BIODIESEL PRODUCTION FROM CANDLENUT AND CALODENDRUM CAPENSE SEEDS: PROCESS DESIGN AND TECHNOLOGICAL ASSESSMENT

By

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A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Chemistry, University of Nairobi.

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2013
DECLARATION

I hereby declare that this thesis is my original work and has not been presented for a degree in any other university

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ACKNOWLEDGEMENTS

I owe special debt of gratitude, appreciation and special thanks to my first supervisor Prof. John M. Onyari for guiding and supervising this research with a lot of dedication. To my other supervisors; Prof. James Nyang’aya, Prof. Paul M. Shiundu and Prof. Francis Mulaa greatest thanks for your continuous guidance, encouragement and criticism during experimental work and thesis preparation.

I say thanks to all who helped me during experimental work, technicians Mrs. Rose Mutungi, Mr. Kimega and Emma of the Physical Chemistry laboratory of University of Nairobi (UoN), Mr. Njoroge of Analytical chemistry laboratory of UoN, Mr.Alfred Odhako of science workshop of UoN, Mr. Kogi and Mr. Kennedy of the thermodynamics laboratory in the department of mechanical and manufacturing engineering of UoN. Thanks to Msc. Biochemistry students Mr. Mwangi and Mr.Nelson for their immense support during culturing of enzymes.

I express my special gratitude to Eng. Richard Kimilu for his guidance and ideas during carrying out engine tests.

Special thanks to Prof. Meroka Mbeche, Prof. Macgrey and Prof.Geoffrey Kamau, for their immense encouragement and moral support during registration of Msc course.

Thanks to Aunt Teresa, Brother Moenga, Sister Jerusha, great friends David Oseko, Benard Nyankabaria, and Beatrice Mwende for their moral and financial support throughout my education.

Thanks to the University of Nairobi for the laboratory facilities and for providing conducive environment for studies and research work. Finally to the World Federation of Scientists and University of Nairobi I say thanks for the award of scholarships which made my studies and research work possible.

Mogire D.N.
DEDICATION


To Thomas Ndaya and Florence Nyaechi for their parental care, prayers, love, patience and support throughout my studies. To Uncle Samuel Ouru for his advice, encouragement and financial support. To Godfrey Moriasi and Evans Matayo for their immense moral support; without their love, encouragement and financial support I could have not reached this far.
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<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>BHP</td>
<td>Brake Horse Power</td>
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<tr>
<td>BS</td>
<td>British Standards</td>
</tr>
<tr>
<td>BSFC</td>
<td>Brake Specific Fuel Consumption</td>
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<tr>
<td>BSP</td>
<td>Biomass Support Particles</td>
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<tr>
<td>BTE</td>
<td>Brake Thermal Efficiency</td>
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<tr>
<td>CFPP</td>
<td>Cold Filter Plugging Point</td>
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<tr>
<td>CI</td>
<td>Compression Ignition</td>
</tr>
<tr>
<td>CP</td>
<td>Cloud Point</td>
</tr>
<tr>
<td>DF2</td>
<td>Grade two diesel fuel</td>
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<tr>
<td>EGR</td>
<td>Exhaust Gas Recirculation</td>
</tr>
<tr>
<td>EN</td>
<td>European Standards</td>
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<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>ID</td>
<td>Ignition Delay</td>
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<tr>
<td>ISO</td>
<td>International Organization for Standards</td>
</tr>
<tr>
<td>KEBS</td>
<td>Kenya Bureau of Standards</td>
</tr>
<tr>
<td>KIRDI</td>
<td>Kenya Industrial Research Institute</td>
</tr>
<tr>
<td>MDG</td>
<td>Millennium Development Goals</td>
</tr>
<tr>
<td>No. 1-D</td>
<td>Grade number one diesel fuel</td>
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<tr>
<td>No. 4-D</td>
<td>Grade number four diesel fuel</td>
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<td>Selective Catalytic Reduction</td>
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<td>Straight Vegetable Oils</td>
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<td>Tetrahydrofuran</td>
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<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
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<tr>
<td>ULSD</td>
<td>Ultra –Low Sulphur Diesel</td>
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<td>WVO</td>
<td>Waste Vegetable Oil</td>
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ABSTRACT

This project was based on biodiesel production from *candlenut* and *calodendrum capense* seeds using conventional and biotechnological technique and determination of the oil yields and biodiesel quality. The driving force for large-scale use of biodiesel has been the need to reduce the harmful emissions that result from the burning of petroleum oil as well as our dependence on diminishing reserves of petroleum oil. The aim of the study was to extract oil from *Candlenut* tree and *Calodendrum capense* seeds using conventional techniques and determine conditions for optimum oil yields. The oil from the two non-edible plant feedstocks was obtained using soxhlet solvent extraction and mechanical screw pressing machine at Kenya Industrial Research Institute (KIRDI).

The preliminary tests like the acid value, viscosity, density, iodine value and calorific value were done to ascertain the quality of the oil. Transesterification was done using methanol and potassium hydroxide as a catalyst. The use of enzyme as a catalyst in transesterification was done using lipase enzyme cultured from Lake Bogoria water. Lipase-catalyzed transesterification of *candlenut* oil and *calodendrum capense* oil using methanol for biodiesel production in amyl alcohol and t-butanol alcohol was investigated. The optimum conditions for transesterification were investigated. Infrared spectroscopy was used to ascertain the efficiency of the acid catalyzed transesterification process. Thin Layer Chromatography was also used in the case of enzymatic transesterification. The engine performance tests of B5 and B20 for both *candlenut* and *calodendrum capense* were also investigated. The engine tests parameters investigated; brake specific fuel consumption, thermal efficiency, brake horse power and exhaust temperature were compared to commercial diesel.

The oil yield for *candlenut* seeds varied from 32.3% to 35.4% and for *calodendrum capense* seeds, the oil content was 35.2%. Factors which govern transesterification process such as the quantity of the catalyst, reaction time, speed, temperature and amount of methanol used were investigated and optimum conditions determined (temperature of 65°C, one hour reaction time, rotation speed of 1100rpm, 6:1 molar ratio of methanol to oil and optimum potassium hydroxide catalyst). For lipase enzymes catalyzed transesterification, it was observed that 6 ml of t-butanol alcohol, 6:1 molar ratio of methanol to oil, 2ml of lipase catalyst, temperature 45°C, 150 rpm and 24hrs yielded the highest biodiesel conversion of 92.6%. Overall, the lipase catalyzed transesterification method yielded higher conversion in comparison to acid catalyzed transesterification (64.8 to 72.1%).
The methyl esters that were obtained after transesterification were then blended with commercial diesel to obtain B5, B10, B20 and B100. The Infrared spectrum for the methyl esters gave a significant peak at 1720 cm$^{-1}$ and it was also similar to that obtained for fossil diesel.

The physical properties studied for biodiesel and the blends for both candlenut and calodendrum capense were similar to those of diesel fuel. The neat candlenut oil was found to have a high iodine value of 136.5g I$_2$/g oil but the methyl esters were within the allowed limits of 115g I$_2$/100g oil and 120g I$_2$/100g oil as per ASTM D6751 and EN 14214 respectively. The kinematic velocities for B100 biodiesel for both candlenut and calodendrum capense were comparable to those of the blends (B5, B10, B20) and the diesel fuel. The kinematic velocities decreased with increase in temperature from 15 to 60$^\circ$C. The acid value for neat biodiesel (B100) and the blends for both candlenut and calodendrum capense were found to be within the allowed maximum limit of 0.8mgKOH/g as per ASTM D664. The calorific values increased with the decrease in the biodiesel percentage in the blends. The calorific value for B5 calodendrum capense (42.2MJ/Kg) and candlenut (41.5MJ/Kg) were the highest and close to the value obtained for diesel fuel (43.4MJ/Kg). The flash point decreased with the decrease in the biodiesel percentage in the blends with the B5 for both candlenut and calodendrum capense being close to that of diesel fuel.

The specific engine consumptions of the biodiesel blends as well as diesel oil decreased with increasing load from 5.593 to 33.570 KW and tended to increase with further increase in brake horse power. The thermal efficiency for B5 candlenut blend increased from 12.64% at BHP 5.59 KW to maximum 32.27% at BHP 27.96 KW and started decreasing. There was an increase in the thermal efficiency for both B5 and B20 calodendrum capense blends. For both B5 and B20 candlenut and calodendrum capense blends the exhaust temperature increased with brake horse power.

The amount of oil that was obtained from mechanical extraction of both the plant seeds promotes planting more hence obtaining alternative fuel and conserving the environment. The results on physical properties of the biodiesel for both the candlenut and calodendrum capense and those of the fossil diesel showed similarities. The lipase catalyzed transesterification gave a high yield of methyl esters which promotes the green chemistry and reduction of environmental pollution resulting on use of alkali catalysts. The engine tests results for B5 and B20 blends for candlenut and calodendrum capense showed that biodiesel obtained from these two plants can be used in a diesel engine without any modification hence serve as alternative fuel.
CHAPTER ONE
INTRODUCTION

Petroleum fuels have remained almost entirely unchallenged since the motor vehicle was invented. However, their reserves are not uniformly distributed and their increased use contributes to a variety of local and regional air pollution problems and potential climatic change (Poulton, 1974). Although studies indicate the existing oil reserves can meet the world’s oil requirements for the next 30-60 years (Eastop et al., 1995; Hansen et al., 1989), concerns have been raised on the impact of the use of fossil fuels on the environment. The recent witnessed fuel crises and the world oil price fluctuations have generated the desirability to develop renewable fuels to decrease the dependence on fossil fuels. The need to reduce the growth of the consumption of fossil fuels, for economic and environmental reasons can best be accomplished by using renewable substitutes (Guibet, 1997; Pramanik, 2002). Kenya which does rely on fossil fuel imports is feeling the environmental effects and the oil price fluctuations.

Kenya is an energy intensive developing country fully dependent on oil imports, which means it is feeling the devastating effects of high oil prices on all sectors of the economy. Price rises of the current magnitude imply, amongst other effects, a significant reduction of economic growth rates, an erosion of trade balances, rising unemployment, lower import capacity, the destruction of the effects of debt relief efforts, a hike in inflation rates and a blow to agricultural production and marketing. Kenya’s oil import bill/year increased from $1.489 billion (2006) to $1.742 billion (2007). In 2008, an increase of 62% in petrol imports to Kshs 197 billion or about $2.54 billion. The cost of oil imports is dictated by factors well beyond the control of the country and thus the need to have secure local oil supplies which should be in line with achieving the vision 2030, as well as MDG’s and sustainable development goal.

High price fluctuations on petroleum and its products have been so unpredictable varying from $50 (Sept. 28, 2004); $72 (April 19, 2006), $130 (May, 2008), $146 (July, 2008), $70 (June 2009), $59.62 (July 2010), $91.38 (Dec.2010), $119.79 (Feb.2011), $102.59 (Nov.2011), $109.39 (Feb.2012) and currently at $98.45(June 10, 2013). These high prices and fluctuations have caused great economic uncertainties and recessions in the world’s economy. Due to this, it has led to countries going for renewable energy such as solar, wind, geothermal and biodiesel.
Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. Climate change due to global warming has its links with the effects of environmental degradation (for example, CO₂ emissions from fossil fuels).

Kenya is a signatory to the Kyoto Protocol; by reducing carbon emissions through large afforestation programs (biofuels) it provides the opportunity to trade in carbon credits with the countries that immediately require them under the Kyoto Protocol. The transport industry is a major contributor to the emission of greenhouse gases (CO₂, NOₓ, SOₓ etc) and it is therefore desirable to replace the fossil diesel with biodiesel with a view to minimizing such greenhouse gas emissions.

Production of biofuels at competitive prices can offset some of these problems. Kenya consumes around 55,000 barrels of oil per day. A single 200,000 tons per year biodiesel plant would be able to replace slightly more than 5 per cent of this total amount—a significant proportion.

Kenya is a largely agrarian society, with 75% of its population employed in the farming sector, mostly as subsistence farmers. It is one of Africa's medium-sized countries, and has an abundance of potential arable land, estimated to be around 15.8 million hectares, of which it currently utilizes around 33 per cent.

Biodiesel from *Jatropha curcas* and *Croton megalocarpus* has previously been investigated in Kenya (Kimilu et al., 2011, Wanjala, 2009). In this study attention is focused on biodiesel from other renewable energy resources in Kenya and other East African countries. Use of biodiesel is expected to improve air emissions quality. In global context, biofuels (comprise biodiesel, bioethanol and other biomass based fuels) have assumed significant importance due to signing of Kyoto protocol, environmental legislations, Environmental Management Systems (EMS) and other international agreements. Interest in Biofuels is also due to energy security concerns (transport, agriculture & industry); afforestation programs; creation of rural employment and diversification of economy as a result of changing patterns in energy supply, demand and cost (Http://unfccc.int/files/kyoto_protocol 2009).

The energy trend offers a challenge as well as an opportunity to look for substitutes of fossil fuels for both economic and environmental benefits. Investigation and development of biofuels as an alternative and renewable source of energy for transportation has become a major target in the effort towards energy self-reliance. Biofuel commands crucial advantages such as technical
feasibility of blending, superiority from the environment and emission reduction angle, its capacity to provide energy security to remote and rural areas and employment generation. Moreover, biofuel will also provide rich biomass and nutrients to the soil and check degradation of land. The consumption and demand for the petroleum products are increasing every year due to increase in population, standard of living and urbanization. The increase in crude oil import affects the country’s economy and its development. The acid rain, global warming and health hazards are the results of ill effects of increased polluted gases like SO$_x$, CO$_x$ and particulate matter in atmosphere.

Today’s diesel engines require a clean burning, stable fuel that performs well under the variety of operating conditions. Biodiesel is the only alternative fuel that can be used directly in any existing unmodified diesel engine. Because it has similar properties to diesel fuel, biodiesel can be blended at any ratio with diesel fuel. In most of the developed countries, biodiesel is produced from edible oils such as soybean, rapeseed, sunflower, peanut, etc. To avoid food versus energy debate, it is more desirable to use non-edible oils for biodiesel production. This is because edible oils are already in demand in food applications and often more expensive than diesel fuel. Among the nonedible oil sources, Calodendrum Capense and Candlenut seeds have been identified as potential biodiesel sources and comparing with other sources, they have added advantages such as rapid growth, higher seed productivity, suitable for tropical and subtropical regions of the world.

The Biofuels have assumed significant importance globally as the world addresses changing patterns in energy supply and demand. Before 2030 the world is projected to experience net deficits of petroleum supplies as new oil discoveries are offset by depletions. Further, as the world focuses on global climate change, biofuels have assumed importance as the most practical alternative to petroleum fuels in efforts to reduce carbon emissions in the transport sector. While biofuels comprise biodiesel, bioethanol and other biomass based fuels; this project addresses biodiesel as the area that requires immediate prioritization. Bioethanol and other biomass based fuels will be addressed in different project that might be undertaken.

