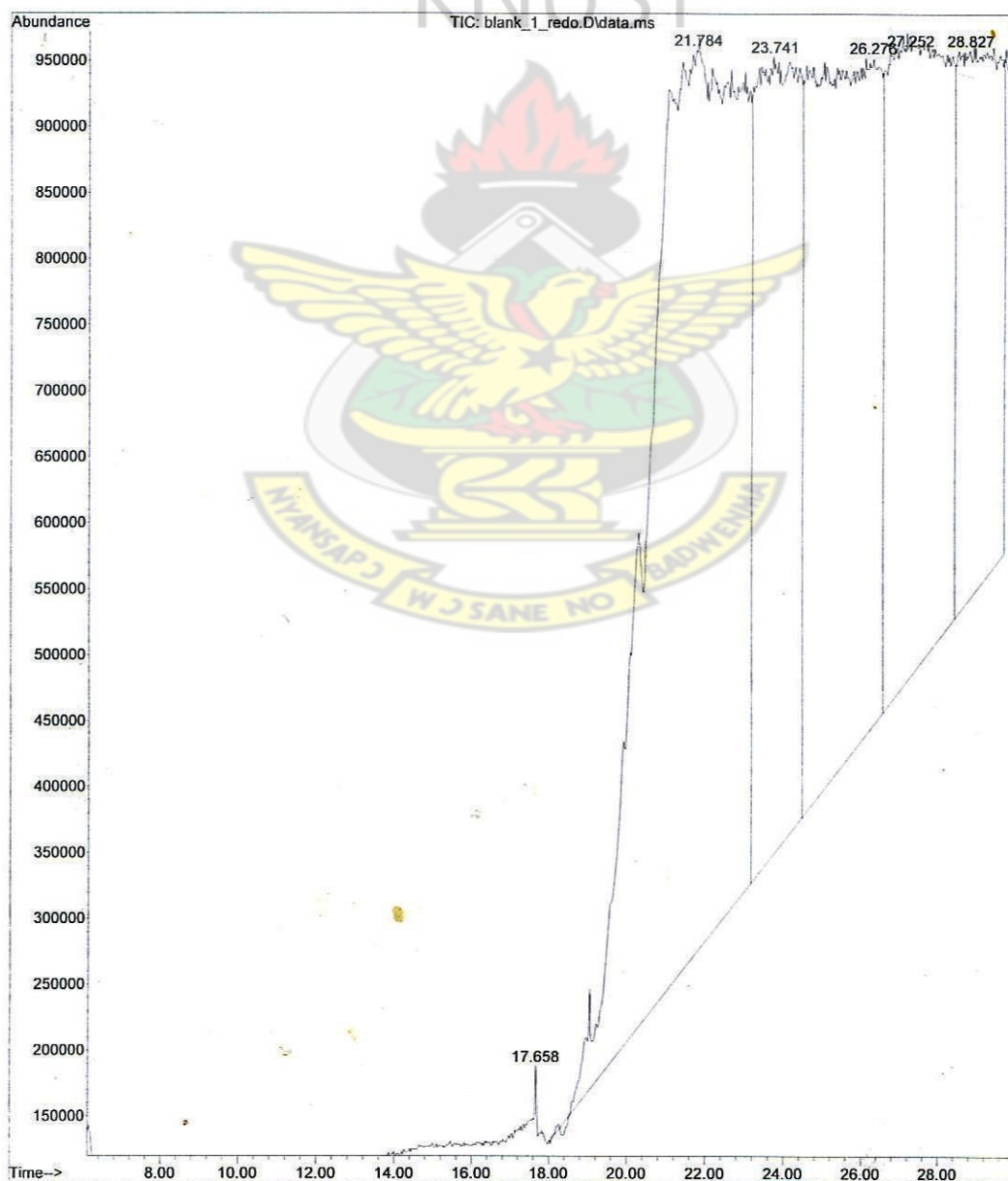


BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

APPENDIX E. Mass spectra of GC-MS Analysis to Determine Percent Composition of Methyl Oleate Esters in Biodiesel Samples

E.1 Blank Sample

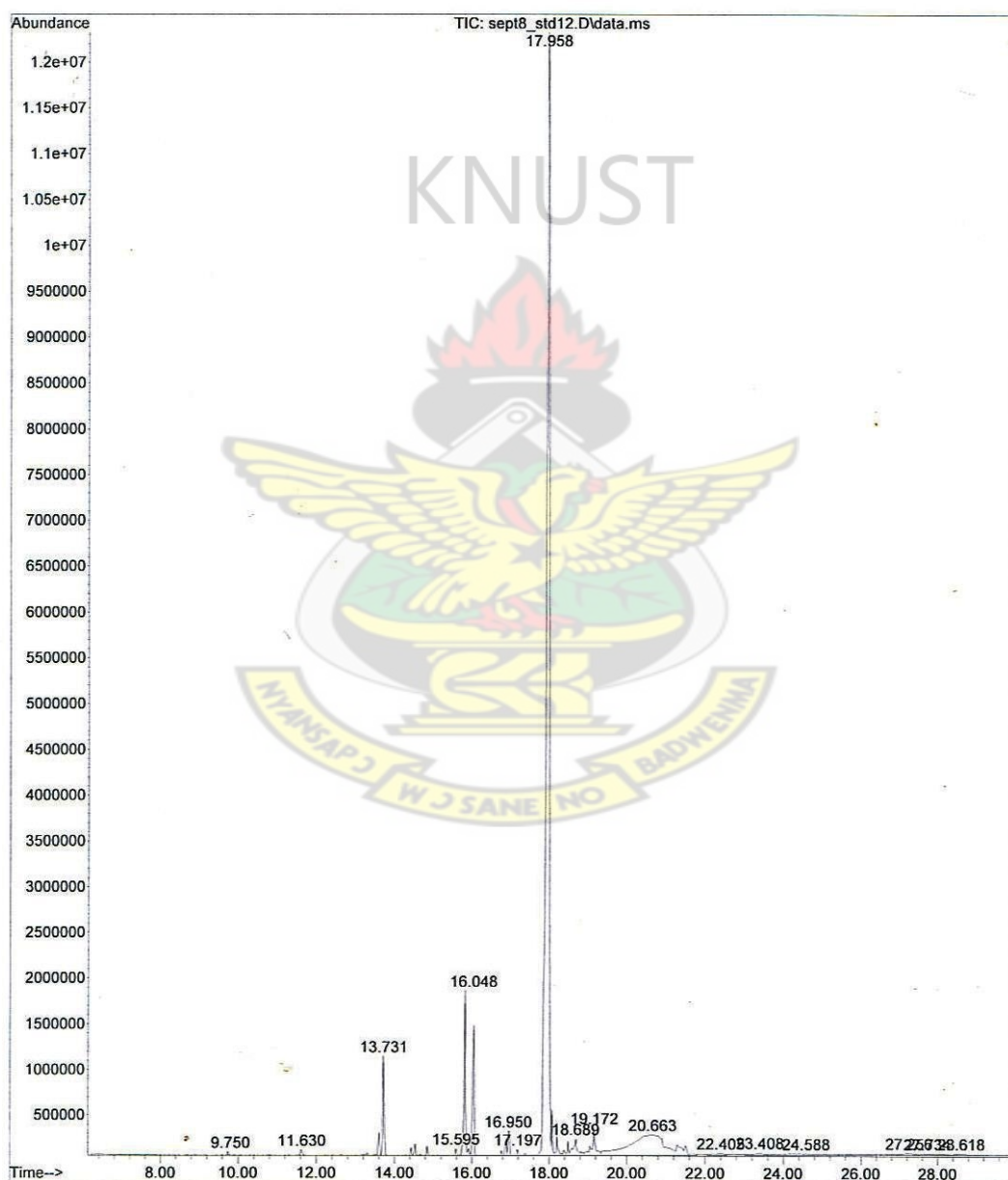
File :D:\Patrick Boakye\blank_1_redo.D
Operator : Patrick
Acquired : 1 Sep 2011 15:44 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: blank
Misc Info :
Vial Number: 1



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.2 Standard 1 (12.5 % Methyl Oleate)

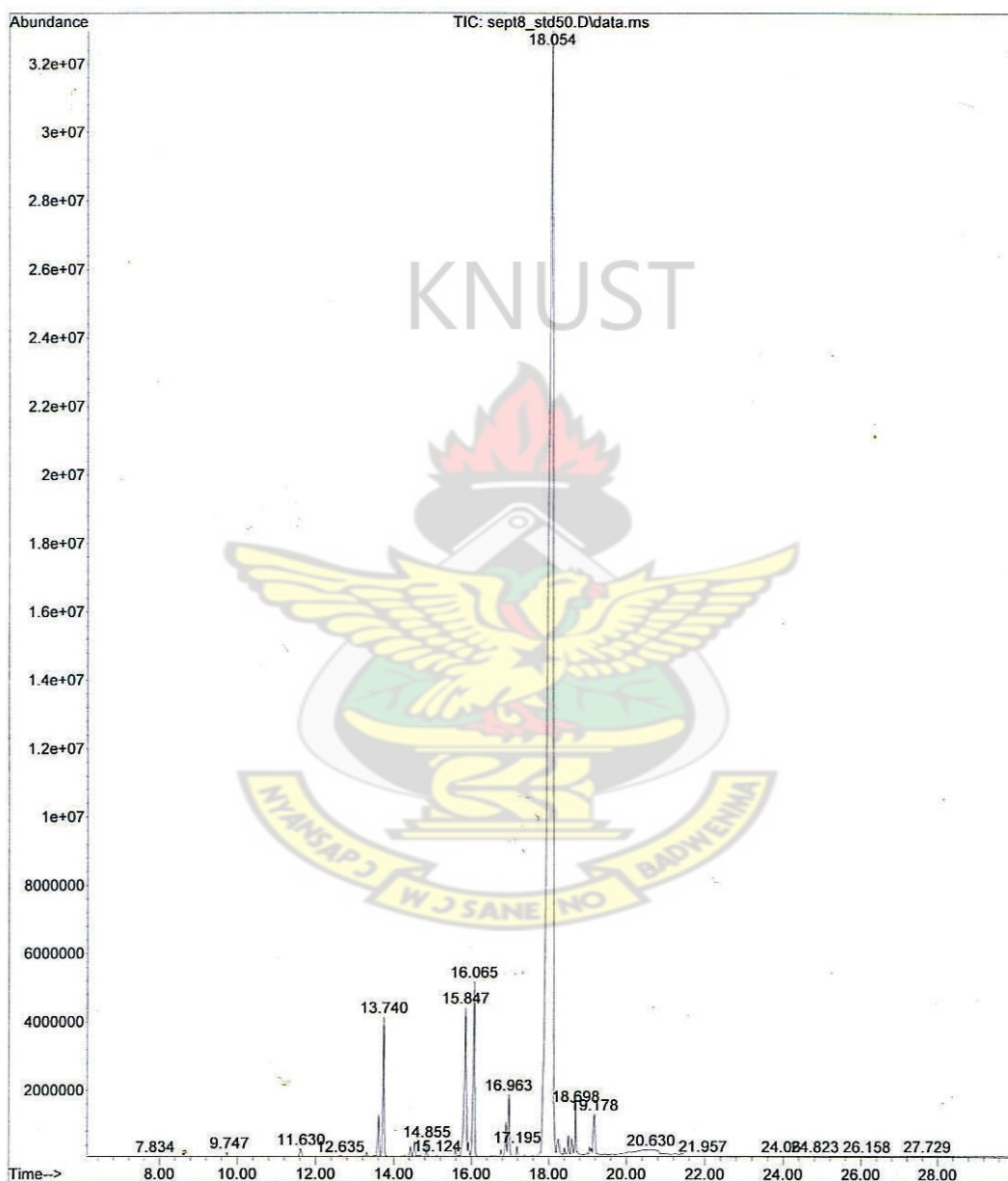
File :D:\Patrick Boakye\sept8_std12.D
Operator : P Boyake
Acquired : 8 Sep 2011 16:57 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: std 1
Misc Info :
Vial Number: 2



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.3 Standard 2 (25 % Methyl Oleate)

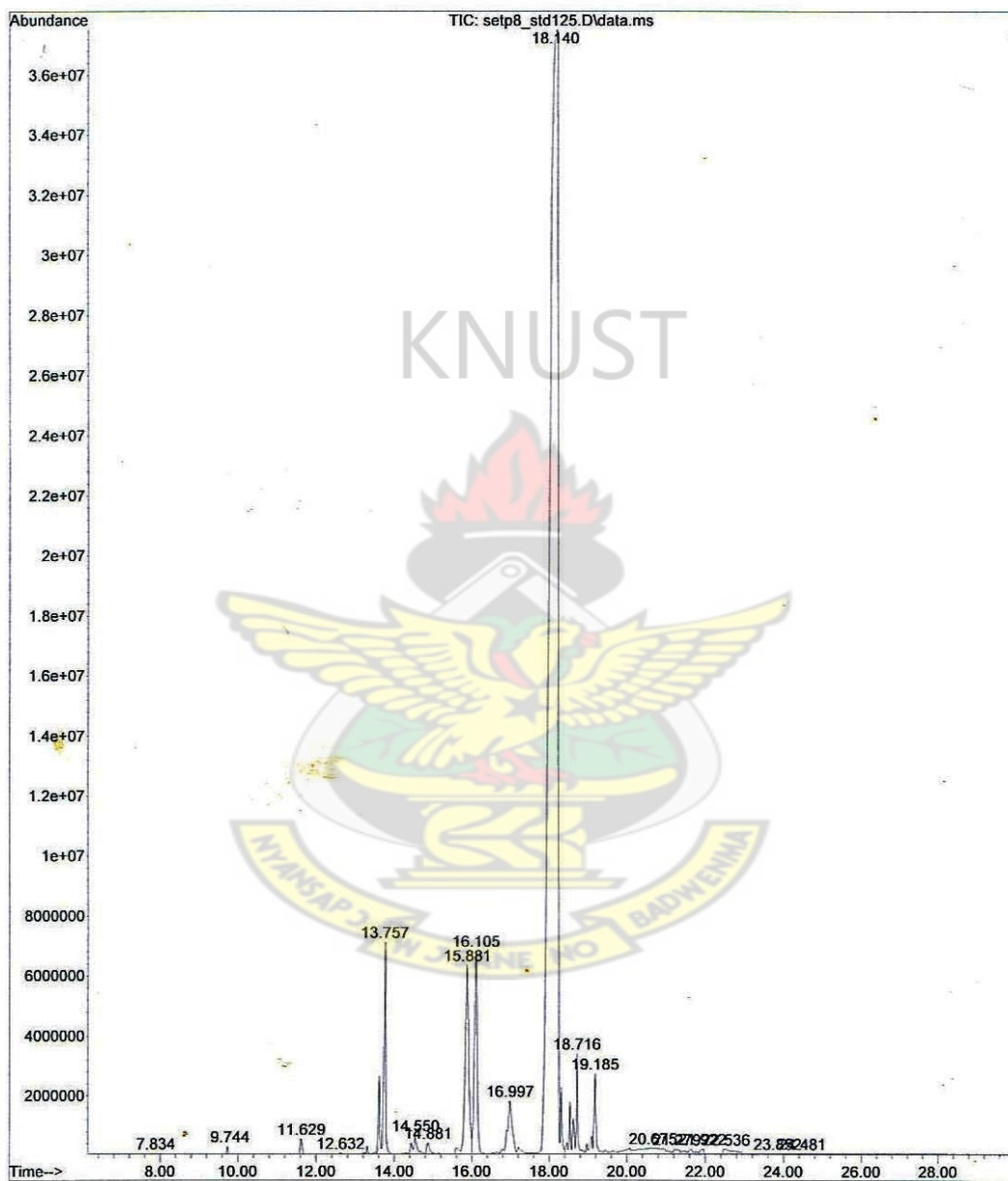
File :D:\Patrick Boakye\sept8_std50.D
Operator : P Boyake
Acquired : 8 Sep 2011 17:31 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: std 2
Misc Info :
Vial Number: 3



E.4 Standard 3 (50 % Methyl Oleate)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

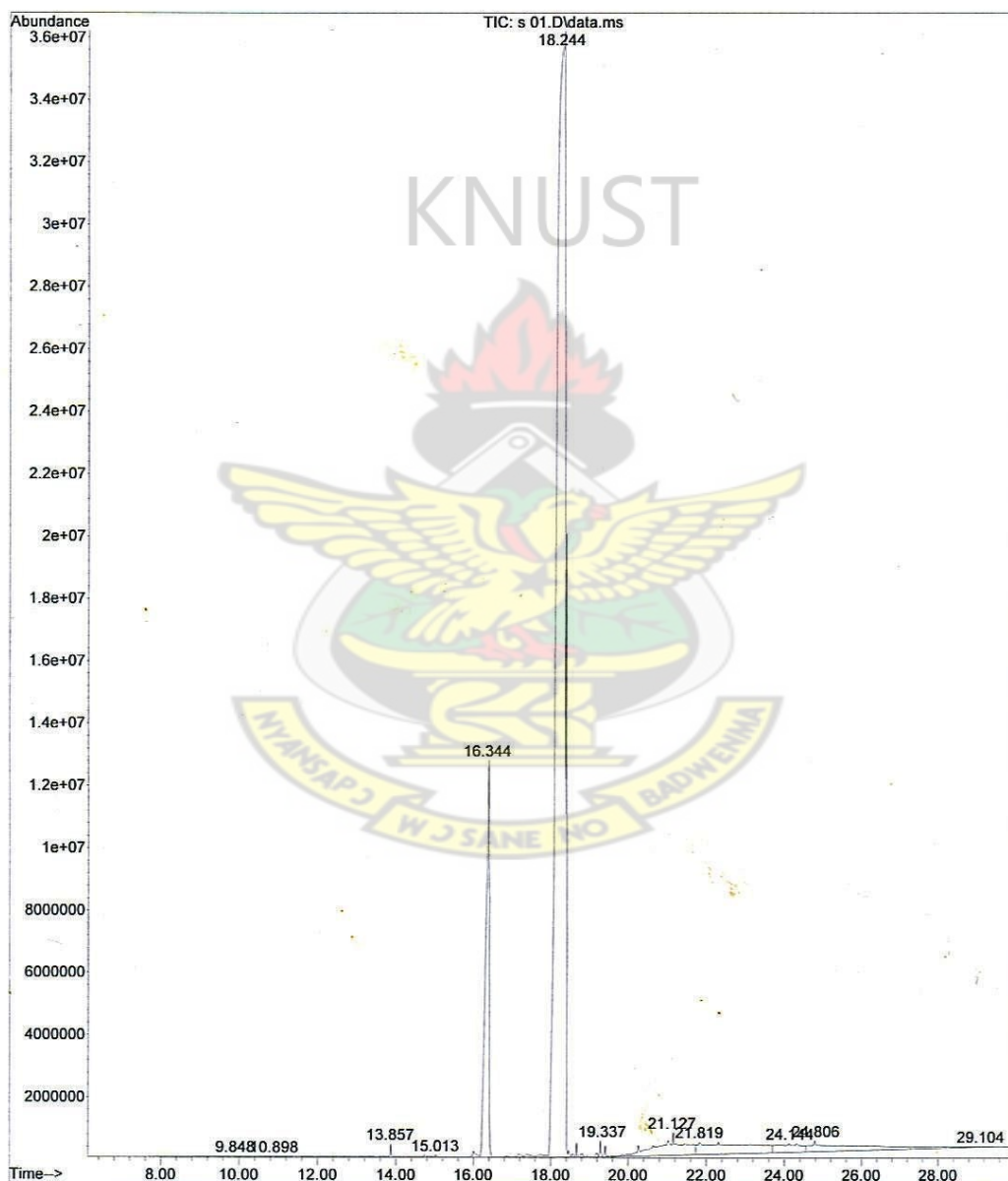
File : D:\Patrick Boakye\setp8_std125.D
Operator : P Boyake
Acquired : 8 Sep 2011 18:06 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: stdn 3
Misc Info :
Vial Number: 4



