EVALUATION OF TRANSESTERIFIED WASTE VEGETABLE OIL FOR USE AS BIODIESEL FUEL

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A research thesis submitted to the Graduate School in partial fulfilment for the requirements of the Master of Science in Chemistry of Egerton University

EGERTON UNIVERSITY

JULY, 2010

DECLARATION AND RECOMMENDATION

Declaration

I, Opondo Raphael Nyayieka, hereby declare that this study and thesis is my original work and has not been submitted wholly or in part for any award in any other institution of learning to the best of my knowledge.

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We wish to confirm that this study and thesis write up was done under our supervision and has our approval to be presented for examination as per the Egerton University regulations.

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DEDICATION

To my family and especially my wife for her dedication, patience, commitment, hard work and struggle while I was away for studies, and the entire Nyayieka family for their moral support and encouragement.

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ABSTRACT

Biofuels made from plant sources, usually used to run in diesel engines are of two types namely bioethanol and biodiesel. Bioethanol is mostly derived from maize and sugar cane molasses, while biodiesel is derived from vegetable oils and animal fats. A wide range of bio-fuels can be used as renewable resources of energy, including tallow and waste vegetable oil from hotels and fish vendors. Presently waste vegetable oil is discarded into sewerage systems, causing pollution in water ways and thus adds to the cost of treating effluent. The study involved the use of waste vegetable oil and fat as raw materials for conversion into biodiesel through transesterification reaction with methanol and sodium hydroxide catalyst. The project evaluated biodiesel on the short-term performance of the selected diesel engine. During the study, transesterification batch reactor was fabricated for biodiesel production. The operating conditions for the reactor were 60 L vegetable oil, 10 L methanol, temperature (65-68°C), time of reaction 3 hours and the catalyst was 250 g anhydrous sodium hydroxide. The diesel engine operating combustion conditions were obtained at engine speed rating of 1750 rpm for both fossil diesel and waste vegetable oil biodiesel. The average fuel consumption was 0.3396 kg/kWh for fossil diesel and 0.3804kg/kWh for biodiesel respectively. The results were promising as performance was similar to that of conventional diesel fuel. Both chemical and physical tests were carried out on waste vegetable oil biodiesel and fossil diesel as reference and results found comparable with those of conventional diesel fuel and in conformity with American Society for Testing and Materials (ASTM D 6751) standard specifications for pure biodiesel (B100). The results were found to be in conformity with those of conventional diesel fuel. Production of biodiesel from waste vegetable oil or non-edible oil crops would not compete with human uses of edible oils. Biodiesel is biodegradable, non-toxic, renewable and sustainable. Due to the high prices of petroleum fuel, biodiesel could reduce the country's dependence on foreign petroleum imports, hence saving on foreign exchange and adding value to waste vegetable oil and animal fat.

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LIST OF ABBREVIATIONS AND ACRONYMS

ABE – Activated bleaching earth

AR – Analar reagent grade

ASTM – American society for Testing and Materials

AV – Acid value

Bat – Batch

B100 – Pure biodiesel

bhp – Brake horse power

B.P – Brake Power

CEN – European Committee for standardization

CFPP – Cold filter plugging point

CP – Cloud Point

cSt – Centistokes viscosity unit

DG – Diacylglycerol

DIN V 56106 Germany standard specifications for pure biodiesel

EN 14214 – European standard specifications for pure biodiesel

FAME – Fatty acid methyl ester

F test – Returns the result of two –tailed probability of the Analysis of Variances (ANOVA),

Kpa – Kilopascals

KS 1309-03 – Kenya Standard specifications for Petroleum products

Lb – pounds

MG - Monoacylglycerol

mm^2/s – millimeters squared per second, (viscosity unit)

NO$_x$ – Oxides of nitrogen

ppm – Parts per million

Rpm – Revolutions per minute

RVOB–Refined vegetable oil biodiesel

SVO – Straight vegetable oil

TG – Triacylglycerol

WVOB – Waste vegetable oil biodiesel

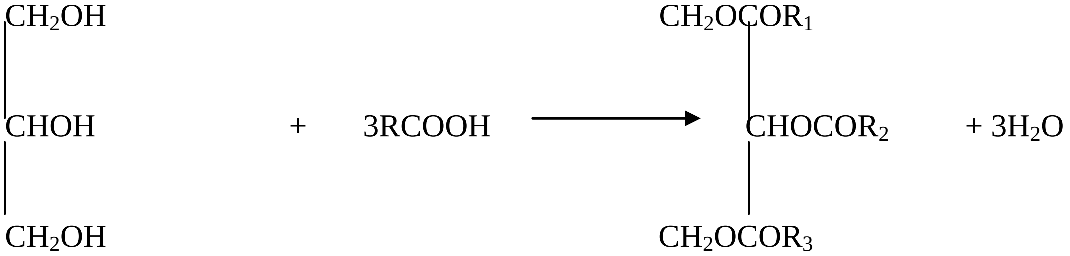
CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

1.1.1 Oils and fats

Many vegetable oils and some animal fats are “drying” or “semi-drying” and it is such property that makes many oils such as linseed, tung and some fish oils suitable as the base of paints and other coatings. It is also this property that further restricts their use as fuels. Fats and oils occur naturally and widely in nature in both animals and plants (Vicente *et al.,* 2007). Fat is a solid at room temperature while oil is a liquid. They are a mixture of glycerides of various fatty acids and commonly known as triaclyglycerols or simply triglycerides. These are formed by the reactions of three molecules of fatty acids with one molecule of glycerol to yield one molecule of triaclyglycerol and three molecules of water as given below (Patterson, 1989).



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH \longrightarrow \begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + 3H_2O \qquad (1)$$

Glycerol Fatty acids Triglyceride Water

Where R_1, R_2, R_3 – are long chain fatty acids and may be the same or different.

1.1.2 Biodiesel as fuel

Biodiesel as a fuel is comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. In this context, it can be used in diesel engines and heating systems (Marchetti *et al*., 2007). Biodiesel has clear advantages in comparison with conventional diesel fuel. It is a renewable fuel, constituting a supplement to petroleum-based diesel fuel. This, in turn implies less dependence on crude oil foreign imports. More-over, it has a favourable energy balance (Pereira and Mudge, 2004) and it is also non-toxic, biodegradable and has a low emission profile (cleaner engine emissions), all of which is better for environmentally pollution prone areas (large cities, mines and lakes). In addition, biodiesel is virtually compatible with commercial diesel engines and practically no engine modifications are required. Biodiesel also has superior lubricating property (Issariyakul *et al.,* 2007).

Three main processing techniques used to convert vegetable oils and animal fats to fuel form include pyrolysis, micro emulsification and transesterification (Ranganathan *et al*., 2008). Pyrolysis refers to chemical change caused by application of heat in absence of air or oxygen to get simpler compounds from complex compound. The process is also known as cracking. especially for hydrocarbons. Vegetable oils can be cracked to reduce viscosity and improve cetane number of resulting biodiesel fuel. The products of cracking are alkanes, alkenes, and carboxylic acids. Vegetable oils from soya bean, rape seed and cotton seed have been successfully cracked with appropriate catalysts to get biodiesel (Ma and Hanna 1999; Shi and Bao, 2008). By using pyrolysis technique good flow characteristics are achieved due to reduction in viscosity. The disadvantages of this process are the high cost of equipment and a separate distillation equipment to remove various fractions. Also the product obtained is similar to gasoline as it contains sulphur and this makes it less environmental friendly (Amigan *et al*., 2008).

Micro emulsification is another technique that has been used to produce biodiesel. The components include diesel fuel, vegetable oil, alcohol, surfactants and cetane number improvers in suitable proportions (Ranganathan *et al*., 2008). Low molecular weight alcohols such as methanol, ethanol and iso-propanol are used as viscosity lowering additives while higher alcohols are used as surfactants and alkyl nitrates are applied as cetane improvers. The disadvantage of the micro-emulsification is that it is only for a short term gain. Because prolonged usage leads to problems like injector needle sticking, carbon deposits formation and incomplete combustion.

The most common way to produce biodiesel is by transesterification in which triacylglycerols as the main components of vegetable oils, react with an alcohol in the presence of a catalyst to produce biodiesel and glycerol as the by-product. The stoichiometry of methanolysis reaction requires 3 moles of methanol and 1 mole of triglyceride to give 3 moles of fatty acid methyl ester (biodiesel) and 1 mole of glycerol (Kemp, 2006). The biodiesel obtained by transesterification process is a mixture of monoalkyl esters of higher fatty acids (fatty acid methyl ester-FAME, or ethyl ester). The high viscosity component glycerol is removed and hence the product has low viscosity like the conventional diesel fuel and so can be used as a supplement to fossil diesel in diesel engines without modification (Gumus, 2008).

Transesterification reaction can be catalyzed by alkali, mineral acid, lipase enzymes, heterogeneous catalysts or using alcohols in their supercritical state (Kumar and Sharma, 2008).

In the alkali process, sodium hydroxide, potassium hydroxide or their methoxides may be used along with methanol as the alcohol. Alkali process is the most efficient, cost-effective and least corrosive. There may be risk of free fatty acids or water contamination and soap formation due to competing hydrolysis reaction. Saponification reaction is shown in equation 2. This undesirable reaction reduces the ester yields and considerably makes it difficult to recover the glycerol due to the formation of emulsion. Use of potassium carbonate catalyst may offer some solution as it forms bicarbonate which does not hydrolyze the esters (Encinar *et al*., 2007). The reaction is given in equation 3. Saponification reaction**:**

$$\underset{\text{Free fatty acid}}{RCOOH} + \underset{\text{Sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{Salt}}{RCOO^-Na^+} + \underset{\text{Water}}{H_2O} \qquad (2)$$

Potassium carbonate catalyst:

$$K_2CO_3 + R'OH \rightleftharpoons R'OK + KHCO_3 \qquad (3)$$

Where:

R = carbon chain of the fatty acid.

R’ = alkyl group of the alcohol.

Base catalyzed transesterification reaction is the most popular method used in commercial industries for biodiesel production due to the above advantages. Acid catalysis is not used due to corrosive nature of the acids which may cause damage to the equipment and also the rate of reaction is too low. Enzymes may be immobilized in a suitable support for use as catalyst. But they are expensive to produce in bulk and also there is risk of inhibition when methanol is used. At the same time the rate of reaction is low (Shimada *et al*., 2002). Hence commercial application is a problem and research studies are going on. The problem with heterogeneous catalysts such as amorphous zirconia, titanium, aluminium and potassium doped zirconias include exhaustion of catalysts and low conversions to biodiesel hence not applied commercially

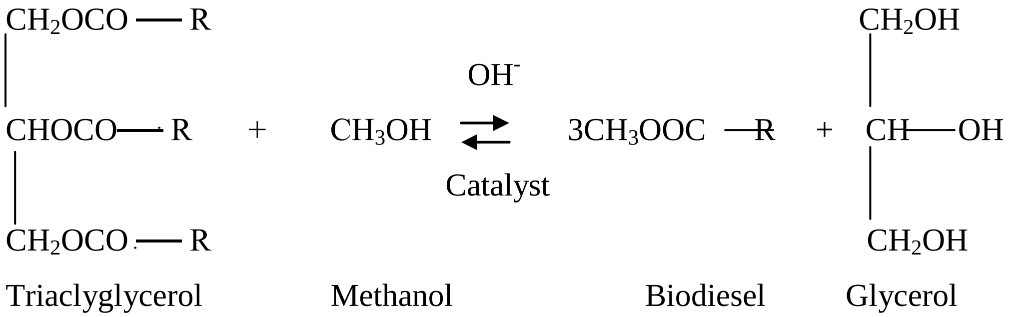
(Hama *et al*., 2004). Use of alcohols at supercritical state requires high temperature and pressure equipment which are expensive and also at high temperature above 400°C there is risk of thermal decomposition of esters. The method is still under experimental stage.

Transesterification reaction consists of three consecutive reversible reactions with intermediate formation of diglycerides and monoglycerides as shown below. The products of the reactions are the bio-diesel and glycerol.

$$\text{Triaclyglycerol (TG)} + \text{R'OH} \rightleftharpoons \text{Diglycerides (DG)} + \text{R'COOR}_1 \qquad (4)$$

$$\text{Diglycerides (DG)} + \text{R'OH} \rightleftharpoons \text{Monoglycerides (MG)} + \text{R'COOR}_2 \qquad (5)$$

$$\text{Monoglycerides (MG)} + \text{R'OH} \rightleftharpoons \text{Glycerol (GL)} + \text{R'COOR}_3 \qquad (6)$$



$$\begin{array}{l} CH_2OCO-R \\ | \\ CHOCO-R \\ | \\ CH_2OCO-R \end{array} + CH_3OH \underset{\text{Catalyst}}{\overset{OH^-}{\rightleftharpoons}} 3CH_3OOC-R + \begin{array}{l} CH_2OH \\ | \\ CH-OH \\ | \\ CH_2OH \end{array} \qquad (7)$$

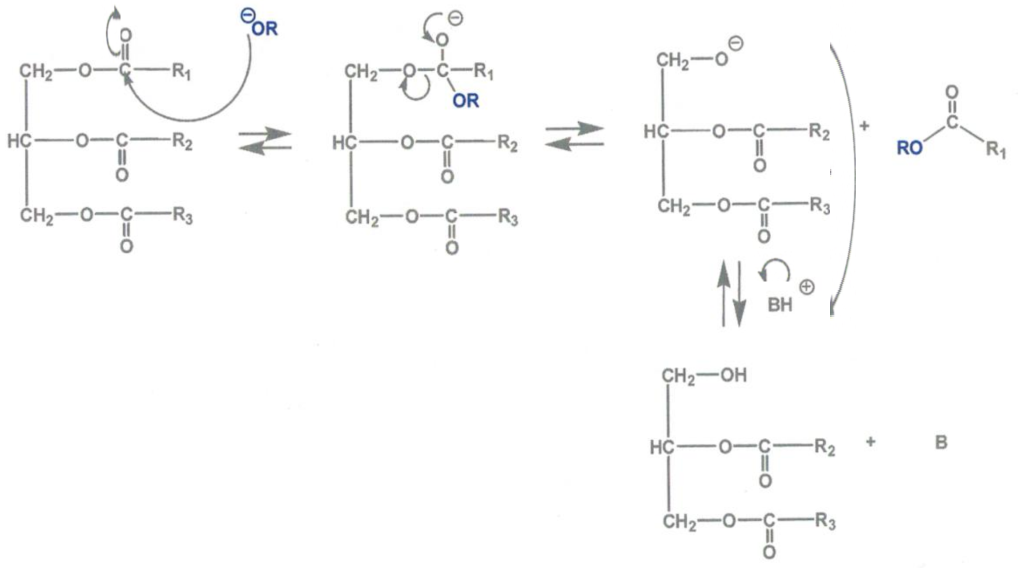
Where:

R_1, R_2, R_3 are carbon chain of the fatty acids.

R' = alkyl group of the alcohol.

The variables affecting transesterification reaction include alcohol to oil ratio, catalyst type and concentration, reaction temperature, time of the reaction and rate of agitation. The alcohol to vegetable oil molar ratio that should be used varies from N = 1:1 to 6:1. (Refaat, *et al.,* 2007). However, a molar ratio of 6:1 chosen as it is the most common ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The alcohol chosen for this work is methanol since it is cheap, readily available and commonly used for biodiesel production. Catalyst concentration levels greater than 1% may favour the backward reaction since transesterification is an equilibrium reaction and hence reversible. The reaction can occur even at room temperature. However, higher temperatures increases the rate of the reaction and thus reduces the time to reach equilibrium and for that reason the temperature range should be from 25°C to 120°C. Sodium hydroxide catalyst is chosen for this work because it is readily available and cheap compared to potassium hydroxide. Rate of agitation is also important since transesterification reaction can only occur in the interfacial region between the liquids and also due to the fact that fats and alcohols are not totally miscible. The reaction is a relatively slow process and a vigorous mixing is required to increase the area of contact between the two immiscible liquids. The time of reaction may range from 30 minutes to 8 hours depending on the feedstock used and the type of base. Acid catalyzed reaction is generally a slow process and may take 8 or more hours, compared to base catalyzed reaction which is faster. Base catalyzed transesterification reaction mechanism is given below.

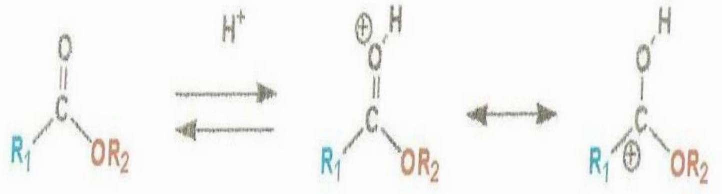
(8)



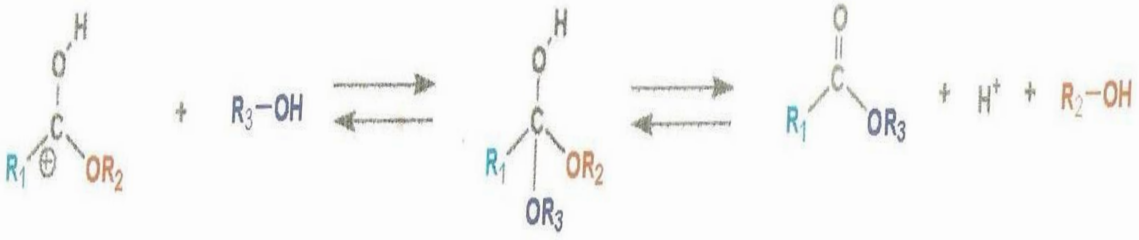
(9)

In this reversible transesterification reaction an excess of alcohol (R’OH), is usually used to drive the reaction towards the formation of the desired biodiesel product. The first step is the reaction of the base (B), with the alcohol (ROH), producing an alkoxide (RO^-) and the protonated base (BH^+). The nucleophile (RO^-) attacks the carbonyl group of the triacylglycerol to generate a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglycerides are formed. The latter deprotonates the catalyst thus regenerating the active species which is now able to react with a second molecule of the alcohol starting another catalytic cycle. Diglycerides and monoglycerides are similarly converted by the same reaction scheme to form a mixture of alkyl esters and glycerol as the by-product (Bunkyakiat and Kunchana, 2006).

This type of reaction has several limitations. RO^- has to fit in the space where there is a slight positive charge on the C=O. So methanol radical (MeO^-), works well because it is small. As the alkyl group (R), on the nucleophile radical RO^- gets bigger, reaction rates decrease. This effect is called steric hindrance. That is why methanol and ethanol are typically used for transesterification reaction (Vera *et al*., 2005). Acid catalyzed transesterification reaction mechanism is given in equation 10 and 11 (Vera *et al*., 2005).