Use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials (Arjun et al., 2008). As early as 1980s Munavu and Onyari (1982) studied the oil content and properties of over 15 non-conventional
seed oils in Kenya and this included *Calodendrum capense* and *Jatropha curcus* seeds. Azam et al., (2005) studied the prospects of using fatty acid methyl esters (FAME) of some 26 non-traditional plant seed oils including *Jatropha*, as potential biodiesel. They were found to be suitable for use as biodiesel and they met the major specification of biodiesel for use in diesel engine. Subramanian et al., (2005) reported that there are over 300 different species of trees which produce oil bearing seeds. Thus, there is a significant potential for non-edible oil source from different plants for biodiesel production as an alternative to petrodiesel.

Biodiesel is most commonly made by transesterification process of the oil through the use of a catalyst and an alcohol, typically methanol. The chemical reaction that occurs through this process breaks down the oil molecules and replaces the glycerine portion of the molecule with an alcohol molecule. The glycerine separates to the bottom and is drained off resulting in biodiesel. The biodiesel is then typically washed, to remove any extra impurities and is then used as a fuel in a diesel engine without making any modifications to the engine. The use of enzymes (lipases) is timely as we embrace the practice of green production technologies (Green chemistry) which ensures sustainable use of resources, energy and maintenance of a clean environment.

### 1.1.1 Vegetable Oils

Conventional vegetable oils such as linseed, cotton seed, soybean, sunflower, castor, peanut, coconut, palm and others have emerged as prime candidates of alternative fuels used in diesel engines. Currently the larger portion of these conventional vegetable oils produced locally are used in production of human and animal food, cooking oil, soap and other industrial chemicals. Kenya imports about 80% of the vegetable oil and other associate foods in its requirements. Munavu and Odhiambo (1984) identified several indigenous and non-conventional sources of vegetable oils and further established that their properties are similar to those of conventional vegetable oils.

Most vegetable oils can be substituted directly for diesel fuel but may create problems mostly resulting from incomplete combustion which result to injector nozzle coking and even failure due to polymerization of the oil (Fuels et al., 1984). Other than operational factors such as cold starting unreliable ignition, misfire and reduced thermal efficiency have added to the general advance of unmodified vegetable oils as long term diesel fuel replacement in Direct Injection
engines and small capacity Indirect Injection diesel engines where the detrimental effects have been greatest.

A more satisfactory fuel is obtained by chemically changing the vegetable oil into a form whose characteristics resemble that of the diesel fuel it is designed to substitute. Used vegetable oil is increasingly being processed into biodiesel, or (more rarely) cleaned of water and particulates and used as a fuel (Zhang et al., 2003). To ensure that the fuel injectors atomize the fuel in the correct pattern for efficient combustion, vegetable oil fuel must be heated to reduce its viscosity to that of diesel, either by electric coils or heat exchangers.

### 1.1.2 Non-conventional vegetable oils

The oil contents of some of the seeds examined by Munavu and Odhiambo (1984) are shown in the table 1.1. The oil seed of over 20% is considered worth of extraction. The oil content of *Calodendrum capense* is high and hence it is viable for biodiesel production as they are readily available.

**Table 1.1: The percentage oil content of seed oil**

<table>
<thead>
<tr>
<th>Oil Seed</th>
<th>Oil Content %</th>
<th>Oil Seed</th>
<th>Oil Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Afzelia Cuanzensis</td>
<td>14.4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Craibbia elliotti</td>
<td>32.2&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Annona Squamosa</td>
<td>29.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Croton Megalocarpus</td>
<td>49.0&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Areeasstrum Romanzofianum</em></td>
<td>57.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td><em>Cucumsus spp</em></td>
<td>24.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Azadirachta Indica</em></td>
<td>56.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td><em>Cupressus lusitanica</em></td>
<td>18.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Balanites Aegyptiaca</em></td>
<td>44.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td><em>Erythrina abyssinica</em></td>
<td>15.3&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Bauhinia purpurea</em></td>
<td>22.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td><em>Passiflora edulis</em></td>
<td>36.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Caesalpenia Decapetala</em></td>
<td>24.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td><em>Sesamum indic</em></td>
<td>45.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Calodendrum Capense</em></td>
<td>60.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td><em>Sterula Africana</em></td>
<td>21.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Citrullus Vulgaris</em></td>
<td>26.8&lt;sup&gt;b&lt;/sup&gt;</td>
<td><em>Jatropha curcas</em></td>
<td>50.0&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>b</sup>, percent of whole seed ; <sup>c</sup>, percent of whole kernel

### 1.1.3 Biodiesel

Biodiesel refers to a diesel-equivalent processed fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oils or animal fats, which can be used (alone, or blended with conventional diesel fuel) in unmodified diesel-engine vehicles. Biodiesel is distinguished from the straight vegetable oils (SVO) or waste vegetable oils (WVO) used (alone, or blended) as fuels in some diesel vehicles.
Biodiesel is a variety of ester-based oxygenated fuels derived from natural, renewable sources such as vegetable oils. Biodiesel operates in compression ignition engines like petroleum diesel thereby requiring no essential engine modifications. Moreover, it can maintain the payload capacity and range of conventional diesel. It has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression–ignition (diesel) engines. The fuel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultra-low sulfur diesel fuel (ULSD, <15 ppm S), such as inherent lubricity, low toxicity, derivation from a renewable and domestic feedstock, superior flash point, biodegradability, negligible sulfur content, and lower overall exhaust emissions (Moser, 2009a, 2009b).

Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability versus petrodiesel, and in some cases, higher NO\textsubscript{x} exhaust emissions (DeOliveira et al., 2006; Knothe, 2008). Many of these deficiencies can be mitigated through cold flow improver (Sern et al., 2007; Hancsok et al., 2008; Moser, 2008a,); additives, blending with petrodiesel (Benjumea et al., 2008; Moser, 2008b), and/or reducing storage time (Bondiol et al., 2003).

Additional methods to enhance the low-temperature performance of biodiesel include crystallization fractionation (Dunn et al., 1997; Kerschbaum et al., 2008) and transesterification with long- or branched-chain alcohols (Lee et al., 1995; Foglia et al., 1997; Wu et al., 1998). Strategies to improve the exhaust emissions of biodiesel, petrodiesel, and blends of biodiesel in petrodiesel include various engine or after-treatment technologies such as selective catalytic reduction (SCR), exhaust gas recirculation (EGR), diesel oxidation catalysts, and NO\textsubscript{x} or particulate traps (McGeehan, 2004; Knothe, 2006). However, feedstock acquisition currently accounts for over 80% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry (Paulson and Ginder, 2007; Retka-Schill, 2008). One potential solution to this problem is employment of alternative feedstocks of varying type, quality, and cost. These feedstocks may include soapstocks, acid oils, tall oils, used cooking oils, and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae. However, many of these alternative feedstocks may contain high levels of free fatty acids (FFA), water, or insoluble matter, which affect biodiesel production.
The main advantages of using biodiesel fuels as 100% mono alkyl esters of vegetable oil and animal fat or biodiesel blends (up to 20% blend to the diesel fuel) are producing less smoke and particulates and having higher cetane numbers (Antolin et al., 2002; Encinar et al., 2007). In addition, the production of biodiesel should be encouraged especially in developing countries because of the following considerations:

- Biodiesel is produced from sustainable/renewable biological sources.
- Ecofriendly and oxygenated fuel.
- It provides a market for excess production of vegetable oils and animal fats.
- It decreases the country's dependence on imported petroleum and thus enhances energy security and also reduces expenditure on imports.
- Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle.
- The exhaust emissions from biodiesel are lower than with regular diesel fuel (sulfur free, less Carbon monoxide, Hydrocarbons, Particulate matter and aromatic compounds emissions).
- Biodiesel has excellent lubricating properties and its fuel properties are the same as those of conventional fuel and can be used in existing unmodified diesel engines.
- Jobs creation and diversification of rural economies.
- It will conserve our forests and reduce deforestation where more will be planted to get seeds for biodiesel processing hence encourage Afforestation.
- The production of biodiesel will increase carbon trading opportunities.
- Non-toxic, biodegradable, and safe to handle.

Much work has been done on other feedstock such as *Jatropha curcas*, *Croton megalocarpus* (Kimilu et al., 2011, Wanjala, 2009, Kimilu, 2007) and *Ricinus communis* for biodiesel production. In this project we targeted biodiesel production from *Candlenut* seeds and *Calodendrum capense* seeds.

1.1.4 Environmental Considerations

Emissions from the use of biodiesel in combustion engines are greatly reduced compared to conventional petroleum diesel fuels by up to 100% sulfur dioxide, 48% carbon monoxide, 47%
particulate matter, 67% total unburned hydrocarbons, and up to 90% reduction in mutagenicity (EPA 2002; Song et al. 2002; Hess et al. 2005, Hess et al., 2007; Lapuerta et al., 2008). Perhaps the most significant reduction based on life cycle analysis is the 78% reduction in carbon dioxide, which is considered the most important greenhouse gas in climatic models. Zhang et al., (2003) showed that biodiesel has much higher biodegradability than low-sulfur diesel fuel and the addition of biodiesel to diesel fuels actually promotes the biodegradability of diesel fuel, making the blends more environmentally attractive. Chang et al., (1998) compared the emission characteristics between particulate matter, SO\textsubscript{x} and HC both experimentally and numerically. They showed that pure biodiesel could significantly reduce total particulate and HC emissions in comparison with conventional diesel at full load engine conditions. Sharp et al., (2000) measured the regulated and unregulated emissions from diesel engines fuelled with biodiesel-blended fuels. In their research, it was shown that measured HC emissions were generally eliminated and CO was reduced roughly 40% by using biodiesels whereas NO\textsubscript{x} emissions increased by 12% because oxygen in the fuel increases the combustion temperature. To overcome the increase of NO\textsubscript{x} emissions by using biodiesel, Yoshimoto and Tamaki (2001) suggested that exhaust gas recirculation (EGR) and water emulsion could be a proper method to reduce the combustion temperature and NO\textsubscript{x} emissions. In addition, they showed that NO\textsubscript{x} emissions decreases significantly without an increase in smoke emissions in the case of a single-cylinder engine fuelled with biodiesel by combining 21% EGR and 30% water emulsion by volume. Ramadhas et al., (2005) found that the compression ignition engine fuelled with biodiesel derived from rubber seed oil had a higher carbon deposits inside the combustion chamber than engines fuelled with conventional diesel. Consequently, more frequent cleaning on the filter, pump, and the combustion chamber is required for the use of biodiesel-blended fuels (Knothe et al., 2006).

Figure 1.1 shows the emission reductions for biodiesel B100 and B20 compared to conventional petroleum diesel fuels DF2 (Adapted from National Biodiesel Board, http://www.biodiesel.org/).
Figure 1.1: Emission reductions for biodiesel B100 and B20 compared to conventional petroleum diesel fuels DF2

Percent reduction in emissions of pollutants in 100% biodiesel (B100) and 20% biodiesel blend (B20). TH is total hydrocarbons, CO\textsubscript{X} is carbon dioxide, CO is carbon monoxide, PM is particulate matter, NO\textsubscript{X} is nitrogen oxides, SO\textsubscript{X} is sulfates, PAH is polycyclic hydrocarbons, and NPAH is nitrated PAHs.
1.2 Background

In 1911, Rudolf Diesel presented the world with the compression ignition engine, which at that time did not have a specific fuel (Knothe, 2001). Diesel claimed that the engine could be fed by vegetable oils which could help the agricultural development in countries using this engine. Biodiesels are derived from vegetable oils or animal fats, more specifically from the respective alkyl esters. The esters from vegetable oils are considered to be superior since they have a higher energetic yield and essentially no engine modifications are necessary for their use. Biodiesels have been traced back to the mid-1800s, where transesterification (described in Chapter 2) was used to make soap and the alkyl esters (biodiesels) were just considered byproducts. Early feedstocks were soybean, corn, peanut, hemp oils, and tallow (Freedman et al., 1986).

Vegetable oils were found to be problematic due to their greater viscosity, which affects piston, injector deposits and oil thickening (Baldwin et al., 1982; Fuels et al., 1984; Ryan et al., 1984; Van Der Wat and Hugo, 1982). Conversion of the oils to their alkyl esters reduced the viscosity to near the diesel fuel levels and produced fuel with properties that were similar to petroleum based diesel fuel and which could be used in existing engines without modifications.

In 1973, the OPEC nations cut down their oil exports to the West, resulting in the oil crisis of the 1970s. Prices of oil increased dramatically and people started to look into renewable sources of energy. Many of the federal renewable energy programs were initiated during the 1970s including the National Renewable Energy Laboratory. Once prices began to fall in 1979, tax incentives and other support for the renewable energy industry ended, thanks to shortsighted policies. The initial steps taken toward a renewable energy initiative were abandoned. The driving force for large-scale use of biodiesel has been the need to reduce the harmful emissions that result from the burning of petroleum oil as well as our dependence on diminishing reserves of petroleum oil. The ease in which biodiesel can be used as an alternative to regular petroleum diesel fuel, along with its economic and environmental benefits, has made it an attractive choice. The recent fluctuations of prices and environmental effects of fossil fuels have led to countries going for alternative renewable fuels such as biodiesel.
1.3 Problem Statement

For the past few years Kenya has faced a crisis of oil supply and unpredictable prices due to its dependence on fossil fuels. Kenya consumes about 55,000 barrels of oil per day and depends on imports for its supply in fossil fuels. Between March 2008 and March 2009, Kenya imported US$2.8 billion worth of petroleum products (Kshs 199,999 million as per the Economic survey 2011), which represents much more than the combined income from its two top export categories (US$0.9 billion for tea, US$0.7 billion for horticulture). The cost of oil imports is dictated by factors well beyond the control of the country and thus the need to have secure local oil supplies which should be in line with achieving the vision 2030, as well as MDG’s and sustainable development goal. The unpredictable rise in oil prices, increasing global demand, declining supply of oil reserves, and the threat of global warming and climate change due to combustion engine emissions highlight the energy crisis and challenges facing the world today. Use of fossil fuels lead to increase in greenhouse gases (SO\textsubscript{2}, NO\textsubscript{2}, CO\textsubscript{2} etc.) that lead to destruction of ozone layer and contribute to climate change. These problems provide adequate reasons and incentives to focus on renewable energy alternatives to fossil fuels. Diversification of renewable energy sources such as solar energy, wind energy; geothermal energy and biofuels have not been utilized. It is estimated that a single 200,000 tons per year biodiesel plant could be able to replace more than 5% of Kenya’s total amount of imported fuel thus significantly reduce the imported fuel cost. Therefore biodiesel fuel is expected to play an important role as alternative to diesel that would reduce the greenhouse gas emissions. Currently, biodiesel is produced industrially by reacting methanol with various vegetable oils using alkaline catalyst. This process has its drawbacks hence the proposal to use local enzymes catalysts and develop green chemistry technology to be used in the transesterification process. Recently there have been reports in the media of biodiesel being sold in some regions in Kenya, yet the quality of the oils and performance testing has not been done to evaluate short and long term effects. The proposed plants (Calodendrum Capense and Candlenut) for biodiesel production are not used as food crops and will not affect food security and hence they are suitable for biodiesel production. Biodiesels offer a significant opportunity for further reductions in dependence on fossil fuels and reduction of greenhouse gas emissions (CO\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{x} etc) that contribute to environmental pollution, destruction of ozone layer and global warming.
1.4 Objectives

1.4.1 Broad Objective
To extract oil from Candlenut tree (*Aleurites moluccanus*) and *Calodendrum capense* seeds using conventional and non-conventional techniques and determine conditions for optimum oil yields.