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.5 Soya bean Fresh Oil Biodiesel, SBFOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio; 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

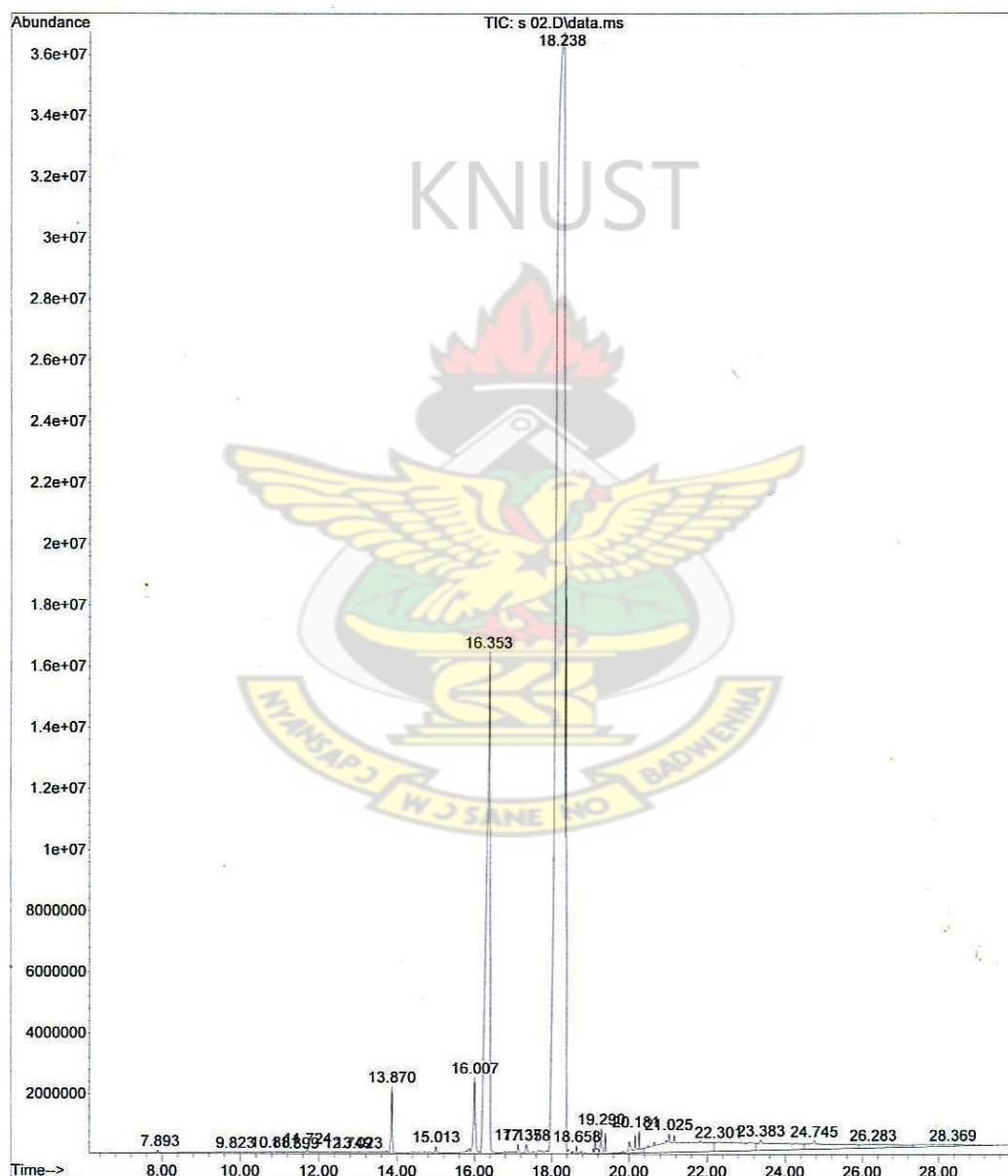
File :D:\Patrick Boakye\s 01.D
Operator : Patrick
Acquired : 1 Sep 2011 18:36 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 01
Misc Info :
Vial Number: 6



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.6 Cottonseed Fresh Oil Biodiesel, CSFOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio; 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

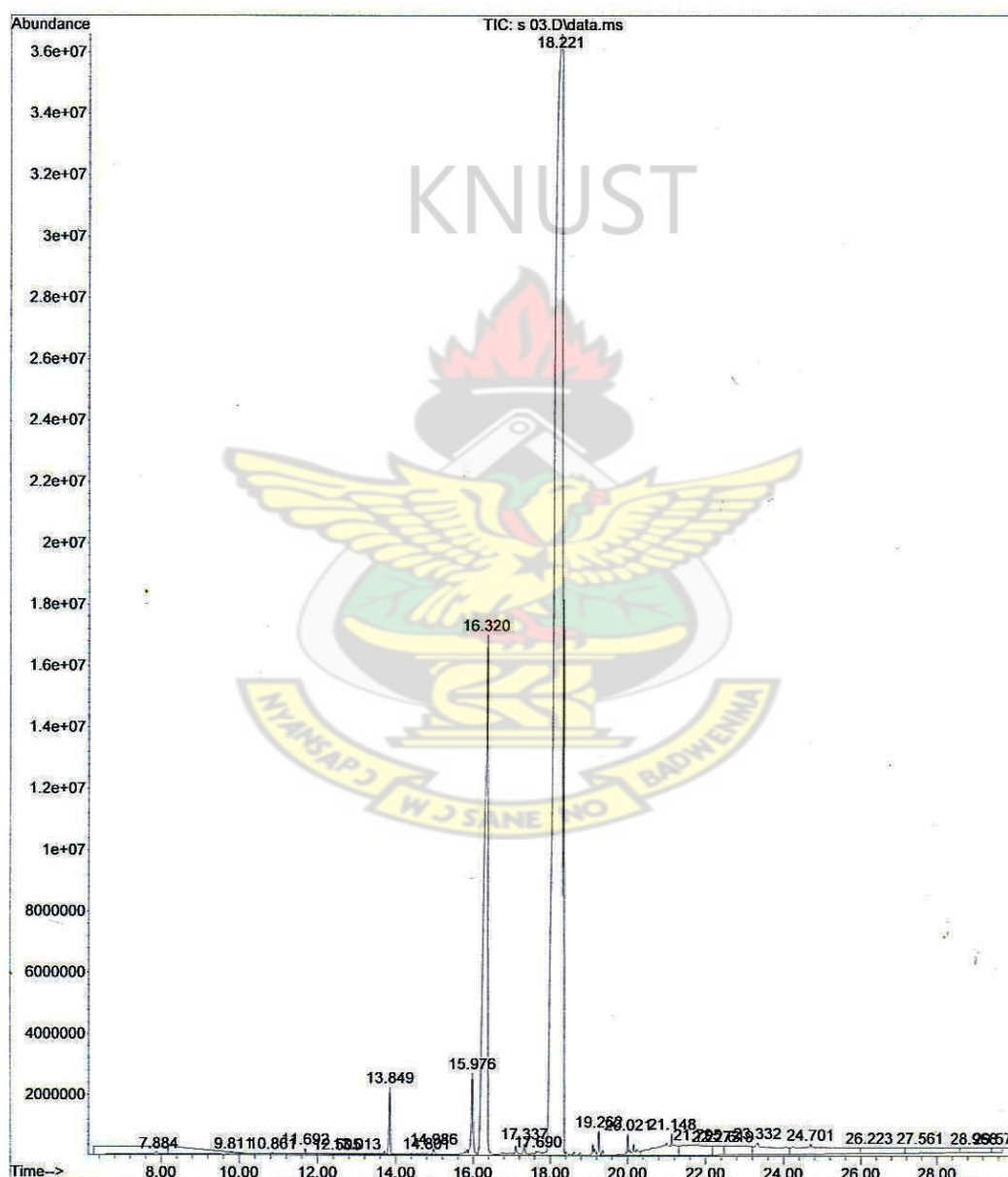
File :D:\Patrick Boakye\s 02.D
Operator : Patrick
Acquired : 1 Sep 2011 19:11 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 02
Misc Info :
Vial Number: 7



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.7 Blend of Fresh Oil Biodiesel, BFOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio; 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

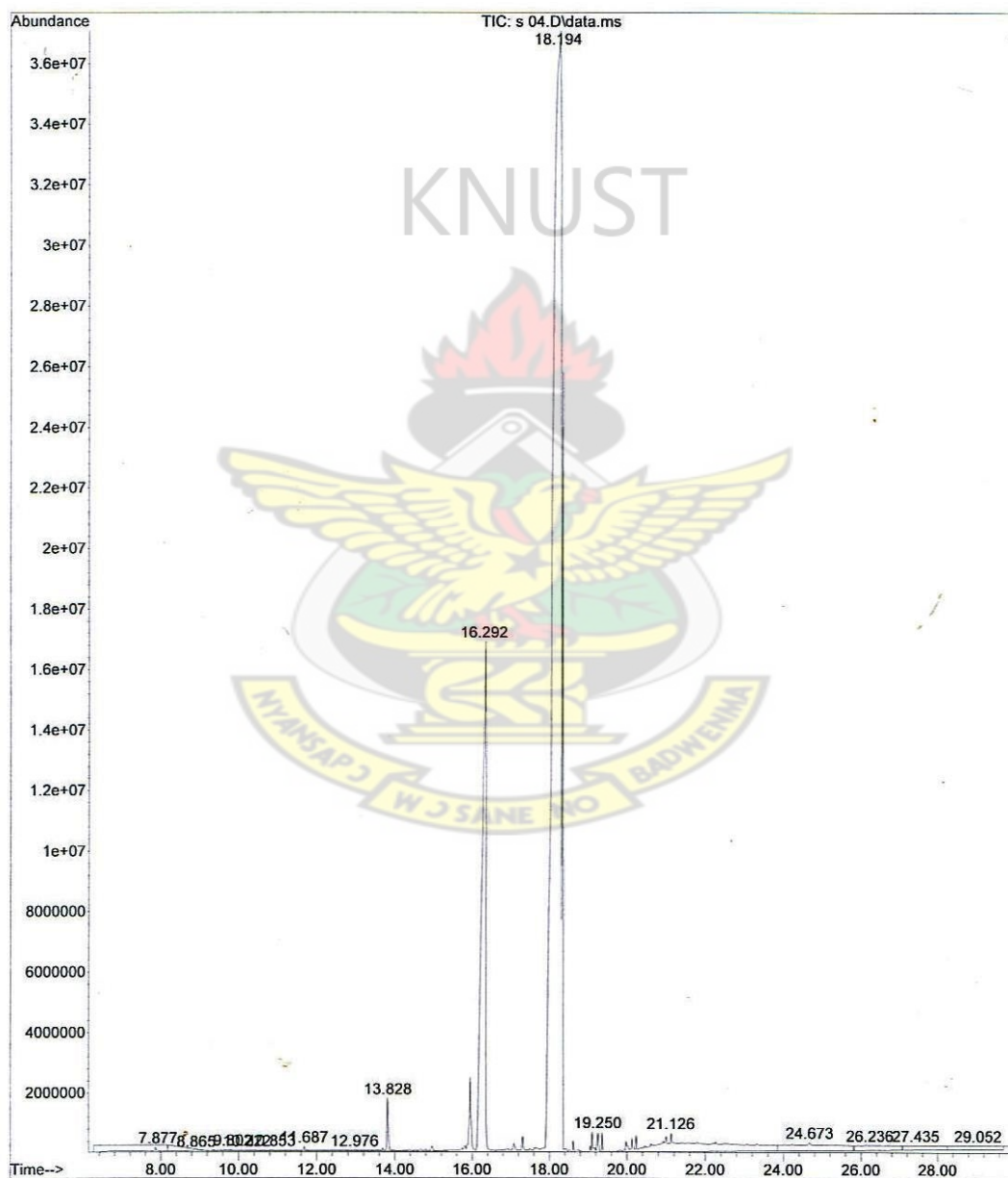
File :D:\Patrick Boakye\s 03.D
Operator : Patrick
Acquired : 1 Sep 2011 19:45 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 03
Misc Info :
Vial Number: 8



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

E.8 Blend of Waste Oil Biodiesel, BWOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio; 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

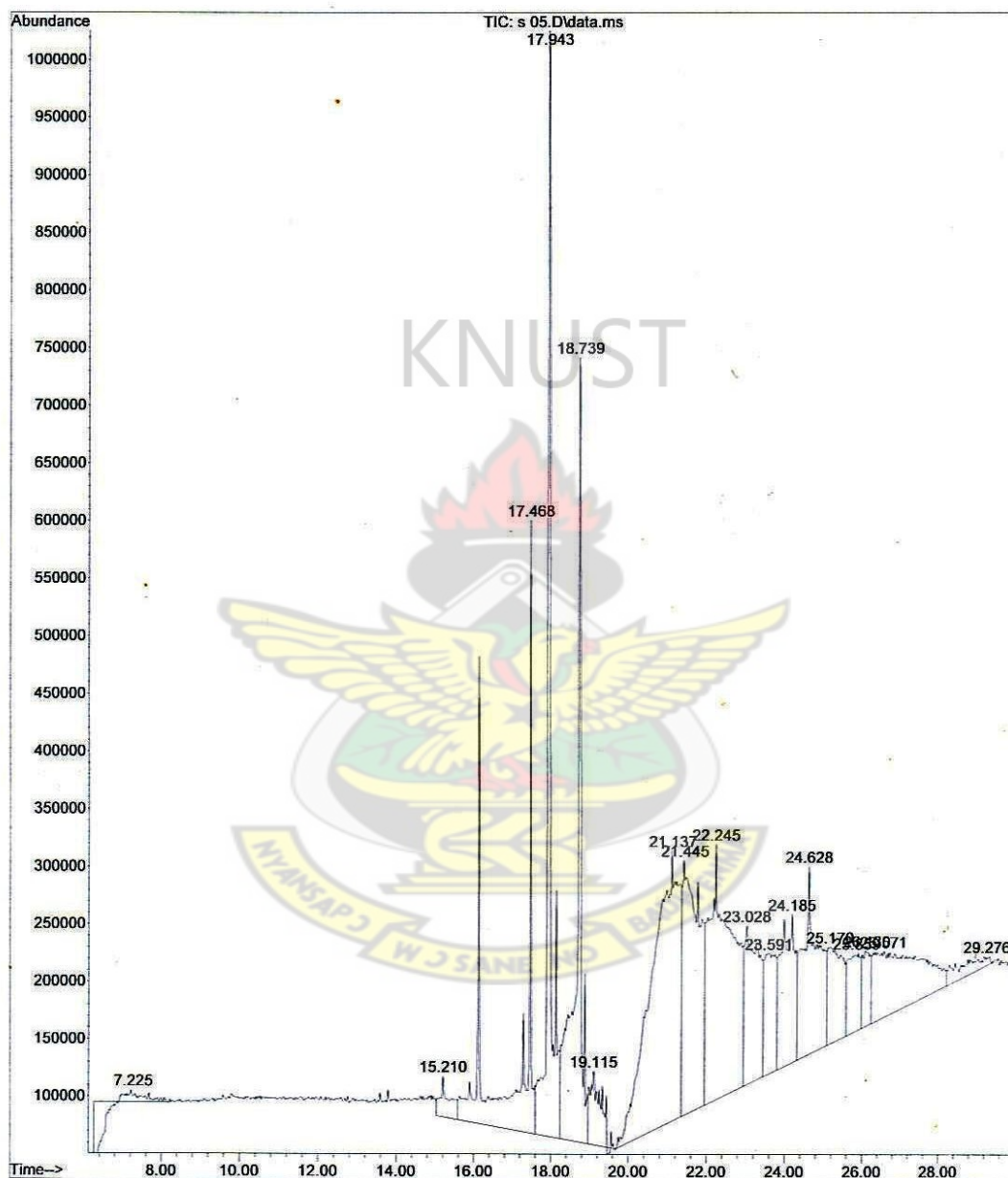
File :D:\Patrick Boakye\s 04.D
Operator : Patrick
Acquired : 1 Sep 2011 20:20 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 04
Misc Info :
Vial Number: 9



E.9 *Jatropha curcas* Oil (Not Transesterified)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