(10)



(11)

The acid catalyzed transesterification reaction for a monoglyceride, is given above but can be extended to di-and triglyacylglycerols. The protonation of the carbonyl group of the ester leads to the carbocation. After nucleophilic attack of the esters, tetrahedral intermediate is produced which eliminates glycerol to form a new ester and a catalyst regenerated (H^+).

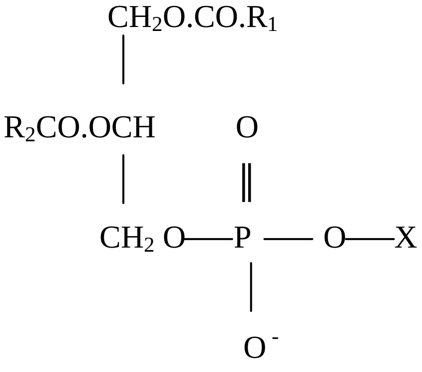
Simple triaclyglycerols are made up of fatty acids with a chain length greater than 12 carbon atoms. The vast majority of these fatty acids are made up of 16 and 18 carbon atoms (Shah and Gupta, 2007). Most physical and chemical properties result from the various fatty acids esterified with glycerol because the fatty acid portion of the triaclyglycerols make the greatest portion (90%) while the glycerol is only 10%. The chemical structures of triaclyglycerols are very complex due to the combination and permutations of the fatty acids that can be esterified at the three-enzymatically non-equivalent hydroxyl groups of glycerol (Weiss, 1992).

1.1.3 Saturated versus unsaturated fatty acids

Saturated fatty acids are the most stable fatty acids and whether in the free state or combined in triaclyglycerols, they pack together more easily when solid because of their regular contour. Thus they have higher melting points than the unsaturated fatty acids. The most common saturated fatty acids include palmitic (C16), stearic (C18) and lauric (C12), although naturally occurring examples with chains up to 32 carbon atoms in length have been discovered (Marjorie and Ada, 1990).

Experience has shown that the use of unsaturated triacylglycerol oils as fuel may cause significant problems that can affect the viability of their fuel use. The main problem is the high viscosity of the triglyceride oils and their chemical instability (Al-Widyan and Al-Shyoukh, 2002). They can cause difficulties in starting engines in cold conditions and formation of deposits on injectors (Geller *et al*., 1999). The viscosity of plant and animal fats and oils varies from hard crystalline solids to light oils at room temperature. In most cases, these oils or fats are actually a complex mixture of various fatty acid triglycerides, often with the various components having widely varying melting points. This may give the oil or fat a temperature range over which solidification occurs, with the oil gradually thickening from a thin liquid, through to a thick liquid, then a semi-solid and finally to a solid (Angelo, 1992). Drying of oils results from the double bonds (and sometimes triple bonds) in the unsaturated oil molecules being broken by atmospheric oxygen and being converted to peroxides. Cross-linking at this site can then occur and the oil irreversibly polymerizes into a plastic-like solid. In high temperature commonly found in the internal combustion engines, the process is accelerated and the engine can quickly become gummed-up with the polymerized oil (Goodrum *et al*., 2005).

Transesterifying waste vegetable oil to convert it to biodiesel is expected to give biodiesel with desirable properties such as high lubricity (Dmytryshyn *et al*., 2004). Monounsaturated fatty acids have double bonds that are potential centres of chemical reaction and hence disruption. Up to five or six double bonds are found in the longer chains of naturally occurring unsaturated fatty acids. Since the double bonds introduce an uneven feature into the chains they pack together less easily, depressing the melting point. The most common unsaturated fatty acid, oleic acid, contains 18 carbon atoms and one double bond between carbon atoms 9 and 10, counting in the usual way from the carboxyl end of the chain as number one (Allen *et al*., 1994). Polyunsaturated fatty acids contain two or more carbon-carbon double bonds within the hydrocarbon chain. The most common and most important examples are linoleic acid and linolenic acid (Robbelen *et al*., 1989). Crude vegetable oils also contain small amounts of phospholipids and glycolipids. These are undesirable in the biodiesel production and so are removed through degummimg of the raw oil. The phospholipids are chemically characterized by having a polar group, consisting of phosphate joined to either choline, ethanolamine, or serine, attached to position 1 of the glycerol backbone and one or generally two acyl groups esterified to positions 2 and 3 (Bournay *et al*., 2005). This is shown below. When X is serine the compound is called phosphatidylserine. Similarly when X is choline or ethanolamine, it is termed phosphatidylcholine or phosphatidylethanolamine. The general structure of some phospholipids is given in equation 12.



$$\begin{array}{llllll} & CH_2O.CO.R_1 & & & & \\ & | & & & & \\ R_2CO.OCH & & O & & & \\ & | & \| & & & \\ & CH_2\,O - & P & - & O - & X \\ & & | & & & \\ & & O^- & & & \end{array} \qquad (12)$$

R_1 and R_2 represent long chain fatty acids.

Waste edible oils and fats pose significant disposal problems in many parts of the world. In the past much of these waste products have been used in the production of animal feeds. However, due to possible links between a disease such as mud cow disease and this practice, the use of waste edible animal fats for animal feed is not as common as it once was, resulting in disposal problems. In Australia such wastes have been used in the production of animal feeds (Park *et al*., 2007). Since it is often difficult to prevent the contamination of waste vegetable oils with animal products during cooking, waste vegetable oil often must be treated in a similar manner as would waste animal fats.

1.2 Chemical composition of petroleum based diesel fuel

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including normal, iso, and cyclo-paraffins), and 25% aromatic hydrocarbons such as naphthalenes and alkyl benzenes (Arzamendi *et al*., 2007). The average chemical formula for common diesel fuel is $C_{12}H_{26}$, ranging from approximately $C_{10}H_{22}$ to $C_{15}H_{32}$. Diesel is produced from petroleum, and is sometimes called petro-diesel when there is a need to distinguish it from diesel obtained from other sources like bio-diesel derived from pure vegetable oil or recycled waste vegetable oil (WVO). As a hydrocarbon mixture, diesel is obtained in the fractional distillation of crude oil between 250 and $350^{\circ}C$ at atmospheric pressure. The density of diesel is about 850 Kg/m^3 whereas petrol has a density of about 720 Kg/m^3 about 15% less. When burnt, diesel typically releases about 40.9 MJ/kg while petrol releases 34.8 MJ/kg also about 15% less (Addison, 2006). Diesel fuel contains higher quantity of sulphur. High level of sulphur in diesel is harmful for the environment. It prevents the use of catalytic diesel particulate filters to control diesel particulate emissions. However, lowering sulphur also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Biodiesel as diesel additive can turn out to be effective lubricant (Gerhard and Gerpen, 2005).

1.3 Statement of the problem

Fossil diesel is getting depleted and thus there is need to develop renewable and sustainable fuel sources. The price of edible plant oil is usually higher than that of fossil diesel, making biodiesel production from edible oil very expensive and not sustainable. Using cheap waste vegetable oil as alternative biodiesel feedstock would reduce the cost of production of biodiesel and add value since edible oil as feedstock is costly. Presently waste vegetable oil is discarded into sewage systems, causing pollution in water ways and thus add to the cost of treating effluent. Producing biodiesel from waste vegetable oil is expected to be cost-effective and environmentally beneficial since it provides a cleaner way for disposal of waste. Over-use of waste vegetable oil causes distaste in consumer preference in the food outlets. Transesterifying such waste vegetable oil for use as biodiesel would reduce health problems like stomach-ache and cancerous compounds produced in the oxidation of lipids that may be caused by its over-use.

1.4 Hypotheses

i. Fabricated transesterification reactor is suitable for biodiesel production.

ii. Biodiesel prepared from waste vegetable oil as feed stock has low viscosity and high volatility.

iii. The performance of waste vegetable oil biodiesel in diesel engine in terms of fuel Consumption and thermal efficiency is not different from that of fossil diesel.

1.5 Objectives

1.5.1 Main objective

To add value to waste vegetable oil by converting it to biodiesel for use as diesel fuel supplement and help reduce the cost of fuel and lower environmental pollution.

1.5.2 Specific objectives

i. To fabricate a transesterification batch reactor for production of Biodiesel.

ii. To prepare biodiesel from waste vegetable oil and refined vegetable oil.

iii To determine operating combustion conditions for waste vegetable oil biodiesel.

iv. To carry out chemical and physical tests on waste vegetable oil biodiesel and compare the results with those of refined vegetable oil biodiesel and conventional diesel.

v. To compare the rate of waste vegetable oil biodiesel consumption and thermal efficiency with that of fossil diesel in a diesel engine.

1.6 Justification

The world is faced with challenges of minimizing emission of green house gases and other pollutants as well as overcoming the shortage of power supply. There is thus need to develop alternative cost-effective biodiesel feedstock in form of waste vegetable oil and animal fat that are capable of powering everyday life without bringing harmful environmental changes. The fact that biodiesel does not contain polycyclic aromatic hydrocarbons and has a high flash-point makes it a safe alternative fuel to handle, store and transport (Amigan, *et al.*, 2008).Reducing fuel viscosity by methyl or ethyl ester formation to improve injector performance will be a partial solution to some of the diesel engine fouling problems, so evident when vegetable oils are used as supplement to diesel fuel. Production of biodiesel from waste oils or wild seed crops would not compete with food uses of edible oils and thus there would be value addition. Kenya's expenditure on oil and imports of other petroleum products is continuously increasing owing to high price of crude oil in the global market. The country spends about 40% of its annual foreign exchange earnings on such products, and this strengthens the need to venture into cheaper and cleaner biofuels. Biodiesel which is renewable, biodegradable and domestically produced has a potential of proving a solution by reducing the country's dependence on foreign oil imports. Conversion of waste oils and fats to biodiesel has environmental advantages such as sustainability or enhancing production by use of non-edible oil crops. Significant reduction in Green house gas emissions to the level of 41% with biodiesel can be achieved compared with burning traditional fossil fuel (Demirbas, 2007). Biodiesel fuel releases carbon dioxide (the major culprit in global warming), that was once used in photosynthesis while the plant oil was growing and so the net carbon dioxide emission to the atmosphere is zero, as the level of carbon-dioxide is maintained (Gumus,2008).

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Classification of oils

2.1.1 Fixed oils

Fixed oils as a class of vegetable oil are dominantly obtained from animal and plants and they are glycerides of monobasic organic acids (fatty acids). The group is mainly used in food industry since it is consumable by human beings and animals. It can further be classified according to the degree of saturation of the fatty acids attached to the glycerol molecule backbone. Saturated fatty acids have single bonds between the carbon chains and are fairly straight and packed closely together. This is why they are solids at room temperature The structural formula of stearic acid (C18:0), is shown in equation 13.

$$CH_3(CH_2)_{16}COOH \qquad (13)$$

Non-drying oils are those that do not absorb oxygen from the air nor do they dry up to form a skin. Their iodine value is low usually less than 100. Examples are coconut oil, palm oil and castor oil (Swern, 1979). Semi-drying oils contain intermediate proportion of unsaturated acids with one or two double bonds. Examples are oleic and linoleic acids. They absorb oxygen from the atmosphere slowly and thicken after sometime, but do not dry up. Their iodine value is between 94 and 140. Examples include sesame oil, corn oil, cotton seed oil or mustard oil (Engler *et al*., 1983). The single double bond in oleic acid occurs between carbon number 9 and 10 and has a cis configuration. The Structural formula of oleic acid is shown in equation 14.

$$CH_3(CH_2)_7CH{=}CH(CH)_7COOH \text{ (cis)} \qquad (14)$$

. Drying oils are mainly composed of unsaturated fatty acids especially those that contain more than two double bonds such as linolenic acid. They absorb oxygen from the air and dry up to form a hard skin (Ryan *et al*., 1984). From a chemical point of view, good oil for biodiesel production should be rich in long chain and low unsaturation level fatty acids for improved oxidative stability, since polyunsaturated fatty acids are more prone to auto-oxidation (Vincente *et al* ., 2007). The two double bonds in linoleic acid occur at carbon position number 9 and 12 respectively and are both cis in configuration. It is referred to as polyunsaturated fatty acid since it possesses two double bonds. The structural formula of linoleic acid is given in equation 15.

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (cis). (15)

Linolenic acid has three double bonds along the carbon chain occurring at position 9, 12 and 15 and thus does not pack closely together. This is why unsaturated fat is liquid at room temperature (Gumus, 2008). The melting points of polyunsaturated fatty acids such as linoleic and linolenic are all very low. The structural formula of linolenic acid is shown in equation16.

$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CH\,(CH_2)_4COOH$ (cis) (16)

2.2 Other types of oils

2.2.1 Essential oils

These are volatile oils that are odorous and equally obtained from various plants and animals. They may contain esters and even unsaturated alcohols such as citronellol and Linalol They are used mostly in the pharmaceutical and Cosmetic industries and not suitable for biodiesel production (Asiedu, 1989).

2.2.2 Mineral oils

They are obtained from crude petroleum oil by distillation and are saturated hydrocarbons or paraffins having 5 to 30 carbon atoms (Weiss, 1992).

2.3 Sources of vegetable oils

Vegetable oils may be edible or non-edible. Edible oils include coconut oil, cotton seed oil, groundnut, sesame, soybean, sunflower, corn, palm oil, rapeseed oil, avocado oil and many others. The common non-edible oils include Jatropha and castor (Ulberth and Roubicek, 1993). Some oils like jatropha and croton seed oils are not edible because they contain toxic phorbic acid.

2.4 Straight vegetable oil (SVO) as fuel

The first known use of vegetable oil as fuel for a diesel engine was a demonstration of an engine built by the Otto Company and designed to burn mineral oil which was run off of pure peanut oil at the 1900 World fair in Paris (Nabi *et al*., 2006). When Rudolf Diesel invented the diesel engine he designed it to run on peanut oil, but later it was operated on cheaper petroleum oil (Zang *et al*., 2007). In 1912 presentation to the British Institute of Mechanical Engineers, he cited a number of efforts in this area and remarked, ‘‘The fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now” (Tahir *et al.*, 1981). Periodic petroleum shortages spurred research into vegetable oil as a diesel substitute during the 30s and 40s and again in the 70s and early 80s when straight vegetable oil (SVO) enjoyed its highest level of scientific interest. The 70s also saw the formation of the first commercial enterprise that allowed consumers to run on straight vegetable oil in their automobiles (German *et al*., 1985). In the 1900s Bougainville conflict, islanders cut off from oil supplies due to a blockade used coconut oil to fuel their vehicles (Haas *et al*., 2006). While engineers and enthusiasts have been experimenting with used vegetable oils as fuel for a diesel engine since 1900, in all the literature, only one peer reviewed study exists that compares long term use of vegetable oil and conventional diesel as fuels which shows no noticeable difference in rate of deterioration of the engine burning vegetable oil, for one particular model of engine (German Deutz F31912W; Barsic and Humke, 1981). Most diesel engines are suitable for use of SVO with suitable modifications. Principally, the viscosity of the SVO must be reduced by preheating it, typically by using heat from the engine or electricity, otherwise poor atomization, incomplete combustion and carbonization may result (Zhang *et al*., 2007). One common solution is to add an additional fuel tank for “normal” diesel fuel (diesel or bio-diesel) and three way valve to switch between this additional tank and the main tank of SVO (Ghadge and Rutherman, 2006). Thus the engine is started on diesel, switched over to vegetable oil as soon as it is warmed up and switched back to diesel shortly before being switched off to ensure it has no vegetable oil in the engine or fuel lines when it is started from cold again. Production of vegetable oils for fuel use is theoretically limited only by the agricultural capacity of a given economy (Fuls, 1983). Despite being energetically favourable, direct use of straight vegetable oils in fuel engines is problematic. Due to the high viscosity (about 11 to 17 times higher than diesel fuel), and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Further more, acrolein (a highly toxic substance), is formed through thermal decomposition of glycerol (Nabi *et al*., 2006).

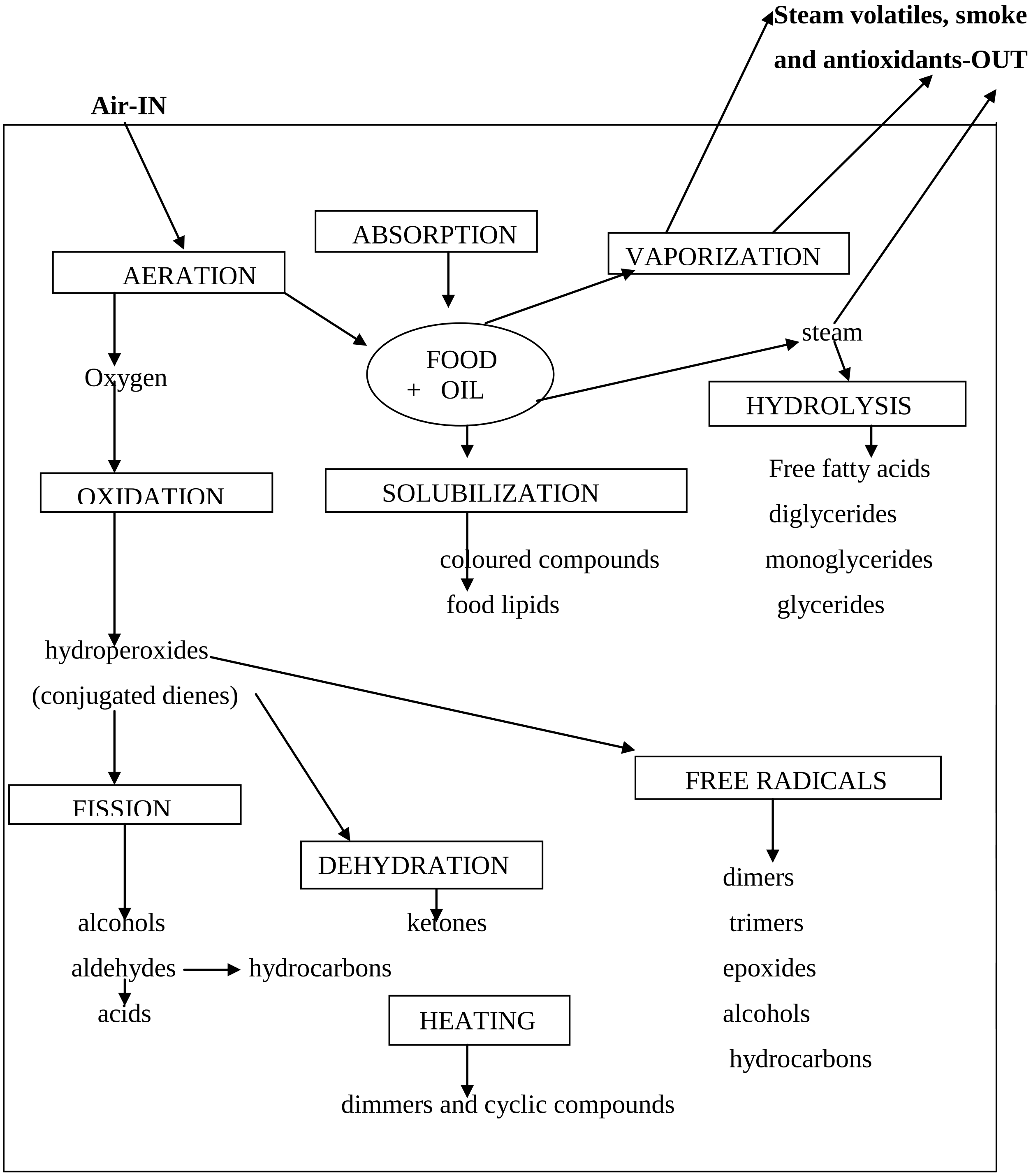
2.5 Waste vegetable oil (WVO) as fuel

One possibility for the disposal of waste triacylglycerol oils from used cooking oils or that derived from activated bleaching earth (ABE), is as a fuel for transport or other industrial uses (Calais and Clark, 2007). Waste vegetable oils from ABE obtained from oil processing industries are disposed as a waste in dumping sites or even in sewers (Park *et al*., 2007). Conversion of waste vegetable oils and animal fats to biodiesel has some environmental advantages such as recycling of already existing carbons in the atmosphere. Thus life-cycle CO_2 emissions are substantially reduced (Lopez *et al.*, 2007). Waste oil contains no sulphur so SO_2 emissions are not present when running on biodiesel. Oxides of nitrogen (NO_x) emissions would most likely be similar or slightly elevated say by 10% as compared to fossil fuels. There is high prospect of biodiesel production from waste vegetable oil triglycerides. Oils including vegetable oils and animal fats are principally triglycerides formed from glycerol and higher fatty acids (C_{12}-C_{22}) such as lauric, myristic, palmitic stearic, oleic, linoleic and lenolenic acids (Barnwal and Sharma, 2005).