1.4.2 Specific Objectives
1. To extract oil from Candlenut and *Calodendrum capense* using conventional methods.
2. To develop efficient methods for conversion (transesterification) of the oil into biodiesel (methyl esters).
3. To develop a new novel transesterification techniques based on lipase enzymes and evaluate the efficiency of the process.
4. To prepare blends of Candlenut and *Calodendrum capense* biodiesel with commercial diesel and determine the biodiesel properties.
5. To perform engine testing of the Candlenut and *Calodendrum capense* blends and evaluate performance compared with commercial diesel sample.
CHAPTER TWO

LITERATURE REVIEW

2.0 Description of Plant Resources

2.1 Calodendrum Capense (Cape Chestnut)

*Calodendrum capense* is a very ornamental tree, suitable for use as a shade or specimen tree in gardens and parks, also as a street tree. It does best in deep fertile, well-composted soil with plenty of moisture, particularly during spring and summer, and requires a warm sunny position. To develop and maintain its shapely canopy, it requires protection from strong, sustained winds. It’s a member of the Rutaceae, the buchu and citrus family that occur in warm temperate regions of the world, with 22 genera and 290 species in southern Africa. One of the diagnostic features of this family is the presence of oil glands on the leaves, visible as tiny translucent dots when held up to the light. Another common feature, caused by the oil, is the strong scent of the leaves, particularly when they are crushed.

2.1.1 Geographic distribution

*Calodendrum capense* (Cape Chestnut) is an African tree which was first studied at the cape in South Africa and cultivated widely for its prolific flower display. It is found in wooden ravines, in evergreen fringe forest, at the coast and sometimes in scrubland. It is not restricted to any specific habitat.

It is native to a swath of the east side of the continent from the equatorial highlands of Kenya at its northern limit southwards through isolated mountains in Tanzania to both sides of Lake Malawi, the Mashonaland Plateau and Eastern Highlands of Zimbabwe, and then along the lower slopes of the Drakensberg Mountains of south Africa and in coastal forest from Port Elizabeth to Cape Town. In Uganda, the species occurs only rarely is scattered parches of woodland in Mbarara District (Leistner, 2000). In Kenya, it is found majorly in Muguga and Karura, Nairobi Arboretum, Ngong forest, as well as in Chiromo campus, University of Nairobi and Kenyatta university compound.
2.1.2 Cultivation

*Calodendrum capense* trees are propagated by seed or cuttings. Fresh seed can be sown in deep seedling trays filled with river sand. The seeds normally germinate in 10-40 days, with a germination rate of 80-90%. Germination may be erratic if old seeds are sown. The species can be propagated successfully from cuttings made from half-grown shoots, but they must be treated with a root-stimulating hormone. Young trees are easily planted out. Artificial propagation by wildings and seedlings is possible. Those grown from seeds will flower after 6-7 years, and those from cuttings after 3 to 4 years. It prefers a sunny, open position in rich, moist, well-drained soil. Tolerates frost and some coastal exposure when established, but should be protected from frost when young. Apply mulch in spring to keep roots cool and moist. Keep moist in dry weather, but drier at other times (Palmer and Pitman, 1972).

In a forest environment, this tree can reach heights of up to 20 m, but at the forest margin or in the open it is shorter, approximately 7 m with a more spreading canopy. In general this is a handsome well-shaped tree with a single trunk and a dense rounded canopy. The trunk is smooth and an attractive mottled streaky grey, buttressed and lichen-covered in older specimens. The leaves are dark green, relatively large (5-22 cm long x 2-10 cm wide), simple, with untoothed undulated margins, and elliptic in shape (Coates and Keith, 1977).

2.1.3 Uses and environmental importance

*Calodendrum Capense* is a slow growing, attractive tree for parks, avenues and large gardens. It makes an attractive specimen tree, especially on a lawn, with its light grey bark, large leaves, masses of pink flowers and knobby fruit. The tree provides valuable shade and also acts as windbreaks.

The timber is white or yellow and fairly hard but bends well and is easily worked. It is used for tent bows, yokes, planking, shovel handles, wagon-making and furniture, and is considered one of the most generally useful hard wood. The tree is also suitable for firewood and charcoal (Venter et al., 1984).

The bark is used as an ingredient of skin ointments and is sold at traditional medicine markets. The tree provides bee forage (apiculture). Leaf-fall is very heavy hence the tree provides mulch which improves the soil fertility. The tree can be intercropped with bananas.
Seeds are crushed and boiled to obtain a lemon-yellow, rather bitter, fixed oil that is suitable for making soap. The Cape Chestnut oil is popular oil in African skin care. Its inherent ultra violet protection and its high content of essential fatty acids and antioxidants and its mild smell destined it for natural cosmetics (http://en. Wikipedia.org/wiki/ Calodendrum).

2.2 Candlenut tree (Aleurites moluccanus)

Candlenut tree also known as candleberry or varnish tree is a flowering tree in the spurge family, Euphorbiaceae. A fast growing species, it is often found in disturbed rainforests. It is described as a bushy tree with a wide spreading crown. It makes a suitable shade tree and a good ornament with large leaves and attractive white flowers (Elbert et al., 1989).

It is an evergreen or partly deciduous, medium or large tree, up to 15-24m, with wide spreading branches. Has a grey trunk; heart-shaped or ovate-lanceolate, leathery, bright green leaves, 7 to 12 inches long (17-30 cm) and 6 inches wide (15 cm), with conspicuous veins; the young foliage has a silvery, powdered appearance (Scott and Craig, 2000). Propagation is through seeds and require moderate to abundant water; prefers a good drainage. Seeds are 4–6 centimeters (1.6–2.4 in) in diameter; the seed inside has a very hard seed coat and a high oil content, which allows its use as a candle, hence its name (http://en.wikipedia.org/wiki/ Aleurites moluccana).

2.2.1 Uses and environmental importance

The kernel contains about 60% of oil and burns easily with a smoky flame. It justifies its use at one time as a primitive candle by some native people of the pacific, who stung the kernels together on sticks (Elevitch et al., 2006). The candlenut oil is similar to linseed or tung oil and can be used in making paints, varnishes, soap, and as a wood preservative for boats (Morrison et al., 2002). The candlenut oil cake is high in nitrogenous content and makes a useful fertilizer for agricultural purposes. The purging effect allows the nut to be utilized as a laxative. The oil is also used as hair stimulant or additive to hair treatment systems. (http://canoeplants.com/kukui.html, 2009).

The timber is silvery white, very plain and, although light and soft, is fairly tough. When draining boards were of wooden construction and kitchen shelves were often left unpainted. Candlenut was popular for the purpose, because it retained its whitish colour for a long time.
Several parts of the plant have been used in traditional medicine in most of the areas where it’s native. The pulped kernels or boiled leaves are used in poultices for headache; fevers, ulcers, swollen joints, and gonorrhea. In ancient periods the nuts were burned to provide light (http://www.ars-grin.gov/ "Aleurites moluccanus. The nuts were stung in a row on a palm leaf midrib, lit one end and one by one every 15 minutes or so. This led to their use as a measure of time, one could instruct someone to return home before the second nut burned out (Krauss and Beatrice, 1993).

Fishermen made use of the nuts where they would chew the nuts and spit them on the water to break the surface tension and remove reflections, giving the greater underwater visibility. The coating of the candlenut oil helped preserve the fishing nets. Pipe nuts are pounded into a paste and used as soap or shampoo. Dead wood of candlenut is eaten by a larva of coleopteran called Agrionome fairmaire, the larva is eaten by some people.

An average tree may produce 100-150 lbs of nuts a year, yielding about 35-45% of oil. When planted on a commercial scale in certain subtropical climate, it said to give 5 tons of seed (1800lbs oil) per acre of mature trees (Dunford et al., 2002).

2.3 Vegetable Oil Properties and Characteristics

Most vegetable oil is composed specific category of organic compounds called “triglycerides” (TG). A TG molecule is made up of three fatty acid units attached to a three-carbon backbone. Some physical properties of the most common fatty acids occurring in vegetable oils as they relate to their use as biodiesel are listed in table 2.1.
Table 2.1: Selected properties of some common fatty acids

<table>
<thead>
<tr>
<th>Trivial name (Acronym)</th>
<th>Mol. wt</th>
<th>M.P (°C)</th>
<th>B.P (°C)</th>
<th>Cetane Number</th>
<th>Heat of Combustion(Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylic acid (Octanoic acid); 8:0</td>
<td>144.22</td>
<td>16.5</td>
<td>239.3</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>Capric acid (Decanoic acid); 10:0</td>
<td>172.27</td>
<td>31.5</td>
<td>270</td>
<td>47.6</td>
<td>1453 (25°C)</td>
</tr>
<tr>
<td>Lauric acid (Dodecanoic acid);12:0</td>
<td>200.32</td>
<td>44</td>
<td>131¹</td>
<td>58.9</td>
<td>1763.25 (25°C)</td>
</tr>
<tr>
<td>Myristic acid (Tetradecanoic acid) 14:0</td>
<td>228.38</td>
<td>58</td>
<td>250.5¹⁰⁰</td>
<td>64.9</td>
<td>2373.91 (25°C)</td>
</tr>
<tr>
<td>Palmitic acid (Hexadecanoic acid); 16:0</td>
<td>256.43</td>
<td>63</td>
<td>350</td>
<td>72.6</td>
<td>2384076 (25 °C)</td>
</tr>
<tr>
<td>Stearic acid (Octadecanoic acid) 18:0</td>
<td>284.48</td>
<td>71</td>
<td>360</td>
<td>85.3</td>
<td>2696.12 (25 °C)</td>
</tr>
<tr>
<td>Oleic acid (9Z–Octadecenoic acid); 18:1</td>
<td>282.47</td>
<td>16</td>
<td>286¹⁰⁰</td>
<td>54.2</td>
<td>2657.4 (25°C)</td>
</tr>
<tr>
<td>Linoleic acid (9Z, 12Z–Octadecadienoic acid); 18:2</td>
<td>280.45</td>
<td>-5</td>
<td>229-30¹⁶</td>
<td>65</td>
<td>2695.4 (25°C)</td>
</tr>
<tr>
<td>Linolenic acid (9Z, 12Z, 15Z–Octadecatrienoic acid); 18:3</td>
<td>278.44</td>
<td>-11</td>
<td>230-2¹⁷</td>
<td>33</td>
<td>2437.2 (25°C)</td>
</tr>
<tr>
<td>Erucic acid (13Z- Docosenoic acid); 22:1</td>
<td>338.58</td>
<td>33-4</td>
<td>265¹³</td>
<td>2413 (25°C)</td>
<td></td>
</tr>
</tbody>
</table>


a) Z Denotes cis (double bond) configuration.

b) The numbers denote number of carbon and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Superscripts in boiling point column denote pressure (mmHg) at which the boiling point was determined.

The most common derivatives of fatty acids for fuels are methyl esters (FAME). These are formed by transesterification of the fatty acid with methanol in the presence of usually a basic
catalyst to give FAME. Other alcohols have been used to generate esters such as ethyl, propyl and butyl ester.

Selected physical properties of methyl ester as they relate to their use as fossil Diesel (DF) are listed in Table 2.2;

**Table 2.2: Selected properties of some common methyl esters**

<table>
<thead>
<tr>
<th>Trivial name (Acronym)</th>
<th>Mol. Wt</th>
<th>M.P (°C)</th>
<th>B.P (°C)</th>
<th>Cetane Number</th>
<th>Heat of Combustion (Kg-cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylcaprylate (Methyl octanoate); 8:0</td>
<td>158.24</td>
<td>193</td>
<td>33.6</td>
<td>1313</td>
<td></td>
</tr>
<tr>
<td>Methylcaprate (Methyl decanoate); 10:0</td>
<td>186.30</td>
<td>224</td>
<td>47.7</td>
<td>1625</td>
<td></td>
</tr>
<tr>
<td>Methyllaurate (Methyl dodecanoate); 12</td>
<td>214.35</td>
<td>5</td>
<td>266 766</td>
<td>61.4</td>
<td>1940</td>
</tr>
<tr>
<td>Methylmyristate (methyl tetradecanoate); 14:0</td>
<td>242.41</td>
<td>18.5</td>
<td>295 751</td>
<td>66.2</td>
<td>2254</td>
</tr>
<tr>
<td>Methylpalmitate (Methyl hexadecanoate); 16:0</td>
<td>270.46</td>
<td>30.5</td>
<td>415-8 747</td>
<td>74.5</td>
<td>2550</td>
</tr>
<tr>
<td>Methylstearate (Methyl octadecanoate) 18:0</td>
<td>298.51</td>
<td>39.1</td>
<td>442-3 747</td>
<td>86.5</td>
<td></td>
</tr>
</tbody>
</table>


a) Z Denotes Cis (double bond) configuration.
b) The numbers denote number of carbon and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.
c) Superscripts in boiling point column denote pressure (mmHg) at which the boiling point was determined.