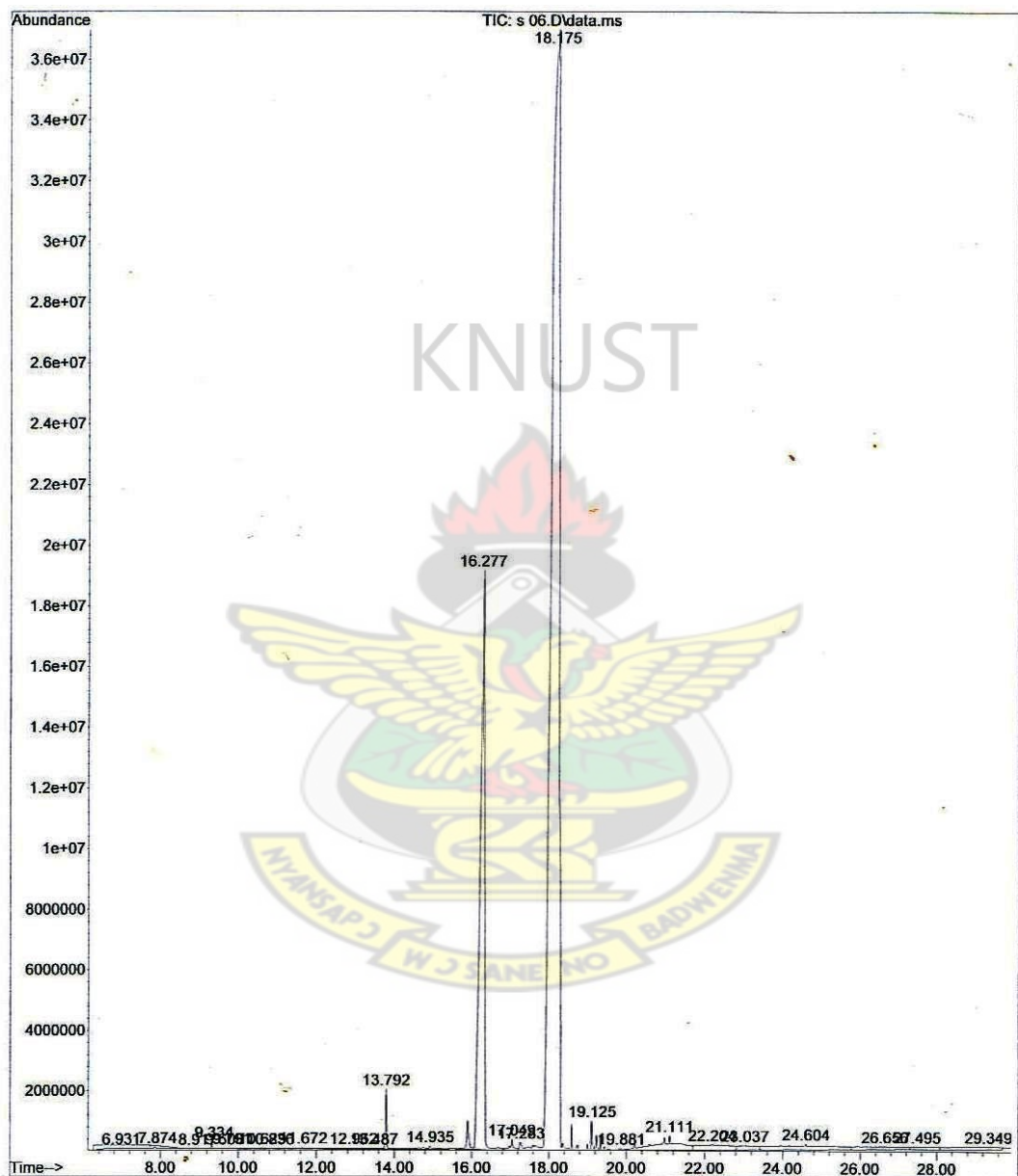
File : D:\Patrick Boakye\s 05.D
Operator : Patrick
Acquired : 1 Sep 2011 20:54 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 05
Misc Info :
Vial Number: 10



E.10 Soya bean Waste Vegetable Oil Biodiesel, SWVOB*, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

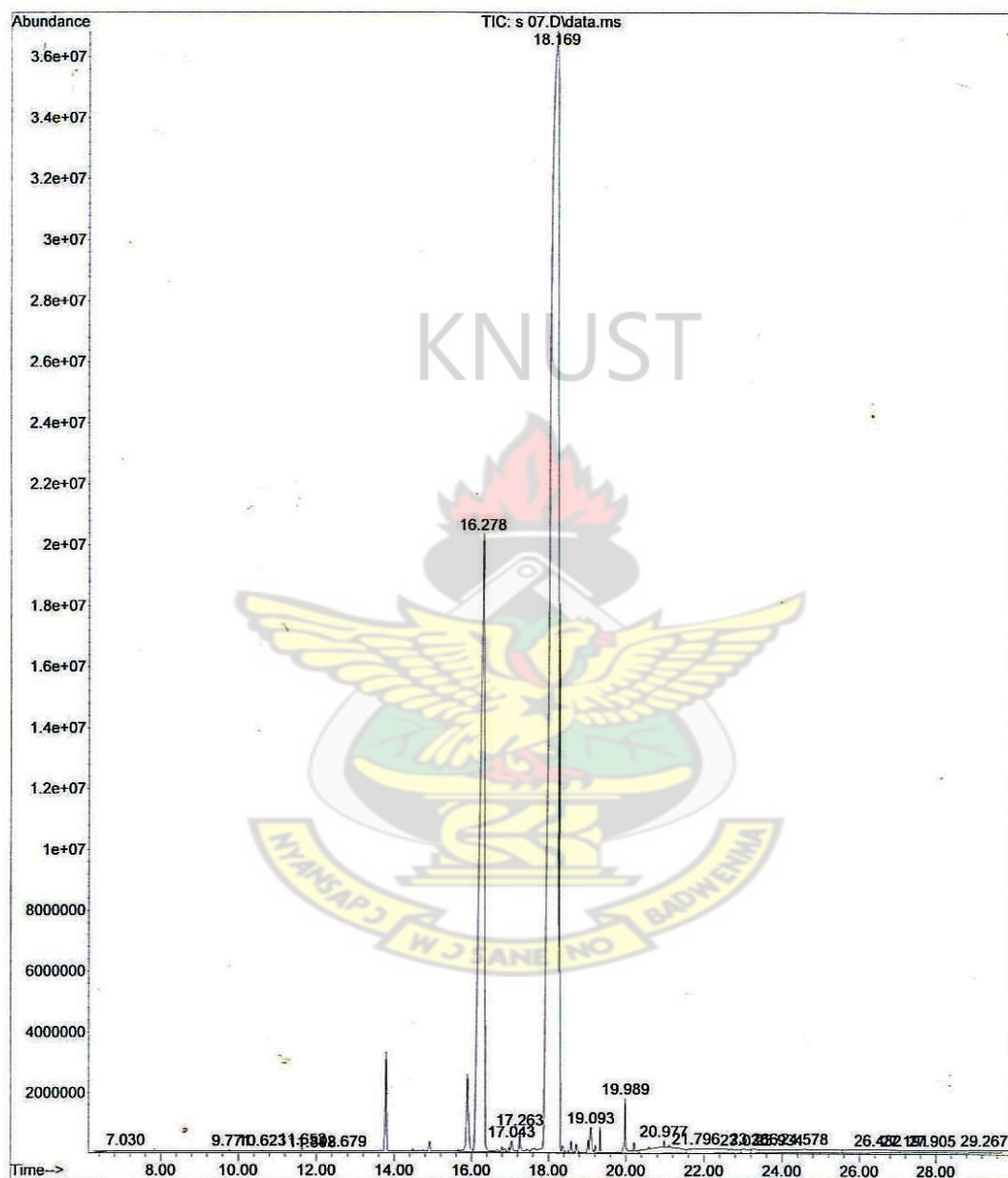
File :D:\Patrick Boakye\s 06.D
Operator : Patrick
Acquired : 1 Sep 2011 21:28 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 06
Misc Info :
Vial Number: 11



E.11 Soya bean Waste Vegetable Oil Biodiesel, SWVOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio; 60 °C Reaction Temperature; 80 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

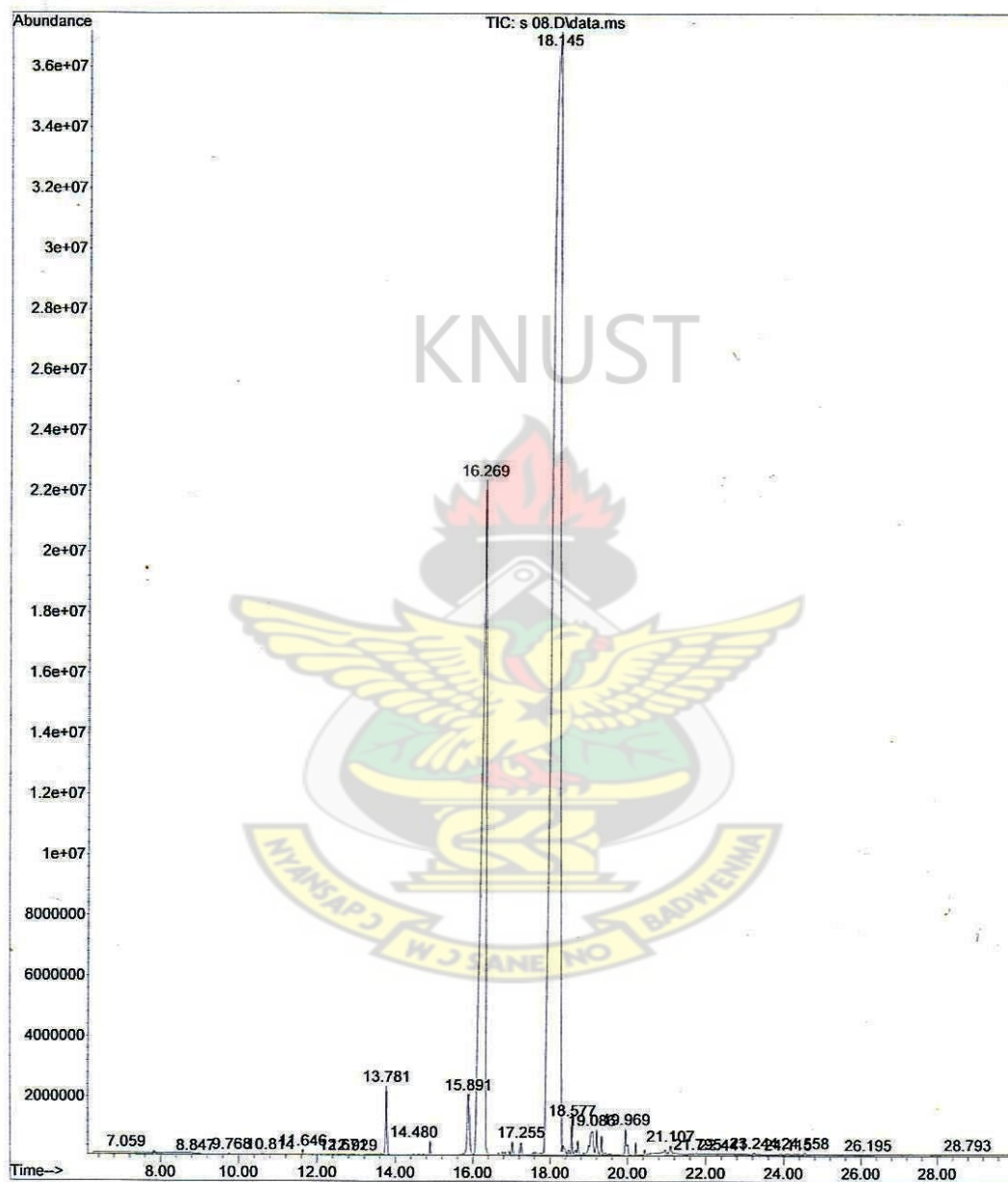
File :D:\Patrick Boakye\s 07.D
Operator : Patrick
Acquired : 1 Sep 2011 22:03 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 07
Misc Info :
Vial Number: 12



E.12 Cottonseed Waste Vegetable Oil Biodiesel, CWVOB*, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

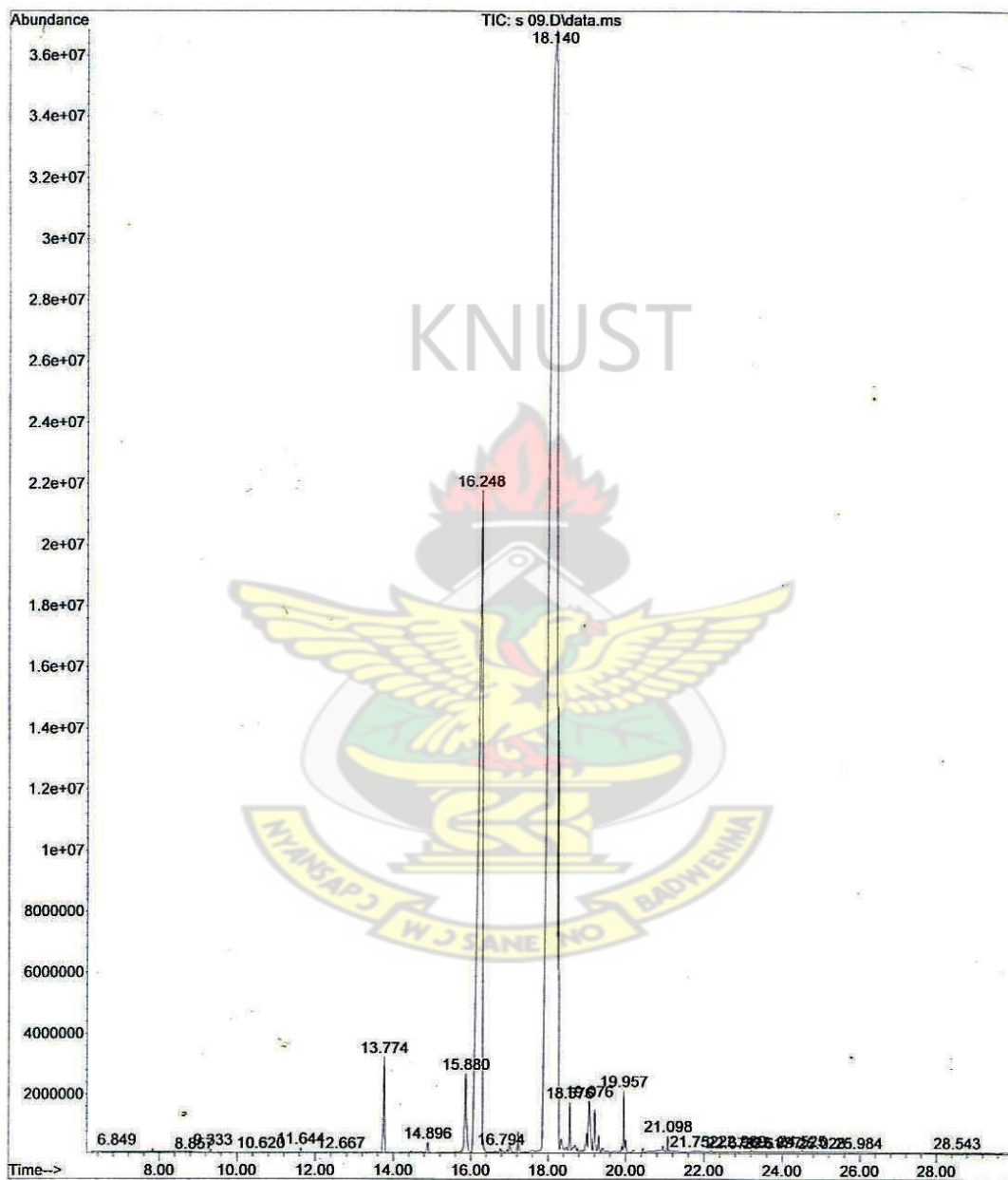
File :D:\Patrick Boakye\s 08.D
Operator : Patrick
Acquired : 1 Sep 2011 22:37 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 08
Misc Info :
Vial Number: 13



E.13 Cottonseed Waste Vegetable Oil Biodiesel, CWVOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio 60 °C Reaction Temperature; 40 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

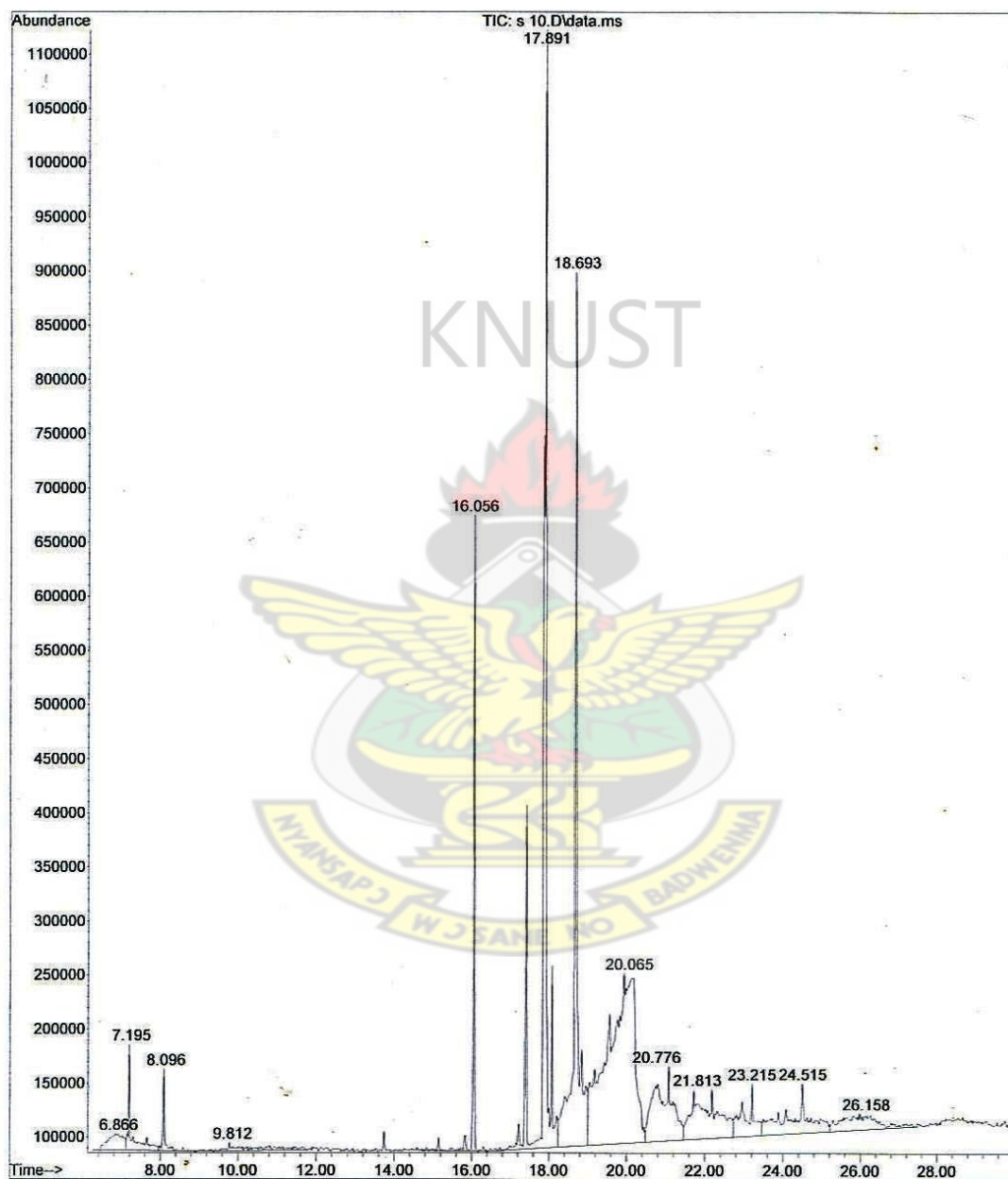
File : D:\Patrick Boakye\s 09.D
Operator : Patrick
Acquired : 1 Sep 2011 23:12 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 09
Misc Info :
Vial Number: 14