A variety of plants can be used to produce bio-diesel. These include rape-seed mainly in the European Union and, soybean and corn in the United States. Other biodiesel feed stocks include mustard, flax, Canola, sunflower, hemp, jatropha and even algae grown on sewage sludge show promise. Waste vegetable oils, animal fats and also grease waste can be used (Miao and Qingyu, 2006). A company in New Zealand has successfully developed a system for using sewage waste as a substrate for algae and then producing bio-diesel from the waste (Demirbas, 2007). Worldwide production of vegetable oils and animal fats is not yet sufficient to replace liquid fossil fuel use (Schoedder, 1981). Furthermore, some environmental groups object to the vast amount of farming and the resulting over-fertilization, pesticide use and land use conversion to that they say would be needed to produce the additional vegetable oil. This calls for cheaper alternative sources such as waste vegetable oils (Pizzaro and Park, 2007). Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel. However, the available quantities are far less than those of petroleum based fuel that is burned for transportation and home heating in the world. Waste vegetable oils can be collected from a wide variety of catering establishments and oil processing factories and refined then converted into biodiesel (Beer *et al.*, 2001).

2.6 Conversion of vegetable oil to biodiesel

Biodiesel is a monoalkyl ester of long chain fatty acids derived from vegetable oils or animal fats, for use in the compression ignition diesel engines. Biodiesel has some clear advantages over straight vegetable oils. It works in any diesel engine without any conversion or modifications to the engine or the fuel system. It also has better cold-weather properties than SVO, but not as good as petro-diesel. Biodiesel is safe, biodegradable and reduces air pollutants such as particulates, carbon monoxide and hydrocarbon (Felizardo *et al*., 2007). Blends of 20 percent biodiesel with 80 percent diesel (B20), can be used in unmodified diesel engines. It can also be used in its pure form referred to as B100, but may require certain engine modifications to avoid maintenance and performance problems (Addison, 2006). The biodiesel process turns the oils and fats into esters separating out the glycerol. The process is called transesterification, which substitutes alcohol for the glycerol in a reaction, using caustic soda or potash as a catalyst (Ferrari *et al*., 2005). The alcohol used can either be pure methanol which makes methyl ester or absolute ethanol (ethyl ester). Transesterifying triglyceride oils and fats largely eliminates the tendency of the oils and fats to undergo polymerization and auto-oxidation as well as reducing the viscosity of the oil to about the same as petroleum diesel fuel (Bruwer *et al*., 1981). Biodiesel has shelf life of about six months to one year if kept in tightly closed containers. Biodiesel can react with oxygen from the air to form acids, hydrocarbons and polymers.



Source: Adapted from Marjorie and Ada (1990).

Figure 1. Changes occurring during deep-fat frying

The chemical and physical events that occur during frying are summarized in (Figure 1). Fat gets absorbed by the food being fried. The availability of water affects the rate of hydrolytic degradation. The degradation results in the formation of free fatty acids, diglycerides, monoglycerides and glycerides. Smoking during deep-fat frying gives out steam volatiles and antioxidants through vaporization. Frying fat gradually absorbs oxygen from the air (aeration), and oxidizes as food is cooked thereby forming hydro-peroxides, and conjugated dienes. These in turn through fission activity gives out alcohols, aldehydes, acids and hydrocarbons. The presence of free radicals results in formation of dimmers, trimers, epoxides, alcohols, hydrocarbons and cyclic compounds through polymerization. Dehydration of the oil gives out ketones and hydrocarbons in the cooking process. Solubilization results in coloured compounds and food lipids which can under-go further changes. Thus, in addition to the degradation associated with smoking, frying fat gradually oxidizes, polymerizes, and increases in viscosity and the tendency to foam. Changes in sensory quality, functional properties, and nutritional value accompany the chemical changes as well (Kusdiana and Saka, 2004). Some people do use frying oils again and again and this may lead to adverse health effects such as stomach-ache and cancerous compounds produced in the oxidation of lipids due to spoiled oil or rancidity. From literature studies oil is considered over used when it contains about 20% polymeric materials. This can be avoided by recycling such waste vegetable oil as feedstock for producing biodiesel fuel.

2.7 Problems of straight vegetable oil as potential fuel sources

Sunflower oil was tested as a replacement for diesel fuel in agricultural tractors. Sunflower oil viscosity was 14% higher than that of diesel at 37°C. Engine performance using the sunflower oil was similar to that of diesel fuel, but with a slight decrease in fuel economy. Oxidation of the sunflower oil left heavy gum and wax deposits on test equipment, which could lead to engine failure (Tahir *et al*., 1981).

Auld *et al*., (1982), used rapeseed oil to study the effects of using alternative fuel in diesel engines. An analysis of the rapeseed oil showed a relationship between viscosity and fatty acid chain length. Engine power and torque results using rapeseed oil were similar to that of diesel fuel. Results of the short-term test indicated further long-term testing was needed to evaluate engine durability when rapeseed oil was used.

Bettis *et al*., (1984) evaluated sunflower, safflower and rapeseed oils as possible sources of liquid fuels. The vegetable oils were found to contain 94% to 95% of the energy content of diesel fuel, and to be approximately 15 times as viscous. Short-term tests indicated that for the vegetable oils power out-put was nearly equivalent to that of diesel fuel, but long-term durability tests indicated severe problems due to carbonization of the combustion chamber. Pryde, (1985), reviewed the reported successes and short-comings for alternative fuel research. This article stated that short–term engine tests using vegetable oils as a fuel source were very promising. However, long-term engine test results showed that durability problems were encountered with vegetable oils because of carbon build-up and lubricating oil contamination. Thus, it was concluded that raw vegetable oils must either be chemically altered or blended with diesel fuel to prevent premature engine failure.

2.8 Straight vegetable oil (SVO) and diesel blends as potential fuel sources

Research has shown that using the crude (raw) form of vegetable oils or even blends of the latter and diesel fuel works only for urgent short-term engine operation. Even then, major problems in engine operation are reported mainly due to the vegetable oil high viscosity and low volatility compared to diesel fuel (Karhale *et al.,* 2008).

Vegetable oil fuel blends of varying percentages refer to fuels of which raw vegetable oils have been mixed at the indicated percentage with conventional diesel fuel on a volume basis. Studies in New Zealand by Simis *et al*., (1981) indicated that vegetable oils particularly rapeseed oil, could be used as a replacement for diesel fuel. Their initial short-term engine tests showed that a 50% vegetable oil fuel blend had no adverse effects. While in long-term tests they encountered injector pump failure and cold starting problems. Carbon deposits on combustion chamber components were found to be approximately the same as that found in engines operated on 100% diesel fuel. These researchers concluded that rapeseed oil had great potential as a fuel substitute but further testing was required.

A research done by International Harvester Company (Fort and Blumberg, 1982) reported that cottonseed oil, diesel fuel blends behaved like petroleum-based fuels in short-term performance and emissions tests. The experimental fuels performed reasonably well when standards of judgment were power, fuel consumption, and emissions. However, engine durability was an issue during extended use of these fuel blends because of carbon deposits and fueling system problems. This is also confirmed by Tyson (2001). Other research at International Harvester Company (Baranescu and Lusco, 1985) was done using three blends of sunflower oil and diesel fuel. Results indicated that the sunflower oil caused premature engine failure due to carbon build-up. It was noted that cold weather operation caused fuel system malfunctions. There was mixed results by Wagner and Peterson (1983), when using rapeseed oil as a substitute fuel. Attempts to heat the oil fuel mixture prior to combustion exhibited no measurable improvement in fuel injection. Severe engine damage was noted during short-term engine testing due to the use of rapeseed oil. A long-term test using a 70% rapeseed, diesel blend was successful for 850 hours with no apparent signs of wear, lubricating oil contamination or loss of power (Tickell and Kaia, 1999). Engine testing by Ziejewski and Kaufman (1982), at Allis Chalmers company using a 50/50 blend of sunflower oil and diesel fuel was unsuccessful. Carbon build-up on the injectors, intake ports and piston rings caused engine operating difficulties and eventual catastrophic failure.

Sapaun *et al*., (1996), reported that studies in Malaysia with palm oil as diesel fuel substitute, exhibited encouraging results. Performance tests indicated that power out-puts were nearly the same for palm oil, blends of palm oil and diesel fuel, and 100% diesel fuel. Short-term tests using palm oil fuels showed no signs of adverse combustion chamber wear, increase in carbon deposits or lubricating oil contamination. In the literature cited production of biodiesel from soya beans and its use in the USA is growing rapidly in various states as a new energy economy fuel (Greg, 2005).

2.9 Future of biodiesel

Biodiesel has potential as renewable fuel. Fatty acid methyl ester (biodiesel) production from waste activated bleaching earth (ABE) discarded by the crude oil refining industry was investigated using fossil fuel as a solvent in the Lipase enzyme catalyzed esterification of triglycerides in a pilot plant. The result demonstrated a promising reutilization method for the production of fatty acid methyl ester (FAME), from industrial waste resources containing vegetable oils for use as a biodiesel fuel (Kojima *et al*., 2004). Production costs of biodiesel are high due to the high vegetable oil prices and some technological issues such as the large tracts of land required. In the European Union production of biodiesel is mainly from rape seed oil and may break even at petroleum prices around £ 60 per barrel (Demirbas, 2007). Sensitivity analyses of different processes for biodiesel production showed that plant capacity, the price of waste cooking oil and the selling price of biodiesel are the major factors affecting the economic feasibility of the biodiesel production (Zhang *et al*., 2007). In Taiwan commercial feasibility on utilizing spent bleaching earth as one of waste edible oil sources was demonstrated. Until then it was mostly disposed off to landfills or composted in soils without any efficient use (Tsai *et al*., 2007). Economics of Peanuts for Biodiesel Production was studied in Georgia, based on the biodiesel value of the oil and the value of the meal. It was concluded that the minimum input peanut production for biodiesel appeared far from feasible since the production was mainly for the edible oil market (Schumaker *et al*., 2007). In another study, Gumus, (2008), evaluated hazelnut kernel oil methyl ester and its blends with fossil diesel and concluded that it could be used as an alternative fuel in existing diesel engines without modification.

Biodiesel has a number of disadvantages which can be overcome. From literature studies biodiesel has a slight increase in nitrogen dioxide (NO_2), emissions over petroleum diesel especially by older diesel engines. These NO_2 emissions can be eliminated by the use of a catalytic converter. Biodiesel does not store well for periods of time. In cold climates biodiesel will separate, congeal and in general break down while in storage. Without preservatives biodiesel has shelf-life of 6 months, in ideal conditions. Biodiesel is subject to algae growth as water accelerates microbial growth and is naturally more prevalent in biodiesel fuels than in petroleum-based diesel fuels. Care must be taken to remove water from fuel tanks. A special algaecide for diesel can be added to the fuel to inhibit algae growth. Biodiesel has a higher viscosity and density than that of fossil diesel. This is not a problem in warm tropical climates but may cause problems in starting engines especially in cold climates. The problem is solved through the use of winterizing agents which are also used in petroleum diesel fuels.

The global biodiesel industry has grown significantly over the past decade. The European Union (EU), has arguably been the global leader in biodiesel production. The EU biodiesel production has more than doubled in the last two years, rising from 1.9 million L in 2004 to 4.9 million L in 2006 (Qiang *et al.,* 2008). Biodiesel production in the United States of America (USA), has also increased dramatically in the past few years. Production grew at a pace of 113 million gallons per year between 2004 and 2006. According to the USA National Biodiesel Board (NBB), there are 105 plants in operation as of early 2007 with an annual production capacity of 964 million gallons (Carriquiry, 2007; USA NBB). The global biodiesel market is estimated to reach 37 billion gallons by 2016, growing at an average annual growth of 42% (Sims, 2007). Africa has not been left behind. Projects across Africa aim to enhance bio-fuel production and use. In South Africa, finance minister Trevor Manuel proposed that the government provide incentives to boost synthetic-fuel and bio-fuel investments. In Nigeria, Lemna International and other companies recently signed contracts to build bio-fuel-production factories. Similar projects are underway in Swaziland. Also in November 2006, Senegal partnered with Brazil and India, to cooperate in bio-fuels production. In Malawi, the government put laws in place that require 5% of all fuel to be environmentally friendly bio-fuel. Despite the ongoing struggles, and the apparent distance of success, Kenya will keep pursuing the bio-fuel industry. It is a useful test bed for the agricultural, technological and environmental challenges that will face other developing countries intent on finding new sources of energy and income.

Table 1. Fatty acid composition of common vegetable and animal oils

Fat/ Oil	**Fatty acid composition (%)**								
	Octanoic 8:0	Decanoic 10:0	Lauric 12:	Myristic 14:0	Palmitic 16:	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3
Coconut oil	8	8	47	18	9	3	6	2	-
Palm Oil	-	-	-	1	45	4	40	10	-
Palm Kernel	8	4	48	16	8	3	15	2	-
Beef tallow	-	-	-	3	24	19	43	3	-
Lard	-	-	-	2	26	24	44	10	-
Cotton seed oil	-	-	-	1	22	3	19	54	-
Neem Seed oil	-	-	-	-	18	20	41	1	20
Rapeseed Oil (Spring)	-	-	-	-	4.4	1.8	59.8	20.6	11.1
Rapeseed oil (Winter)	-	-	-	-	3.2	1.1	14.8	12.7	-

Source: Bio-diesel by Frisby and Schumacher, (1990).

From **table 1** Coconut oil consists of short chain fatty acids mainly lauric acid and only with 6% oleic and 2% linoleic. It is classified as non-drying and saturated. The other oils follow the same trend. Neem seed oil contains unsaturated fatty acids with 41% oleic acid and 20% linolenic acid (Kirk and Sawyer, 1991). The main fatty acid content in cotton seed oil is linoleic acid 54%, followed by palmitic acid 22% and oleic 19%. While for spring rape seed oil the main fatty acid content is oleic acid 59.8%, followed by linoleic at 20.6%. These are the main fatty acid contents of common vegetable oils, edible and non-edible and animal fats that are used to make biodiesel fuel.

Table 2. Biodiesel properties

Oil	**Viscosity (cSt or mm^2/s)**	**Cloud Point (˙C)**	**Cetane No.**	**Heat Energy (MJ/kg)**	**Weight density (Kg/m^3)**
Soybean	35	- 4.4	38	39.7	920
Soy ester	5	0.11	45	40.2	910
Sunflower	33	-3.89	37	39.7	910
Sunflower ester	5	0.11	49	38.1	870
Canola	37	-4.4	37	39.8	910
Canola ester	6	10	54	40.5	870
Crambe	54	10	44	40.5	890
Diesel	3	-15	47	40.7	850

Source: Bio-diesel by Frisby and Schumacher, (1990).

As can be seen in **table 2** the viscosity of triacylglycerols and fats is reduced to almost twice that of petroleum diesel fuel. For soya bean oil viscosity is reduced from 35 cSt to 5 cSt for the Soya methyl ester, while the density reduced from 920 kg/m^3 to 910 kg/ m^3. Similarly for sunflower oil its viscosity reduced from 33 cSt to 5 cSt and density from 910 kg/ m^3 to 870 kg/ m^3 for sunflower methyl ester. The trend continues in the similar fashion for other oils like canola and crambe and their methyl esters. In comparison fossil diesel fuel has viscosity of 3 cSt and density of 850 kg/ m^3. Feed-stocks whose oil has high specific energy are more likely to produce biodiesel with high amounts of energy on combustion.

In **table 3** it is observed that the higher the iodine value the more unsaturated the oil (the greater the number of double bonds) and the higher is the potential for the oil to polymerize. Some oils have low iodine number (IV) and are suitable without any further processing other than extraction and filtering for use as neat or straight vegetable oils (SVO). Usually the majority of vegetable and animal oils have an iodine value which may cause problems if used as a neat fuel (Yang *et al*., 2007). Generally speaking an iodine number of less than about 25 is required if the neat oil is to be used for long-term applications in unmodified diesel engine and this limits the types of oil that can be used as fuel. Only coconut oil has an iodine value low enough to be used without any potential problems in an unmodified diesel engine. But with a melting point of 25°C, the use of this oil in cooler areas would lead to problems (Gerpen *et al*., 2006). The low melting-point of coconut oil is due to low molecular weight short chain fatty acids in the molecule.