**2.3.1 Fatty Acid Methyl Esters Composition of Non-Conventional Oils**

The physical and chemical properties of biodiesel to a large extent depend on its chemical constitution. Vegetable oils are chemically simple since not more than six or seven fatty acid esters of glycerol make up the oil mixture. Fatty acid may be saturated or unsaturated by various degrees as shown in Table 2.2. The degree of saturation determines the viscosity of the oils as well as stability of the oil with respect to atmospheric oxidation. High saturation leads to low viscosity as well as to low stability in the presence of oxygen. The fatty acid ester compositions of non-conventional vegetable oil are shown in Table 2.3 below;
Table 2.3: major fatty acids in weight (wt) % of some non-conventional oil seed

<table>
<thead>
<tr>
<th>Non-Conventional Oil Seed</th>
<th>Fatty Acid composition (% by mass of methyl esters)</th>
<th>Palmitic 16:0</th>
<th>Stearic 18:0</th>
<th>Oleic 18:1</th>
<th>Linoleic 18:2</th>
<th>Linoleic 18:3</th>
<th>Arachidic 20:0</th>
<th>&gt;20:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia podalyifolia</td>
<td></td>
<td>11.9</td>
<td>2.0</td>
<td>17.7</td>
<td>65.0</td>
<td>65.0</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>Alerites molucana</td>
<td></td>
<td>7.7</td>
<td>3.8</td>
<td>23.7</td>
<td>40.4</td>
<td>24.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Annona squamosal</td>
<td></td>
<td>14.9</td>
<td>5.1</td>
<td>45.5</td>
<td>32.6</td>
<td>32.6</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>Azadirachta Indica</td>
<td></td>
<td>20.8</td>
<td>19.7</td>
<td>35.6</td>
<td>20.1</td>
<td>20.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Balanites Aegyptiaca</td>
<td></td>
<td>20.9</td>
<td>19.7</td>
<td>25.7</td>
<td>32.4</td>
<td>32.4</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Bauhinia purpurea</td>
<td></td>
<td>21.8</td>
<td>15.2</td>
<td>10.0</td>
<td>49.8</td>
<td>49.8</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Caesalpenia Decapetala</td>
<td></td>
<td>9.0</td>
<td>4.7</td>
<td>16.9</td>
<td>68.7</td>
<td>68.7</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Calodendrum capense</td>
<td></td>
<td>23.6</td>
<td>4.5</td>
<td>33.7</td>
<td>35.6</td>
<td>35.6</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Croton megalorcarpus</td>
<td></td>
<td>5.4</td>
<td>4.0</td>
<td>9.0</td>
<td>78.1</td>
<td>1.2</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Erythrina abyssinica</td>
<td></td>
<td>14.5</td>
<td>4.1</td>
<td>50.2</td>
<td>21.1</td>
<td>21.1</td>
<td>2.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Erythrina lysistememon</td>
<td></td>
<td>25.3</td>
<td>5.7</td>
<td>26.5</td>
<td>35.6</td>
<td>35.6</td>
<td>2.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Passiflora adilus</td>
<td></td>
<td>10.1</td>
<td>2.3</td>
<td>15.7</td>
<td>71.1</td>
<td>71.1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The oils differ mainly by the percentage composition by mass of the major fatty acids i.e palmitic, stearic, oleic, linoleic and arachidic acids. For comparisons purposes the fatty acid composition of some conventional vegetable oils are shown in Table 2.4.

Table 2.4: Fatty acid composition (% by mass of methyl esters) of conventional oil seed

<table>
<thead>
<tr>
<th>Conventional Oil Seed</th>
<th>Fatty acid composition (% by mass of methyl esters)</th>
<th>Palmitic 16:0</th>
<th>Stearic 18:0</th>
<th>Oleic 18:1</th>
<th>Linoleic 18:2</th>
<th>Linoleic 18:3</th>
<th>Arachidic 20:0</th>
<th>&gt;20:0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunflower (Kenya)</td>
<td></td>
<td>8.0</td>
<td>6.1</td>
<td>17.3</td>
<td>68.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Soybean</td>
<td></td>
<td>6.4</td>
<td>4.2</td>
<td>23.9</td>
<td>61.4</td>
<td>3.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Buffalo gourd</td>
<td></td>
<td>9.0</td>
<td>4.0</td>
<td>27.0</td>
<td>58.0</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>Peanut oil</td>
<td></td>
<td>8.3</td>
<td>3.1</td>
<td>56.0</td>
<td>26.0</td>
<td>-</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>Safflower</td>
<td></td>
<td>6.4</td>
<td>4.5</td>
<td>13.8</td>
<td>75.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Calodendrum Capense* (CL) was studied by Munavu and Odhiambo (1984) and it was shown that its fatty acid composition profile closely resembled those of conventional vegetable oil in table
2.4. The suitability of fats and oils as fossil diesel (DF) results from their molecular structure and high energy content. Long chain, saturated, unbranched hydrocarbons are specifically suitable for use in place of conventional DF as shown by cetane number (CN) in Table 2.1 and their respective methyl esters in Table 2.2, corresponding to components of diesel fuel the long, unbranched hydrocarbon chains in fatty acids meet this requirement. Saturated fatty acids compounds have higher CNs than unsaturated compounds as shown in Tables 2.1 to 2.4 (Munavu and Odhiambo, 1984).

2.4 Diesel Engines

A diesel engine also known as a compression ignition engine is an internal combustion engine that uses the heat of combustion to initiate ignition to burn the fuel, which is injected into the combustion chamber during the final stage of combustion. The diesel engine is modeled on the diesel cycle and the thermodynamic cycle developed by Rudolph in 1897 (Http://en.wikipedia.org/wiki/ Internal combustion engine).

The diesel engine has the highest thermal efficiency of any regular internal or external combustion engine due to its very high compression ratio. The diesel internal combustion engine differs from the gasoline powered Otto cycle by using highly compressed, hot air to ignite the fuel rather than using a spark plug (compression ignition rather than spark ignition). In the diesel engine, only air is initially introduced into the combustion chamber. The air is then compressed with a compression ratio typically between 15:1 and 22:1 resulting in 40-bar (4.0 MPa; 580 psi) pressure. The high compression heats the air to 550°C. At about the top of the compression stroke, a fuel is injected directly into the compressed air in the combustion chamber. The fuel injector ensures that the fuel is broken down into droplets, and that the fuel is evenly distributed. The heat of the compressed air vaporizes fuel from the surface of the droplets. The vapour is then ignited by the heat from the compressed air in the combustion chamber, the droplets continue to vaporize from the surface and burn, getting smaller, until all the fuel in the droplets has been burnt. The start of vaporization causes a delay period during ignition, and the characteristics diesel knocking sound as the vapour reaches ignition temperature and causes abrupt increase in pressure above the piston (http://www.britannica.com).

Ignition occurs in regions of fuel-air mixture that have fuel-air ratios close to the chemically correct ratio or the stoichiometric ratio. Combustion proceeds very rapidly due to the backlog of
prepared or nearly prepared fuel-air mixtures formed during the ignition delay period. The rapidly rising temperatures and pressure in the cylinder accelerate the combustion in an uncontrolled manner until the backlog is depleted. This portion of the combustion process is usually called premixed combustion (Http://en.wikipedia.org/wiki/ Internal combustion engine). The remainder of the fuel in the spray core is still too rich to burn, so combustion slows down and is controlled by the rate at which the air is entrained and a combustible mixture formed. This portion of the combustion process is called mixing controlled or diffusion burning. Thus, while chemical kinetics dominates the ignition delay, the high temperatures and pressures of the post-ignition gases promote very fast reaction rates that make fuel-air mixing the rate determining process (Garpen et al., 2004).

Diesel engines have many advantages over the internal combustion engines:-They burn less fuel than petrol engine performing the same work, due to the engine’s higher temperature of combustion and greater expansion ratio. Gasoline engines are typically 25% efficient while diesel engines can convert over 30% of the fuel energy into mechanical energy.

They have no high-tension electrical ignition system to attend to, resulting in high reliability and easy adaptation to damp environments. The absence of coils and spark plug wires also eliminates a source of radio frequency emissions which can interfere with navigation and communication equipment, which is especially important in marine and aircraft applications.

They can deliver much more of their rated power in continuous basis than petrol engines. The life of a diesel engine is generally about twice as long as that of a petrol engine due to increased strength of parts used. Diesel fuel has better lubrication properties than petrol as well. Diesel fuel is considered safer than petrol in many applications. Although diesel fuel will burn in open air using a wick, it will not explode and does not release a large amount of flammable vapor. The low vapor pressure of diesel is especially advantageous in marine applications, where the accumulation of explosive fuel-air mixtures is a particular hazard. For the same reason, the diesel engines are immune to vapor lock (Singer et al., 1978).

For any given partial load the fuel efficiency (mass burned per energy produced) of a diesel engine remains nearly constant, as opposed to petrol and turbine engines which use proportionally more fuel with partial power outputs. They generate less waste heat in cooling and exhaust. The carbon monoxide content of the exhaust is minimal; therefore diesel engines are
used in underground mines. Biodiesel is an easily synthesized, non-petroleum-based fuel (through transesterification) which can run directly in many diesel engines, while gasoline engines either need adaptation to run synthetic fuels or else use them as an additive to gasoline, making diesel engines the clearly preferred choice for sustainability (Hardenberg, 1999). Diesel engines can be grouped into two types as described below.

2.4.1 Indirect Injection Engine
An indirect diesel engine delivers fuel into a chamber off the combustion chamber, called a pre-chamber, where combustion begins and then spreads into the main combustion chamber, assisted by turbulence created in the chamber. This system allows for smoother, quieter running engine, and because combustion is assisted by turbulence, injector pressures can be lower using a single orifice tapered jet injector. The pre-chamber had the disadvantage of increasing heat loss to the engine’s cooling system, and restricting the combustion burn, which reduces the efficiency by 5-10%. Indirect injection engines have poor fuel economy as compared to direct injection engines (Lilly, 1984). This is because the combustion tends to continue during a longer part of the expansion stroke.

Pumping loses are also greater on account of the flow through the narrow passages connecting the pre-chamber and the main inside the cylinder. Further the heat loses tend to be higher because of the greater surface area of the two combustion chambers and due to higher gas velocities generally prevailing in this type of configuration. Indirect engines are cheaper to build and it is easier to produce smooth, quiet-running vehicles with a simple mechanical system.

2.4.2 Direct Injection Engine
Direct injection injectors are mounted in the top of the combustion chamber. The problem with these vehicles was the harsh noise that they made. Fuel combustion was about 15 to 20% lower than indirect injection diesels. This type of engine was transformed by electronic control of the injection pump. The injection pressure was still only around 300 bars, but the injection timing, fuel quantity and turbo boost were electronically controlled. This gave more precise control of these parameters which eased refinement and lowered emissions. In the direct injection engine, the fuel is injected into a combustion chamber directly above the piston crown. This type of combustion chamber design is usually called open chamber, and can either be disc, wedge, hedge
or bowl in piston (Heywood, 1998). To have complete combustion within a short time available, sufficiently rapid fuel-air mixing rates are paramount (Columbia encyclopedia, 2010).

2.5 Diesel Engine Fuel Requirements

One of the most important properties of a diesel fuel is its readiness to autoignite at the temperatures and pressures present in the engine cylinder when the fuel is injected. The laboratory test that is used to measure this tendency is the Cetane Number Test (ASTM D 613). Fuels with a high cetane number will have short ignition delays and a small amount of premixed combustion since little time is available to prepare the fuel for combustion (Gerpen et al., 2004).

The energy content of a fuel is characterized by the amount of heat released when the fuel, starting at ambient conditions, is burned and the products are cooled to ambient conditions. This is defined as the enthalpy of combustion (or the heat of combustion) since the combustion process produces water and energy will be different depending on whether the water is liquid or vapor. Two separate cases are considered. First, if all of the water in the exhaust products is assumed to be liquid, the heat extracted will be the higher heating value or the gross heating value. If all of the water is considered to be vapor, then the heat extracted is the lower heating value or the net heating value. Since engines do not have the ability to condense water in the exhaust, the lower heating value is the most commonly used measure of fuel energy content.

Biodiesel fuels do not contain aromatics but they contain fatty acids with different levels of unsaturation (Gerpen et al., 2004). Fuels with more unsaturation tend to have slightly lower energy contents (on a weight basis) while those with greater saturation tend to have higher energy content and is more dense than the diesel fuel. The energy content is only 8% less on a per gallon basis. The actual heating value for diesel fuel will vary depending on the refinery in which it was produced, the time of year, and the source of the petroleum feedstock. Beyond these differences, the heating value will depend on the composition of the fuel.

The density of the fuel is not itself an important parameter for the diesel engine but it is generally related to the fuel’s energy content. The higher the density, the greater the potential energy, since biodiesel has a higher density than diesel fuel, biodiesel is expected to have high energy content.
Diesel fuel contains small amounts of long chain hydrocarbons, called waxes that crystallize at temperatures within the normal diesel engine operating range. If temperatures are low enough, these wax crystals will agglomerate and plug fuel filters and prevent engine operation. At a low enough temperature, the fuel will actually solidify. Additives, known as pour point depressants, are used to inhibit the agglomeration of the wax crystals, which then lowers the point at which fuel filter plugging occurs.

Many of the parts in the diesel fuel injection system are made of high-carbon steels and thus are prone to corrosion when in contact with water. Water damage is the leading cause of premature failure of fuel injection systems. Diesel fuel containing excessive water that enters the injection system can cause irreversible damage in a very short time. Some compounds in diesel fuel, especially sulfur compounds, can be corrosive. Since copper compounds are particularly susceptible to this type of corrosion, copper is used as an indicator of the tendency of the fuel to cause corrosion.

Diesel fuel filters are designed to capture particles that are larger than 10 microns in size. Some newer engines are even equipped with filters that capture particles as small as 2 microns. These filters should stop foreign materials from entering the fuel injection system. However, when fuels are exposed to high temperatures and the oxygen in air, they can undergo chemical changes that form compounds that are insoluble in the fuel. These compounds form varnish deposits and sediments that can plug orifices and coat moving parts causing them to stick.

When diesel fuel burns, it should be converted entirely to carbon dioxide and water vapor. Inorganic materials present in the fuel may produce ash that can be abrasive and contribute to wear between the piston and cylinder. When fuel is exposed to high temperatures in the absence of oxygen, it can pyrolyze to a carbon-rich residue which can limit the range of motion of moving parts.

Under ideal circumstances, all of the carbon in the diesel fuel will burn to carbon dioxide and all of the hydrogen will burn to water vapor. In most cases, virtually all of the fuel does follow this path. However, if sulfur is present in the fuel, it will be oxidized to sulfur dioxide (SO₂) and sulfur trioxide (SO₃). These oxides of sulfur can react with water vapor to form sulfuric acid and other sulfate compounds. The sulfates can form particles in the exhaust and elevate the exhaust
particulate level. Biodiesel contains no aromatics which are believed to contribute to higher particulate and nitrogen oxides emissions (Knothe et al., 2006).

The viscosity of the diesel fuel determines whether the fuel can fit the design specifications of the engine in which it’s to be used in. The fuel viscosity must be specified within a fairly narrow range. Hydrocarbon fuels in the diesel boiling range easily meet this viscosity requirement.

The volatility of diesel should always be below the flammability limit or the flash point i.e. the temperature at which the fuel will give off enough vapor to produce a flammable mixture. This has been a concern for mixtures of ethanol and diesel fuel because ethanol reduces the flash point of diesel fuel to the point where it needs to be treated in the same manner as gasoline.