E.14 Blend of Fresh Oil (Not Transesterified)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

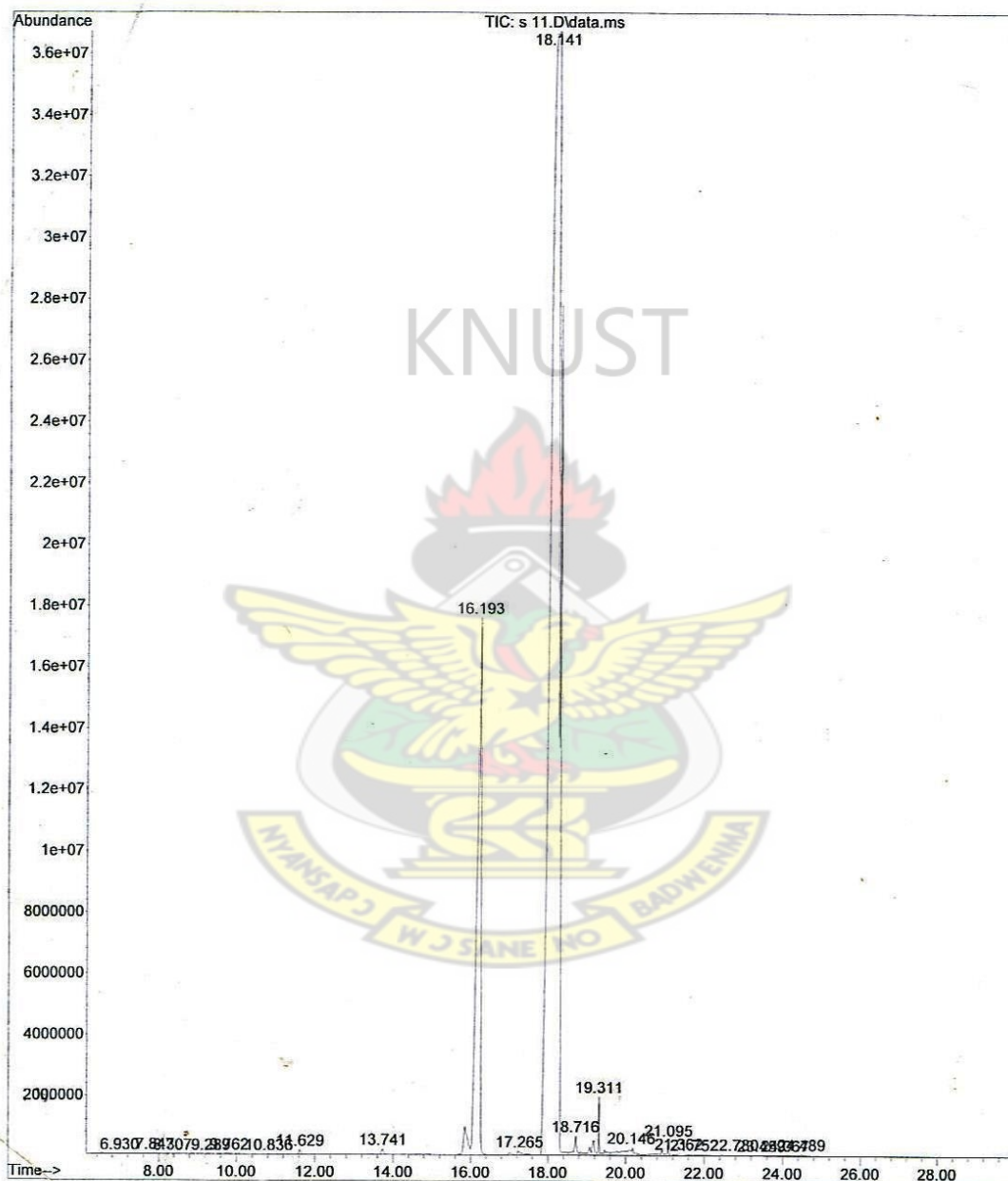
File :D:\Patrick Boakye\s 10.D
Operator : Patrick
Acquired : 1 Sep 2011 23:46 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 10
Misc Info :
Vial Number: 15



E.15 *Jatropha curcas* Oil Biodiesel, JCOB, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:8 Oil: Methanol Molar Ratio 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

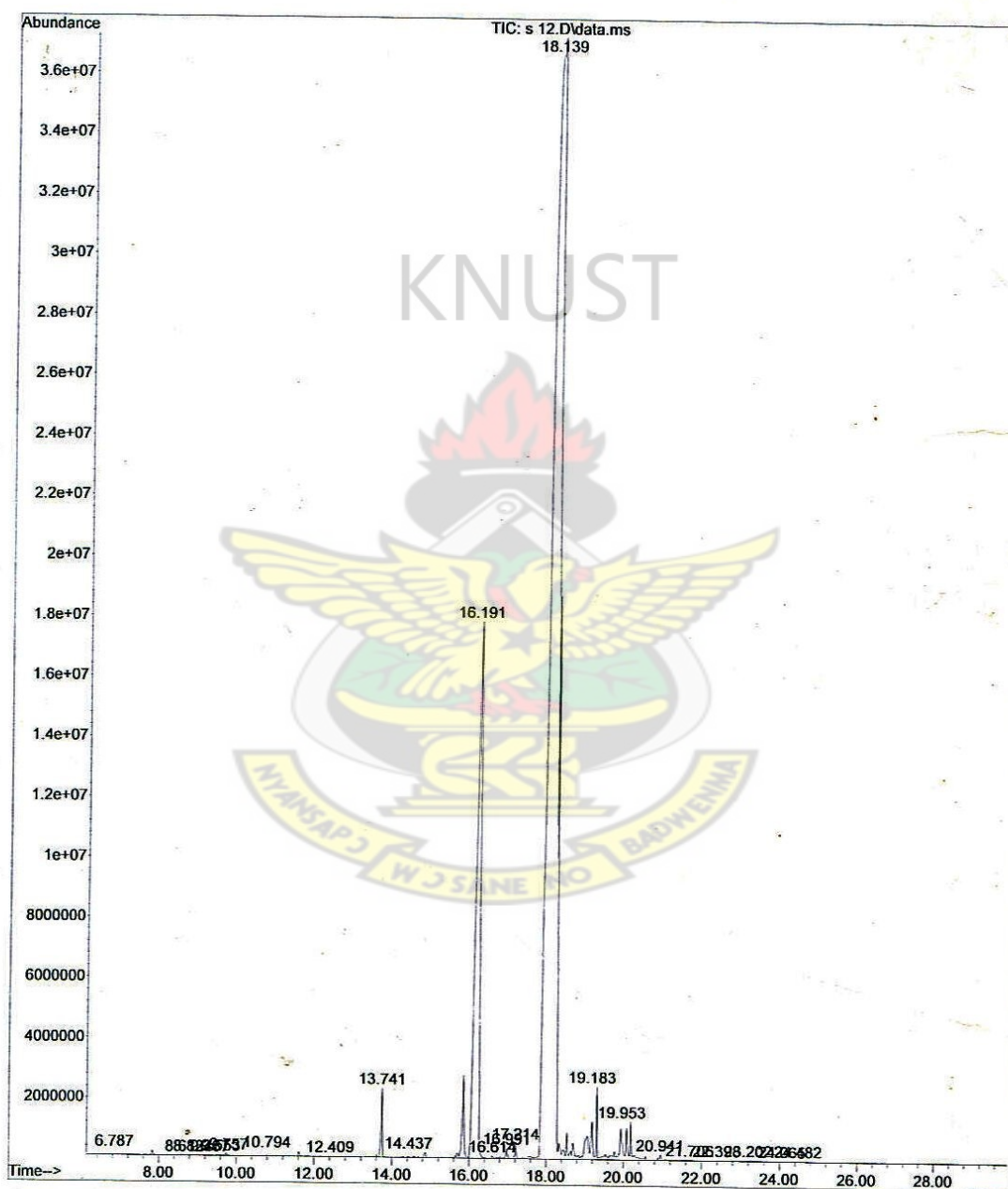
File :D:\Patrick Boakye\s 11.D
Operator : Patrick
Acquired : 2 Sep 2011 00:21 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 11
Misc Info :
Vial Number: 16



E.16 *Jatropha curcas* Oil Biodiesel, JCOB*, (Reaction conditions: 4 wt. % K_2CO_3 ; 1:6 Oil: Methanol Molar Ratio 60 °C Reaction Temperature; 120 min Reaction Time at 600 rpm Stirring Speed)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

File :D:\Patrick Boakye\s 12.D
Operator : Patrick
Acquired : 2 Sep 2011 00:55 using AcqMethod PATRICK.M
Instrument : GCMS
Sample Name: 12
Misc Info :
Vial Number: 17



APPENDIX F Publications

F.1 Influence of Reaction Parameters on Waste Vegetable Oil Transesterification Using Unsupported Potassium Carbonate (*Draft Manuscript*)

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¹Abstract

In this study, unsupported potassium carbonate (K_2CO_3) was used as a catalyst to assess its feasibility for transesterification of waste vegetable oil (WVO). The results suggest that K_2CO_3 is better than other known alkali catalysts such as KOH and NaOH. It was observed that 4 wt % of oil amount of catalyst with 1:6 oil to methanol molar ratio at 60 °C reaction temperature were the best conditions for the transesterification reaction. Also, the best reaction time for the conversion of the Cottonseed waste vegetable oil (CWVO) to fatty acid methyl ester (FAME) was 40 min while that of the Soya bean waste vegetable oil (SWVO) was 80 min. The combination of these parameters of catalyst amount, oil to methanol molar ratio, reaction temperature as well as reaction time gave a FAME yield of 99.46 % and 99.51 % respectively for CWVO and SWVO.

Keywords: Waste vegetable oil; Transesterification; Potassium carbonate; Fatty Acid Methyl Ester (FAME).

¹ Abbreviations: *Waste Vegetable Oil (WVO)*, *Cottonseed waste vegetable oil (CWVO)*, *Fatty acid methyl ester (FAME)*, *Soya bean waste vegetable oil (SWVO)*

1.0. Introduction

A greater percentage of energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these sources are limited and exhaustible and will be depleted in the near future (MacLamb, 2011). Thus, looking for alternative sources of energy that are inexhaustible and renewable, such as hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable energy sources have the potential to solve many socio-economic and environmental problems, from job creation, air pollution control and global warming mitigation to environmental improvements and sustainable development and resource exploitation (MacLeana and Laveb, 2003).

The American Society for Testing and Materials (ASTM) defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. “Bio” represents its renewable and biological source in contrast to traditional petroleum-based diesel fuel. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel has many merits. It is derived from a renewable resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Körbitz, 1999; Agarwal and Das, 2001). Biodiesel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996). It provides lubricating properties that can reduce engine wear and extend engine life (Wedel, 1999). It also gives a better engine performance due to its higher cetane

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

number. Thus, these merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally sensitive areas.

Additionally, because biodiesel can be refined under normal atmospheric temperature and pressure, it can be produced economically across a variety of places and scales; from urban to rural, small to commercial. The ease of production also contributes to biodiesel's high net energy balance; for example, soybean-biodiesel produces a 93 % energy gain compared to 25 % for corn-ethanol (Kurki, Hill and Morris, 2006).

However, biodiesel has currently not yet been commercialized globally (Yan and Lin, 2009; Thamsiroj and Murphy, 2009). The major bottleneck is the high cost of edible plant and vegetable oils as raw materials used for biodiesel production, which greatly prohibits its widespread application. Moreover, the land use for production of edible oil as feedstock for biodiesel production competes with the use of land for food production. One way of reducing the cost of biodiesel production is to employ low quality feedstocks such as waste or used vegetable oils, non-edible oils and soap stock (by-product of vegetable oil refinery), which are cheaply available and can be regarded as attractive feedstocks for biodiesel production (Canakci and Sanli, 2008; Felizardo *et al.*, 2006; Zhang and Jiang, 2008; Öner and Altun, 2009). The use of waste cooking oil as biodiesel feedstock reduces the cost of biodiesel production (Canakci, 2007) since feedstock costs constitute approximately 70-95 % of the overall cost of biodiesel production (Connemann and Fischer, 1998). Hence, the use of waste cooking oils and non- edible oils should be given higher priority over the edible oils as biodiesel feedstock.

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Furthermore, management of such waste cooking oils and fats pose a significant challenge because of their disposal problems and possible contamination of water and land resources. Even though some of the waste oil is used for soap production, a higher percentage is discharged into the environment. As large amounts of waste vegetable oils are illegally dumped into rivers and landfills, causing environmental pollution (Yang *et al.*, 2007), the use of waste vegetable oil for biodiesel production as petrodiesel substitute offers significant advantages because of the reduction in environmental pollution.

K_2CO_3 provides practically complete alcoholysis with least amount of soap production as compared to other alkali or base catalysts, such as NaOH, KOH, $NaOCH_3$ and $KOCH_3$ (Baroi *et al.*, 2009; Hartman, 1956). According to US patents 6890451 B2 (Sapienza *et al.*, 2005) and 7138071 B2 (Sapienza *et al.*, 2006), glycerol containing K_2CO_3 can be an excellent environmentally benign anti-icing or de-icing agent. Thus, it is used on airport runways and also on the wings, fuselage, and tail of aircrafts for de-icing. Unsupported K_2CO_3 is a better alternative for biodiesel production. However, the manufacturing of K_2CO_3 can be expensive as it involves the reaction of CO_2 with KOH, which is itself synthesized by electrolysis of KCl solution (Baroi *et al.*, 2009). On the other hand, most biomass such as plantain peels, cocoa pods and *Jatropha curcas* seedcake contains potassium. Hence the production of K_2CO_3 from these biomass sources will help reduce its cost thereby reducing the overall cost of biodiesel production.

The purpose of the present study was to investigate the optimization of parameters governing the transesterification of waste vegetable oils using unsupported K_2CO_3 as catalyst. The study is innovative because previous studies on transesterification of waste vegetable oils into biodiesel have, to date, not considered K_2CO_3 as catalyst.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Table 1 (Appendix A.1) shows the estimated amounts of waste vegetable oil (WVO) in some countries. Unfortunately published data from Sub-Sahara Africa is not available. However, given current population sizes and the large number of restaurants, hotels, road side food providers and households in Sub-Saharan African cities and towns that use vegetable oils for cooking, it is conceivable that similar large quantities of waste oils abound. Thus, significant quantities of waste vegetable oils may be available as potential biodiesel feedstock.

2.0. Materials and Methods

Anhydrous grade (99.95 %) methanol was purchased from Alfa Aesar (Oakville, Ontario, Canada) and ACS grade (99 %) K_2CO_3 were obtained from Western University Civil and Environmental Engineering and Chemical and Biochemical Engineering Laboratories, Canada. Both triolein (≈ 99 %) and methyl oleate (≈ 99 %) were bought from Sigma Aldrich (Oakville, Ontario, Canada). Soya bean and Cottonseed oils were purchased and given to food vendors at Kwame Nkrumah University of Science and Technology, Kumasi, Ghana to fry fish and chicken and thereby simulate waste oil generation.

The WVO samples were filtered under vacuum to remove traces of food particles that might have been carried over in the process of collecting the waste oil samples. The WVO samples were stored in plastic containers which were tightly covered to prevent oxidation. The samples were sent to Western University, London, Canada where they were stored in a cold and dark room at 5 °C under argon to prevent oxidation. A 250 ml Erlenmeyer flask was modified and used as the reactor. The top of the flask was made narrower to fit into the bottom part of the 24/40 size Liebig condenser. A bent glass tube of 19/26 size filled with anhydrous calcium sulphate and blocked at both ends with cotton wool was connected to the top of the condenser to ensure the entrance of moisture free air into the system. The flask was

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modified to have two more openings (Figure 1 of Appendix B.1). One opening was to fit the temperature sensing probe inside the reactor. The oil feed and the methanol-carbonate solution were introduced into the reactor through the second opening.

2.1. Transesterification of the WVO samples

An amount of unsupported Potassium carbonate (K_2CO_3) catalyst (ranging from 1 to 7 wt % of waste oil in increments of 1% in seven separate experiments) was added to 30 mL of anhydrous grade (99.95 %) methanol to produce a carbonate solution. The catalyst was added to the methanol and heated to dissolve at 60 °C whilst condensing the methanol into the mixture. Exactly 100 g of oil was heated to 60 °C and charged into the reactor containing the carbonate-alcohol mixture to aid in an increase of reaction. The mixture was stirred continuously while maintaining the temperature at 60 - 65 °C for 2 hours. The mixture was left for 8 hours undisturbed in a separatory funnel to allow separation of glycerol from the ester phase. After separation, the crude biodiesel was washed 3-4 times with warm distilled water followed by 0.1 % H_2SO_4 to remove trace amounts of catalyst in the methyl ester phase. The washing was repeated until a clear water layer of neutral pH was obtained. The washed biodiesel was first dried using anhydrous sodium sulphate. A rotary evaporator was used to remove excess methanol that might have been carried over during the washing process.

Once the optimum catalyst amount resulting in a higher yield was obtained, the second part of the experiment was pursued by maintaining the optimum catalyst amount (4 w % of oil) at a reaction temperature of 60 °C for 2 hours while the oil to methanol molar ratios were varied at 1:4, 1:6, 1:8. The ratio that gave the highest yield was chosen as the best. The optimized catalyst weight and oil to methanol molar ratio was maintained while transesterification

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reactions were carried out at times 40 min, 80 min and 120 min to determine an optimum reaction time. Lastly, the optimized catalyst amount, oil to methanol molar ratio and reaction time were maintained while the reaction temperature was varied from 55 °C, 60 °C and 65 °C to obtain the best yield. It was ensured that all the reaction contents were preheated to the desired temperature. The 8 hour reaction time was selected based on the preliminary experimental run with 1:6 oil to methanol molar ratio with the fixed amount of catalyst.

3.0. Results and Discussion

Some of the properties of the Cottonseed waste vegetable oil (CWVO) and Soya bean waste vegetable oil (SWVO) determined are represented in Table 2 (Appendix A.2). The analyses were done in conformity with ASTM D 6751.

The data show that the CWVO and SWVO samples contained lower percentage free fatty acid of 0.462 % and 0.547 % respectively, which were considered relatively low; therefore, a one-step alkali transesterification was employed.

The yields of the fatty acid methyl esters (FAME) produced were estimated using a mass balance approach and the purity of FAME was confirmed with the gas chromatography-mass spectrometry (GC-MS).