Table 3.Melting points and iodine values of oils

Oil	**Approximate melting point (˙C)**	**Iodine value (IV)**
Coconut	25	10
Palm kernel	24	37
Mutton tallow	42	40
Beef tallow	-	50
Palm oil	35	54
Olive	-6	81
Castor	-18	85
Peanut	3	93
Rapeseed	-10	98
Cotton seed	-1	105
Sunflower	-17	125
Soybean	-16	130
Tung	-2.5	168
Linseed	-24	178

Source: Calais and Clark (2007.

Table 4. Emissions data

Blend Soya Oil/diesel (%)	**Oxygen (%)**	**Hydrocarbons (ppm)**	**Carbon (II) Oxide (%)**	**Carbon (IV) Oxide (%)**
100	18.42	4.4	0.011	1.40
90	18.27	5.0	0.017	1.50
80	18.30	3.8	0.020	1.57
70	18.20	4.9	0.016	1.40
60	18.17	3.4	0.018	1.40
50	18.39	3.6	0.011	1.40
40	18.07	6.5	0.020	1.52
30	18.32	5.8	0.018	1.43
20	17.90	4.5	0.020	1.41
10	18.40	4.8	0.011	1.40
0	18.40	3.7	0.018	1.42

Source:Biodiesel Overview by Sheehan *et al*., (1998).

Exhaust emission levels are periodically analyzed for air pollutants. **Table 4** illustrates the non-visible emissions data by various soya oil and diesel blends. The characteristics for a number of soya oil and diesel blends are given. In the literature studies, more amount of carbon-dioxide exhaust emission of fossil diesel is an indication of the complete combustion of the fuel. Higher amount of biodiesel in fossil diesel blends emits low amount of carbon-dioxide as a consequence of higher viscosity of biodiesel (Gumus, 2008). The emitted carbon-dioxide is readily absorbed by crops and hence CO_2 is kept in balance. The carbon monoxide emissions increase with engine load, since the air-fuel ratio decreases with increase in load. This is typical of all internal combustion engines. An excess of oxygen supply is needed for complete combustion of fuel.

CHAPTER THREE

METHODOLOGY

3.1 Materials

The materials used for the transesterification of waste vegetable oil included reagent grade methanol (99%) and the catalyst were anhydrous sodium and Potassium hydroxide (85-90%). Other materials were recovered, filtered used vegetable frying oils, reaction three necked flask, condenser, thermometer (0 -110˚C) and heater with stirrer. Transesterification reactor was fabricated and reaction operating conditions determined.

3.2 Methods

3.2.1 Laboratory scale biodiesel synthesis

A mass of 0.75 g of sodium hydroxide (or 1.0 g of potassium hydroxide), catalyst was dissolved in 60 ml of pure methanol. The mixture was then warmed in hot water while stirring until all the alkali dissolved. The resulting mixture was added to 100 g of oil (either refined or waste vegetable oil) sample in a three-necked 500 ml reaction flask placed on a heater. The mixture was refluxed for at least 1 hour with moderate stirring at 65 - 68˚C (Appendix 4). At the end of the reaction the residual methanol was recovered through distillation. The mixture was then transferred to a separating funnel and left to settle for at least 8 hours, by gravity into phases the lighter upper phase was bio-diesel and the lower heavier phase glycerol. The two phases were separated. The bio-diesel phase was washed with warm distilled water 3-4 times until the wash water pH was neutral. The bio-diesel was finally distilled under vacuum to remove any water droplets and kept in the sample container. In preparing biodiesel from waste vegetable oil and refined vegetable oil, ten test runs were done in each case and the results obtained given in **tables 16 and 17**. The following chemical and physical tests were carried out on waste vegetable oil biodiesel refined vegetable oil biodiesel and fossil diesel. Acid value, saponification value, peroxide value, density, viscosity, caloric value (or heat of combustion), and flash-point were determined and the results summarized in **table 5**. Thermal efficiency and fuel consumption were also tested and the results recorded (Appendix 6 to 13). In order to determine fatty acid contents of waste vegetable frying oil it was converted to its respective ester by the transesterification technique. Additional water washing and drying over anhydrous sodium sulphate was done to obtain samples pure enough (Auld *et al*., 1982). Density was determined by using glass hydrometer as per USA standard specification, ASTM D 1298. Kinematic viscosity is a measure of resistance to flow of a given fluid. It was measured at 40°C using Pensky martens viscometer as per ASTM D 445. Heat of combustion or caloric value of fuel was determined in a bomb calorimeter with an adiabatic water jacket as per ASTM D 240, standard specification (Auld *et al*., 1982).

The biodiesel was evaluated as a fuel in short-term test runs in a diesel engine at the University of Nairobi Thermo Laboratory. During test runs the following parameters were recorded for investigation. Brake power, specific fuel consumption (at intervals), the temperature of incoming and outgoing air, oil, engine cooling water, and fuel (at intervals). The conventional diesel fuel was used in parallel runs in the diesel engine and the same data recorded to detect any changes in performance during the testing procedure. Filters were located ahead of the pump to minimize mixing of the oil types between tests.

3.2.2 Transesterification reactor

The transesterification reactor was fabricated from stainless steel material type 316 (plate 1). The stainless steel sheets were measured using tape for appropriate lengths and widths before welding into a tank to form a jacket. The inner reaction vessel was similarly made and inserted into the already made jacket before finishing up the various parts. The associated condenser was similarly made from stainless steel sheets type 316. In determining operating reaction conditions for the reactor, there was scaling up, the amount of catalyst was increased to 250 g, waste vegetable oil to 60 L and alcohol to 10 L. The molar ratio of methanol to oil was at 6:1. The temperature range maintained at (65-68°C) for 3 hours, with vigorous agitation using stirring motor for the first 5 minutes followed by moderate circulation for 30 minutes using recirculation pump. The associated reflux condenser was also fabricated from stainless steel materials (Plate 2).

Plate 1.Transesterification reactor (Capacity 60 L /hr biodiesel)

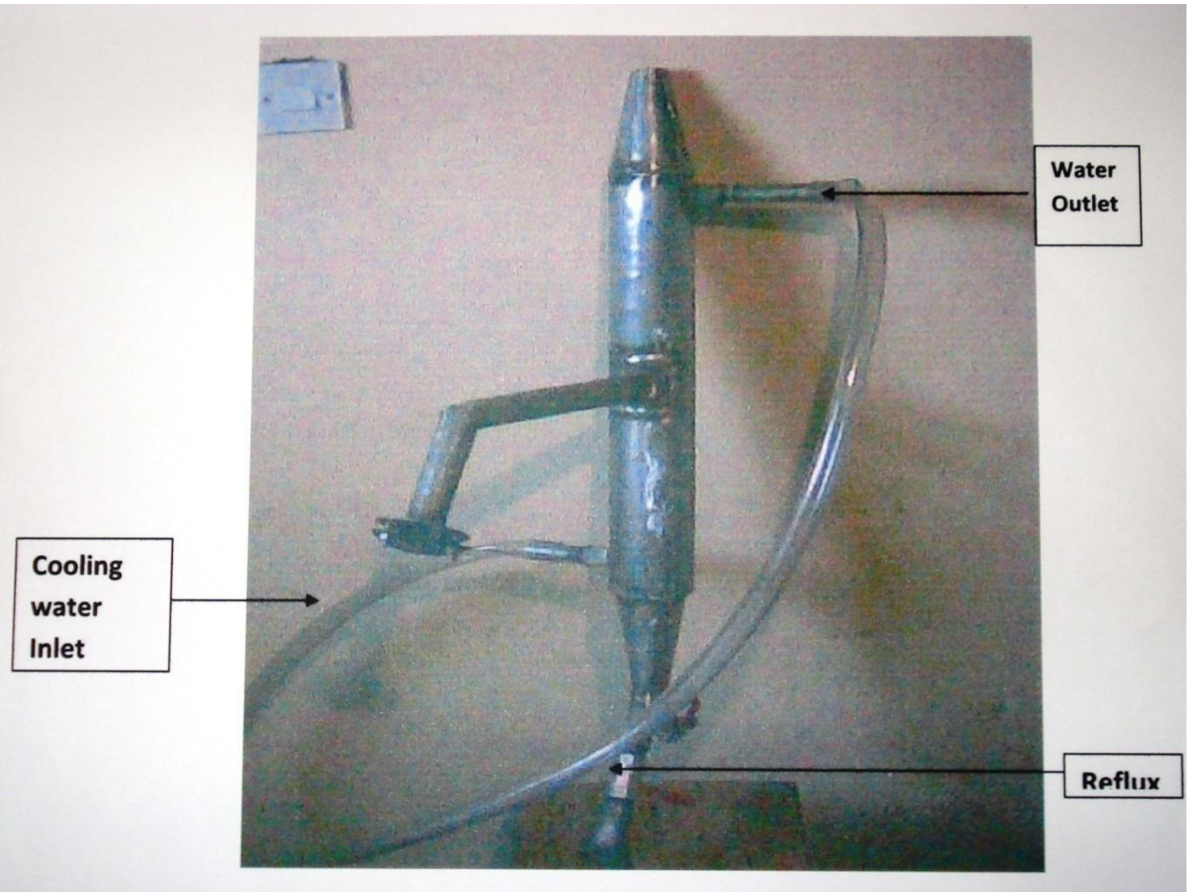


Plate 2. Reflux condenser

3.3 Chemical and physical analysis

The refined vegetable oil biodiesel, waste vegetable oil biodiesel and conventional diesel fuel were tested for the following parameters in line with USA standard specifications for pure biodiesel ASTM D 6751.

3.3.1 Flash-point

This is the lowest temperature corrected to a barometric pressure of 101.3 Kpa (760 mm Hg), at which application of an ignition source causes the vapour of a specimen to ignite under specified conditions of test. It is a determinant for flammability classification of materials. The flash-points of model refined oil, waste frying oil, bio-diesel and diesel fuel were determined using Pensky-martens closed cup apparatus as per ASTM D 93 standard specifications. Measured 10 mL sample placed in the Pensky martens metallic crucible and closed the lid to avoid any spillage of the test sample. The thermometer was fixed into position and biodiesel sample heated. A burning splint was brought to the mouth of the Pensky martens Crucible after every five minutes as heating continued until a pop sound that extinguished the splint was heard. The temperature was then recorded as the flash-point of the sample. The procedure was repeated for the various samples. Each sample run three times and results summarized in **table 5.**

3.3.2 Kinematic viscosity

Viscosity is the resistance to flow of liquid under test. It was determined following ASTM D 445 standard specification. A sample was poured into the viscometer with the narrow bore closed to avoid air entering that might create bubbles which otherwise would interfere with sample movement. After filling the larger bore by capillary action the sample was placed in a water bath maintained at 40°C and the time taken for the sample to move from point A to B recorded. This was multiplied by a constant specific for every viscometer (S_3 viscometer used), to give a measure of the sample viscosity at 40°C. The procedure was repeated for the remaining samples and results recorded **table 7.**

3.3.3 Density

For density the hydrometer method was used. Hydrometer range used was 856.3-921.3. The SI unit for density is Kg/m^3. The hydrometer was dipped into the liquid and allowed to float and reading taken below the meniscus level. The temperature of the sample was also taken at the same time of reading the density and correction done at 20°C. The above procedure was repeated for the rest of the samples and recorded in **table 6**.

3.3.4 Free fatty acid (FFA)

The acid value is the milligrams of potassium hydroxide needed to neutralize the free fatty acid in one gram of oil or fat. The titration was performed with a standard solution of 0.1M alcoholic potassium hydroxide.

Alternatively a sample was dissolved with stirring in hot 95 % ethanol and titrated with 0.1 M aqueous sodium hydroxide using phenolphthalein indicator.

FFA % = $v/1000 \times 0.1 \times 282/w \times 100$

Where: v = ml of sodium hydroxide solution used.

0.1 = molarity of sodium hydroxide solution used.

282 = molecular weight of oleic acid taken as basis for calculation.

w = weight in (g) of sample. FFA% is approximately ½ A.V.

Acid value (A.V) will be given by the number of milligrams of potassium hydroxide needed to neutralize the free fatty acid in one gram of oil/fat.

Thus;

A.V = $v/1000 \times 0.1 \times 56.1/w$

Where: 56.1 = equivalent weight of potassium hydroxide solution used.

v = ml of potassium hydroxide solution used.

0.1 = molarity of potassium hydroxide solution used.

w = weight in (g) of sample.

3.3.5 Total acid number

The total acidity is a measure of the combined organic and inorganic acidity. The inorganic acidity is a measure of the mineral acid present in the fuel sample. The organic acidity is obtained by deducting inorganic acidity from the total acidity. Total acid number was determined as per ASTM D 664 standard specification. A standard alcoholic KOH solution was prepared by dissolving 6 g of solid KOH in 1 Litre of anhydrous propan-2-ol in a 2 litre volumetric flask. The mixture was boiled gently for 10-15 minutes with stirring on a heater. To the mixture was added 2 g of barium hydroxide ($Ba(OH)_2$), and again boiled for 10-15 minutes. The solution then cooled to room temperature and allowed to stand for several hours and the supernatant liquid filtered through sintered glass funnel. The solution finally stored in a chemically resistant dispensing bottle out of contact with cork, rubber or saponifiable stop-cock, lubricant and protected by a guard tube containing soda-lime. Titration solvent was prepared by adding 500 mL of toluene to 5mL of distilled water and 495 mL of anhydrous propan-2-ol then kept in a bottle and lid closed. 20 g of waste vegetable oil biodiesel sample was weighed and placed into a 250 ml conical flask. The testing was done in triplicate. To the flask was added 100 mL of titration solvent and 4 drops of p-naphtholbenzein indicator. The mixture was titrated with vigorous shaking, against 0.1 M alcoholic KOH solution to a definite blue colour. Titre value was taken as A. Blank titration was also run and titre value taken as B, and the calculation carried out as follows:

Total acid No (in mg KOH/g) = $(A - B) \times M \times 56.1/W$

Where:

A = volume of KOH used in sample titration

B = volume of KOH used in blank titration.

W = weight of sample in grams

M = molarity of KOH.

3.3.6 Sulphated ash.

Ash is the percentage by weight of an inorganic residue obtained by combustion of oil in the presence of air. Thus it is inorganic impurities and salts present in the oil. On the other hand, sulphated ash is the residue remaining after a fuel has been carbonized, and the residue subsequently treated with sulphuric acid and heated to a constant weight. The test monitors mineral ash residual when a fuel is burned. This is given in ASTM D 874 standard specification in **table 5**. The test is used to indicate the concentration of known metals containing additives in new oil. When phosphorus is absent in the oil barium, calcium, magnesium, sodium and potassium are converted to their sulphates and tin zinc to their oxides. Sulphur and chlorine do not interfere but when phosphorus is present with metals it remains partially or wholly in the sulphated ash as metal phosphates. The sample is ignited and burned until only ash and carbon remain. After cooling the residue is treated with sulphuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled retreated with sulphuric acid and heated at 775°C to constant weight.

3.3.7 Water and sediment

The test specified in ASTM D 2709, is important as a measure of cleanliness of the fuel. For pure biodiesel (B100), it is especially significant because water can react with the esters making free fatty acids, soap and can support microbial growth in the fuel tanks. It should be kept out of the biodiesel production process as much as possible. Sediments may plug fuel filters and thus contribute to the formation of deposits on fuel injectors and other engine damage. Sediment levels can increase over time as the fuel degrades during long storage. Dean and stark apparatus was used to determine water content of samples. A measured 100 mL of waste vegetable oil biodiesel sample was mixed with 100 mL of petroleum spirit (boiling point 100°-120°C), as solvent carrier and placed in the round bottom distillation flask, fitted the condenser. The mixture was placed in a heating mantle and heat applied. This was continued for 3 hours. The test was repeated for refined vegetable oil biodiesel and fossil diesel samples.

3.3.8 Copper strip corrosion

Detection of copper strip corrosion from petroleum products by copper-strip tarnish test is given in ASTM D 130 standard specification. It is an important test in that it determines the corrosiveness of fuel to the engine parts, some of which are made of copper alloys. The test is an indication of corrosiveness of metals used in the construction of diesel equipment such as engine parts, injectors or fuel tank. A polished copper strip was immersed in 5 mL of waste vegetable oil biodiesel in a boiling tube and dipped in a water bath maintained at a temperature of 100˚C for 3 hours. At the end of the period, the copper strip removed and compared with standard strips. The test repeated for refined vegetable oil biodiesel and fossil diesel.

3.3.9 Calorific value of fuel

This is the heat of combustion of fuel. Referred to as the specific energy of fuel, it indicates the oil or fuel’s energy released when it is burned. Feed-stocks whose oil has high specific energy are more likely to produce biodiesel with high amounts of energy on combustion. Calorific value was determined by igniting a small sample of about 1g in an oxygen bomb calorimeter. A thermometer accurate to two decimal places was used to sense the temperature rise due to heat released by the combustion process. The gross heat was calculated from temperature, fuel and bomb data using the formulae provided with calorimeter. The gross heat of combustion is the heat released by the combustion of a unit mass of fuel. The bomb calorimeter was calibrated by the combustion of benzoic acid as fuel. An adiabatic calorimeter jacket was used in both tests.

3.3.10 Carbon residue

Carbon residue is what remains after the fuel has been burned in an electric furnace at a specified temperature. The test was determined as follows. A weighed 5 g of waste vegetable oil sample in a crucible was placed in the furnace set at 500˚C, and then heated slowly for 2 hours until carbon residue remained. This was repeated for refined oil biodiesel and fossil diesel. The residue was weighed and the difference in weight obtained and recorded in **table 15.**

3.3.11 Saponification value

Saponification value is a measure of the tendency of soap formation and this can affect the smooth running of the diesel engine. The procedure involved weighing 4.5 g of sample into a conical flask and then adding 50 mL of 0.5 M alcoholic KOH. The mixture was refluxed for 30 minutes and slowly titrated against 0.5 M HCl using phenolphthalein indicator. The blank was also run at the same time and under the same conditions.

3.3.12 Peroxide value

Peroxide value is a measure of the degree of oxidation of the fuel sample under test. The test may also be applied to fats and oils to gauge rancidity or off-flavour. To determine the peroxide value, 1.42 g of sample was weighed and added to a 250 ml conical flask. Solvent mixture was made up of 2 volumes of glacial acetic acid and 1 volume of chloroform was added to the flask. To the mixture was also added 1 mL of KI and 35 mL of distilled water and the whole shaken thoroughly before titrating against 0.02 M sodium thiosulphate solution. Starch solution (1%) was used as the indicator. The blank was also run under the same conditions.