2.6 Diesel Fuel Specification

The ASTM identifies five grades of diesel fuel. Grade No. 1-D and Low Sulfur 1-D; this is a light distillate fuel for application requiring higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses. The specification for this grade of diesel fuel overlaps with kerosene and jet fuel and all three are commonly produced from the same base stock. One major use for No. 1-D diesel fuel is to blend with No. 2-D during winter to provide improved cold flow properties (Gerpen et al., 2004).

Grade number 2-D and Low Sulfur 2-D; this is a middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load. Grade number 2-D is more dense than 1-D and so it provides more energy per gallon. This makes it the preferred fuel for on-highway trucks. Grade number 4-D is a heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

2.7 Ignition Indices

Cetane number (CN) is related to the ignition delay time a fuel experiences once it has been injected into a diesel engine. It is an engine based and is similar to the octane test engine used for rating gasoline. Indirect injection engine is used in carrying out this test. The engine speed is fixed at 900 r.p.m while the engine is naturally aspirated, the intake air temperature is held at 65.5°C. The test is based on careful adjustment of the fuel/Air and the compression ratio to
produce a standard ignition delay, the period between the start of the fuel injection and the start of combustion of 13 degrees while operating on the test. The cetane number standard test procedure is defined by ASTM D 613.

The engine is switched to operate on a blend of two reference fuels. Different blends are tested until a formulation is found that restores the ignition delay to 13 degrees. The primary reference fuels are n-cetane (n-hexadecane), which has a cetane number of 100 and heptamethlynonane (HMN) which has a cetane number of 15 (Knothe et al., 1997). When the ignition delay is restored to 13 degrees, the cetane number is computed from the following relationship

\[
\text{Cetane number} = \% \text{n-cetane} + 0.15 (\% \text{HMN}) \tag{Equation 2.1}
\]

The Kenya Bureau of Standards (Appendix I) specification for conventional DF2 requires a minimum of CN of 40. This means that the fuel would have ignition delay performance equivalent to that of a blend of 40% n-cetane and 60% (HMN) by volume. The CN scale clarifies an important aspect of the compounds comprising DF long chain; unbranched, saturated hydrocarbons (Alkanes) have high CNs and poor ignition quality (Freedman and Bagby, 1990). Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines; all biodiesel have been found to contain higher cetane number values, so they would tend to improve operation of the engine with respect to pure diesel (based on this value alone). However, both too high and too low CN can cause operational problems (in case of too high CN, combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke; in case of too low CN, engine roughness, misfiring, higher air temperatures, slower engine warm-up and also incomplete combustion occur. For conventional diesel fuel, higher CNs has been correlated with reduced nitrogen oxides \((\text{NO}_x)\) exhaust emissions. This correlation has led to efforts to improve the cetane number of biodiesel fuels by means of additives known as cetane improvers. Despite the inherently relatively high CNs of fatty compounds, \(\text{NO}_x\) exhaust emissions usually increase slightly when operating a diesel engine on biodiesel.
2.8 Mechanical extraction of vegetable oil

The vegetable oil processing starts with the shelling of the seed nuts (Candlenut or Calodendrum capense nuts). The shelling is done using two stones to crack each nut and separating the kernel and shell simultaneously. The mechanical nut-crackers deliver a mixture of kernels and shells that must be separated. The kernel/shell separation is usually performed in a clay-bath, which is a concentrated viscous mixture of clay and water. The density of the clay-bath is such that the shells sink while the lighter kernels float to the top of the mixture. The floating kernels are scooped in baskets, washed with clean water and dried. Periodically, the shells are scooped out of the bath and discarded. Oil seeds have oil-containing cells within their kernels. To extract this oil, the seed is first pretreated to weaken the cell walls of the oil-containing cells. The pretreated process include breaking, grinding, rolling, pressing or pelleting of the seed as explained above. This process is done to reduce the oil viscosity and adjust seed moisture content. Only sufficient mechanical and thermal energies are employed, for large excesses of either are detrimental. The following methods are commonly used to extract oil from seeds.

Mechanical extraction processes are suitable for both small- and large- capacity operations. The three basic steps in these processes are (a) kernel pre-treatment, (b) screw-pressing, and (c) oil clarification as shown in Figure 2.1. An oil expeller or press is usually used to extract oil from the pre-treated seeds where the seeds are subjected to high pressures. The oil oozes out through a compartment walls and is collected. Line (A) is for direct screw pressing without kernel pre-treatment; Line (B) is for partial kernel pre-treatment followed by screw pressing; and Line C is for complete pre-treatment followed by screw pressing.

2.8.1 Kernel pre-treatment

Proper kernel pre-treatment is necessary to efficiently extract the oil from the kernels. The feed kernels are first cleaned of foreign materials that may cause damage to the screw-presses, increasing maintenance costs and down time, and contamination of products. Magnetic separators commonly are installed to remove metal debris, while vibrating screens are used to sieve sand, stone and other undesirable materials. A swinging hammer grinder, breaker rolls or a combination of both then breaks the kernels into small pieces. This process increases the surface area of the kernels, thus facilitating flaking. The kernel fragments subsequently are subjected to flaking in a roller mill.
A large roller mill can consist of up to five rollers mounted vertically above one another, each revolving at 200-300 rpm. The thickness of kernel cakes is reduced progressively as it travels from the top roller to the bottom. This progressive rolling initiates rupturing of cell walls. The flakes that leave the bottom nip are from 0.25 to 0.4 mm thick. The kernel flakes are conveyed to a stack cooker for steam conditioning, the purpose of which is to adjust the moisture content of the meal to an optimum level, reduce viscosity of oil and coagulate the protein in the meal to facilitate separation of the oil from protein materials.
The meal flows from the top compartment down to the fifth compartment in series. At each stage a mechanical stirrer agitates the meal. Steam trays heat the cookers, and live steam may be injected into each compartment when necessary. The important variables are temperature, retention time and moisture content. In the palm kernel, the meals are normally cooked to a moisture content of 3% at 104-110°C.

2.8.2 Screw-pressing
The properly cooked meal is then fed to the screw-press, which consists of an interrupted helical thread (worm) which revolves within a stationary perforated cylinder called the cage or barrel. The meal is forced through the barrel by the action of the revolving worms. The volume axially displaced by the worm diminishes from the feeding end to the discharge end, thus compressing the meal as it passes through the barrel.

The expelled oil drains through the perforation of the lining bars of the barrel, while the de-oiled cake is discharged through an annular orifice. In order to prevent extreme temperatures that could damage the oil and cake quality, the worm-shaft is always cooled with circulating water while the barrel is cooled externally by recycling some cooled oil.

2.8.3 Oil clarification
The expelled oil invariably contains a certain quantity of ‘fines and foots’ that need to be removed. The oil from the presses is drained to a reservoir. It is then either pumped to a decanter or revolving coarse screen to remove a large part of the solid impurities. The oil is then pumped to a filter press to remove the remaining solids and fines in order to produce clear oil prior to storage. The cakes discharged from the presses are conveyed for bagging or bulk storage.

As can be seen from Figure 2.1 above, not all crushers use the same procedure for mechanical extraction of kernel oil. There are three variations: direct screw-pressing, partial pre-treatment, and complete pre-treatment.
2.8.4 Direct screw-pressing
Some mills crush the kernels directly in the presses without any pre-treatment. Double pressing usually is required to ensure efficient oil extraction. The screw-presses used normally are less than 10 tonnes per unit per day.

2.8.5 Partial pre-treatment and complete pre-treatment
The kernels are first broken down to smaller fragments by grinding prior to screw-pressing. In some cases, cooking is also carried out. The full pre-treatment processes described earlier are carried out prior to screw-pressing.

2.9 Solvent extraction
Solvent extraction processes can be divided into three main unit operations: kernel pre-treatment, oil extraction, and solvent recovery from the oil and meal. In solvent oil extraction, the oil in the pretreated seeds is chemically extracted. The available routes of solvent oil extraction are percolation, immersion, direct solvent and pre-pressing followed by solvent extraction methods. The percolation extraction process is the most popular method in current use. The pretreated seeds (flakes or cakes) are laid on a perforated bed and the liquid solvent pumped over the bed of flakes or cakes percolates down the bed, and leaves at the bottom through the perforations on the bed. The solution of vegetable oil and solvent called “miscella” is collected then distilled in a desolventiser where the solvent is separated from the oil.
In emersion, the pretreated seeds are immersed in a solvent for some time to allow the oil in the seed cake dissolve in the solvent forming a “miscella” which is treated as in percolation method. This method is best suited to extract efficiently very fine particles that could otherwise choke the bed of percolation extractor.
Direct solvent extraction is generally used for low oil content (less than 20% oil) seeds, while pre-press followed by solvent extraction is used for high oil content (greater than 20% oil) seeds. By improved pre-treatment techniques, the ratio of solvent to solids can be reduced, which give both richer miscellas (solutions of vegetable oil and solvent) going to the distillation system and a reduction of the solvent hold up in the extracted meal fed to the desolventiser.
The extraction process consists of "washing" the oil from the flakes with hexane solvent in a countercurrent extractor or any other solvent that boil fairly at low temperatures. Then the
solvent is evaporated (i.e., desolventized) from both the solvent/oil mixture (micella) and the solvent-laden, defatted flakes. The oil is desolventized by exposing the solvent/oil mixture to steam (contact and non-contact). Then the solvent is condensed, separated from the steam condensate, and reused. Residual hexane not condensed is removed with mineral oil scrubbers. The desolventized oil, called "crude" oil, is then refined. Solvent extraction recovers almost all the oil, leaving only one percent or less oil in the flakes. This method results in higher capacity; lower power consumption, lower wear and tear / maintenance and high extract efficiency. Thus it could be used as complement equipment to extract the oil remained in cakes.

2.10 Production of Biodiesel

A number of studies have shown that triglycerides hold promise as alternative diesel engine fuel (Freedman et al., 1984). However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct-injection and indirect-type diesel engines.

The high viscosity, carbon deposits, acid composition, free fatty acid content of such oils, gum formation due to oxidation and polymerization during storage and combustion, oil ring sticking, lubricating problems, cooking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, thickening and gelling of the lubricating oil as a result of contamination by vegetable oils, lower volatilities content which causes formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics are some of the more obvious problems (Adam, 2002). Consequently, considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Problems encountered in substituting triglycerides for diesel fuels are mostly associated with high viscosity, low volatility and polyunsaturated character. The following processes have been used in attempts to overcome these drawbacks and allow vegetable oils and oil waste to be utilized as a viable alternative fuel.
2.10.1 Pyrolysis
This refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. Thermal decomposition of triglycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics, and carboxylic acids. Different types of vegetable oils reveal large differences in composition when they are thermally decomposed. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Khotoliya et al., (2007) found out that pyrolyzate had lower viscosity, flash point and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate was lower. Pyrolyzed soybean oil, for instance, contains 79% carbon and 12% hydrogen. It also has low viscosity and a high cetane number compared to pure vegetable oils. However, while pyrolyzed vegetable oils possess acceptable amounts of sulfur, water, and sediment, as well as giving acceptable copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. In addition, though the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during thermal processing also eliminates any environmental benefits of using an oxygenated fuel.

2.10.2 Dilutions
Dilution of vegetable oils can be accomplished with such materials as diesel fuels, solvent or ethanol. Pramanik (2003) blended Jatropha curcas oil with diesel oil in varying proportions and found out that the viscosity of the resulting fuel blends was close to that of the diesel fuel. Important physical and chemical properties performed on these fuel blends gave results that were comparable to those of diesel fuel.

2.10.3 Micro-emulsification
The use of microemulsions with solvents such as methanol, ethanol, and 1-butanol has been studied as a means of solving the problem of high viscosity of vegetable oils. Microemulsions are isotropic, clear or translucent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed-phase particles is less than one-fourth the wavelength of visible light. Microemulsion-based fuels are sometimes also termed “hybrid fuels,” although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels (Goering et al.,...
Microemulsions are classified as non-ionic or ionic, depending on the surfactant present. Microemulsions containing, for example, a basic nitrogen compound are termed ionic while those consisting, for example, only of a vegetable oil, aqueous ethanol, and another alcohol, such as 1-butanol, are termed non-ionic. Non-ionic microemulsions are often referred to as detergentless microemulsions, indicating the absence of a surfactant.

2.10.4 Transesterification

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol (Ma et al., 1998a; Ma et al., 1998b and Ma et al., 1999). This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance. Thus, fatty acid methyl esters (known as biodiesel fuel) obtained by transesterification can be used as an alternative fuel for diesel engines.

Biodiesel is made by chemically altering the molecular structure of any organic oil through the use of a chemical catalyst and an alcohol (Darnako and Cheryan, 2000). To do this, oil is simply heated to a designated temperature (to help with the chemical reaction) and then a mixture of catalyst and an alcohol are added to the oil. The oil, catalyst, and alcohol mixture are then mixed for a period of time and then allowed to settle. If successful, the chemical reaction between the oil, alcohol, and the catalyst will have broken down the oil into several layers. The top layer will be biodiesel, chemically called an Ester, the next layer may contain soap, and the bottom layer will be glycerine.

Once the layer separation has occurred, the glycerine and soap are drained off. The biodiesel is then washed with a mist-wash, a bubble-wash, or both. The washing is done to remove any additional soap, alcohol, or other impurities in the biodiesel. After it's been washed, it is then dried to remove any water. Commonly, it is then filtered through fuel filters and is then ready to be used. Biodiesel fuels produced from various vegetable oils have viscosities close to those of diesel. Their volumetric heating values are a little lower, but they have high cetane numbers and flash points.
2.11 The Process of Transesterification

ASTM International defines Biodiesel as a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats as per the requirements of ASTM D6751 (ASTM 2008a,b,c,d). Vegetable oils and animal fats are principally composed of triacylglycerols (TAG) consisting of long chain fatty acids chemically bound to a glycerol (1, 2, 3-propanetriol) backbone as shown in figure 2.2 and figure 2.3.

R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> represent the hydrocarbon chains of the fatty acyl groups of the triglyceride. In their free form, fatty acids have the configuration shown below where R is a hydrocarbon chain > 10 carbon atoms.