3.1. Effect of catalyst amount on percentage yield of FAME

Different amounts of catalyst ranging from 1 to 7 wt. % of oil were used for the transesterification reaction to determine an optimum yield of FAME and the results are presented in Table 3 below. The results showed that 4 g of K_2CO_3 (wt. % of WVO) gave the highest conversion of FAME (95.35 %), when 100 g of waste vegetable oil was reacted with methanol at a 1:6 oil to methanol molar ratio at a temperature of 60 °C and a stirring speed of 600 rpm for 2 hours.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

The data in Figure 2 (Appendix B.2) shows that when the catalyst amount was 1 wt. % of oil, the yield of FAME was 11.09 %. This indicates that 1 wt. % of K_2CO_3 was not sufficient to catalyze the transesterification reaction. This amount of catalyst gave a lower yield because the reaction intermediate was unstable. An increase in the conversion of the waste vegetable oils to FAME (fatty acid methyl ester) occurred with a corresponding increase in catalyst amount to 4 wt % of oil. The yield decreased when the amount of catalyst was increased from 4 to 7 wt. %. The instability in the FAME produced at lower catalyst amount may be responsible for the variability seen in Figure 2 (Appendix B.2).

Previous studies by Baroi *et al.* (2009) and Dorado *et al.* (2004) have shown that excess alkali catalyst causes saponification of triglycerides resulting in the formation of soap and hence an increase in the viscosity of the reactants, which ultimately resulted in reduced FAME conversion. Thus secondary saponification might have been responsible for the significantly lower conversion of the waste vegetable oil to biodiesel (FAME) when the catalyst amount was increased from an optimum value of 4 wt. % of oil (i.e. from 5 to 7 wt. %). For 5 and 6 wt. % of catalyst, the FAME yield was almost the same, as shown in Table 3. Also, the decrease in the FAME yield with catalyst above the optimum amount of 4 wt. % was due to the reduction in the molar concentration of FAME in the biodiesel phase which might have resulted from the solubilization of soap and other components into the biodiesel phase. The qualitative analysis of soap formed, which was presented by Baroi *et al.* (2009) using FTIR-ATR on *Jatropha* biodiesel, agrees with the increased solubilization of soap into the biodiesel phase at catalyst amount above the optimum value and that there are no side reactions during the settling of biodiesel from the glycerol phase. Work by Platonov *et al.* (2002) revealed that more than 99% of $KHCO_3$ produced from the solubility reaction between anhydrous K_2CO_3

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and methanol remained in the solid phase along with unreacted K_2CO_3 at room temperature (25 °C). This is illustrated in equation 2 below.



The equilibrium of the above reaction is shifted towards product formation as a result of the phase distribution of $KHCO_3$ between the solid and liquid phase. $KHCO_3$ dissolves when the temperature is increased, thus the rate of backward reaction is favoured causing the concentration of CH_3OK to decrease while that of $KHCO_3$ increases. Also, Arzamendi *et al.* (2008) showed that $KHCO_3$ was a poor catalyst with negligible catalytic activity when compared to K_2CO_3 . Hence CH_3OK formation as illustrated in equation 1 is the main catalyst compound contributing to the transesterification process (Baroi *et al.*, 2009). Other studies using different and traditional catalysts have reported similar yields but lower catalyst amounts and different operating conditions. For example, Peng *et al.* (2008) reported an optimum heterogeneous catalyst (SO_4^{2-}/TiO_2-SiO_2) of 3 wt. % for simultaneous esterification and transesterification of waste oil. In that study, however, a reaction temperature of 200 °C was used to obtain yields of approximately 95%. Hoque *et al.* (2011) found that an alkaline catalyst amount of 1.25 wt. % was optimal in the transesterification of waste cooking oil to achieve a yield of approximately 88% at 65 °C. Unfortunately no other studies involving K_2CO_3 and waste oil have been reported, making comparison to the present study impossible.

3.2. Effect of oil to methanol molar ratio on the percentage yield of FAME

To assess the effect of oil to methanol molar ratio on biodiesel yield, the optimized amount of catalyst (4 wt.% of oil) was selected while the oil to methanol molar ratio was varied as 1:4, 1:6, and 1:8. A 60 °C reaction temperature was maintained while stirring was done at 600 rpm for 2 hours. The results are presented in Table 4 (Appendix A.4).

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Figure 3 (Appendix B.3) shows the biodiesel yield from Cottonseed waste vegetable oil (CWVO) and soyabean waste vegetable oil (SWVO).

The results show that when a 1:4 oil to methanol molar ratio was used the FAME yield was lower than when 1:6 and 1:8 oil to methanol molar ratio was used for both waste vegetable oil samples. This indicates that the amount of methanol was insufficient and hence, resulted in incomplete conversion of triglycerides to methyl esters. Also, when the oil to methanol molar ratio was 1:8 the FAME yield was low as compared to the 1:6 oil to methanol molar ratio. Thus, excess methanol dilutes the catalyst concentration, leading to a reduction in oil conversion. This finding is consistent with the work of Alamu (2007) who observed that biodiesel yield increases as the oil to methanol ratio increases only up to a threshold mix. The results of the present study indicate that the optimum oil to methanol molar ratio for the transesterification of the Cottonseed and Soya bean waste vegetable oils was 1:6.

The study by Hoque *et al.* (2011) indicated that the optimum oil/methanol molar ratio for the transesterification of beef fat, chicken fat and used cooking oil was 1:6. In that study the maximum yield at optimum conditions with a 1:6 oil to methanol molar ratio were 87.4 %, 89 % and 88.3 % for beef fat, chicken fat and used cooking oil respectively. These findings and those obtained in the present study are in agreement with those of many other studies which suggest that the optimum molar ratio of oil to methanol for the maximum biodiesel yield from used cooking oil and animal fat is between 1:4.8 and 1:6.5 (Freedman *et al.*, 1984; Hoque *et al.*, 2011).

3.3. Effect of reaction time on the percentage yield of FAME

Using the optimum catalyst amount and oil to methanol molar ratio, separate experiments were conducted at different reaction times of 40, 80 and 120 min for the two WVO samples. The optimum reaction time for the transesterification of the waste vegetable oils are shown in Figure 4 (Appendix B.4).

The results indicate that 40 min of reaction time gave an optimum yield of 98.09 % FAME from CWVO. After 40 mins of reaction time, the methyl ester concentration reduced. This could have been due to a possible conversion of some of the methyl esters into soap (saponification which usually occurs in the reverse direction). For the Soya bean waste vegetable oil feedstock the FAME yield increased until 80 min of reaction time when an optimum yield of 98.48 % was obtained. After 80 min of reaction time, there could also have been possible conversion of methyl esters into soap.

Some studies on biodiesel production from triglycerides show that the maximum reaction time for transesterification reaction time is 120 min, beyond which saponification occurs (Hogue *et al.*, 2011; Patil and Deng, 2009). The different reaction times observed for the various feedstocks could be associated with the difference in the molecular structure of the oil feeds, which contain different saturated fatty acids. While some fatty acids have lower activation energy, others have higher activation energy and require longer periods of heating and stirring to react.

3.4. Effect of reaction temperature on the percentage yield of FAME

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Using the optimum catalyst amount, oil to methanol molar ratio and reaction time, temperature was varied (55 °C, 60 °C and 65 °C) in separate experimental runs to study its effects on the transesterification reaction. The results are presented graphically in Figure 5 (Appendix B.5).

The results show that the optimum reaction temperature for both waste oils is 60 °C with a corresponding FAME yield of 99.45 % and 99.51 % for CWVO and SWVO respectively. The yields at 55 °C were slightly lower with relatively higher standard deviations than the yields at 60 °C. At 65 °C which was above the optimum temperature of 60 °C the FAME yield decreased. Some studies have shown that the saponification of triglycerides by alkali catalyst is much faster than alcoholysis at temperatures above 60 °C (Patil and Deng, 2009; Eevera *et al.*, 2009). Furthermore, transesterification above 60 °C reaction temperature causes excessive methanol loss due to evaporation and significantly reduces the yield of biodiesel. Hoque *et al.* (2011) showed that the optimum reaction temperature for the transesterification of used cooking oil that gave a maximum FAME yield of 87.6 % was achieved at 65 °C. This yield is lower than those obtained in the current study. Hence a reaction temperature of 60 °C was considered optimal for the transesterification of both waste cooking oils.

Some characteristics of the biodiesel produced from the waste vegetable oil (WVO) feedstocks are shown in Table 5 (Appendix A.5). The results indicate that the viscosity of both feedstocks reduced from 34.7 cP and 32.4 cP to 4.0 cP and 3.8 cP respectively for Cottonseed waste vegetable oil biodiesel (CWVOB) and soyabean waste vegetable oil biodiesel (SWVOB) following transesterification. Also, the acid values of 0.12 mgKOH/g oil for CWVOB and 0.28 mgKOH/g oil for SWVOB are lower than the ASTM maximum permissible level of 0.8 mgKOH/g oil.

The optimized reaction conditions for the transesterification of Cottonseed and Soya bean waste oils with their corresponding FAME yields are shown in Table 6 (Appendix A.6).

4.0. Conclusions

Waste vegetable oils are alternative feedstock for biodiesel production and can reduce the demand on food crops for renewable fuel production. In previous biodiesel production experiments from various feedstocks, K_2CO_3 was used as a supported catalyst. In most of these reported studies high reaction temperatures had to be used to give acceptable yields in reasonable times. In the present study, K_2CO_3 was used as an unsupported catalyst to understand its catalytic activity in the transesterification of waste vegetable oils. Based on the results, the following conclusions are drawn:

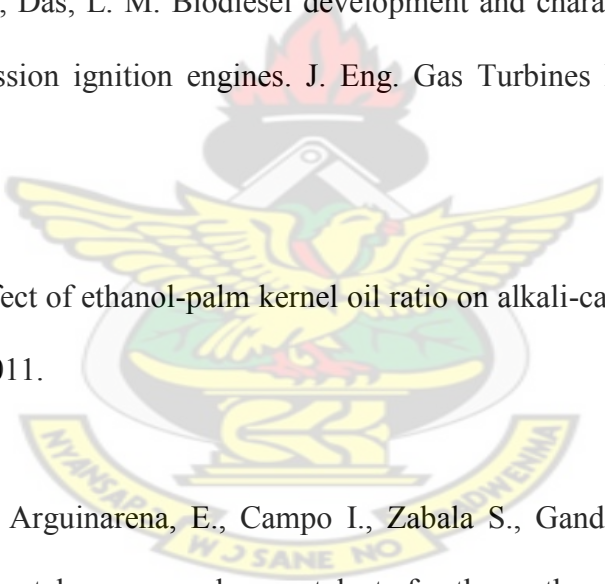
- A catalyst amount of 4g wt % of oil was found to be sufficient to complete the transesterification of waste vegetable oils.
- The optimized oil to methanol molar ratio for the transesterification of both waste vegetable oils was 1:6.
- The best reaction time for the transesterification of Cottonseed waste vegetable oil was 40 mins whereas that of Soya bean waste vegetable oil was 80 min.
- The optimized reaction temperature for the process was 60 °C.

Transesterification reduced the viscosity, acid value and water content of the FAME produced thereby improving the quality of biodiesel and potentially enhancing energy efficiency of engines that may run on such fuel.

Acknowledgements

The research was funded by a Canada Africa Research Grant (CAREG) awarded to Dr. E.K. Yanful and Dr. Ebenezer Mensah by the International Development Research Centre through the Association of Universities and Colleges of Canada. The support provided by technical staff in the Departments of Civil and Environmental Engineering and Chemical and Biochemical Engineering is gratefully acknowledged.

References

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- [1] Agarwal, A. K., Das, L. M. Biodiesel development and characterization for use as a fuel in compression ignition engines. J. Eng. Gas Turbines Power. 2001, 123, pp. 440–447.
- [2] Alamu O .J. Effect of ethanol-palm kernel oil ratio on alkali-catalyzed biodiesel yield. Fuel. 2007, 08.011.
- [3] Arzamendi G., Arguinarena, E., Campo I., Zabala S., Gandia L. M. Alkaline and alkaline- earth metals compounds as catalysts for the methanolysis of sunflower oil, Catalysis Today. 2008, pp. 305 -313.
- [4] Baroi C, Yanful E. K, Bergougnou M. A. Biodiesel production from *Jatropha curcas* oil using potassium carbonate as unsupported catalyst. International Journal of Chemical Reactor Engineering; 2009, Vol. 7, Article A72.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

- [5] Canakci M. The Potential of Restaurant Waste Lipids as Biodiesel Feedstocks. *Bioresource Technology*. 2007, 98, pp. 183–190.
- [6] Canakci M, Sanli H. Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Industrial Microbiology and Biotechnology*; 2008, 35:431–41.
- [7] Carter, D., Darby, D., Halle, J., Hunt, P. How to Make Biodiesel; Low-Impact Living Initiative, Redfield Community, Winslow, Bucks. 2005, ISSN 0-9649171-0-3.
- [8] Chhetri, A. B., Watts, K. C. and Islam, M. R. Waste Cooking Oil as an Alternate Feedstock for Biodiesel Production, *Energies*. 2008, 1, 3-18.
- [9] Connemann, J.; Fischer, J. Biodiesel in Europe: biodiesel processing technologies. Paper presented at the International Liquid Biofuels Congress, Brazil. 1998, pp. 1-16.
- [10] Dorado, M. P.; Ballesteros, E.; Lopez, F. J.; Mittelbach, M. Optimization of alkali catalyzed transesterification of brassica oil for biodiesel production. *Energy and Fuels*. 2004, Vol. 18, Issue 1, pp. 77-83.
- [11] Eevera T., Rajendran K., Saradha S. “Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions”, “Renewable Energy”, 2009, Vol. 34, Issue 3, pp. 762 – 765.

**BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS
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- [12] Felizardo P, Correia MJN, Raposo I. Production of biodiesel from waste frying oils. *Waste Manage*; 2006, 26:487–94.
- [13] Furniss, B.S, Hannaford A.J, Smith P.W.A and Tatchell A.R. *Vogel's Textbook of practical organic chemistry*, 5th Ed. 1989, pp 164, 165, 168 and 236.
- [14] Graille J. “Vegetable oil alcoholysis pilot trials using natural catalysis to produce diesel fuels”, “*Oleagineux*”, 1986, Vol. 41, Issue 10, pp. 457 – 464.
- [15] Graille J., Lozano P., Pioch D., Geneste P. “Alcoholysis tests of vegetable oils with natural catalyzers for the production of diesel fuels”, “*Oleagineux*”, 1985, Vol. 50, Issue 5, pp. 271 – 276.
- [16] Hartman, L. “Methanolysis of triglycerides”, “*Journal of the American Oil Chemist's Society*”, 1956, 33, 129.
- [17] Korbitz, W. Biodiesel production in Europe and North American, an encouraging prospect. *Renew. Energy*. 1999, 16, 1078–1083.
- [18] Krawczyk, T. Biodiesel. *INFORM*. 1996, 7 (8), 801–822.
- [19] Kulkarni, M. G.; Dalai, A. K. Waste Cooking Oils an Economical Source for Biodiesel: A Review. *Ind. Eng. Chem. Res*. 2006, 45, 2901-2913.

- [20] Leung, D. Y. C.; Guo, Y. Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel processing Technology*. 2006, 87, 883-890.
- [21] MacLeana H. L, Laveb L. B. Evaluating automobile fuel/propulsion system technologies. *Prog Energy Combust Sci*; 2003, 29:1–69.
- [22] McLamb E. Fossil Fuels vs. Renewable Energy Resources. *Ecology Global Network*. 2011. <http://www.ecology.com/2011/09/06/fossil-fuels-vs-renewable-energy-resources>. [Accessed on 04/05/2012]
- [23] Öner C, Altun S. Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. *Appl Energy*; 2009, 86:2114–20.
- [24] Patil P. D., Deng S. “Optimization of biodiesel production from edible and non-edible vegetable oils”, “*Fuel*”, 2009, Vol. 88, Issue 7, pp. 1302 – 1306.
- [25] Peng B., Shu Q., Wang J., Wang G., Wang D. and Han M. Biodiesel production from waste oil feedstocks by solid acid catalysis. *Process Safety and Environmental Protection*. 2008, Vol. 86, Issue 6, pp. 441–447.

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

- [26] Platonov A. Y., Evdokimov A. N., Kurzin, A. V., Maiygorova, H. D. “Solubility of Potassium carbonate and Potassium Hydrocarbonate in Methanol”, “J. Chem. Eng. Data.”, 2002, 47, 1175 – 1176.
- [27] Radich, A. Biodiesel performance, costs, and use. US Energy Information Administration. 2006. (Online) Available at <http://www.eia.doe.gov/oiaf/analysispaper/biodiesel/index.html>. [Accessed on 18/08/2011]
- [28] Sapienza R., Johnson A., Ricks, W. “Environmentally benign anti – icing or de-icing fluids”, “US Patent 7138071 B2”, Date issued: 21 Nov, 2006.
- [29] Sapienza R., Johnson A., Ricks W. “Environmentally benign anti – icing or de-icing fluids employing triglyceride processing by-products”, “US Patent 6890451 B2”, Date issued: 10 May, 2005.
- [30] Thamsiroj T., Murphy J. D. Is it better to import palm oil from Thailand to produce biodiesel in Ireland than to produce biodiesel from indigenous Irish rape seed. Appl Energy; 2009, 86:595–604.
- [31] Wedel V R. Technical handbook for marine biodiesel in recreational boats. Prepared for National Renewable Energy Laboratory, US Department of Energy, Subcontract No. ACG-7-16688-01 under Prime Contract No. DE-AC36-83CH10093. 1999, pp. 32.

- [32] Yan J, Lin T. Biofuels in Asia. *Appl Energy*; 2009, 86:S1–S10.
- [33] Yang H-H.; Chien, S-M.; Lo, M-Y.; Lan, J. C.-W.; Lu, W-C.; Ku, Y-Y. Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. *Atmospheric Environment*. 2007, 41, 7232–7240.
- [34] Zhang J. J., Jiang L. F. Acid-catalyzed esterification of *Zanthoxylum bungeanum* seed oil with high free fatty acids for biodiesel production. *Bioresour Technol*; 2008, 99:8995–8.
- [35] Zheng S.; Kates, M., Dube, M .A.; McLean, D. D. Acid-catalyzed production of biodiesel from waste frying oil. *Biomass and Bioenergy*. 2006, 30, 267-272.

APPENDIX A – TABLES

Appendix A.1

Table 1: Quantities of waste vegetable oil generated in some countries.