3.4 Rate of fuel consumption and thermal efficiency at various throttle speeds

A 6- cylinder turbo-charged diesel engine was used. Engine specifications:

Engine type 2, Bore = 100 mm, Stroke = 100 mm, Compression Ratio = 16: 1

Displacement = 5416 cm^3.

3.4.1 The Engine

The engine was coupled to a G-type Froude Hydraulic dynamometer for absorption and measurement of the power developed. The power developed by the engine was controlled by regulating the amount of water going into the dynamometer. The load on the engine and the speed shown on the dials on the dynamometer were read directly.

3.4.2 Cooling system

The engine cooling water flow was assisted by a pump. The external circuit was via a head tank, fitted with a thermometer. The water temperature in the head tank was kept constant by supplying water from the mains and allowing the same amount of hot water to pass to waste from the system. Thermometers were provided to measure the inlet and outlet water temperatures. A flow-meter was used to measure the mass flow rate of water.

3.4.3 Fuel system

Fuel from the tank was supplied to the fuel injector pump through a capillary tube via a fuel filter. From the injector pump, the fuel was supplied at high pressure, correctly metered and timed to the injector nozzles in the cylinder head. The fuel quantity supplied to each cylinder was controlled by the position of the injector pump rack. The fuel atomized by the injector nozzles mixed with air and then burned in the combustion chamber of the engine. To measure the fuel consumption the supply was taken from a bulb pipette, the supply from the fuel tank being cut off. The time taken to consume 100 mL of fuel was then recorded.

3.4.4 Test procedure

The throttle was set to give a speed of 1250 revolutions per minute (rpm) at a light load. The load was then adjusted to give a reading of 1 Lb (0.4536 kg), on the dynamometer dial. When conditions were steady the following observations were made and relevant readings recorded for speed, load, fuel consumption, cooling water inlet and outlet temperatures, room temperature and barometric pressure. The above procedure was repeated at a load of 2 Lbs (0.9072 kg), 3 Lbs (1.3608 kg), 4 Lbs, (1.8144 kg), 5 Lbs (2.2680 kg), 6 Lbs (2.7216 kg), and 7 Lbs (3.1752 kg), at the same constant speed. The entire procedure again was repeated at speeds of 1500, 1750, and 2000 revolutions per minute (Rpm). Brake power is a measured of the output of the engine. It was measured by running the engine against some form of absorption brake, hence the name. The engine wais connected to a dynamometer loaded in such a way that the torque exerted by the engine was measured. Brake power of an engine is given by the formula: Brake power (kW) = W x N x bhp/200 x 1000. Where: W = Load (kg), N = Speed (rpm) bhp = 746 kW. Power input (watts) = energy input/time (hrs).

The rate of fuel consumption was measured by allowing the fuel to run through a special measuring device (a bulb pipette). The time for the engine to consume 100 mL of fuel was noted by means of a stop watch. Alternatively, a flow-meter calibrated to give the fuel consumption in litres per hour could be read directly. Mass of fuel consumed = density x volume of fuel. Rate of fuel consumed = mass of fuel consumed/ time (hrs).

Energy of fuel consumed (energy input) = mass of fuel consumed x its calorific value. Power input (watts) = energy input/time (hrs). Brake specific fuel consumption (B.S.F.C) in (kg/kWh or L/kWh), is the amount of fuel required in kg or litres, to develop a brake power of 1 kilowatt for a period of 1 hour at the load considered. B.S.F.C (kg/kWh) = Rate of fuel consumption/brake power. Brake thermal efficiency (%) is the actual amount of fuel consumed to give a particular brake power. The overall efficiency of the engine is thus given by the brake thermal efficiency. Brake Thermal Efficiency (%) = Brake Power x 100/power input.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

During the study, a 60 L per hour transesterification batch reactor was fabricated for bio-diesel production. The optimum operating conditions for the fabricated transesterification reactor were 60 L waste vegetable oil, 10 L methanol, temperature (65- 68°C) and the catalyst was 250 g sodium hydroxide. Vigorous agitation using a stirring motor was done for the first 5 minutes followed by moderate circulation for 30 minutes with a recirculation pump. The mixture was refluxed for 3 hours per batch. The diesel engine optimum operating combustion conditions were obtained at engine speed rating of 1750 rpm for both fossil diesel and biodiesel fuels at average fuel consumption of 0.3396 kg/kWh for diesel and 0.3804 kg/kWh for biodiesel respectively.

The various chemical and physical tests carried out on diesel, refined vegetable oil and biodiesel are given in **table 5**. Density measured at convenient temperatures using glass hydrometer is reduced to 20°C, by application of international standard tables. Different products have different acceptable ranges of densities at 20°C set by American Society for testing and Materials standard. If the density of a product does not lie in the expected range then it may suggest contamination. Hence more rigorous tests are done to confirm contamination. The colour visual test is done for the purpose of customer's satisfaction. So the test is significant. Flash-point can indicate the possible presence of highly volatile and flammable materials in a relatively non-volatile or non-flammable material. Saponification value is a measure of the tendency of soap formation and this can affect the smooth running of the diesel engine. Peroxide value may show the degree of oxidation of the fuel sample under test. The test is mainly applied to fats and oils to gauge rancidity or off-flavour. Peroxides in oxidized oil may decompose further into various carbonyl and other compounds. This decomposition accelerates as the temperature is raised. Thus the peroxide value may be reduced by heating the oil in the absence of air or oxygen. Calorific value of fuel is best determined by burning of sample in an atmosphere of compressed oxygen contained in a steel bomb. The test is very important as it gives the amount of heat contained in the fuel under consideration. Biodiesel has a slightly lower heat value compared to diesel and so more of it is burned per unit volume in the diesel engine.

Table 5. Chemical and physical analysis of pure biodiesel (B100) and fossil diesel.

Test Parameters			**Biodiesel**							
		Diesel	**RVOB**	**WVOB**	**Kenya KS 1309-1 (Diesel)**			**USA ASTM D 6751 (pure Biodiesel)**		
						Limit		**Limit**		
						min	**max**		**min**	**max**
1	Kinematic viscosity @ 40°C cSt	3.2	3.92	3.96	KS 1099(a) Annex A	1.9	6.0	ASTM D445	1.9	6.0
2	Copper strip corrosion, 3hrs @100°C	1a	1b	1b	KS 1289(b) Annex D	1	-	ASTM D130	-	No. 3
3	Density @ 20°C, Kg/m^3	845	871	877	KS 1289	820	870	-	-	-
4	Flash-point,Pensky martens Closed cup°C	60	132	135	KS 161-17©	60	-	ASTM D93	130	-
5	ASTM colour	1.0	0.8	0.8	KS 1309-1 Annex A	-	3.5	ASTM D1500	-	-
6	Water content % (v/v)	< 0.05	< 0.05	< 0.05	KS 1309-1 Annex F	-	0.05	ASTM D2709	-	0.05
7	Sulphated ash % (w/w)	0.011	0.022	0.024	KS 1309-1 Annex G	-	0.01	ASTM D874	-	0.02
8	Total acid No. mg KOH/g	0.512	0.553	0.562	KS 1309-1 Annex K	-	0.8	ASTM D664	-	0.8
9	Gross Calorific value MJ/kg	43.788	40.359	39.323	-	-	-	ASTM D240	-	-
10	Carbon residue Wt %	< 0.05	< 0.05	< 0.05	KS 1309-1 Annex J	-	0.15	ASTM D4530	-	0.05
11	Saponification value mg KOH/g	-	183.48	178.69	-	-	-	-	-	-
12	Peroxide value	-	13.19	15.38	-	-	-	-	-	-

Key: RVOB- Refined vegetable oil biodiesel; Waste vegetable oil biodiesel.

In **table 5** chemical and physical tests carried out on waste vegetable oil biodiesel, refined vegetable oil biodiesel and diesel fuel are summarized. For all the tests done each sample was tested in triplicate.

4.1 Determination of fuel density

The determined density value of 877 kg/ m^3 for waste vegetable oil biodiesel sample was within the specified range given in **table 5** for Kenya standard specification for fossil diesel, ranging from 820-870 kg/m^3. American standard has no specification for biodiesel density.

Table 6 Determination of fuel density

SAMPLE	APPARATUS-Glasss Hydrometer DENSITY (Kg/m^3) (Corrected)
Fossil diesel	845 ± 2
Refined vegetable oil biodiesel (RVOB)	871 ± 3
Waste vegetable oil biodiesel (WVOB)	877 ± 3
Corrected density = observed density + (observed temperature - 20°C) X Correction coefficient = 844.9 + (26.5 -20) x 0.00064 = 844.9 + 0.00416 = 844.90416 = 845 The rest calculated similarly.	

Densities of biodiesel fuels are generally higher than those of fossil diesel which have impacts on cetane number, calorific value (heating value) and fuel consumption, as the amount of fuel introduced into the combustion chamber is determined volumetrically. However, Tat and Gerpen (2000) showed that temperature-dependent changes in biodiesel densities are similar to those of fossil diesel. Density values for biodiesel (fatty acid methyl ester-FAME), depend on their fatty acid composition as well as on their purity. On one hand, density increases with decreasing chain length and increasing number of double bonds (Refaat *et al*., 2007)), explaining high values for fuels rich in unsaturated compounds, such as sunflower oil methyl ester (885 kg/m^3) or linseed oil methyl ester (891 kg/m^3). On the other hand, density can be decreased by the presence of low-density contaminants like methanol. Because biodiesel has a higher density more is consumed per unit volume compared to fossil diesel. Thus in terms of density conventional diesel is better than biodiesel.

4.2 Kinematic viscosity measurements

Kinematic viscosity is a measure of resistance to flow of fuel. It is an important parameter as it shows how easily fuel would flow in the fuel system and through the nozzles in the vehicle. It is determined at 40°C. The kinematic viscosity is limited to 3.5-5 mm^2/s in the European biodiesel standard in (Appendix 3), with the exception of the American specifications, which allow broader range of values from 1.9-6 cSt (or mm^2/s) as given in Appendix 2.

Table 7 Kinematic viscosity measurements

SAMPLE	APPARATUS –U-tube glass viscometer S-3 KINEMATIC VISCOSITY (Centistokes cSt or mm^2/s) @ 40°C
Fossil diesel	3.20 ± 0.07
Refined vegetable oil biodiesel	3.92 ± 0.04
Waste vegetable oil biodiesel	3.96 ±0.03

Kinematic viscosity = time taken in seconds x viscometer constant.

Each sample tested three times and results read directly and recorded in **table 7**. The corresponding limit for conventional diesel fuel in the European standard is considerably lower ranging from 2-4.5 mm^2/s. The value for biodiesel samples of 3.92-3.96 mm^2/s were within the range specified. Viscosity increases with higher contents of high molecular compounds like glycerides or polymers, which can be found in used frying oil. Hence the kinematic viscosity of waste vegetable oil biodiesel was the highest at 3.96 cSt and that of fossil diesel was the lowest at 3.92 cSt.

4.3 Determination of flash-point of fuel

Flash-point is a measure of flammability of fuels and hence an important safety criterion in transport and storage. The American standard gives a minimum of 130°C, while the European standard defines a flash-point minimum of ≥ 120°C for biodiesel fuels in (Appendix 3). For fossil diesel ≥ 55°C is specified as minimum. Each sample tested three times and results read directly and recorded in **table 8**. The biodiesel samples gave a flash-point range of 132-135°C, which was well above the specified minimum.

Table 8 Determination of Flash-point of fuel

SAMPLE	APPARATUS –PENSKY-MARTENS FLASH-POINT °C
Fossil diesel	60 ± 2
Refined vegetable oil biodiesel	132 ± 2
Waste vegetable oil biodiesel	135 ± 1

In general the flash-points of petro-diesel samples are only about half the values of those for biodiesel, which constitutes an important safety asset for the bio-fuels. From **table 8**, the flash-points of pure biodiesel samples are considerably higher than the prescribed limits, so that values of 170°C are reported for pure rape seed biodiesel. However, flash-points rapidly decrease with increasing amounts of residual alcohol. Thus these two parameters are strictly correlated. The higher flash-point of waste vegetable oil biodiesel makes it a safe fuel to use, handle and store. Flash-point is an indicator of unreacted alcohol remaining in the fuel.

4.4 Determination of water content of fuel

Biodiesel quality standards limit water content to 500 ppm, with the American standard covering both the content and sediment with one limit of 0.05% (v/v) as given in (Appendix 2). The respective maximum concentration for fossil diesel fuel is less than half these values, but it is easily met due to the non-polar nature of fossil fuel. From **table 5**, the determined value for the biodiesel sample of < 0.0 5% (v/v) is within the required specification, as no water droplets carry-over was observed during testing using Dean and Stark apparatus. Water is introduced into biodiesel during the production process (for example in the final washing step) and thus has to be reduced to values well below the limit by drying. Biodiesel is dried by heating under vacuum to remove water droplets. However, even, very low water contents achieved directly after the production do not guarantee that biodiesel storage 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. Moisture may condense in the storage tank especially during cold weather resulting in hydrolytic reaction. Free water promotes biological growth, so that sludge and slime formation thus induced may cause blockage of fuel filters and fuel lines. So strict control of water contamination of fuel is required.

4.5 Copper strip corrosion test

Copper -strip corrosion- the tendency of biodiesel fuel to cause corrosion to copper, zinc and bronze parts of the diesel engine and tank. It was determined using freshly polished copper strips and class 1a and 1 b obtained were within the standard specifications. This is shown in **table 9**. For the US standard the maximum is class 3 while for the European standard the rating must not exceed class 1, respectively (Appendix 2 and 3). In biodiesel samples corrosion might be induced by some sulphur compounds and by acids, so that the parameter is correlated with acid number. In practice, however, fatty acid methyl ester (FAME), samples have turned out to be very unlikely to give ratings higher than class 1. Copper metal can corrode very fast as compared to other metals and that is why it is used in this test. If a product is used on a copper strip and it passes the test then most likely it will too on other metals. Copper and its alloys are used in making machine and engines parts.

Table 9 Standard copper strips with markings

Freshly Polished Copper Strip	1a	1b	2a	2b	2c	2d	2e	3a	3b	4a	4b	4c
	Slight tarnish		Moderate Tarnish					Dark tarnish		Corrosion		

The strips were found to be slightly tarnished (1a and 1b) which are within the required (ASTM D1500), standard specifications. The copper strip corrosion test is given in various classes, with class 1a and 1b indicating slight tarnish. class 2a-e shows moderate tarnish on copper strip. While class 3a and 3b gives dark tarnish on copper strip and the last class 4a-c shows complete corrosion on the copper strip. Copper metal can react with oxygen from the air to form copper oxide and moisture may speed up the corrosion process.

4.6 Sulphated ash test

Sulphated ash test is important because from resulting ash metallic contaminants in the fuel such as sodium, zinc, calcium and magnesium may be determined from the resulting ash by digestion with mineral acid. The metals are undesirable as their presence may lead to corrosion of the combustion chamber. Each sample tested three times and results recorded in **table 10**.

Table 10 Sulphated ash test

SAMPLE	SULPHATED ASH (% w/w)
Fossil diesel	0.01 ± 0.001
Refined vegetable oil biodiesel	0.02 ± 0.001
Waste vegetable oil biodiesel	0.03 ± 0.001

The results compared with the corresponding US standard in Appendix 2 and are within the specified limits.

4.7 Total acid number measurements

The total acidity is a measure of the combined organic and inorganic acidity in a fuel sample and inorganic acidity is a measure of the mineral acid present. The results for total acid number for fossil diesel, refined vegetable oil methyl ester and biodiesel are given in **table 11**.

Total acid number (fossil diesel) = (A-B) x 0.114695x 56.1/W. Where:

W = weight of sample taken

A = Sample titre value

B = Blank titre value

Molarity of KOH = 0.114695

Molecular weight of KOH = 56.1

Total acid number (fossil diesel) = (1.8- 0.1) x0.114695 x 56.1/22.623 = 0.512 .

Similarly, the total acid number for Refined vegetable oil biodiesel (RVOB) and waste vegetable oil biodiesel were calculated.

Table 11.Total acid number measurements

SAMPLE	TOTAL ACID NUMBER in mg KOH/g
Fossil diesel	0.512 ± 0.01
Refined vegetable oil biodiesel	0.553 ± 0.07
Waste vegetable oil biodiesel	0.562 ± 0.01

For acid value the respective limit in the European standard (appendix 3), is ≤ 0.5 mg/KOH/g, whereas, the American standard allows slightly higher value of ≤ 0.8(Appendix 2). From **table 11** the total acid number or value determined for biodiesel sample of 0.553 - 0.562, was within the range required. Acid number of biodiesel depends on the type of feedstock used for fuel production and on its respective degree of refinement. On the other hand, acidity can also be generated during the production process, especially by mineral acids introduced as catalysts or by free fatty acids resulting from acid-work-up of soaps. Use of waste vegetable oils with high free fatty acid content also plays some part although this can be neutralized by using more alkali catalyst. The degree of fuel aging during storage must also be considered as the acidity gradually increases due to hydrolytic cleavage of ester bonds. High fuel acidity is associated with corrosion and formation of deposits within the engine. However, it has been shown that free fatty acids as weak carboxylic acids pose far lower risks than strong mineral acids. This is an indication of the level of free fatty acids or processing acids in biodiesel. Acids in oil are the acidic elements of organic and inorganic acids, esters, phenol compounds lactones and resins. Water soluble acids can cause corrosion in the burning chambers and exhausts of engines and in burner tips.

4.8 Determination of Calorific Value (C.V) of fuel

The heat of combustion of fuel is best determined by a method which permits the burning of the material in an atmosphere of compressed oxygen, contained in a steel bomb. The bomb is placed in a calorimeter and heat released by combustion is measured by observing the temperature rise of the water in the calorimeter.

Table 12 Determination of Calorific Value (C.V) of fuel

SAMPLE	**GROSS CALORIFIC VALUE OF FUEL in MJ/Kg**
Fossil diesel	43.91 ± 0.02
Refined vegetable oil biodiesel	40.49 ± 0.02
Waste vegetable oil biodiesel	39.45 ± 0.03

In calorimetry corrections must be made in order to obtain meaningful results. Heat losses from the calorimeter to the surroundings normally involve an application of Newton's law of cooling. However, using an adiabatic bomb calorimeter a heat loss correction has been eliminated. Nevertheless, two other corrections call for some consideration, they are the nitrogen correction and the heat evolved by the wire and cotton forming the fuse. The first step is to determine the water equivalent of the apparatus. The results are recorded for standard benzoic acid for calibration of the bomb before testing the sample.