R<sub>1</sub>—C—OH

The chemical process by which biodiesel is prepared is known as the transesterification reaction, which involves a TAG reaction with a short-chain monohydric alcohol normally in the presence of a catalyst at elevated temperature to form fatty acid alkyl esters (FAAE) and glycerol (Agarwal, 2004). The conversion of TAG to biodiesel is a stepwise process whereby the alcohol initially reacts with TAG as the alkoxide anion to produce FAAE and diacylglycerols (DAG, reaction [1], figure 2.5) which react further with alcohol (alkoxide) to liberate another molecule of FAAE and generate monoacylglycerols (MAG, reaction [2], figures 2.5). Lastly, MAG undergoes alcoholysis to yield glycerol and FAAE (Peterson et al., 1991), reaction [3], figure 2.5 with the combined FAAE collectively known as biodiesel. Three moles of biodiesel and one mole of glycerol are produced for every mole of TAG that undergoes complete conversion. The
basic chemical process that occurs during the transesterification reaction is indicated in figure 2.4 and 2.5 below.

**Fig. 2.4:** Chemical process that occur during transesterification reaction.

The catalyst may be acidic, basic (KOH, NaOH, NaOCH₃, etc.), or enzymatic (lipase) (Gerpen et al., 2004).

**Fig.2.5:** Trans-esterification triacylglycerol’s to yield fatty acid alkyl esters (biodiesel).

The mixture of methyl esters produced by this reaction is referred to as biodiesel. The above reaction is currently the most widely used industrial biodiesel production method, due to the low cost and high availability of methanol. The fuel properties of biodiesel are determined by the amounts of each fatty acid in the feedstock used to produce the esters. The transesterification is an equilibrium reaction as shown (figure 2.6) below. In order to achieve a high yield of the ester the alcohol has to be used in excess to push the reaction to the right.
Fig. 2.6: **Equilibrium representation of transesterification reaction.**

This reaction is reversible, although the reverse reaction (production of MAG from FAAE and glycerol, for instance) is negligible largely because glycerol is not miscible with FAAE, especially fatty acid methyl esters (FAME) when using methanol as the alcohol component (figures 2.5 and 2.6). The reaction system is biphasic at the beginning and the end of biodiesel production, as methanol and vegetable oil and glycerol and FAME are not miscible. Methanol commonly used in the commercial production of biodiesel, since it is generally less expensive than other alcohols, but ethanol prevails in regions such as Brazil where it is less expensive than methanol. Other alcohols aside from methanol and ethanol are also of interest for biodiesel production because FAAE produced from higher alcohols may have different fuel properties in comparison to methyl or ethyl esters (Knothe, 2005). Inexpensive homogenous base catalysts such as sodium or potassium hydroxide or methoxide are typically used in the commercial preparation of biodiesel from refined or treated oils. The classic alcoholsysis conditions described by Freedman et al., (1984) include a TAG reaction with an excess of six molar equivalents of methanol (with respect to TAG) and 0.5 weight percent (wt.%) alkali catalyst (with respect to TAG) at 60°C for 1 h to produce fatty acid methyl esters (FAME, biodiesel) and glycerol. The chemical composition of biodiesel is dependent upon the feedstock from which it is produced, as vegetable oils and animal fats of differing origin have dissimilar fatty acid compositions (Table 2.5). The fatty ester composition of biodiesel is identical to that of the parent oil or fat from which it was produced.

A recent report (International Grains Council, 2008) indicated that rapeseed oil was the predominant feedstock for worldwide biodiesel production in 2007 (48%, 4.6 million metric tons, MMT). The remaining oils included soybean (22%, 2.1 MMT) and palm (11%, 1.0 MMT), with the rest (19%, 1.8 MMT) distributed among other unspecified vegetable oils and animal fats. The leading vegetable oils produced worldwide during the 2008 fiscal year biodiesel production vary with location according to climate and availability.
Table 2.5: Typical fatty acid composition (wt. %)\textsuperscript{a} of a number of common feedstock oils\textsuperscript{b} and fats that may be used for biodiesel production

<table>
<thead>
<tr>
<th>Fatty acid\textsuperscript{c}</th>
<th>CO</th>
<th>PO</th>
<th>SBO</th>
<th>SFO</th>
<th>COO</th>
<th>CSO</th>
<th>CCO</th>
<th>CF</th>
<th>BT</th>
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<td>C6:0</td>
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<td></td>
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<tr>
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<td>1</td>
<td></td>
</tr>
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<td>1</td>
<td>18</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
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<td>3</td>
<td>6</td>
<td>20</td>
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<tr>
<td>C16:1</td>
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<td></td>
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<td></td>
<td>1</td>
<td>8</td>
<td>4</td>
<td></td>
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<tr>
<td>C18:1</td>
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<td>39</td>
<td>23</td>
<td>29</td>
<td>28</td>
<td>17</td>
<td>6</td>
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<tr>
<td>C18:2</td>
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</tr>
<tr>
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<td></td>
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<td></td>
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<tr>
<td>Others</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Gunstone et al., (2007)

\textsuperscript{a} trace amounts (<1%) of other constituents may also be present

\textsuperscript{b} CO canola (low erucic acid rapeseed oil) oil, PO palm oil, SBOsoybean oil, SFO sunflower oil, COO corn oil (maize), CSOcottonseed oil, CCO coconut oil, CF chicken fat, BT beef tallow

\textsuperscript{c} C6:0 methyl caproate, C8:0 methyl caprylate, C10:0 methyl caprate,C12:0 methyl laurate, C14:0 methyl myristate, C16:0 methylpalmitate, C18:0 methyl stearate, C20:0 methyl arachidate, C22:0methyl behenate, C16:1 methyl palmitoleate, C18:1 methyl oleate,C18:2 methyl linoleate, C18:3 methyl linolenate, C20:1 methyleicosenoate

Generally, the most abundant commodity oils or fats in a particular region are the most common feedstocks. Thus, rapeseed and sunflower oils are principally used in Europe for biodiesel production, palm oil predominates in tropical countries, and soybean oil and animal fats are most common in the USA (Demirbas, 2006). However, even combining these feedstocks do not suffice to fully replace the volume of conventional petroleum diesel fuel. Therefore, exploration of additional feedstocks (such as Candlenut and Calodendrum capense used in this study) for
biodiesel production has been continuously gaining significance. Biodiesel standards are in place in a number of countries in an effort to ensure that only high-quality biodiesel reaches the marketplace. Current research focuses primarily on the basic and enzymatic approaches because acidic catalysts require a long reaction time. In the enzymatic approach, lipases are isolated from many types of microorganisms and catalyze the transesterification reaction. This project will explore the basic and enzymatic methods, as well as methods to improve upon the current drawbacks of biodiesel production.

2.12 Basic Transesterification

Methanolysis of vegetable oils using an alkaline catalyst is currently the most widely used industrial biodiesel production method, due to the low cost and high availability of methanol. The addition of methanol to a vegetable oil causes the large branched molecules of vegetable oils to break down into smaller, linear methyl ester oils. This process requires a large excess of methanol to drive the reaction to completion as well as base catalysts such as sodium hydroxide, potassium hydroxide, or sodium methoxide (Freedman et al., 1986 and Srivastava and Prasad (2000).

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in figure 2.7 below. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol (Schuchardt et al., 1998). Research has shown that transesterification using an alkali catalyst results into high conversion oil plant and animal fats to biodiesel and a fast reaction rate. Despite this, several problems still exist: The byproduct of methyl ester formation is glycerol, which can be difficult to remove from the biodiesel, the need to remove base from the wastewater, side reactions due to contamination by
free fatty acids and water and saponification, which requires the pretreatment of waste oils before they can be reused in further reactions.

\[
\begin{align*}
\text{ROH} + B & \rightleftharpoons \text{RO}^- + \text{BH}^+ \quad \text{..........................1} \\
\text{R'COO} & \rightleftharpoons \text{CH}_2 \\
\text{R''COO} & \rightleftharpoons \text{CH} \\
\text{H}_2\text{C} & \rightleftharpoons \text{OCR} \\
\text{OR} & \rightleftharpoons \text{O} \\
\text{R'COO} & \rightleftharpoons \text{CH}_2 \\
\text{R''COO} & \rightleftharpoons \text{CH} \\
\text{H}_2\text{C} & \rightleftharpoons \text{OCR''} \\
\text{OR} & \rightleftharpoons \text{O} \\
\text{R'COO} & \rightleftharpoons \text{CH}_2 \\
\text{R''COO} & \rightleftharpoons \text{CH} \\
\text{H}_2\text{C} & \rightleftharpoons \text{OCR} \\
\text{OR} & \rightleftharpoons \text{O} \\
\text{R'COO} & \rightleftharpoons \text{CH}_2 \\
\text{R''COO} & \rightleftharpoons \text{CH} \\
\text{H}_2\text{C} & \rightleftharpoons \text{OH} \\
\text{B} & \rightleftharpoons \text{BH}^+ \quad \text{..........................4}
\end{align*}
\]

Fig. 2.7: Base catalyzed transesterification process

2.12.1 Steps in base catalyzed production of biodiesel

The most important issue during biodiesel production is the completeness of the reaction. The basic chemical process that occurs during the reaction is indicated by the following sequence events.

The first step is the mixing of alcohol and catalyst, the catalyst used in most cases is sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator. The amount of KOH or NaOH is normally reached based on the amount needed to neutralize the free fatty acids in the oil as determined by titration (Demirbas, 2003).
The alcohol/catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of alcohol (around 70 °C) to seep up the reaction and the reaction takes place. Near the end of the reaction mixing speed must be reduced to improve separation of glycerin and the reaction would proceed faster in the top layer. Recommended reaction time varies from 1 to 8 hours, and some systems recommend the reaction take place at room temperature (Foidl et al., 1996). Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. Care is taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of excess methanol that is used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off at the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster. Once the glycerin and biodiesel phase have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care is taken to ensure no water accumulates in the recovered alcohol stream.

The glycerin by-product contains unused catalyst and soap that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as a fertilizer. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold as crude glycerine. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets.

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst, soap, remnant glycerin and excess methanol. The use of warm water (40 to 60 °C) prevents precipitation of unsaturated fatty acid esters and retards the formation of emulsions with the use of gentle washing action. Softened water (slightly acidic)
removes calcium and magnesium contamination and neutralizes remaining base catalysts. In some processes this step is unnecessary. This is normally the end of the production process resulting in clear amber-yellow liquid with viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an addition step to remove small amounts of color biodiesel to produce a colorless biodiesel.

Keith (2007) gave a brief description of the main washing methods as described below:

**Mist washing:** Mist washing was developed as a way to address emulsification issues. This system uses a very fine mist head from a garden supply store, suspended over a container of biodiesel, with a way to drain the water after it falls through the fuel. The mist stirs up the fuel less than in bubble washing, and removes soaps gradually. The gentler agitation gives less of an opportunity for the soaps and many mono and diglycerides to form emulsion.

**Bubble washing:** Bubble washing involves gently adding 1/3 water to 2/3 biodiesel, adding a cheap aquarium air stone and air pump setup to the water portion (water sinks to the bottom and biodiesel will float on top) and bubbling air through the water. The air bubbles allow a sort of indirect agitation of the two fluids-they pick up a tiny amount of water and gently carry it through the biodiesel, picking up soaps and other contaminants. When the bubble bursts at the surface it drops the water which picks up more of the soaps and contaminants on its way back down. After about 6 hours of this (low-wattage) ‘washing’, the air is stopped, then the water is drained, more fresh water is added, and the process repeats. These ‘wash water changes’ are repeated about 3 times on average- until the water measures the same PH as the tap water, and is perfectly clear (Keith, 2007).

**Stir Washing:** This method involves mixing the biodiesel with water and stirring to a homogeneous state preferably by use of a motor driven impeller. The mixture is then allowed to settle for an hour in a settling tank. In a mixture of good quality, the biodiesel separates and forms a clear layer on top of the water and is siphoned or decanted out. This process is repeated at least twice. It’s more advantageous compared to other methods because it is quick and effective and there is no masking of poor reaction or oxidation since biodiesel is actively agitated.

A dry fuel is ‘clear’ –referring to lack of haze, not color- it does not contain much water (in reality biodiesel will absorb some water and harmless amount of moisture from the atmosphere).
The water content in biodiesel can be reduced by any of the following methods:

**Vacuum driers:** In vacuum driers the biodiesel is subjected to highly reduced pressure. This allows the water in the biodiesel to evaporate at low temperature. Vacuum driers can be either batch or continuous, in which the biodiesel is dried in batches (or in turns) or continuously respectively (Keith, 2007).

**Falling film evaporator:** In a falling evaporator, a thin film of the biodiesel runs down a heated surface of the evaporator. The direct contact with the heated wall evaporates the water rapidly. Falling film evaporators allow for rather high heating and evaporation rates. In this process caution is taken in avoiding high temperatures that lead to darkening of the biodiesel, which is a sign of polymerizing of the poly-unsaturated methyl ester.

**Bubble-drying:** Bubble drying uses the same principle as bubble washing discussed above, the exception is that here water is not used. Air is bubbled through the biodiesel, enhancing the evaporation of water in the biodiesel. It has the same disadvantage of oxidizing and polymerizing the biodiesel as occurs in bubble washing (Keith, 2007).

**Evaporation:** Biodiesel when exposed to an open place for a day or longer it clears on its own. This process can be accelerated by heating the biodiesel to 40-50 °C, and allowing it to cool in a vented container.

### 2.13 Biodiesel quality

Biodiesel characteristics vary slightly with the feedstock used. This does not however diminish the final quality of the processed biodiesel. Home brewers in Europe have reported excellent results of home-made biodiesel, which have passed biodiesel standards such as of European EN 14214, Germany’s DIN 51606 and America’s US ASTM D-6751-02 (Keith, 2007).

#### 2.13.1 Biodiesel quality testing

As for fuels, the quality testing of biodiesel is essential to ensure safe running in the diesel engine. Free glycerin, poorly converted oils/fats and sodium lye are contaminants which have severe impact on the fuel system of a diesel engine. Sodium and potassium arise from the addition of catalyst, and result in high ash levels in the engine. They are however limited to a combined maximum of 5 ppm. Several standards for testing biodiesel have been developed where biodiesel is commercially in use. These include the US D6751-02 Standard Specification for Biodiesel Fuel (B100) Blend stock for distillate fuel, and EU standard, DIN EN 14214.
However, for quality checks where standard tests are not available, Keith (2007) has proposed the following tests that can be used to check quality of biodiesel.

**Wash test:** In a half litre glass jar 150ml of unwashed biodiesel was mixed with 150ml of water, the lid was then screwed tightly and the jar shaken violently for ten seconds or more, until a homogeneous mixture was formed. The mixture was then left to settle. For a good quality biodiesel, the biodiesel was supposed to separate from the water in half an hour or less, with amber biodiesel on top and milky water below. If it turns into something like mayonnaise and won’t separate, or separates slowly with a white creamy layer sand-witched between water and biodiesel, the fuel was of poor quality.

**Reprocessing test:** A small amount of the finished biodiesel was reprocessed again as if were virgin vegetable oil. If more glycerin drops out, then the fuel was not of good quality.