Country	Amount of WVO generated ,tonnes/year
United States of America	118,939,655 (Radich A, 2006)
Canada	135,000 (Chhetri et al, 2008)
United Kingdom	200,000 (Carter <i>et al</i> , 2005)
10 EU Countries	1,000,000 (Kulkarni and Dalai, 2006)

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Appendix A.2

Table 2: Some characteristics of the waste vegetable oil samples

Property	Unit	CWVO	SWVO
Density @ 15°C	g/mL	0.915	0.913
Kinematic viscosity	cP	34.7	32.4
Acid value	mgKOH/g oil	0.920	1.088
% FFA	%	0.462	0.547
Water content	%	< 0.05	< 0.05

Appendix A.3

Table 3: Effect of catalyst amount on percentage yield of FAME

Catalyst amount/g (wt% of oil)	Washed sample (after 8 hours of settling)	
	Average % yield of FAME	Error % (S D)
1	11.09	0.5118
2	89.12	0.4693
3	92.10	0.4602
4	95.35	0.0811
5	93.45	0.0870
6	93.10	0.0925
7	92.46	0.3125

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Appendix A.4

Table 4: Effect of oil to methanol molar ratio on the percentage yield of FAME

Sample ID	Oil: Methanol Molar ratio	Washed sample (after 8 hours of settling)	
		Average % yield of FAME	Error % (SD)
CWVO	1:4	82.32	0.1742
	1:6	93.29	0.1145
	1:8	92.14	0.2467
SWVO	1:4	88.03	0.0847
	1:6	95.90	0.0583
	1:8	92.84	0.2147

Appendix A.5

Table 5: Characteristics of biodiesel produced from waste vegetable oil

Property	Unit	CWVOB	SWVOB	ASTM D6751-02
Density @ 15 °C	g/mL	0.880	0.885	N/A
Kinematic				
viscosity	cP	4.0	3.8	1.9-6.0
Acid value	mgKOH/g oil	0.12	0.28	Max 0.80
Water content	%	< 0.05	< 0.05	Max 0.05

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

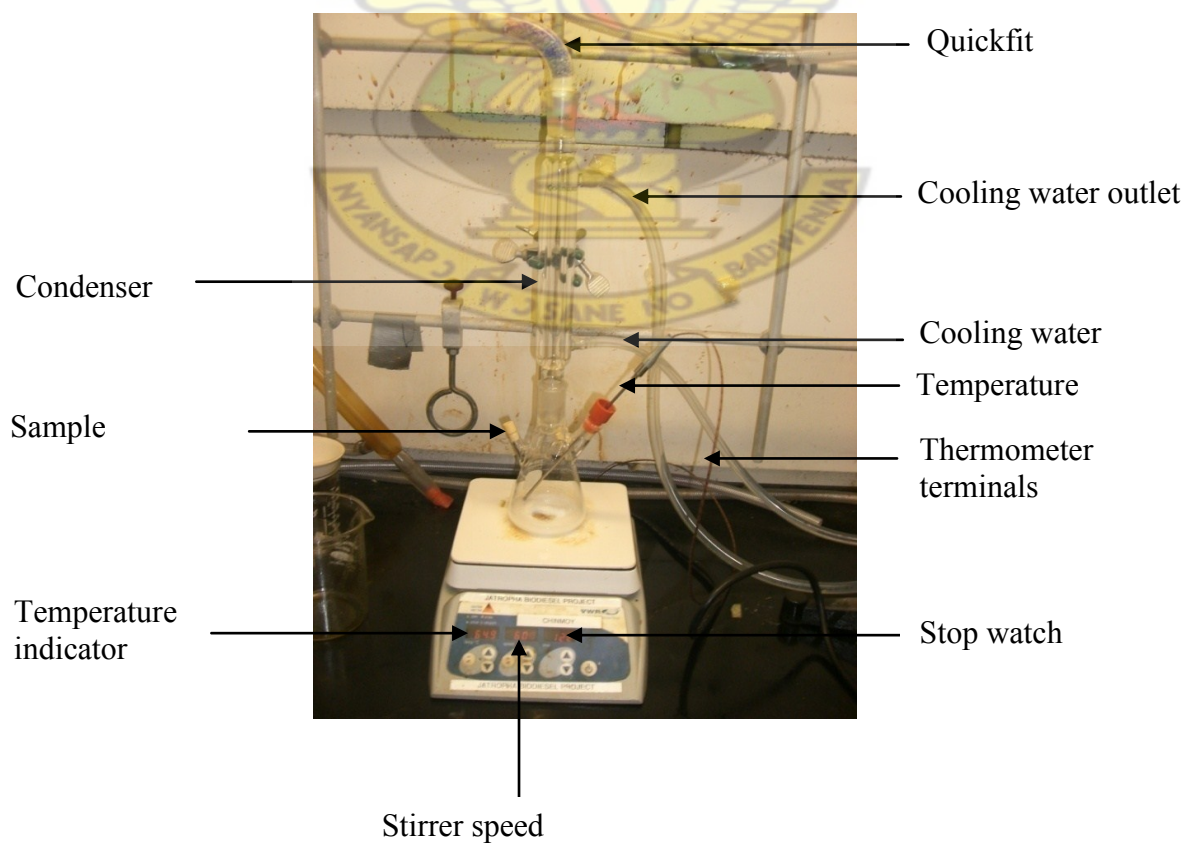
Appendix A.6

Table 6: Summary of optimised reaction parameters for the various feedstocks

Sample ID	Catalyst Amount (wt% of Oil)/g	Molar Ratio Oil: Methanol	Temperature /°C	Reaction Time /min	% FAME Yield
Cottonseed Waste Vegetable Oil	4	1:6	60	40	99.46
Soya bean Waste Vegetable Oil	4	1:6	60	80	99.51

APPENDIX B – FIGURES

Appendix B.1



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Figure 1: Experimental Set up



Appendix B.2

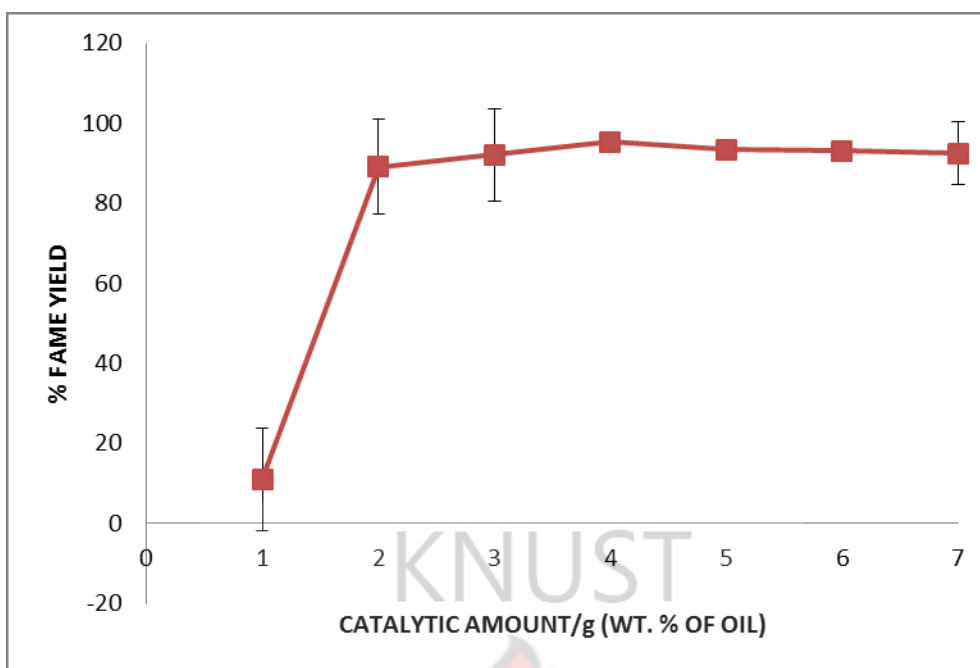


Figure 2: Effect of catalyst amount on percentage yield of FAME.

Appendix B.3

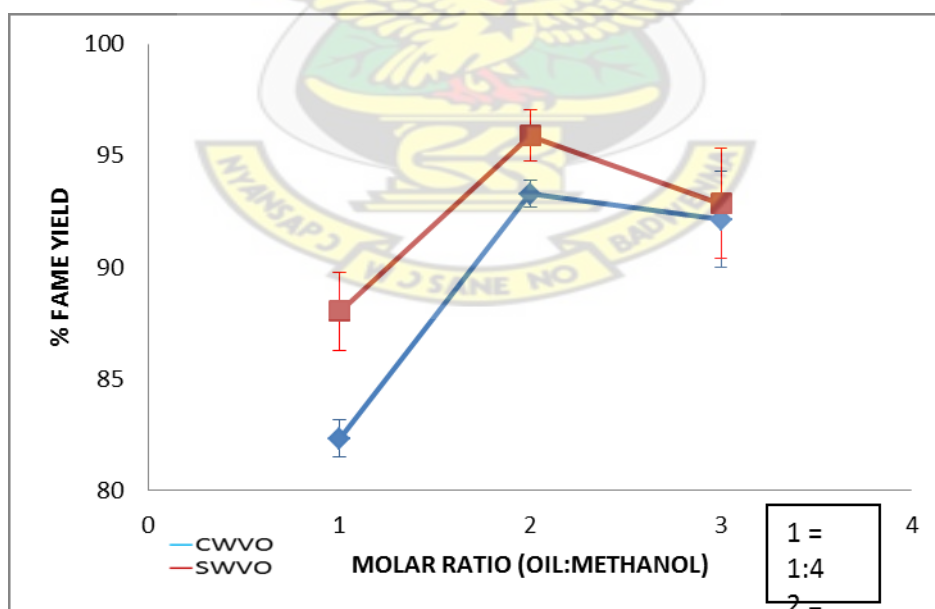


Figure 3 . Effect of oil to methanol ratio on the percentage yield of some FAME

Appendix B.4

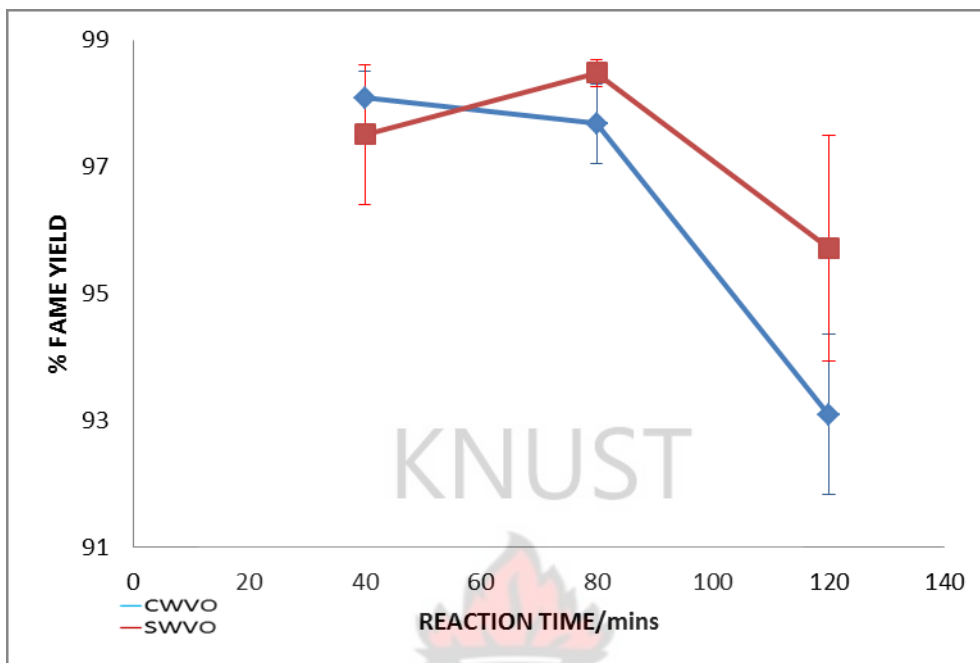
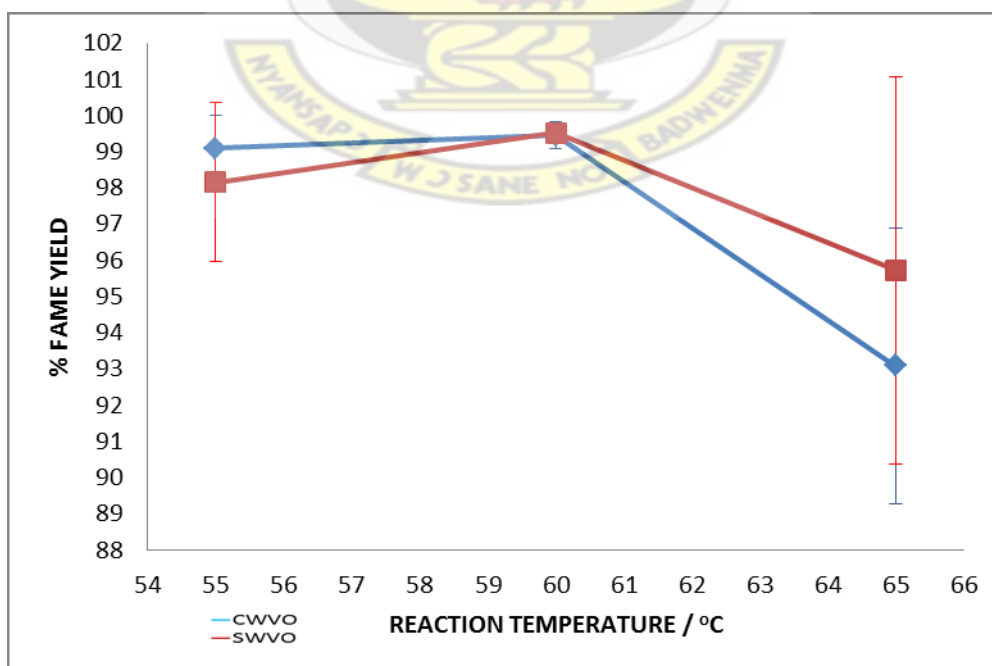


Figure 4. Effect of reaction time on the percentage yield of FAME from Cottonseed waste vegetable oil (CWVO) and soyabean waste vegetable oil (SWVO)

Appendix B.5



BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Figure 5: Effect of reaction temperature on the percentage yield of FAME from Cottonseed waste vegetable oil (CWVO) and soyabean waste vegetable oil (SWVO)



F.2 Full Title: Effect Of Reaction Parameters on a Two-Stage Biodiesel Production from *Jatropha curcas* Oil Using Unsupported Potassium Carbonate (*Draft Manuscript*)

Short Title: Reaction Parameters' Effect on *Jatropha* Biodiesel Using Unsupported Potassium Carbonate

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ABSTRACT

BACKGROUND: In this study, the free fatty acid (FFA) content of crude *Jatropha curcas* oil was lowered from 5.70% to 1.31% in the process of esterification using sulphuric acid ahead of transesterification constituting a two-step process for biodiesel production. Transesterification reactions are influenced by reaction parameters including catalyst amount, oil to methanol molar ratio, reaction time and reaction temperature which effect were assessed in this paper.

RESULTS: A 4g K₂CO₃ catalyst amount (wt% *Jatropha* oil), an oil to methanol molar ratio of 1:8, 120 min reaction time and 60 °C reaction temperature were the best reaction parameters obtained for the two-step biodiesel production using a *Jatropha curcas* oil with initial high FFA content.

CONCLUSION: The combination of these best reaction parameters gave a fatty acid methyl ester (FAME) yield of 94.80 % which is 1.24 % higher than the best case for each single parameter.

NOTATION:

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

Keywords: Biodiesel, Esterification, Transesterification, Potassium carbonate, fatty acid methyl ester (FAME)

1.0. INTRODUCTION

The dwindling reserve of fossil fuel and their associated environmental problems have increased the need to seek other alternative renewable and sustainable sources for fuel production. The use of biofuel as a replacement for fossil fuel is on the increase at a faster rate. Biodiesel, mostly produced from vegetable oils, is mono-alkyl ester and is perceived to replace fossil diesel fuel. Both edible and non-edible vegetable oils can be used as feedstock in the production of biodiesel. However, edible oils are commonly used feedstock in the current biodiesel production industries. According to Food and Agriculture Organization's (FAO) reports, edible plants containing oil are used for the production of biodiesel among which about 84 % of the biodiesel is from rapeseed oil (RSO) and the remaining is from sunflower (13 %), palm oil (1 %), soybean and others (2 %) ¹. The use of edible oils for fuel production is a concern as more and more of the global food demand rises. There are also issues of deforestation and ecological imbalance while changing the virgin forests and arable lands to large scale biofuel production ². In other words, the sustainability of edible oils as biodiesel feed is under threat. The high supply cost of these feedstocks which account for more than 70 % of the overall biodiesel production cost coupled with their competition as food sources have turned the attention to the exploitation of other non-edible feedstocks such as Jatropha, Castor bean oil, Hemp oil, Neem oil, Pongame oil and Sea mango oil. Jatropha, which is claimed to be suitable to be grown in non-arable land, has been hailed as a promising raw material for biodiesel production ³.

Many types of methods have been developed to convert oils such as Jatropha oil into biodiesel. The four main categories are the direct use of vegetable oil, micro-emulsion,

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thermal cracking and transesterification. Direct use of vegetable oil is not applicable to most diesel engines as the high viscosity can damage the engine by causing coking and trumpet formation ⁴. Biodiesel obtained from micro-emulsion and thermal cracking methods would likely lead to incomplete combustion due to a low cetane number and energy content ⁵. Transesterification is the most common method for biodiesel production due to its simplicity, thus this method has been widely used to convert vegetable oil into biodiesel ^{6, 7}. The transesterification process or methanolysis, which refers to a catalysed chemical reaction involving vegetable oil and methanol (MeOH) to yield fatty acid methyl ester (FAME) as the main product and glycerol as a by-product ⁸⁻¹⁰, is shown in equation (1).



where:

TG - triglyceride -

MeOH - methanol

ME - methyl ester,

Potassium Carbonate (K_2CO_3) provides practically complete alcoholysis with the least amount of soap production as compared to other alkali or base catalysts such as NaOH, KOH, NaOCH_3 and KOCH_3 ^{11, 12}. According to US patents 6890451 B2 ¹³ and 7138071 B2 ¹⁴, glycerol containing K_2CO_3 can be an excellent environmentally benign anti-icing or de-icing agent. Thus, it can be used on airport runways and also on the wings, fuselage, and tail of aircrafts for de-icing. Unsupported K_2CO_3 is a better alternative for biodiesel production, for a number of reasons. Among traditional catalysts, KOH and its methylate are the most expensive. KOH is synthesized by electrolysis of KCl solution and the current method of producing K_2CO_3 is by reacting KOH with CO_2 . Thus, K_2CO_3 could be more expensive than

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

KOH¹¹. However, most biomass such as plantain peels, cocoa pods and *Jatropha curcas* cake contains potassium. Hence the production of K₂CO₃ from these biomass sources could help reduce its cost thereby reducing the overall cost of biodiesel production. The purpose of the present study was to investigate the effect of four parameters necessary for transesterification of esterified *Jatropha* oil into biodiesel. This two-step process coupled with using unsupported K₂CO₃ catalyst is the novelty for biodiesel production from *Jatropha* oil with a high FFA content.