Gross calorific value of fossil diesel = Rise in temperature x heat capacity of calorimeter = 3.51 x2036.8/0.1628x1000

= 43.914 MJ/kg

Gross calorific value of refined vegetable oil methyl ester = Rise in temperature x heat capacity of calorimeter = 3.23 x 2036.8/0.1625x1000

= 40.485 MJ/kg

Gross calorific value of biodiesel = Rise in temperature x heat capacity of calorimeter

= 3.19 x 2036.8/0.1647x1000 = 39.449 MJ/kg

The gross calorific value of waste vegetable oil biodiesel obtained was 39.45MJ/kg and this is about 11% lower than that of fossil diesel (43.91 MJ/kg). Thus coupled with its higher viscosity biodiesel consumption in the diesel engine was more compared to fossil diesel. It has been claimed biodiesel gives better lubricity and more complete combustion hence increasing the engine energy output and partially compensating for the higher energy density of fossil diesel (http://en.wikipedia.org/wiki/Biofuel). Also, being oxygenated fuel, despite its lower heating value biodiesel performance in the diesel engine is similar to that of fossil diesel.

4.9 .Saponification value test

Saponification value is the amount of alkali necessary to saponify definite quantity of sample and is expressed as the mg of potassium hydroxide (KOH), required to saponify 1 g of sample. There was slight difference in the values for refined vegetable oil biodiesel (183.48) and waste vegetable oil biodiesel (178.69). The results are given in **table 13.** The test is significant as an indication of cleanliness of fuel and to what extent the soap forming salts have been removed through washing.

Table 13 Saponification value test

SAMPLE	**SAPONIFICATION VALUE in mg KOH/g**
Fossil diesel	Not done
Refined vegetable oil biodiesel	183.48 ± 0.03
Waste vegetable oil biodiesel	178.69 ± 0.04

Saponification value of biodiesel = 56.1 xM ($V_2 - V_1$)/W

Where: Molecular weight of KOH = 56.1

M = Molarity of HCl

W = Weight of sample

V_1 = Titre value of sample

V_2 = Titre value of blank

Saponification value of biodiesel = 56.1 x0.5(30.1 – 4.3)/4.05 = 178.69 mg KOH/g

Saponification value of RVO biodiesel = 56.1 x0.5(30.1 – 1.73)/4.35 = 183.48 mg KOH.

4.10 Peroxide value test

Peroxide test of biodiesel can indicate the on set of auto-oxidation of the fuel, hence the oxidative and storage stability. The peroxide value for fossil diesel was not determined because it has no unsaturated double bonds in its composition but only hydrocarbons. The measured peroxide value for refined vegetable oil biodiesel was 13.19 while that of waste vegetable oil biodiesel was 15.38. The value for biodiesel made from waste vegetable oil is slightly higher than that of biodiesel from refined vegetable oil because of thermal oxidation that had occurred during deep fat frying. The results are recorded in **table 14**.

Table 14 Peroxide value test

SAMPLE	**PEROXIDE VALUE in mg KOH/g**
Fossil diesel	Not done
Refined vegetable oil biodiesel	13.19 ±0.02
Waste vegetable oil biodiesel	15.38 ± 0.02

Peroxide value of biodiesel = 1000 $(V_1 - V_2)$ xM/W

Where: M = Molarity of Sodium thiosulphate

W = Weight of sample

V_1 = Titre value of sample

V_2 = Titre value of blank

Peroxide value of RVO = 1000 (0.97 – 0.0) x 0.02/1.47 = 13.19

Peroxide value of Biodiesel = 1000 (1.1 – 0.0) x 0.02/1.43 = 15.38

Peroxides in oxidized oil may decompose further into various carbonyl and other compounds. This decomposition accelerates as the temperature is raised. Thus the peroxide value may be reduced by heating the oil in the absence of air or oxygen.

4.11 Carbon residue measurements

Carbon residue test served as a measure for the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber when used in an engine. The value obtained for biodiesel sample was < 0.05 and it met the requirement for ASTM, D 4530 standard specification. The standards for biodiesel and conventional diesel fuel consistently limit carbon residue (determined on the 10% distillation residue), to a maximum value of 0.30% (w/w) (Appendix 3). The respective limit in the ASTM standard is lower (≤ 0.050), because it is determined on the original, undistilled sample (ASTM, 2008). For biodiesel carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst.

Table 15 Carbon residue measurements

SAMPLE	CARBON RESIDUE (% w/w)
Fossil diesel	0.01 ± 0.001
Refined vegetable oil biodiesel	0.03 ± 0.001
Waste vegetable oil biodiesel	0.04 ± 0.001

The parameter is also influenced by high concentration of polyunsaturated biodiesel and polymers. Each sample was tested thrice and results recorded in **table 15**.

4.12 Colour test

Colour was determined using Lovibond PFX 880 tintometer with path length 100 mm. Biodiesel sample was poured into the cell and measurement read directly on the screen. The test was repeated for biodiesel made from refined vegetable oil as well as fossil diesel. The results are given in **table 5**. A clear colour simply means that the sample is free from solid matter or suspended solids. Waste vegetable oil biodiesel has a darker colour compared to that of fossil diesel.

4.13 Estimation of waste vegetable oil generation

Based on a figure of 10 batches per day of 50 kg activated bleaching earth (ABE) per batch per industry (taking 5 factories in Kenya). For 1kg spent ABE, waste oil generated would be 325g/1kg = 325x100/1000 = 32.5%. For 10 batches per day for 5 factories annually = 325x50x10 x5x4x12 = 39,000 kg. For 5 days per week collecting 40g of used cooking oil generated per day for approximately 200 cafes in the country = 40x200x5x4x12 = 1920 kg annually.

When about 1920 kg of used cooking oil is added to 39,000 kg of waste vegetable oil extracted from ABE, a total of approximately 40,920 kg of waste oil can be generated for producing biodiesel annually in Kenya. This gives about 40,100 kg (35,168 L), of biodiesel (at 98% yield and only 2% loss). Given that conventional diesel sells at Ksh 60 per litre this can save about Ksh 2.1 million annually in terms of crude oil imports. Biodiesel production can be a viable venture which may add value given that feedstock is obtained cheaply from waste vegetable oil, waste oil from activated bleaching earth and supplemented by non-edible oils that do not compete with food uses of oil.

4.14 Results of biodiesel synthesis from refined vegetable oil and waste vegetable oil

Laboratory scale biodiesel preparation was carry out in a 500 ml round bottom reaction flask using first refined vegetable oil (palm oil) bought from a supermarket and then waste vegetable oil obtained from restaurants in Eldoret town and Moi University hotel. The results are summarized in table 16 and 17 respectively. The anhydrous potassium hydroxide catalyst used ranged from 0.8 to 1.5 g, per 100 g of refined vegetable oil. The temperature was maintained at 65 - 68°C while the time was 1 hour per batch. Methanol was used in all the batches and ranged from 60-80 mL. A total of 10 batches were carried out for each feedstock.

Table 16. Results of biodiesel synthesis from refined vegetable oil

Bat	**Cat**	**MeOH**	**Oil (RVO)**	**Time Hrs**	**Temp ^{0}C**	**YIELDS**			
						Residual MeOH	**GLY**	**Purified (RVOB)**	
Units	**g**	**ml**	**g**	**Hrs**	**^{0}C**	**ml**	**ml**	**g**	**%**
1	0.82	80	100.54	1	65-68	45	14	98	97.5
2	1.28	80	100.59	1	65-68	45	34	96	95.4
3	0.87	80	101.56	1	65-68	46	14	99	97.5
4	1.2	60	102.21	1	65-68	42	20	98	96.2
5	1.21	80	100.56	1	65-68	42	32	98	97.5
6	0.87	60	100.2	1	65-68	34	24	98	97.8
7	1.16	80	101.9	1	65-68	44	22	97	95.2
8	0.88	60	101.14	1	65-68	40	16	98	96.5
9	1.54	80	101.54	1	65-68	28	34	94	92.6
10	1.16	80	96.78	1	65-68	42	20	90	93.0

KEY

CAT – Catalyst Potassium hydroxide (KOH), MeOH – Pure methanol; RVOB – Refined vegetable oil biodiesel; Temp – Temperature; Res – Residual methanol; GLY – Glycerol; Bat- batch.

From **table 16**, the average purified biodiesel yield obtained was 95.9%, after washing biodiesel with distilled water. Excess methanol was used to ensure the equilibrium reaction goes to completion. The results showed that the catalyst about 1% gave high yields and that above 1.5% on the weight of the oil was not suitable to avoid excess soap formation.

Table 17.Results of biodiesel synthesis from waste vegetable oil

Bat	Cat	MeOH	Oil (WVO)	Time	Temp	YIELDS			
						Residual MeOH	GLY	Purified (WVOB)	
Units	**g**	**ml**	**g**	**hrs**	**^{0}C**	**ml**	**ml**	**g**	**%**
1	0.85	60	100.52	1	65-68	35	15	96	95.5
2	1.23	80	100.13	1	65-68	44	30	96	95.8
3	0.86	80	101.6	1	65-68	42	16	95	93.9
4	1.03	60	102.23	1	65-68	36	20	98	95.9
5	1.15	80	100.16	1	65-68	45	34	92	92.0
6	0.84	60	100.22	1	65-68	28	26	96	95.8
7	1.11	80	100.04	1	65-68	35	20	95	94.0
8	0.88	60	100.3	1	65-68	42	22	97	96.7
9	1.50	60	101.21	1	65-68	28	24	95	93.9
10	1.12	80	100.6	1	65-68	37	34	96	95.4

KEY

CAT – Catalyst Sodium hydroxide NaOH; MeOH – Pure methanol; WVOB – Waste vegetable oil biodiesel; Temp – Temperature; Res – Residual methanol; GLY – Glycerol; Bat- batch.

In **table 17**, the average purified biodiesel yield was found to be 94.89% under conditions of the reaction, after washing with distilled water. Excess methanol was used to ensure the equilibrium reaction tilted towards the right. The anhydrous sodium hydroxide catalyst was used and ranged from 0.8 to 1.5 g, per 100 g of filtered waste vegetable oil. The results showed that 1% catalyst gave favourable yields and that above 1.5% on the weight of the oil was not suitable to avoid excess soap formation as in the first test run in **table 16**. Either catalyst could be used but sodium hydroxide catalyst subsequently chosen for further work due to its low cost and availability compared to potassium hydroxide. Methanol was preferred to ethanol because it produces stable esters, has low cost and common international biodiesel standards such as USA, ASTM D 6751 and European EN 14214 are based on FAME (fatty acid methyl ester).

4.15 Results of Specific fuel consumption versus brake power at constant speeds

The following sets of graphs were plotted to indicate the relationship between conventional (fossil), diesel and biodiesel (WVOB) fuels and how well they compare in terms of specific fuel consumption against brake power in diesel engine at various speeds.

4.15.1 Effects of fossil diesel and WVOB consumption on brake power at 1250 rpm

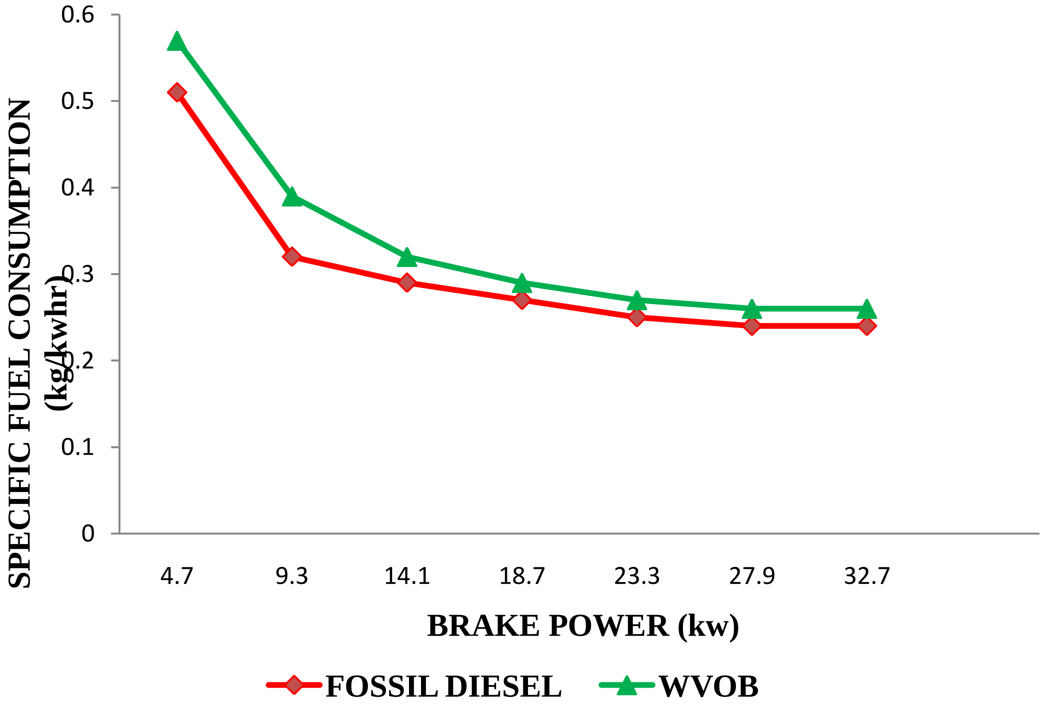


Figure 2.Specific fuel consumption versus brake power at 1250 rpm

From Figure 2, specific fuel consumption reduced with increasing brake power at constant speed for both fossil diesel and waste vegetable oil biodiesel (WVOB). Slightly more WVOB was consumed per unit of power per hour compared to fossil diesel. This is because

WVOB has a lower heat value and higher density. An F test value of 0.7074 indicates that the variation of fossil diesel and biodiesel consumption is not significantly different.

4.15.2 Effects of fossil diesel and WVOB consumption on brake power at 1500 rpm

In Figure 3, again specific fuel consumption reduced with increasing brake power at constant speed for both fossil diesel and waste vegetable oil biodiesel. Slightly more WVOB was consumed per unit of power per hour compared to fossil diesel. Specific fuel consumption increased with increasing engine speed for both fuels but the increase was negligible. The variation of both fuels in consumption rate is not significantly different as the F test of 0.7556 indicates.

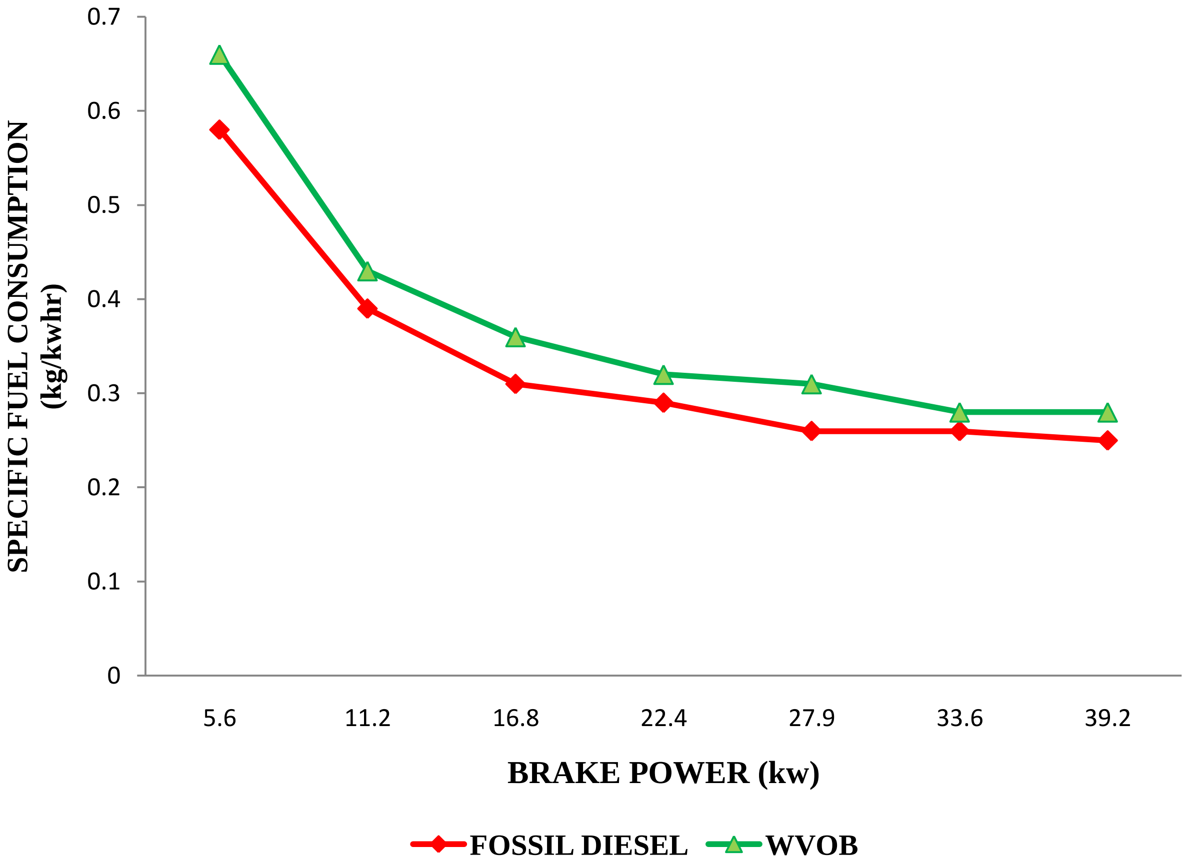


Figure 3.Specific fuel consumption versus brake power at 1500 rpm

4.15 3 Effects of fossil diesel and WVOB consumption on brake power at 1750 rpm

In Figure 4, specific fuel consumption reduced with increasing brake power at constant speed for both fossil diesel and biodiesel. Slightly more waste vegetable oil biodiesel was consumed per unit of power per hour compared to fossil fuel. It was observed that the optimum operating combustion conditions were at a speed of 1750 rpm for both fossil diesel and waste vegetable oil biodiesel at average fuel consumption of 0.3396 kg/kWh for diesel and 0.3804 kg/kWh for waste vegetable oil biodiesel. Specific fuel consumption also increased with increasing engine speed for both fuels but the increase was negligible. F test of 0.7334 shows that the variation of both fuels in terms of consumption rate is not significantly different.