**Methanol test:** In a measuring glass 25ml of biodiesel was dissolved with 225ml of methanol. The biodiesel should be fully soluble in the methanol, forming a clear bright phase. If not, there was contamination of the biodiesel. This method gives indication of impurities in the biodiesel. It is valid only for biodiesel made from vegetable oils and animal fats and is not valid for biodiesel made from oils with a very wide fatty acid patterns, such as fish oils.

### 2.14 Enzymatic Transesterification

Although chemical transesterification using an alkali-catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water requires treatment, and free fatty acids and water interfere with the reaction. Both extracellular and intracellular lipases are also able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous system.

Most lipases used as catalysts in organic synthesis are of microbial or fungal origin, such as *Candida rugosa, Psuedomonas florescenes, Rhizopus oryzae, Burkholderia cepacia, Aspergillus niger, Thermomyces lanuginose* and *Rhizomucor miehei*. Microbial lipases are easy to obtain, by fermentation processes and a few basic purification steps.
One important aspect of lipolytic enzymes is the unique property of interfacial activation, identified by Verger et al., (1973). The activity of lipases is low in monomeric solutions of lipid substrates but is strongly enhanced once organized lipid structures and a configuration change of the enzyme at the water-lipid interface are formed. Lipase-catalyzed separation of vegetable oils into methyl esters gives a very high-purity product that can easily be separated from glycerol. The enzyme can also be reused for multiple reactions. In order for the lipase to maintain its activity for repeated reactions, either the enzyme or the entire cell must be immobilized. Other advantages of using lipases in biodiesel production are: (a) ability to work in very different media which include biphasic system, and monophasic system, (b) they are robust and versatile enzymes that can be produced in bulk because of their extracellular nature in most manufacturing system, (c) when the lipase is used in a packed bed reactor, no separation is necessary after transesterification, and (d) higher thermo stability and short chain alcohol-tolerant capabilities of lipase make it very convenient for use in biodiesel production (Ghaly et al., 2010).

In addition to the type of lipase, other factors affecting the effectiveness of lipase in the production of biodiesel from triacylglycerol are the water content, temperature, number of cycles (for immobilized enzymes) and the type of alcohol and its ratio to oil. One major problem of lipase-catalyzed transesterification is that glycerol competitively inhibits lipase activity by blocking the active sites. Since glycerol is a byproduct of the reaction of triglycerides with methanol, new acyl acceptors that produce other more useful and less detrimental byproducts need to be investigated. One such major success was done by Du et al., (2004) who used methyl acetate as an acyl acceptor. An acyl acceptor functions as the new attachment of fatty acid chains, in place of glycerol. The byproduct of this reaction is triacetylglycerol, which has no negative effects on the reaction, can easily be separated from the biodiesel product, and has a higher value than glycerol for later use.

Addition of a solvent that will not interfere in the reaction is another way to reduce the inhibitory effects of methanol and glycerol. The branched alcohol t-butanol does not interfere with lipase and dissolves both methanol and glycerol. It is nontoxic and relatively low cost. Royon et al., (2007) added t-butanol to a transesterification reaction with a 6:1 methanol to oil ratio, which normally completely inhibits the lipase activity. He observed a high yield of methyl ester in half
the reaction time. Mamoru et al., (2001) used 1, 4-dioxane, benzene, chloroform and tetrahydrofuran as appropriate organic solvents to carry out the transesterification reaction using immobilized *Pseudomonas fluorescens* lipase as catalyst. The lipase tested was found to be active during methanolysis. In contrast the lipase was almost inactive in a solvent free medium. The enzymatic activity increased significantly with 1, 4-dioxane giving the highest yield biodiesel as compared to other solvents used.

Lipases are known to have a propensity to act on long chain fatty alcohols better than on short chain ones. Mamoru et al., (2001) found out that when methanol and ethanol were used as alcohol, organic solvent like 1, 4-dioxane was required. However, the reaction could be performed in absence of such a solvent when 1-propanol and 1-butanol were used as short-chain alcohol. Mittelbach, (1990) and Abigor et al., (2000) reported that using methanol in enzymatic lipase catalyzed transesterification gives very low yields of methyl esters as compared to other alcohols.

The effect of water content on the production of biodiesel from vegetable oil using lipase can be attributed to the fact that lipase acts at the interface between aqueous and organic phases. Activation of enzyme involves unmasking and restructuring the active site through conformation changes of the lipase molecule, which requires the presence of an oil-water interface.

**Use of extracellular lipases:** Various types of alcohols- primary, secondary, and straight- and branched-chain can be employed in transesterification using lipases as catalyst. Linko et al., (1998) have demonstrated the production of variety of biodegradable esters and polysters with lipase as the biocatalyst. In transesterification of rapeseed oil with 2-ethyl-1-hexanol, 97% conversion of esters was obtained using *Candida rugosa* lipase powder. De et al., (1999) investigated the conversion of fatty alcohol (C₄-C₁₈:₁) using immobilized *Mucor miehei* lipase (Lipozyme IM-20) in solvent-free system. The percentage of molar conversion of all corresponding alcohol esters ranged from 86.8 to 99.2%, while the slip melting points of the esters were found to increase steadily with increasing alcohol chain length (from C₄ to C₁₈) and to decline with the incorporation of unsaturation for the same chain length as from (C₁₈ to C₁₈:₁).

Transesterification of the triglycerides sunflower oil, fish oil and grease with ethanol has also been studied. In each case, high yields beyond 80% could be achieved using the lipase from *M.miehei, Candida antartica, Pseudomonas cepacia* respectively (Wu et al., 1999).
Mettelbach, (1990) reported transesterification using the primary alcohols methanol, ethanol, and 1-butanol, with and without petroleum ether as a solvent. Although the ester yields with ethanol and 1-butanol were relatively high, even in reactions without a solvent, with methanol only traces of methyl esters were obtained. Abigor et al., (2000) also found that the conversion of palm kernel oil alkyl esters using *P. cepacia* lipase, ethanol gave the highest conversion of 72%, while only 15% methyl esters was obtained with methanol. Lipases are known to have a propensity to act on long chain fatty alcohols better than on short-chain ones. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanolysis) is likely to be very low compared to that with ethanol in systems with or without a solvent.

**Use of intracellular lipase as a whole cell biocatalyst:** Bioconversion can be carried out using extracellular or intracellular enzymes, but extracellular enzymes require purification by procedures that may be too complex for practical use. Furthermore, enzymes recovered through such operations are generally unstable and expensive (Liu et al., 2000).

To utilize whole cell biocatalysts in a convenient form, cells should be immobilized in such a way that resemble ordinary solid-phase catalysts used conventionally in synthetic chemical reactions. Among many available immobilization methods, a technique using porous biomass support particles (BSPs) developed by Atkinson et al., (1979) have several advantages over other methods in terms of industrial application:

- No chemical additives are required and there is no need for preproduction of cells.
- Aseptic handling of particles is unnecessary and there is a large mass transfer rate of substrate and production within BSPs.
- The particles are reusable and are durable against mechanical shear.
- Bioreactor scale-up is easy and costs are compared to other methods.

Because of its advantageous features, the BSP technique has been applied successfully in a wide variety of microbial, animal, insect and plant cell systems.
2.15 Variables Affecting Transesterification Reaction

2.15.1 Effect of Moisture and Free Fatty Acid

The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. To carry the base catalyzed reaction to completion; a free fatty acid (FFA) value lower than 3% is needed. The higher the acidity of the oil the smaller is the conversion efficiency. Both, excess as well as insufficient amount of catalyst may cause soap formation (Dorado et al., 2004).

The transesterification of beef tallow catalyzed by NaOH in presence of free fatty acids and water was studied by Ma et al. (1998). Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6% of FFA was added, the apparent yield of BTME reached the lowest, less than 5%, with any level of water added.

The products were solid at room temperature, similar to the original beef tallow. When 0.9% of water was added, without addition of FFA, the apparent yield was about 17%. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids. Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids.

The starting materials used for base catalyzed alcoholysis should meet certain specifications. The triglycerides should have lower acid value and all material should be substantially anhydrous. The addition of more sodium hydroxide catalyst compensates for higher acidity, but the resulting soap causes an increase in viscosity or formation of gels that interferes in the reaction as well as with separation of glycerol (Freedman et al., 1984). When the reaction conditions do not meet the above requirements, ester yields are significantly reduced. The methoxide and hydroxide of sodium or potassium should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide.

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and fats that could be converted to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkaline catalyst. Therefore, two-step esterification process is required for these feedstocks. Initially the FFA of these can be
converted to fatty acid methyl esters by an acid catalyzed pretreatment and in the second step transesterification is completed by using alkaline catalyst to complete the reaction (Canakci and Gerpen, 2001).

If the oil or fat contains sufficient amounts of FFA, special processes are required. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to such feedstocks, the free fatty acids react with the catalyst to form soap and water as shown in the reaction scheme 2.8 below; (Gerpen, 2005).

![Reaction between free fatty acid and potassium hydroxide](image)

**Fig. 2.8: Reaction between free fatty acid and potassium hydroxide**

The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap formed inhibits separation of the glycerol from the methyl esters, causes an increase in viscosity of the biodiesel, reduces catalytic efficiency and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters as shown in reaction figure 2.9 below; (Gerpen, 2005).

![Esterification of free fatty acids using acid catalyst](image)

**Fig. 2.9: Esterification of free fatty acids using acid catalyst**

This process can be used as a pretreatment to convert the FFAs to methyl esters and thereby reduce the FFA level. Then, the low FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters (Gerpen, 2005). As shown in the above reaction, water is formed and, if it accumulates, it can stop the reaction well before completion.
Any water added to the entire system quenches a proportional amount of the catalyst. One part of water can quench up to 4.67 parts of catalyst (Peters, 1996).

2.15.2 Catalyst type and concentration

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective (Ma and Hanna, 1999). If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid.

Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe (Ma et al., 1998). The catalysts NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively. Sodium methoxide causes formation of several by-products mainly sodium salts, which are to be treated as waste. In addition, high quality oil is required with this catalyst (Marr et al., 1995). This was different from the previous reports (Freedman et al., 1986), in which ester conversion at the 6:1 molar ratio of alcohol/oil for 1% NaOH and 0.5% NaOMe were almost the same after 60 min. Part of the difference may be attributed to the differences in the reaction system used.

As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil. Refined and crude oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted successful conversion. Methanolysis of soybean oil with the catalyst 1% potassium hydroxide has given the best yields and viscosities of the esters (Tomasevic and Siler-Marinkove, 2003).

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several shortcomings: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and free fatty acid and water interfere the reaction (Devanesan et al., 2007). The drawbacks can be overcome using enzymatic catalysts like lipases which are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems (Fuduka et al., 2001). However, with further increase in the catalyst amount the conversion was slightly
decreased. This was probably because the slurry (mixture of catalyst and reactants) become too viscous giving rise to a problem of mixing and demand of higher power consumption for adequate stirring (Kim et al. 2004; Wan et al., 2009; Xie et al., 2006; Xie and Li 2006).

Acid catalyzed transesterification was studied with waste vegetable oil. The reaction was conducted at four different catalyst concentrations, 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the result showed a decrease in viscosity. When H$_2$SO$_4$ was used instead of HCl it was observed that it had superior catalytic activity in the range of 1.5–2.25 M concentration (Mohamad et al., 2002).

In particular, the by-products, glycerol can be easily removed without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. In general the production cost of a lipase catalyst is significantly greater than that of an alkaline one.

2.15.3 Molar ratio of alcohol to oil and type of alcohol

One of the most important variables affecting the yields of ester formation is the molar ratio of alcohol to vegetable oil employed. The stoichiometric ratio for this reaction requires 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol. Since transesterification is an equilibrium reaction, large excess of alcohol is required to drive the reaction to the right.

Higher molar ratios result in greater ester conversion in a shorter time. Freedman et al., 1986 studied the effect of molar ratios (from 1:1 to 6:1) on ester conversion with vegetable oils. Soya bean sunflower, peanut and cotton seed oils all behaved in the same way, with the highest conversion being achieved at a 6:1 molar ratio. Anh and Tan (2008) also confirmed the dependence of biodiesel yield on methanol/oil ratio. Their results showed that as the ratio increased from 5:1 to 8:1 conversion increased from 50% for the ratio of 5:1 to 64% for the ratio of 8:1. However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in its solubility (Meher et al., 2004; Anh and Tan 2008). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility.

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol
and ethanol are not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Zhou et al., 2003). The emulsions are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, the concentration of mono- and di-glycerides is very low, the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of mono- and di-glycerides.

2.15.4 Effect of reaction time

The conversion rate increases with reaction time. Freedman et al., (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the following conditions; methanol/oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60°C. They observed an approximate yield of 80% after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93-98%). Ma et al., (1998) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute, which they said was due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeded very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min. To achieve reaction in shorter times, non-conventional heating methods can be employed. Nezihe and Aysegul (2007) performed transesterification of cotton seed by microwave irradiation in the presence of methanol and potassium hydroxide (KOH).
To compare the heating systems conventional heating was also employed in transesterification. As a result, 7 min reaction time, 333°K temperature and 1.5% catalyst–oil ratio were obtained as optimum reaction parameters for microwave heating. Similar results were found out for conventional heating but 30 min of reaction time. Saifuddin and Chua (2004) reported similar results. During their study they noted that while the conventional process required 75 min, the microwave assisted process only required 4 min to complete the transesterification reaction. Shorter reaction times with high yields of biodiesel can also be achieved when transesterification is carried out in supercritical conditions and use of co-solvents (Vivek and Giridhar, 2007; Hawash. et al., 2009 and Zhou et al., 2003).

2.15.5 Effect of temperature

Transesterification can occur at different temperatures, depending on the types of catalyst, alcohol and oil used. Freedman et al., (1984) studied the transesterification of refined oil with methanol at 6:1 methanol/oil ratio and 1% NaOH, the reaction with three different temperatures. After half an hour, ester yields were 94%, 87% and 64% for 60°C, 45°C and 32°C, respectively. After one hour, ester formation was identical for 60°C and 45°C runs and only slightly lower for the 32°C run. It’s therefore evident that temperature clearly influenced the reaction rate and yield of esters.