2.0. MATERIALS AND METHODS

Anhydrous grade (99.95 %) methanol was purchased from Alfa Aesar (Oakville, Ontario, Canada) and ACS grade (99 %) K₂CO₃ and H₂SO₄ (99 %) were obtained from the Civil and Environmental Engineering and Chemical and Biochemical Engineering laboratories at Western University. Both triolein ($\approx$ 99 %) and methyl oleate ($\approx$ 99 %) were bought from Sigma Aldrich (Oakville, Ontario, Canada). The *Jatropha* oil was imported from India to Western University, London, Canada, where the research was conducted. The as-received oil was stored in a cold and dark room at 5 °C under argon to prevent oxidation.

The laboratory experiments followed a modified version of the approach used by Baroi *et al.* (2009)¹¹. A 250 mL Erlenmeyer flask was modified and used as the reactor (Figure 1).

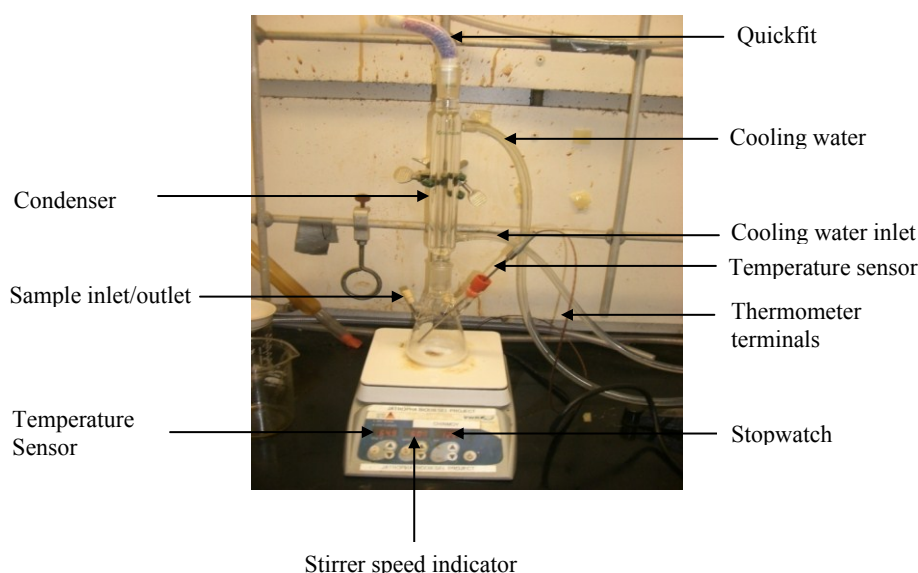


Figure 1: Experimental Set up

The top of the flask was made narrower to fit into the bottom part of the 24/40 size Liebig condenser. An adapter with one socket bent (Quick fit, 19/26) filled with anhydrous Calcium sulphate (CaSO_4) and blocked at both ends with cotton wool, was connected to the top of the condenser. This was to ensure the entrance of moisture-free air into the setup. The flask was modified to have two additional openings, with one opening to fit the temperature sensing probe into the reactor. The oil feed and the methanol-carbonate solution were introduced into the reactor through the second opening.

2.1. ESTERIFICATION AND TRANSESTERIFICATION OF THE JCO SAMPLES

2.1.1 ESTERIFICATION

This procedure was carried out to reduce the high percentage free fatty acid of the feed which could enhance saponification and cause a reduction in the yield of the FAME. For every amount of percentage free fatty acid per gram of oil, 0.05 g H_2SO_4 and 2.25 g of anhydrous CH_3OH were used. The sulphuric acid-methanol solution was added to the oil and heated at 60 °C while stirring at 600 rpm for one hour. After that, the reaction mixture was allowed to settle. The acid-methanol-water mixture which settled on top was separated from the esterified oil. The free fatty acid level content of the esterified oil was then measured. The procedure was repeated three times to ensure the free fatty acid content had been reduced from 5.70 % to 1.31 % for the transesterification reaction.

2.1.2 TRANSESTERIFICATION

Following esterification, an amount of K_2CO_3 catalyst ranging from 1g to 7g wt. % of oil was added in separate experiments to 30 mL of methanol to dissolve and produce a carbonate solution. Dissolution was enhanced by heating the mixture at 60 °C whiles condensing the methanol into the mixture. Exactly 100 g of oil was heated to 60 °C and charged into the reactor containing the carbonate-alcohol mixture to increase reaction rate. The mixture was stirred continuously while maintaining the temperature between 60 - 65 °C for 2 hours. The mixture was left for 8 hours undisturbed in a separatory funnel to allow separation of glycerol from the ester phase. After separation, the crude biodiesel was washed 3-4 times with warm distilled water followed by 0.1 % H_2SO_4 to remove trace amounts of catalyst in the methyl ester. The washing was repeated until a clear water layer of neutral pH was obtained. The washed biodiesel was first dried using anhydrous sodium sulphate. A rotary evaporator was used to remove excess methanol that might have been carried over during the washing process.

After obtaining the optimum catalyst amount that resulted in a high yield, the second part of the experiment followed by maintaining the catalyst at the optimum amount at a temperature of 60 -65 °C for 2 hours, while varying the oil:methanol molar ratio. Three ratios (1:4, 1:6, and 1:8) were investigated with the intention of selecting the one that would give the highest yield. Next, the optimized catalyst weight and oil to methanol molar ratio were maintained

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whilst the reactions were carried at different times namely, 40 min, 80 min and 120 min, to determine an optimum FAME yield. Lastly, the best catalyst amount, oil to methanol molar ratio and reaction time were maintained while varying the reaction temperature (55 °C, 60 °C and 65 °C) to obtain the best yield. It was ensured that all the reaction contents were pre-heated to the desired temperature. The 8 hour separation time was selected based on the preliminary experimental run using 1:6 oil:methanol molar ratio with a fixed amount of catalyst. The figure below summarises the experimental procedure.

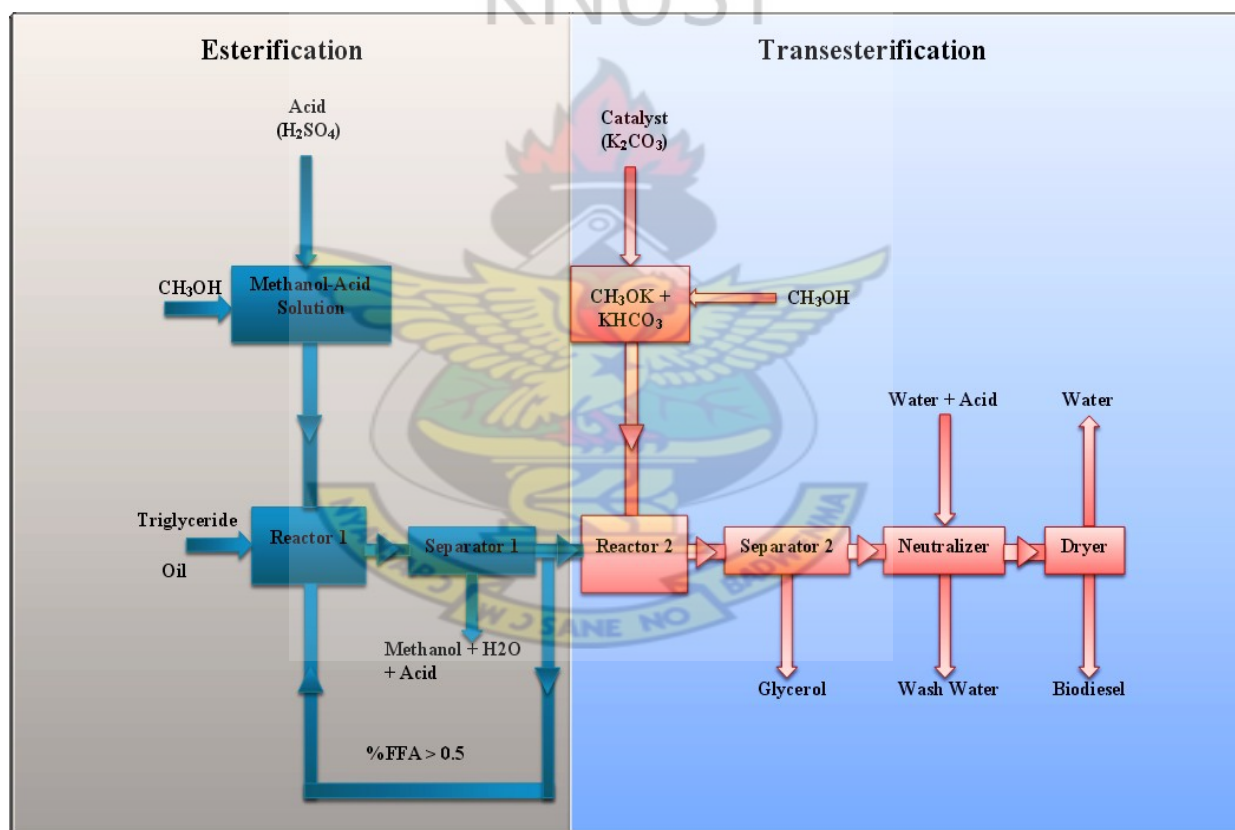


Figure 2: Schematic of batch reaction processes of esterification and transesterification of Jatropha oil.

All tests described above were repeated three times and the mean values are reported with the associated error bars.

3.0. RESULTS AND DISCUSSION

The characteristics of the crude *Jatropha* oil determined according to ASTM D 6751 are presented in Table 1. The data in Table 1 show that the as-received *Jatropha* oil contained high free fatty acid (5.70 %); hence, a two- step transesterification processed was employed. During the acid pre-treatment or esterification phase, the free fatty acid (% FFA) crude *Jatropha* oil was reduced from 5.70 % to 1.31 %. High FFA promotes saponification which could cause difficulty in the phase separation of the biodiesel from the glycerol phase. Thus, the acid pre-treatment converted much of the high FFA to biodiesel with no soap formation before the transesterification reaction to give the highest yield of methyl esters. The yield of the biodiesel produced was estimated using a mass balance approach and the purity of FAME was confirmed using gas chromatography-mass spectrometry (GC-MS).

Table 1: Characteristics of crude *Jatropha* oil used in the study

Property	Unit	<i>Jatropha</i> oil
Density at 15 °C	g/mL	0.907
Kinematic viscosity	cP	32.1
Acid value	mg KOH/g oil	11.298
% FFA	%	5.70
Water content	%	< 0.05

3.1 EFFECT OF CATALYST AMOUNT ON PERCENTAGE YIELD OF FAME

Figure 3 represents the effect of the catalyst amount on the yield of biodiesel. Catalyst amounts of 1 g to 7 g (wt% *Jatropha* oil) were used in separate experimental runs to determine the yield of biodiesel.

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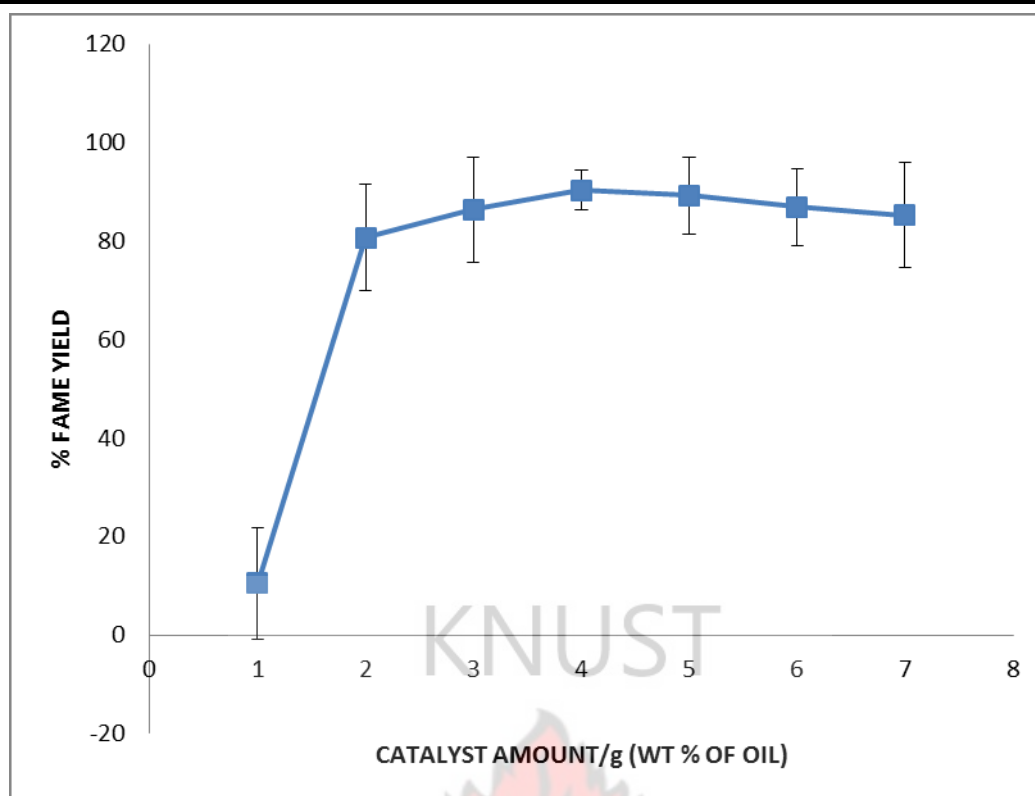


Figure 3: Effect of catalyst amount on percentage yield of FAME

It is observed from Figure 3 that when the catalyst amount was 1 g (wt % of oil), the percentage yield of FAME was 10.47 %. This indicates that 1 g of K_2CO_3 was not sufficient to catalyze the transesterification reaction. The conversion of the esterified Jatropha oil to FAME (fatty acid methyl ester) increased with a corresponding increase in catalyst amount from 1 to 4 g (wt % of oil). The conversion decreased slightly when the weight of catalyst was increased from 5 to 7 g. The results show that 4 g of K_2CO_3 gave the highest conversion or yield of FAME (90.30 %), when 100 g of Jatropha oil was made to react with methanol at a 1:8 oil to methanol molar ratio at a temperature of 60 °C with stirring at 600 rpm for 2 hours. Also, Darkwah *et al.* (2012)¹⁵ showed that 4 g of K_2CO_3 gave the highest conversion of FAME (95.35 %), when 100 g of waste vegetable oil was made to react with methanol at a 1:6 oil : methanol molar ratio at a temperature of 60 °C with stirring at 600 rpm for 2 hours. These results can be compared to those of Baroi *et al.* (2009) who observed that 6 g K_2CO_3 gave the highest conversion (98.214 %), when 100 g of Jatropha oil was reacted with

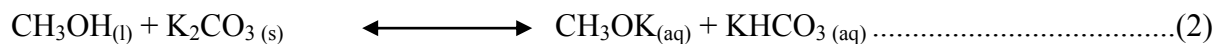
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methanol at a temperature of 60 °C with stirring at 600 rpm for 10 hours using 1:6 oil:methanol molar ratio. The FAME yield of 98.214 % is higher than the 90.30 % obtained in the present study. This is because some of the Jatropha oil used by Baroi *et al.* (2009)¹¹ had been stored for 2 years prior to its use as feed in the present study. The long storage of the Jatropha oil is believed to have promoted rancidity which resulted in the high FFA of 5.68 % as compared to the 1.47 % reported by Baroi *et al.* (2009)¹¹. The possible formation of waxes and other contaminants due to the long storage of the Jatropha oil sample could also affect the yield in the present study. Apart from the work by Baroi *et al.* (2009) and Boakye *et al.* (2012)^{11, 15}, there has been little or no reported study on the use of unsupported potassium carbonate for transesterification of Jatropha oil.

The usage of 1g (wt % Jatropha oil) of catalyst gave a lower yield because the reaction intermediate was unstable. Previous studies showed that excess alkali catalyst cause saponification of triglycerides resulting in the formation of soap and an increase in the viscosity of the reactants that result in reduced FAME conversion^{11, 16}. Hence secondary saponification might be responsible for significantly lower conversion of the Jatropha oil to biodiesel (FAME) when the catalyst amount was increased from an optimum weight of 4 g (i.e. from 5 g to 7 g). Also, the decrease in the FAME yield with catalyst amount above the optimum amount of 4 g appears to have been due to the reduction in the molar concentration of FAME in the biodiesel phase which could result from the solubilisation of soap and other components into the biodiesel phase. The qualitative soap presence analysis by Baroi *et al.* (2009)¹¹, using FTIR-ATR confirmed increased solubilisation of soap into the biodiesel phase at catalyst amounts above the optimum weight and the observation that there are no side reactions during the settling of biodiesel from the glycerol phase. Platonov *et al.* (2002)¹⁷, indicated that more than 99% of KHCO_3 produced from the solubility reaction between

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anhydrous K_2CO_3 and methanol remained in the solid phase along with unreacted K_2CO_3 at room temperature (25 °C). This is illustrated in equation (2) below.



The equilibrium of the above reaction is shifted towards product formation as a result of the phase distribution of $KHCO_3$ between the solid and liquid phases. $KHCO_3$ dissolves when the temperature is increased, thus the rate of backward reaction is favoured causing the concentration of CH_3OK to decrease while that of $KHCO_3$ increases. Also, Arzamendi *et al.* (2008) ¹⁸, showed that $KHCO_3$ was a poor catalyst with negligible catalytic activity when compared to K_2CO_3 . Hence CH_3OK formation (equation (2)) is the main catalytic reaction driving the transesterification reaction (Baroi *et al.*, 2009) ¹¹.

3.2 EFFECT OF OIL TO METHANOL MOLAR RATIO ON THE PERCENTAGE YIELD OF FAME

Figure 4 is a graph of the effect of oil to methanol molar ratio on the yield of fatty acid methyl esters.

The results show that when a 1:4 oil : methanol molar ratio was used, the FAME yield was lower than when 1:6 and 1:8 oil:methanol molar ratios were used. This indicates that the amount of methanol at the lower ratio was insufficient and this resulted in incomplete conversion of triglycerides to methyl esters. Also, when the oil : methanol molar ratio was 1:6, the FAME yield (86.72%) was low as compared to that of 1:8 with a FAME yield of 94.56%. Thus, excess methanol was needed for the transesterification reaction, leading to an increase in oil conversion. Similar observation that the biodiesel yield increased as the methanol to oil ratio increases only up to a threshold mix is reported by other researchers¹⁹.