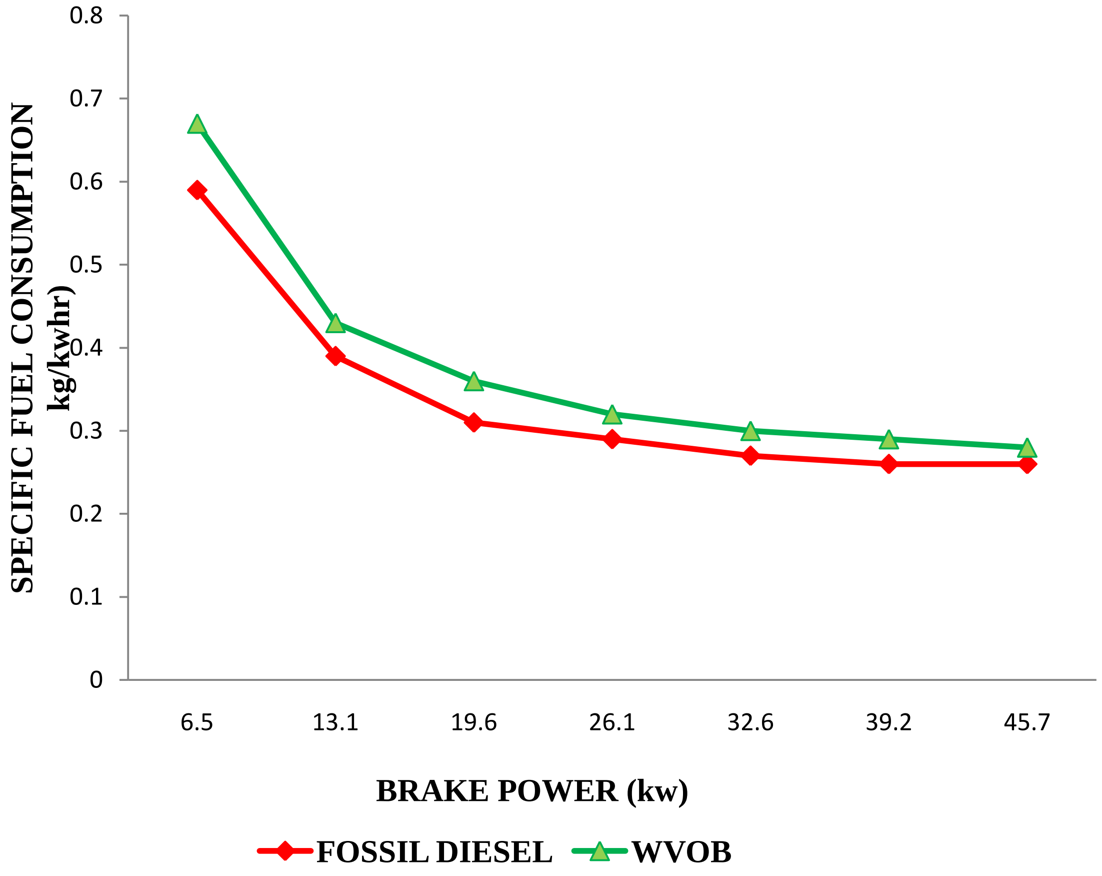


Figure 4.Specific fuel consumption versus brake power at 1750 rpm

4.15.4 Effects of fossil diesel and WVOB consumption on brake power at 2000 rpm

In Figure 5, again specific fuel consumption reduced with increasing brake power at constant speed for both fossil diesel and biodiesel. But slightly more WVOB was consumed per unit of power per hour compared to fossil diesel. Specific fuel consumption increased with increasing engine speed for both fuels but the increase was negligible. If the plots were to be extrapolated, specific fuel consumption was likely to be equal for both fuels at very high brake power. This could indicate that biodiesel consumption rate may be at par or lower than that of fossil diesel for heavy duty applications. F test of 0.3964 shows that the variation of both fuels in terms of consumption rate is not significantly different.

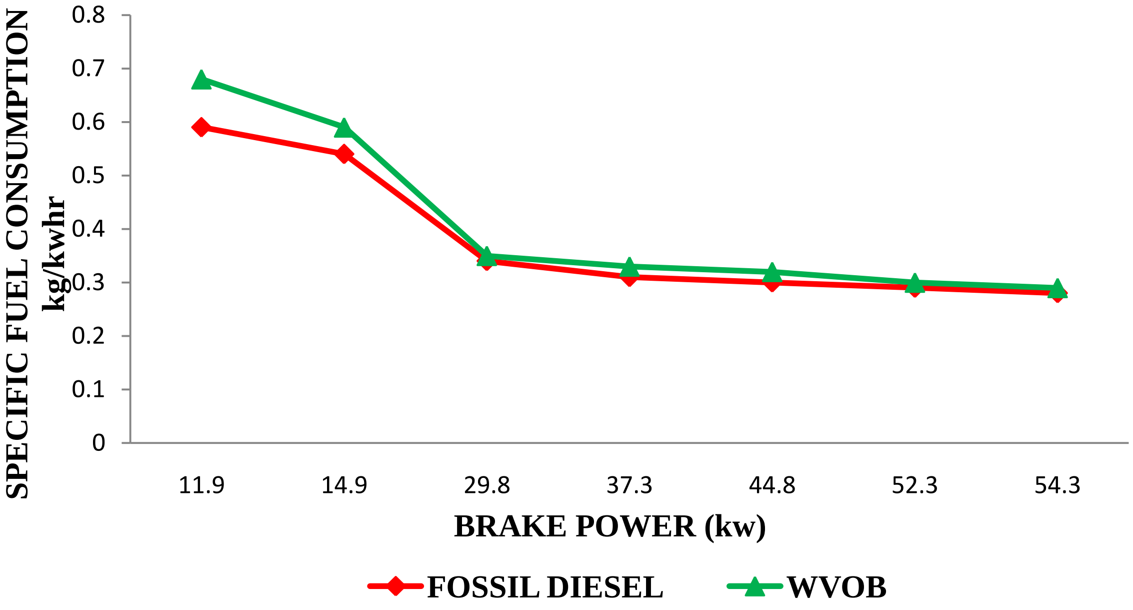


Figure 5.Specific fuel consumption versus brake power at 2000 rpm

4.16 Results of fuel thermal efficiency versus brake power at constant speeds

The following series of graphs dealt with thermal efficiency against brake power for fossil diesel and waste vegetable oil biodiesel and how well they compare in diesel engine at various speeds from 1250 rpm to 2000 rpm.

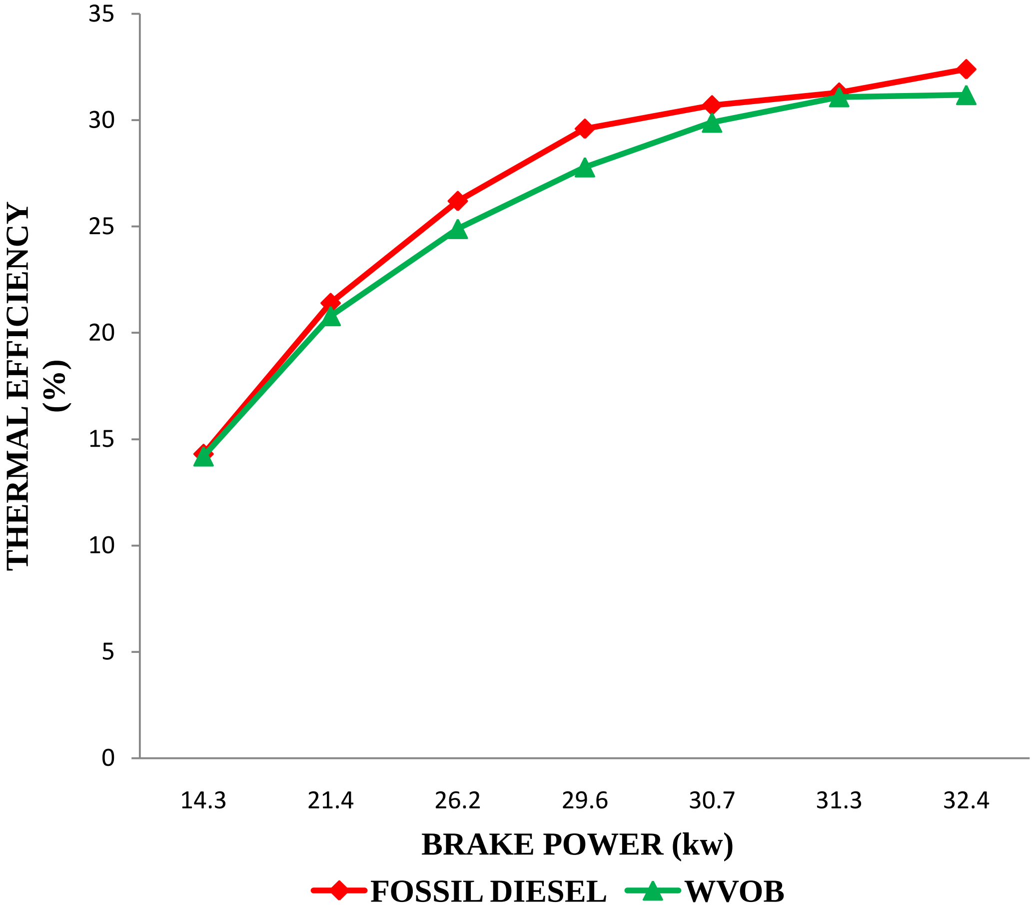


Figure 6. Thermal efficiency versus brake power at 1250 rpm

4.16.1 Effects of fossil diesel and WVOB thermal efficiency on brake power at 1250 rpm

Figure 6 gives a plot of thermal efficiency against the brake power at 1250 rpm. Thermal efficiency increased with brake power at constant speed. The thermal efficiency of both WVOB and fossil diesel were highly comparable, but that of biodiesel slightly lower. The engine used attained a maximum thermal efficiency averaging 32.36% at a constant speed of 1250 rpm. F test gives 0.9186, which indicated that the variation of thermal efficiency with brake Power was not significantly different.

4.16.2 Effects of fossil diesel and WVOB thermal efficiency on brake power at 1500 rpm

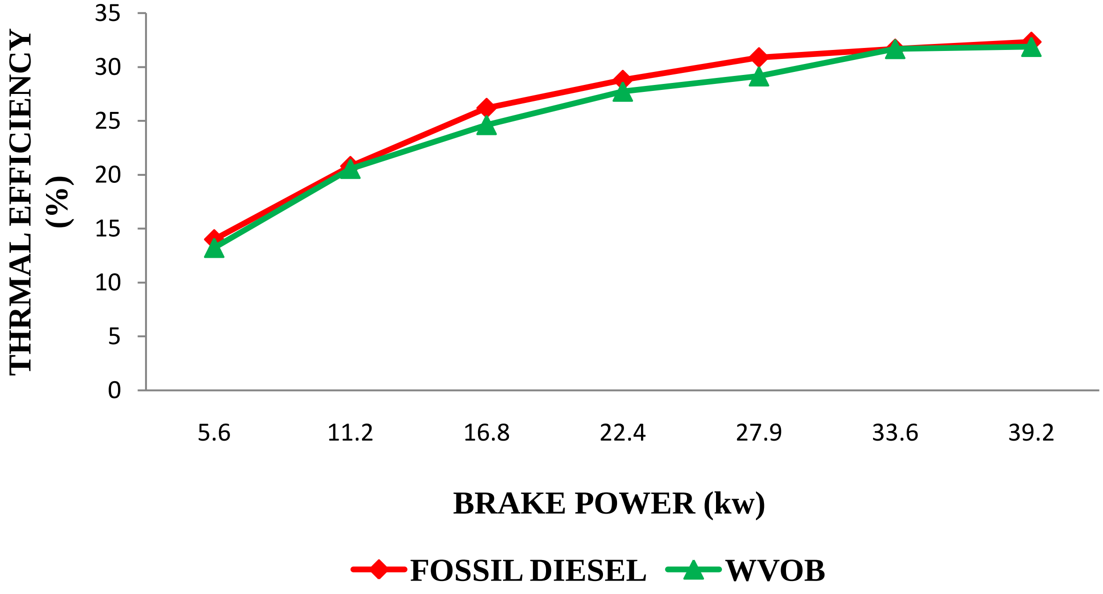


Figure 7.Thermal efficiency versus brake power at 1500 rpm

From the graph in (Figure7), thermal efficiency increased with brake power at constant speed of 1500 rpm. The thermal efficiency of both waste vegetable oil biodiesel and fossil diesel were highly comparable, but that of biodiesel slightly lower. The engine attained a maximum thermal efficiency averaging about 32.34% at a constant speed of 1500 rpm. F test value of 0.9960 shows that the variation of both fuels in terms of thermal efficiency is not significantly different.

4.16.3 Effects of fossil diesel and WVOB thermal efficiency on brake power at 1750 rpm

Figure 8 is a plot of thermal efficiency against the brake power at constant speed of 1750 rpm. Thermal efficiency once more increased with brake power at constant speed. The thermal efficiency of both WVOB and fossil diesel were highly comparable, but that of biodiesel slightly lower due to low calorific value of biodiesel. The engine used attained a maximum thermal efficiency averaging about 33.06% at a constant speed rating of 1750 rpm. The variation in thermal efficiency with brake power for both fuels is not significantly different as given by F test 0.9747.

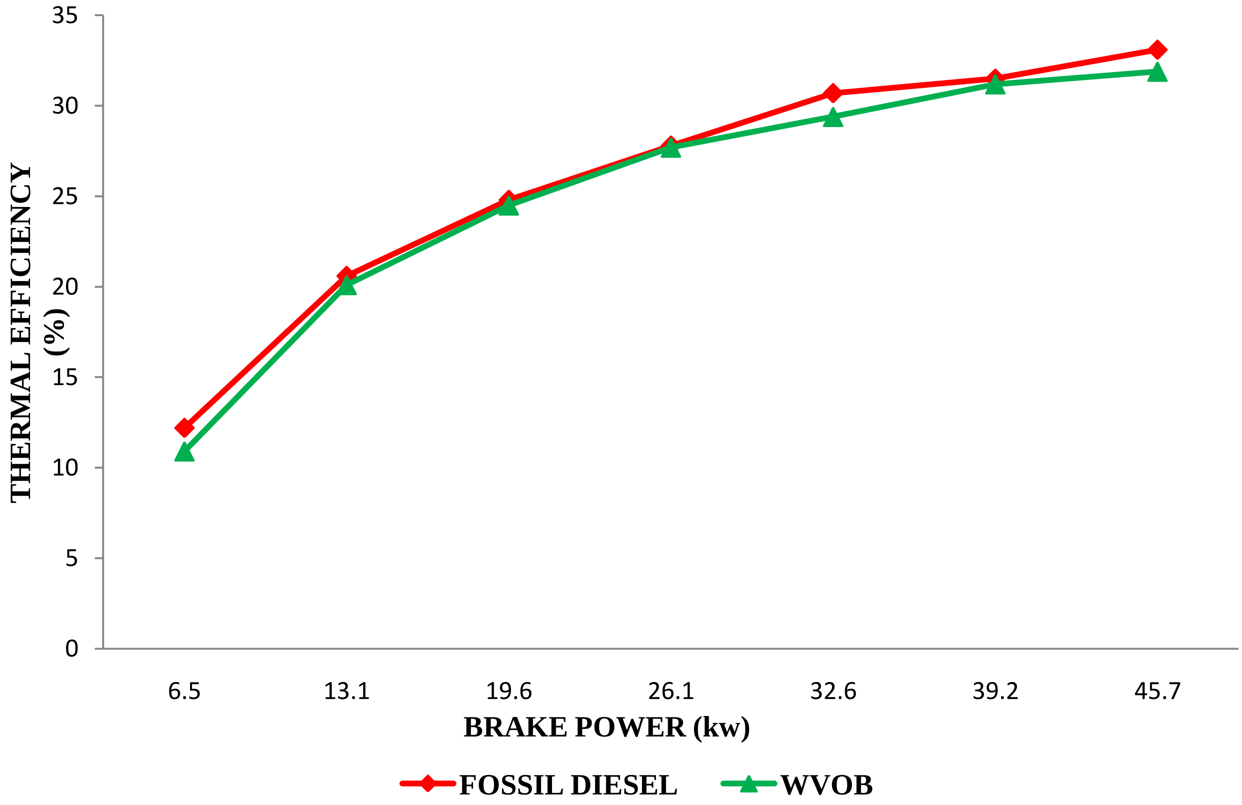


Figure 8.Thermal efficiency versus brake power at 1750 rpm

4.16.4 Effects of fossil diesel and WVOB thermal efficiency on brake power at 2000 rpm

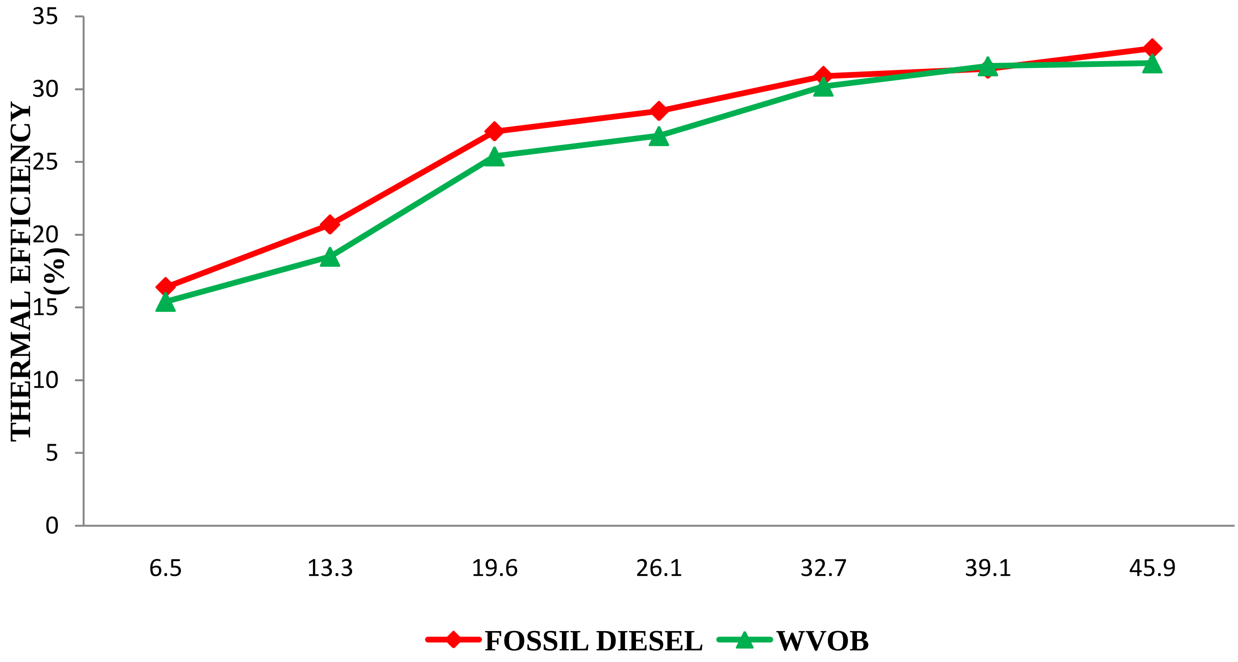


Figure 9.Thermal efficiency versus brake power at 2000 rpm

In Figure 9, thermal efficiency increased as usual with increasing brake power. At some brake power levels the thermal efficiencies realized were almost the same for both fossil diesel and biodiesel. This may mean that properties necessary for proper energy conversions in the diesel engine were all met by the biodiesel. The engine used attained a maximum thermal efficiency averaging about 32.68%. This may mean that properties necessary for proper energy conversions in the diesel engine were all met by the biodiesel. Thermal efficiency generally decreases at elevated brake power. At some point, especially at high speed of 2000 rpm the thermal efficiency of both fossil diesel and waste vegetable oil biodiesel continued to increase with that of biodiesel being higher. This may be due to the high lubricity of biodiesel. F test 0.88481 is a clear indication that the variation of thermal efficiency with brake power is not significantly different.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The experimental work carried out shows that biodiesel of acceptable quality can be produced on a small scale from waste vegetable oils and other low-cost raw materials like non-edible oils (Jatropha and croton seed oils), to add value. With the development of modern technology, biodiesel produced from waste vegetable oils and non-edible oils could be utilized as potential alternative fuel which could be substitute or additive for diesel fuel and other fuels like coal and natural gas for heating purposes. From the comparative fuel consumption rates for both fuels in diesel engine tests, it is clear that biodiesel has very similar properties to petroleum diesel as given in (table 5), and in graphs (Figure 2 and 9). There was no significant difference in the variation of fuel consumption rate and thermal efficiency for both fuels. Therefore waste vegetable oil biodiesel is as good as refined vegetable oil biodiesel and a potential alternative additive to fossil diesel.