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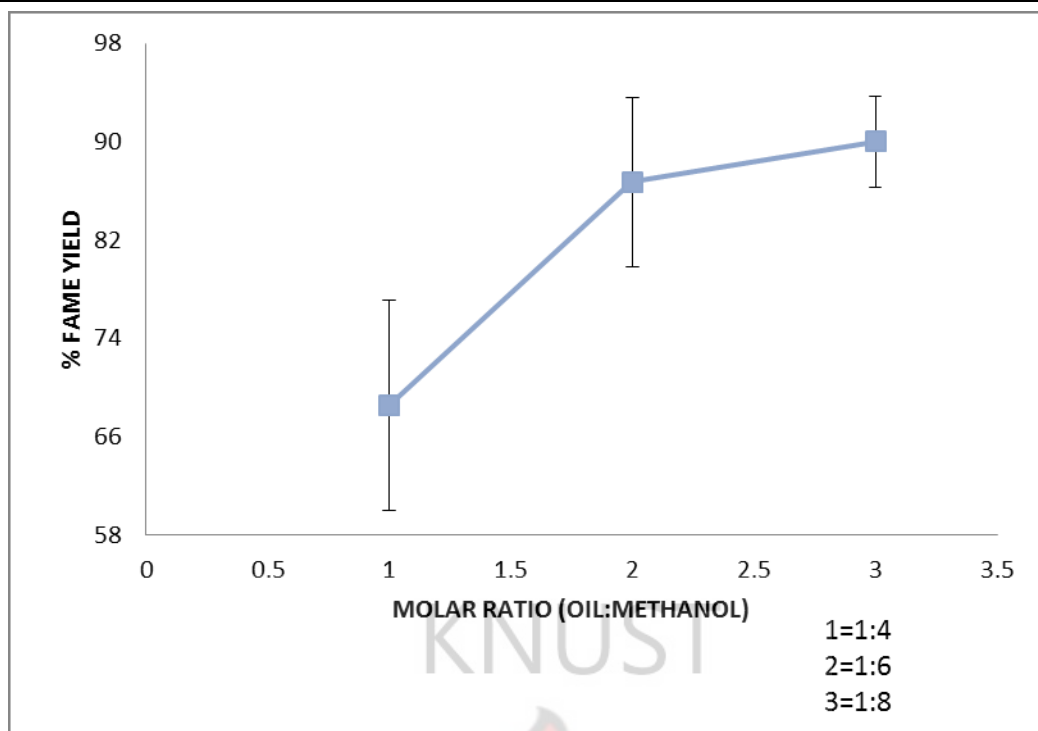


Figure 4: Effect of oil to methanol molar ratio on the percentage yield of FAME

The results clearly indicate that the optimum oil to methanol molar ratio for the transesterification of the *Jatropha* oil was 1:8. A relatively similar results have been reported indicating that 1:10 oil:methanol molar ratio gave the highest conversion (98.79 %), when 100 g of *Jatropha* oil was reacted with methanol at a temperature of 60 °C with stirring at 600 rpm for 10 hours using 6 g of K_2CO_3 as catalyst ¹¹. Although Baroi *et al.* (2009) ¹¹, observed a higher FAME yield, the excess methanol used would increase the separation and purification cost in the process thereby affecting the overall production cost.

3.3 EFFECT OF REACTION TIME ON THE PERCENTAGE YIELD OF FAME

With an optimum catalyst amount and oil to methanol molar ratio, the variation in FAME yield with reaction time during transesterification of the refined *Jatropha* oil is shown in Figure 5 below.

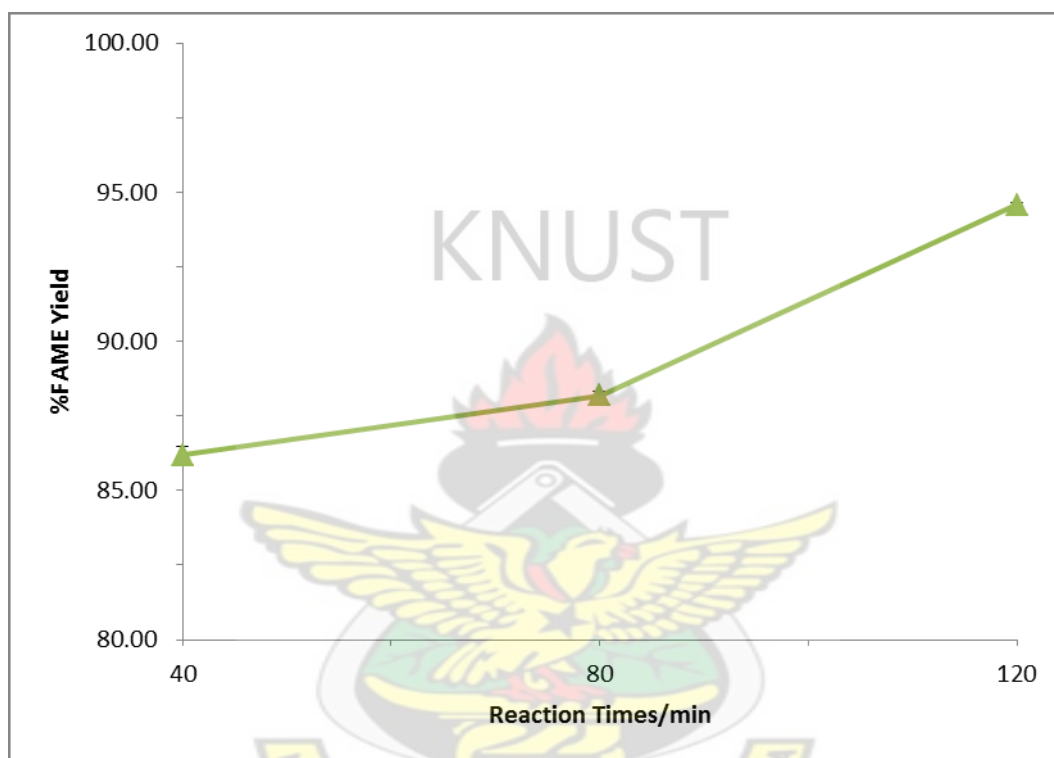


Figure 5: Effect of reaction time on the percentage yield of FAME

The results show that 120 min of reaction time gave the highest yield of 94.574% FAME. Below the 120 min of reaction time, the methyl ester yield was low. This could be due to incomplete conversion of some of the oil into FAME. The optimum reaction time of 120 min for the complete formation of *Jatropha curcas* FAME in the current study is similar to other optimum reaction times reported in many experiments. Investigations into the kinetics of the methanolysis of a mixture of *Jatropha curcas* waste food oil via experiment and simulation methods and reported that biodiesel of 97.1 % purity was obtained at 120 min of reaction

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time with 1:6 oil:methanol molar ratio and 1 wt. % KOH to oil mass ratio at 50 °C reaction temperature²⁰. The optimal value of 93 % yield of *Jatropha* methyl ester is reported for a 120 min of reaction time at 66 °C with 1:11 oil:methanol ratio using 1.1 % of KOH (wt. of oil)²¹. Another research²² shows maximum biodiesel yields (87.4 %, 89 % and 88.3 % for beef fat, chicken fat and used cooking oil respectively) were obtained at reaction periods of 120 min with catalyst concentration of 1.25 wt % of oil, 65 °C and 150 rpm stirring speed. These authors observed that 2-3 hours of reaction time were required for the process to reach equilibrium. Also, they observed a decline in yield after 3 hours which could be due to the reversible nature of the transesterification reaction. Yet another study conducted on the optimization of biodiesel production from *Jatropha curcas* oil reported a maximum yield of approximately 90-95 % at 120 min reaction time, 60 °C reaction temperature with an oil:methanol molar ratio of 1:9 and 0.5 % (w/w) of KOH as catalyst. FAME yield decreased beyond 120 min of reaction time as a result of degradation of the produced FAME²³. Moreover, a two-step acid-base catalysed transesterification study of *Jatropha curcas* oil, gave a maximum yield of 90.1 % at 6 hours reaction time with 1 % (w/w) catalyst concentration for H₂SO₄ and NaOH, 400 rpm of stirring speed and 3:7 oil:methanol molar ratio²⁴. Therefore a maximum reaction time of 120 min was chosen in the current study. This is because prolonged heating might cause the produced FAME to revert back to its original state, thereby reducing the overall biodiesel yield and affecting the economics of production.

3.4 Effect of reaction temperature on the percentage yield of FAME

The yields of biodiesel due to the effect of temperature are illustrated graphically in Figure 6.

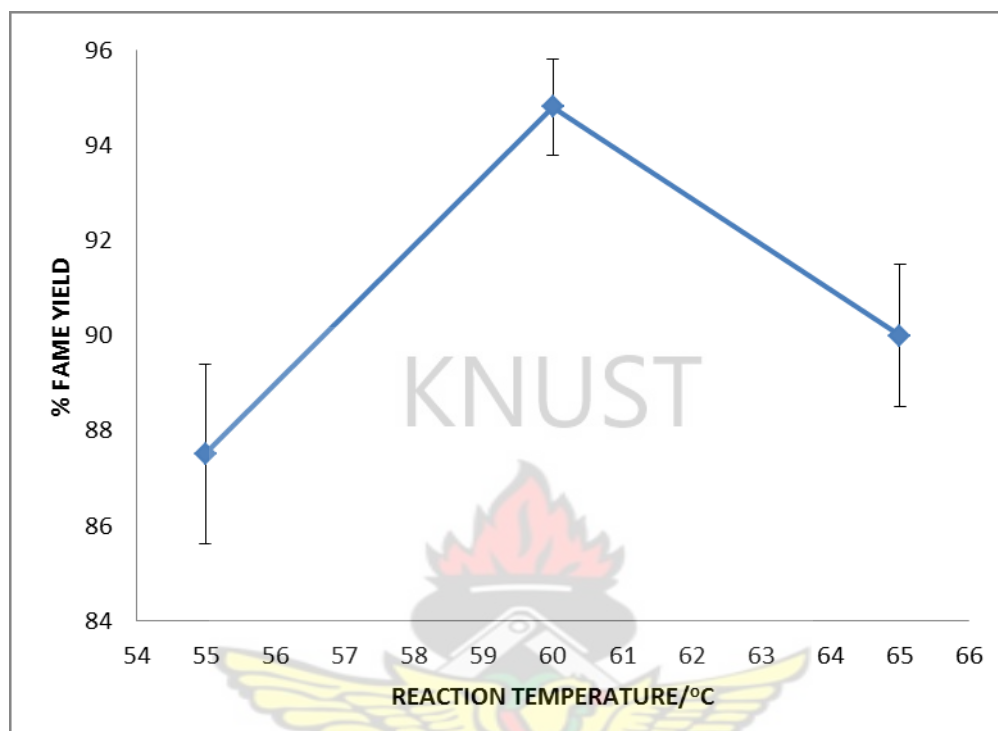


Figure 6: Effect of reaction temperature on the percentage yield of FAME

It was observed that the optimum reaction temperature for the *Jatropha* oil was 60 °C with corresponding FAME yield of 94.80%. From the results, the yields at 55 °C were slightly lower with higher standard deviations compared to the yield at 60 °C. This might have resulted from incomplete conversion of triglycerides to FAME at the lower temperature. At 65 °C which was above the optimum temperature of 60 °C, the FAME yield decreased. Some studies have suggested that the saponification of triglycerides by alkali catalysts is much faster than the transesterification reaction at temperatures above 60 °C^{23, 25}. Also, the study conducted by Baroi *et al* (2009)¹¹ revealed that a reaction temperature was optimum for the production of 98.214 % yield of *Jatropha curcas* oil biodiesel (JCOB). This yield is higher than 94.57 % FAME yield obtained for JCOB in the present study. This might be due to the

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presence of waxes and phospholipids in the *Jatropha* oil sample used in the present study due to prolonged storage.

Therefore 60 °C was determined to be the optimal temperature for transesterification of the *Jatropha* oil.

The characteristics of the biodiesel produced from the *Jatropha* oil are shown in Table 2. The results indicate that the viscosity of the crude *Jatropha* oil decreased from 32.1 cP to 4.1 cP after transesterification. Also, the acid value of the biodiesel was 0.50 mgKOH/g oil which is lower than the maximum permissible level of 0.80 mgKOH/g oil for ASTM standards. These parameters support the high quality of the biodiesel (FAME) produced from the process described in the present study.

Table 2: Characteristics of biodiesel produced from waste vegetable oil

Property	Unit	J(UWO)	ASTM D6751-02
Density at 15 °C	g/ml	0.790	N/A
Kinematic viscosity	cP	4.1	1.9-6.0
Acid value	mgKOH/g oil	0.50	Max 0.80
Water content	%	< 0.05	Max 0.05

The table below shows a summary of the optimized parameters for the transesterification of the *Jatropha curcas* oil into biodiesel using potassium carbonate as a catalyst.

Table 3: Optimised reaction parameters for the transesterification of *Jatropha* oil

Sample ID	Catalyst Amount (wt% of Oil)/g	Molar Ratio Oil: Methanol	Temperature (°C)	Reaction Time (min)	FAME Yield (%)
JCO	4	1:8	60	120	94.80

4. Conclusions

Jatropha curcas is an alternative feedstock for biodiesel production and can reduce the demand on food crops for renewable fuel production. In previous biodiesel production experiments from various feedstocks, K_2CO_3 was used as a supported catalyst. In the present study, it was used as an unsupported catalyst to understand its catalytic activity in the transesterification of *Jatropha* oil after esterification to reduce the hitherto high percentage free fatty acid. Based on the results, the following conclusions were made:

- Acid esterification using H_2SO_4 reduced the high percentage free fatty acid of the *Jatropha* oil from 5.70 % to 1.31 % which made the alkali transesterification feasible for higher oil conversion into FAME.
- A 4 g K_2CO_3 was found to be sufficient to complete the transesterification of the esterified *Jatropha* oil. The optimized oil to methanol molar ratio was 1:8, the best reaction time was 120 minutes, and the optimized reaction temperature was 60 °C.

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References

1. Themes P. Biofuels and commodity markets—palm oil focus, FAO, Commodities and Trade Division (2006). (Online). Available at faorlc.cgnet.com/as/priorities/Bioenergy/pdfs/commodity.pdf [Accessed on 12, 07, 2011].
2. Butler R. A. Why is oil palm replacing tropical rainforests? Why are biofuels fueling deforestation? (2006). (Online), Available at http://www.news.mongabay.com/2006/0425-oil_palm.html. [Accessed on 09, 08, 2011].
3. Lim S, Hong S. S, Tong K. L, and Bhatia S. Supercritical fluid reactive extraction of *Jatropha curcas* L. seeds with methanol: A novel biodiesel production method. *Bioresource Technology* 101 (2010) September 2010, pp. 7169-7172.
4. Agarwal D. and Agarwal A.K. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. *Appl. Therm. Eng.*, 27, pp. 2314–2323 (2007).
5. Leung D.Y.C., Wu X. and Leung M.K.H. A review on biodiesel production using catalyzed transesterification. *Appl. Energy*, 87, pp. 1083–1095 (2010).
6. Helwani Z., Othman M.R., Aziz N., Fernando W.J.N. and Kim J. Technologies for production of biodiesel focusing on green catalytic techniques. *Fuel Process. Technol.*, 90, pp. 1502–1514 (2009).
7. Jain S. and Sharma M. P. Prospects of biodiesel from Jatropha in India: A Review. *Renew. Sust. Energ. Rev.*, 14, pp. 763–771 (2010a).
8. Huber G. W., Iborra S. and Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.*, 106, pp. 4044–4048 (2006).

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9. Lotero E., Liu Y., Lopez D. E., Suwannakarn K., Bruce D. A. and Goodwin J.G. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.*, 44, pp. 5353–5363 (2005).
10. Marchetti J. M., Miguel V.U. and Errazu A. F. Possible methods for biodiesel production
► *Renew. Sustain. Energy Rev.*, 11, pp. 1300–1311 (2007).
11. Baroi C, Yanful E.K, and Bergougnou, M.A. Biodiesel production from *Jatropha curcas* oil using potassium carbonate as unsupported catalyst, *International Journal of Chemical Reactor Engineering*, Vol. 7, Article A72 (2009).
12. Hartman, L. “Methanolysis of triglycerides”, “*Journal of the American Oil Chemist’s Society*”, 33, 129 (1956).
13. Sapienza R., Johnson A., and Ricks W. Environmentally benign anti – icing or de-icing fluids employing triglyceride processing by-products, US Patent 6890451 B2, Date issued: 10 May, 2005.
14. Sapienza R, Johnson A. and Ricks, W. Environmentally benign anti – icing or de-icing fluids, US Patent 7138071 B2, Date issued: 21st Nov, 2006.
15. Boakye, P., Darkwah, L., Mensah, E., and Yanful, E. Influence of reaction parameters on waste vegetable oil transesterification using unsupported potassium carbonate as catalyst (2012). [Submitted to the *Journal of Ghana Institution of Engineers* and presented at the 2013 Engineering Week Celebration “TAKSI-2013” held in Takoradi, Western Region, Ghana on 21st March, 2013].
16. Dorado M.P., Ballesteros E., Lopez F.J., Mittelbach M. Optimization of Alkali-Catalyzed Transesterification of *Brassica carinata* Oil for Biodiesel Production, *Energy and Fuels*, 18, 77 – 83 (2007).
17. Platonov A. Y., Evdokimov A. N., Kurzin, A. V., and Maiygorova, H. D. Solubility of Potassium carbonate and Potassium Hydrocarbonate in Methanol, *J. Chem. Eng. Data.*”, 47, 1175 – 1176 (2002).

BIODIESEL PRODUCTION FROM SELECTED NON-EDIBLE FEEDSTOCKS USING UNSUPPORTED POTASSIUM CARBONATE

18. Arzamendi G., Arguinarena, E., Campo I., Zabala S., and Gandia L.M. Alkaline and alkaline- earth metals compounds as catalysts for the methanolysis of sunflower oil, *Catalysis Today*, 305 -313 (2008).
19. Alamu O.J. Effect of ethanol-palm kernel oil ratio on alkali-catalyzed biodiesel yield. *Fuel*, 08. 011 (2007).
20. Berchmans, H. J. Morishita, K and Takarada, T. Kinetic study of hydroxide-catalyzed methanolysis of *Jatropha curcas*-waste food oil mixture for biodiesel production. *Journal of Chemical Engineering of Japan*, Vol.43, No.8, 661 – 670 (2010).
21. Sahoo, P. K. and Das, L. M. Process optimization for biodiesel production from *Jatropha*, *Karanja* and *Polanga* oils. *Fuel*, 88, pp 1588-1594 (2009).
22. Hoque M.E., Singh A., Chuan Y.L. Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield. *Biomass and Bioenergy*, Vol. 35, Pp. 1582-1587 (2011).
23. Patil P. D. and Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils, *Fuel*, Vol. 88, Issue 7, pp. 1302 – 1306 (2009).
24. Jain S. and Sharma M. P. Kinetics of acid base catalysed transesterification of *Jatropha curcas* oil. *Bioresource Technology*, 101, pp 7701-7706 (2010b).
25. Eevera T., Rajendran K., and Saradha S. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions, *Renewable Energy*, 34, 3, 762 – 765 (2009).