Biodiesel represents a small but tangible way of breaking total dependence on fossil fuels. It is relatively straight-forward to produce and can be blended with petroleum diesel with no modifications to the engine. Biodiesel is environmentally friendly because its combustion emission gases are non-toxic to the atmosphere and reduces global warming (Green House Gas emissions). It is also extremely biodegradable and poses no long-term health problems.

With the inevitable depletion of the non-renewable resources of petroleum fuels and due to its favourable environmental features, biodiesel promises to be the fuel of tomorrow.

Although quantity of waste vegetable oils collectible from restaurants might be less, biodiesel production is viable and add value given that feedstock is obtained cheaply and could be supplemented with sources like oil recovered from activated bleaching earth (ABE), and non-edible oils which do not compete with food uses of oils.

5.2 RECOMMENDATIONS

No work has been done in Kenya to ascertain how much waste vegetable oils is collectible for biodiesel production. Further research may be done in this area. Long-term testing of biodiesel made from waste vegetable oils and animal fats is required especially regarding particulate exhaust emissions. The by-product glycerol could be used for example in the cosmetics, pharmaceutical and soap industries to further reduce the cost of biodiesel production. The recovery of methanol for reuse in the reaction would also reduce biodiesel production cost. Further work on analysis of waste vegetable oil biodiesel composition needs to be done as it requires instruments such as GC and HPLC which are expensive. In a biodiesel production plant, a quality control system would be required at reception, to monitor water content, free fatty acid levels and polymer levels in the incoming waste vegetable oil feedstock and other materials. Further work required to investigate the storage and oxidative stability of waste vegetable oil biodiesel, NO_x emissions and long term use in diesel engines and tractors.

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APPENDICES

APPENDIX 1

Kenya standard for Diesel fuel (Automotive Gas Oil)- KS 1309-1 :2003

S. No.	**Property**	**Limit**		**Test Method**	
		Min	**Max**	**KS 1309-1**	**Equivalent standard US ASTM**
i	Kinematic viscosity @ 40^0C cSt	1.6	5.5	KS 1099(a) Annex A	ASTM D 445 IP 71
)ii	Copper strip corrosion, 3hrs @100^0C	-	1	KS 1289(b) Annex D	ASTM D130 IP 154
iii	Distillation recovery @ 365^0C, % v/v, End-point	90	400	KS 1289 Annex F	ASTM D86 IP 123
iv	Density @ 20^0C, Kg/m^3	0.820	0.870	KS 1289	ASTM D 1298 IP 160
v	Flash-point,Pensky martens Closed cup ^{0}C	60	-	KS 161-17©	ASTM D 93 IP 34
vi	ASTM colour	-	3.5	KS 1309-1 Annex A	ASTM D1500 IP 196
vii	Cetane index (calculated)	48	-	KS 1309-1 Annex B	ASTM D 976
viii	Cloud-point ^{0}C	Report		KS 1309-1 Annex C	ASTM D 2500
ix	Cold filter plugging point (CFPP),^{0}C	-	6	KS 1309-1 Annex D	IP 309
x	Cloud-CFPP ^{0}C	-	12	-	-
xi	Sediment %, (m/m)	-	0.01	KS 1309-1 Annex E	ASTM D 473 IP 53
xii	Water % (v/v)	-	0.05	KS 1309-1 Annex F	ASTM D 95 IP 74/82
xiii	Ash % (m/m)	-	0.01	KS 1309-1 Annex G	ASTM D482
xiv	Sulphur content % (m/m)	-	0.5	KS 1309-1 Annex H	ASTM D1552
xv	Carbon residue Conradson on 10% residue (m/m)	-	0.15	KS 1309-1 Annex J	ASTM D 189 IP13
xvi	Neutralisation value : Strong acid No. mgKOH/g Total acid No. mgKOH/g	 Nil 0.5	 Nil -	KS 1309-1 Annex K	ASTM D 974

Source : Kenya Bureau of Standards, 2003.

Key ; (a) - specification for engine oil

(b) – specification for illuminating kerosene

(c) – Determination of flash-point, closed cup equilibrium method.

APPENDIX 2

U.S.A Standard Specifications for pure biodiesel (B 100)-ASTM D 6751-02.

Property	**Method**	**Limits**	**Units**
Flash point, closed cup	D 93	130 min	**°C**
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity	D 445	1.9 – 6.0	mm^2/s
Sulphated ash	D 874	0.020 max	Wt%
Total sulphur	D 5453	0.050 max	Wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report to customer	**°C**
Carbon residue	D 4530	0.050 max	Wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	Wt%
Total glycerine	D 6584	0.240	Wt%
Phosphorus	D 4951	0.0010	Wt%
Vacuum distillation end-point	D 1160	360°C max, at 90% distilled	**°C**

Source: Gerpen, J. V. *et al.*, (2006**).**

APPENDIX 3

European Standard Specifications for Pure Biodiesel (B100) EN 14214

S. No.	Property	Units	Lower limit	Upper limit	Test Method	
					EN 14214	ASTM D 6751
1	Ester content	%(m/m)	96.5	-	Pr EN 14103d	-
2	Density @ 15^0C	Kg/m^3	860	900	EN ISO 3675	
3	Viscosity @ 40^0C	mm^2/s	3.5	5.0	EN ISO 3104	D 445
4	Flash-point	^{0}C	> 101		ISO CD 3679e	D 93
5	Sulphur content	mg/kg	-	10	-	D 5453
6	Tar remnant (@ 10% Distillation remnant)	% (m/m)	-	0.3	EN ISO 10370	D 1160
7	Cetane No.	-	51.0	-	EN ISO 5165	D 613
8	Sulphated ash	% (m/m)	-	0.02	ISO 3987	D 874
9	Water content	mg/kg	500	-	EN ISO 12937	D 2709
10	Total contamination	mg/kg	-	24	EN 12662	-
11	Copper band corrosion (3 hrs @ 50^0C)	Rating	Class 1	Class 1	EN ISO 2160	D 130
12	Oxidation stability, 110^0C	hours	6	-	EN 14112	To be determined
13	Acid value	mg/KOH/g	0.5		pr EN 14104	D 664
14	Iodine value		-	120	pr EN 14111	
15	Linolenic acid Methyl ester	% (m/m)	-	12	pr EN 14103 d	-
16	Polyunsaturated (> = 4 double bonds) Methylester)	% (m/m)	-	1	pr EN 14103	-
17	Methanol content	% (m/m)	-	0.2	pr EN 14110l	-
18	Monoglyceride content	% (m/m)	-	0.8	pr EN 14105m	-
19	Diglyceride content	% (m/m)	-	0.2	pr EN 14105m	-
20	Triglyceride content	% (m/m)	-	0.2	pr EN 14105m	-
21	Free glycerine	% (m/m)	-	0.02	pr EN 14105m/ pr EN 14106	D 6584
22	Total glycerine	% (m/m)	-	0.25	pr EN 14105m	D 6584

Source : European Standard Specifications for pure Biodiesel, (2009).

APPENDIX 4

Calculations and statistical analysis

The following relationships were used in calculating the data given in appendices 6 to 13.

FUEL	**FUEL CONSUMPTION**	**CALORIFIC VALUE OF FUEL**	**FUEL DENSITY**	**ROOM TEMP ^{0}C**	**BAROMETRIC PRESSURE**
FOSSIL DIESEL	100 ml (100 x 10^{-6} kg)	44 MJ/kg	845 Kg/m^3	25	630 mm Hg
BIODIESEL	100 ml (100 x 10^{-6} kg)	40 MJ/kg	877 Kg/m^3	25	630 mmHg

- Mass of fuel consumed = Density x volume of fuel used
- Rate of fuel consumption = Mass of fuel consumed/time (hrs)
- Energy of fuel consumed (energy input) = Mass of fuel consumed x Calorific value of fuel used.
- Power Input (Watts) = Energy of fuel consumed /time (hrs)
- Brake Power (b.p) (kilowatts-KW) = W x N x bhp/200 x 1000
  Where: W = load (in Lbs), N = speed (rpm), bhp = 746 Watts.
- Thermal Efficiency(%) = Brake power /Power Input
- Brake Specific fuel consumption (B.S.F.C) = Rate of fuel consumption /Brake Power

Statistical analysis

This is based on one way ANOVA, and F- test.

The null hypothesis:

H_0 = There is no significant difference between the variances for fossil diesel and biodiesel fuel consumption rate and thermal efficiency in diesel engine at 0.05% significant level.

H_1 = The alternative hypothesis is that there is significant difference if F- test value is more than 1. Hence the hypothesis is then rejected.

APPENDIX 5

FOSSIL DIESEL CONSUMPTION AT 1250 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**2.7**	**3.4**	**4.4**	**5.3**	**6.2**	**7.2**	**8.7**
Brake Power (Kilowatts)	**4.7**	**9.3**	**14.1**	**18.7**	**23.3**	**27.9**	**32.7**
Thermal Efficiency (%)	**14.3**	**21.4**	**26.2**	**29.6**	**30.7**	**31.3**	**32.4**
Brake Specific fuel consumption Kg/kwh	**0.51**	**0.32**	**0.29**	**0.27**	**0.25**	**0.24**	**0.24**
Power Input (Watts)	**0.33**	**0.43**	**0.53**	**0.63**	**0.76**	**0.86**	**1.08**
Time for 100 ml fuel consumption (hrs)	**0.03**	**0.02**	**0.019**	**0.015**	**0.014**	**0.012**	**0.009**
F- test Result = 0.70744							

APPENDIX 6

FOSSIL DIESEL CONSUMPTION AT 1500 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**3.3**	**4.4**	**5.2**	**6.4**	**7.4**	**8.6**	**9.9**
Brake Power (Kilowatts)	**5.6**	**11.2**	**16.8**	**22.4**	**27.9**	**33.6**	**39.2**
Thermal Efficiency (%)	**14.0**	**20.8**	**26.2**	**28.8**	**30.9**	**31.7**	**31.9**
Brake Specific fuel consumption Kg/kwh	**0.58**	**0.39**	**0.31**	**0.29**	**0.26**	**0.26**	**0.25**
Power Input (Watts)	**0.40**	**0.54**	**0.64**	**0.78**	**0.90**	**1.05**	**1.21**
Time for 100 ml fuel consumption (hrs)	**0.026**	**0.019**	**0.016**	**0.013**	**0.011**	**0.009**	**0.008**
F- test Result = 0.7556							

APPENDIX 7

FOSSIL DIESEL CONSUMPTION AT 1750 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**3.8**	**5.2**	**6.0**	**7.7**	**8.9**	**10.3**	**11.9**
Brake Power (Kilowatts)	**6.5**	**13.3**	**19.6**	**26.1**	**32.7**	**39.1**	**45.9**
Thermal Efficiency (%)	**12.2**	**20.6**	**24.8**	**27.8**	**30.7**	**31.5**	**33.1**
Brake Specific fuel consumption Kg/kwh	**0.59**	**0.39**	**0.31**	**0.29**	**0.27**	**0.26**	**0.26**
Power Input (Watts)	**0.51**	**0.62**	**0.79**	**0.94**	**1.06**	**1.18**	**1.45**
Time for 100 ml fuel consumption (hrs)	**0.02**	**0.015**	**0.012**	**0.01**	**0.0095**	**0.0082**	**0.0071**
F- test Result = 0.7334							

APPENDIX 8

FOSSIL DIESEL CONSUMPTION AT 2000 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**3.9**	**5.4**	**6.7**	**8.1**	**9.4**	**11.6**	**12.7**
Brake Power (Kilowatts)	**6.5**	**13.3**	**19.6**	**26.1**	**32.7**	**39.1**	**45.9**
Thermal Efficiency (%)	**16.4**	**20.7**	**27.1**	**28.5**	**30.2**	**31.5**	**32.8**
Brake Specific fuel consumption Kg/kwh	**0.59**	**0.40**	**0.34**	**0.31**	**0.30**	**0.29**	**0.28**
Power Input (Watts)	**0.53**	**0.65**	**0.81**	**0.95**	**108**	**1.24**	**1.40**
Time for 100 ml fuel consumption (hrs)	**0.022**	**0.016**	**0.013**	**0.010**	**0.0085**	**0.0073**	**0.0066**
F- test Result = 0.3964							

APPENDIX 9

BIODIESEL CONSUMPTION AT 1250 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**2.8**	**3.6**	**4.9**	**6.1**	**6.9**	**8.1**	**9.3**
Brake Power (Kilowatts)	**5.6**	**11.2**	**16.8**	**22.4**	**27.9**	**33.6**	**39.2**
Thermal Efficiency (%)	**14.2**	**20.8**	**24.9**	**27.8**	**29.9**	**31.1**	**31.2**
Brake Specific fuel consumption Kg/kwh	**0.57**	**0.39**	**0.32**	**0.29**	**0.27**	**0.26**	**0.26**
Power Input (Watts)	**0.38**	**0.48**	**0.67**	**0.80**	**0.94**	**1.08**	**1.25**
Time for 100 ml fuel consumption (hrs)	**0.031**	**0.025**	**0.018**	**0.014**	**0.013**	**0.011**	**0.009**
F- test Result	**= 0.9186**						

APPENDIX 10

BIODIESEL CONSUMPTION AT 15O0 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed ((kg/h)	**3.7**	**4.9**	**6.1**	**7.1**	**8.6**	**9.5**	**10.9**
Brake Power (Kilowatts)	**5.6**	**11.2**	**16.8**	**22.4**	**27.9**	**33.6**	**39.2**
Thermal Efficiency (%)	**13.2**	**20.6**	**24.6**	**27.7**	**29.2**	**31.6**	**31.7**
Brake Specific fuel consumption Kg/kwh	**0.66**	**0.43**	**0.36**	**0.32**	**0.31**	**0.28**	**0.28**
Power Input (Watts)	**0.45**	**0.54**	**0.68**	**0.81**	**0.96**	**1.06**	**1.24**
Time for 100 ml fuel consumption (hrs)	**0.024**	**0.018**	**0.014**	**0.012**	**0.01**	**0.009**	**0.008**
F- test Result	**= 0.9960**						

APPENDIX 11

BIODIESEL CONSUMPTION AT 1750 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**4.4**	**5.8**	**7.1**	**8.5**	**9.9**	**11.3**	**12.8**
Brake Power (Kilowatts)	**6.5**	**13.1**	**19.6**	**26.1**	**32.6**	**39.2**	**45.7**
Thermal Efficiency (%)	**10.9**	**20.1**	**24.5**	**27.7**	**29.4**	**31.2**	**31.9**
Brake Specific fuel consumption Kg/kwh	**0.67**	**0.43**	**0.36**	**0.32**	**0.30**	**0.29**	**0.28**
Power Input (Watts)	**0.6**	**0.65**	**0.80**	**0.94**	**1.11**	**1.26**	**1.43**
Time for 100 ml fuel consumption (hrs)	**0.02**	**0.015**	**0.012**	**0.01**	**0.008**	**0.007**	**0.006**
F- test Result = 0.9747							

APPENDIX 12

BIODIESEL CONSUMPTION AT 2000 RPM

	Load (kg)						
PARAMETER	**0.4536 (1Lb)**	**0.907 (2Lb)**	**1.3608 (3Lb)**	**1.8144 (4Lb)**	**2.2680 (5Lb)**	**2.7216 (6Lb)**	**3.1752 (7Lb)**
Rate of fuel consumed (kg/h)	**8.1**	**8.8**	**10.3**	**12.1**	**14.4**	**15.8**	**16.3**
Brake Power (Kilowatts)	**11.9**	**14.9**	**29.8**	**37.3**	**44.8**	**52.3**	**54.3**
Thermal Efficiency (%)	**15.4**	**18.5**	**25.4**	**26.8**	**30.9**	**31.6**	**32.8**
Brake Specific fuel consumption Kg/kwh	**0.68**	**0.59**	**0.35**	**0.33**	**0.32**	**0.30**	**0.29**
Power Input (Watts)	**0.78**	**0.92**	**1.10**	**1.29**	**1.45**	**1.65**	**1.66**
Time for 100 ml fuel consumption (hrs)	**0.0108**	**0.0099**	**0.0085**	**0.0072**	**0.0061**	**0.0056**	**0.0054**
F- test Result = 0.8848							