The effect of temperature on the conversion of waste cooking oil to biodiesel at the methanol/oil ratio of 8:1 in the presence of 0.75 wt percentage KOH was studied by Anh and Tan 2008. They observed that by increasing the temperatures from 30°C to 50°C, the conversion increased by 10–13%. However, when the temperature was increased up to 70°C, a slight reduction in the conversion was observed. This is because high temperature enhances both transesterification and saponification reactions. Basri et al., (2010) investigated the influence of temperature on conversion of palm oil to biodiesel at different temperatures. He found out that the conversion increased as the reaction temperature increased with the highest conversion of 99% at 60 °C. However, when the temperature reaches to the boiling point of methanol, a lot of methanol’s bubbles were formed hence inhibit the mass transfer on the phase interface thus lower the conversion (Zabeti et al. 2009).
2.15.6 Mixing intensity
Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide–methanol solution. Once the two phases are mixed and the reaction is started, stirring is no longer needed. Initially the effect of mixing on transesterification of beef tallow was investigated by Ma and Hanna (1999). No reaction was observed without mixing and when NaOH–MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

2.15.7 Effect of using organic cosolvents
One of the study carried out by Meher et al., (2004) reported that the methoxide base catalyzed methanolysis of soybean oil at 40°C (methanol-oil molar ratio 6:1) to form methyl esters proceeded approximately more slowly than butanolysis at 30°C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate mono- and di-glycerides preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. In order to conduct the reaction in a single phase, the use of cosolvents like tetrahydrofuran (THF), 1,4- dioxane and diethyl ether was studied. At the 6:1 methanol-oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produced an oil dominant one phase system in which the rate of methanolysis increased dramatically and occurred as fast as butanolysis. In particular, THF is chosen because its boiling point of 67°C is only two degrees higher than that of methanol.

2.16 Biodiesel Properties and their Tests
The methods and standards used in determining the fuel properties in a given fuels were put forth by ASTM. The following are some of the properties used to characterize diesel fuels needed to provide acceptable engine operation (Kinast, 2003).The property data for major pure components for biodiesel components are shown in the table 2.6 below.
Table 2.6: Major pure component property data for fatty acid methyl esters

<table>
<thead>
<tr>
<th>Ester</th>
<th>Density, g/cc @15.5°C</th>
<th>Viscosity @ 40°C, cSt</th>
<th>Cetane number</th>
<th>Heating value, Mj/Kg</th>
<th>Melting value, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitate</td>
<td>0.867</td>
<td>4.37</td>
<td>74</td>
<td>39.4</td>
<td>30.6</td>
</tr>
<tr>
<td>Stearate</td>
<td>0.867</td>
<td>5.79</td>
<td>75</td>
<td>40.1</td>
<td>39.1</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.878</td>
<td>4.47</td>
<td>55</td>
<td>39.9</td>
<td>-19.8</td>
</tr>
<tr>
<td>Linoleate</td>
<td>0.89</td>
<td>3.68</td>
<td>33</td>
<td>39.7</td>
<td>-35</td>
</tr>
</tbody>
</table>


2.16.1 Flash point

It measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. It is used to assess the overall flammability hazard of a material. Specifically, flash point is used in safety regulations to define "flammable" and "combustible" materials. Higher values indicate materials that are less likely to ignite accidentally. A typical value for Number 2 diesel is 70°C, which is considered safe under normal conditions; D 975 requires a minimum of 52°C. The biodiesels would be considered significantly safer with temperatures between 128°C and 167°C.

The standard procedure for measuring the flash point for diesel and biodiesel fuels is ASTM D93. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed (Gerpen et al. 2004). The flash point needs not to correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame.

2.16.2 Water and Sediment

This property measures the amount of water and sediment in fuel oils. The presence of either water or sediment in biodiesel can indicate incomplete washing or filtering. This test is particularly important when working with biodiesel because it’s usually water-washed to remove
traces of soap and free glycerol. Vacuum drying is usually needed to remove residual water following the washing process. The standard procedure for measuring the water and sediment for diesel and biodiesel fuels is ASTM D2709.

2.16.3 Calorific Value
The calorific value is determined according to ASTM D240, but it is not specified in ASTM D6741 or EN 14214. The calorific value is the thermal energy that is liberated upon combustion, so it is commonly referred as energy content. The heat of combustion is measured with an oxygen bomb calorimeter which is an instrument for measuring calorific values of solid and liquid combustible samples. Heat measured in a bomb calorimeter may be expressed either as calories (cal), British thermal units (Btu) or Joules (J).

Factors that influence the energy content of biodiesel include oxygen content and carbon to hydrogen ratio. Generally, as the oxygen content of FAAE is increased, a corresponding reduction in energy content is observed.

The ASTM has developed a series of standard methods for testing both solid and liquid fuels in an oxygen bomb calorimeter. The heat of combustion determines the suitability of using given oil for fuel. As suggested by Clements and Davis, (1996) the heating value can be approximated using a sample mixing rule of the form:

\[ H_{mix} = \sum x_i H_i \]  

(Equation 2.2)

Where \( H_i \) is the heating value of the pure component as given in Table 2.6

The heating values obtained are within range of other heating values obtained by workers of conventional vegetable oils. The heats of combustion obtained for cotton seed, soybean, groundnut, sunflower oils are 38.9 Kj/g, 39.4 Kj/g, 40.2 Kj/g and 38.7 Kj/g respectively (Broder et al., 1982).

In general the heat of combustion for vegetable oils is slightly lower than that of conventional DF. Since the density of diesel is less than the density of vegetable oils (Appendix III) the ratio of the heat content of CL in comparison to diesel is about 90% on volume basis. This indicates slightly more vegetable oil than DF2 is needed to generate the same amount of power.
2.16.4 Kinematic Viscosity

Viscosity is an important quantity in diesel engine especially for lower grade fuels used in larger engines. Kinematic viscosity provides a measure of the time required for a volume of liquids to flow under gravity through a calibrated glass capillary tube. It is determined using a standard procedure ASTM D445. According to viscous fuels form a dribble at the injector nozzle resulting in injector coking. This deposit impedes subsequent flow of fuel into the combustion chamber resulting in power loss. High viscous fluids atomize poorly and thus there is incomplete combustion. Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of vegetable oils or animal fats. The high kinematic viscosities of vegetable oils and animal fats ultimately lead to operational problems such as engine deposits when used directly as fuels (Knothe and Steidley 2005a,b).

Viscosity affects the atomization of a fuel upon injection into the combustion chamber and thereby ultimately the formation of engine deposit (Fuels et al., 1984). The higher the viscosity, the greater the tendency of the fuel to cause such problems, that is the greater the viscosity, the less readily the liquid flows (Ryan et al., 1984). The viscosity of petroleum oils is a strong function of temperature with the viscosity decreasing as the temperature increases. Viscosity impacts the operation of components such as the fuel pump. The viscosity of transesterified oil (biodiesel) is about an order of magnitude lower than that of the parent oil. Several structural features influence the kinematic viscosities of FAAE, such as chain length, degree of unsaturation, double bond orientation, and type of ester head group.

Janarthanan et al., (1996) tested a number of empirical expressions for representing the temperature dependence of liquid viscosity and suggested that the viscosity for methyl palmitate, stearate and oleate can be approximated by the equation of the form;

\[ \ln \eta = A + B/T + C/T^2 \]  \hspace{1cm} \text{(Equation 2.3)}

And that of methyl linoleate by the equation of the form;

\[ \ln \eta = A + BT + C/T^2 \]  \hspace{1cm} \text{(Equation 2.4)}

Where constants A, B and C are as given in Table 2.7 below;
Table 2.7: Empirical constants for estimating methyl ester viscosity

<table>
<thead>
<tr>
<th>Ester</th>
<th>Constant A</th>
<th>Constant B</th>
<th>Constant C</th>
<th>Temperature range °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitate</td>
<td>-17.7087421</td>
<td>0.0194820</td>
<td>4095.98793</td>
<td>26.7 - 98.9</td>
</tr>
<tr>
<td>Stearate</td>
<td>-12.2620883</td>
<td>0.0109932</td>
<td>3310.50996</td>
<td>48.9 – 110</td>
</tr>
<tr>
<td>Oleate</td>
<td>-9.6133497</td>
<td>0.0075371</td>
<td>2739.10625</td>
<td>26.7 – 110</td>
</tr>
<tr>
<td>Linoleate</td>
<td>-0.5705778</td>
<td>-680.80715</td>
<td>396575.647</td>
<td>37.8 – 100</td>
</tr>
</tbody>
</table>

Source: Clements and Davis (1996).

The estimation of the viscosity of mixtures is one of the most difficult problems in the entire domain of property estimation. A number of expressions have been suggested in the form;

\[
\ln \eta_{\text{mix}} = x_i f(\eta)
\]  

(Equation 2.5)

Where \( f(\eta) \) is chosen by trial and error

A commonly used form of the equation is;

\[
\ln \eta_{\text{mix}} = x_i (\ln \eta)^{1/3}
\]  

(Equation 2.6)

The viscosities obtained for the vegetable oils are 15-20 times higher than the viscosity of DF. High viscosities of oils account for the oil fuel flow problems encountered when vegetable oils are used in diesel engines.

Viscosities are directly proportional to the iodine value of a vegetable oil. Iodine values shown in Appendix III reflect the degree of unsaturation of oil. In general, highly unsaturated oils have higher iodine values and hence have lower viscosities than unsaturated oils. The chain length of the constituent fatty acids or the presences of other substituents also influence viscosity.

Kinematic viscosity has been included in biodiesel standards (1.9- 6.0 mm²/s in ASTM D6751 and 3.5- 5.0 mm²/s in EN 14214). It can be determined by standards such as ASTM D445 or ISO 3104.

2.16.5 Lubricity

Biodiesel possesses inherently good lubricity, especially when compared to petrodiesel (Drown et al., 2001; Goodrum and Geller 2005; Hu et al. 2004; Bhatnagar et al., 2006; Moser et al., 2008a). With the advent of low-sulfur petroleum-based diesel fuels, the issue of diesel fuel lubricity is becoming increasing important. Desulfurization of conventional, petroleum-derived diesel fuel reduces or eliminates the inherent lubricity of this fuel, which is essential for proper
functioning of vital engine components such as fuel pumps and injectors. However, non-sulfur polar compounds are also eliminated from petrodiesel during the desulfurization process and it is likely the loss of these compounds and not the sulfur containing materials that causes the loss of lubricity. Another study states that phenols and polyaromatic compounds are the species imparting lubricity to petrodiesel fuels (Barbour et al., 2000; Dimitrakis, 2003). The poor lubricity of petrodiesel requires lubricity-enhancing additives or blending with another fuel of sufficient lubricity to achieve a satisfactory lubricity value. Various structural features such as the presence of heteroatoms, chain length, and unsaturation influence lubricity of biodiesel. Biodiesel possess at least two oxygen atoms that in large part explains their enhanced lubricities over typical hydrocarbon-containing petrodiesel fuels (Knothe and Steidley 2005b). Several studies on the lubricity of biodiesel or fatty compounds have shown the beneficial effect of these materials on lubricity on convention petroleum-derived diesel fuel, particularly low-sulfur petroleum-derived diesel fuel. Adding biodiesel at low levels (1-2%) restores the lubricity to low-sulfur petroleum-derived fuel. An advantage of biodiesel compared to lubricity-enhancing additives is that biodiesel inherently possesses fuel properties competitive and compatible with the conventional petroleum-based diesel fuel, which those additives usually do not possess. Biodiesel possesses inherently good lubricity, especially when compared to petrodiesel (Hughes et al., 2002). Standard for testing the lubricity of diesel fuel is ASTM D6079 using a high frequency reciprocating rig instrument.

2.16.6 Oxidative stability

Oxidative stability affects biodiesel primarily during extended storage. The influence of parameters such as presence of air, heat, traces of metal, antioxidants, peroxides as well as nature of storage container have been studied (Moser 2009a, 2009b). Generally, factors such as presence of air, elevated temperatures or presence of metals facilitate oxidation. Oxidative stability of biodiesel is determined through measurement of the oil stability index (OSI) by the Rancimat method (EN 14112). The Rancimat method indirectly measures oxidation by monitoring the gradual change in conductivity of a solution of water caused by volatile oxidative degradation products that have been transported via a stream of air (10 l/h) from the vessel (at 110°C) containing the biodiesel sample. The OSI is mathematically determined as the inflection
point of a computer generated plot of conductivity (µS/cm) of distilled water versus time (Knothe, 2007). The units for OSI are normally expressed in hours. Biodiesel fuels with longer OSI times are more stable to oxidation than samples with shorter values. Autoxidation of lipids, including biodiesel, produces free radicals through hydrogen abstraction in the presence of various initiators such as light, heat, peroxides, hydro-peroxides and transition metals. These free radicals further react exothermically with molecular oxygen to produce peroxides, which react with unoxidized lipids to produce addition free radicals (Frankel, 2005). Generally the rate-limiting step in the autoxidation of lipids is initial hydrogen abstraction.

2.16.7 Ash content and Carbon Residue of Petroleum Products
This property measures the amount of ash left after a sample is burned. The presence of ash may indicate undesirable impurities or contaminants. As such, it provides one measure of the suitability of a product for a given application. The maximum acceptable value for diesel meeting D 975 requirements is 0.01% by weight, which should be easily met with most of the biodiesels. ASTM D 482 is a standard test procedure for determining the ash content in diesel fuels.

Carbon residue is a potential indicator of the likelihood that a fuel would form deposits from carbon in an engine's combustion chamber. Carbon residue shows the amount left after evaporation and pyrolysis of an oil, indicating its relative propensity to form coke. The standard test procedure for determining carbon residue of petroleum product is D 4530.

2.16.8 Sulfur content and Copper Strip Corrosion
Sulfur content is used to measures the amount of sulfur in diesel fuels. As part of the fuel, sulfur is converted to sulfur oxides and sulfuric acid, affecting the emissions of the engine. The lack of detectable sulfur in the biodiesels would result in a reduction in the particulate emissions, in comparison to diesel. The current test procedure for amount of sulfur in biodiesel is D 2622, but there is need to change to a new method, when low levels of sulfur are required because it allows diesel fuel to contain up to 0.5% (5000 ppm) yet this value is to be lowered to 15 ppm (EIA, 2001).
Copper strip corrosion measures the degree to which the fuel can have a corroding effect on various metals. Biodiesel easily meets this diesel requirement for low corrosion impacts. The standard test procedure for determining the corrosion abilities of diesel fuels is ASTM D 130.

2.16.9 Specific Gravity

The specific gravity is a relative measure of the density of a substance. In this case, it measures the specific gravity of the biodiesels. It is defined as the ratio of the density of the substance, \( \rho \), to a reference density, \( \rho_{ref} \). The equation for the specific gravity (SG) is \( SG = \frac{\rho}{\rho_{ref}} \). The most common reference density used in the measurement of specific gravity is the density of water at 4°C, which corresponds to a reference density of 1 g/cc.

The density of methyl esters of fatty acids as a function of temperature can be simply estimated using an empirical relation developed by Janarthanan et al., (1996).

\[
\rho_i = a_i t + b_i \quad \text{………………………………………………………………………………. (Equation 2.8)}
\]

Where \( t \) is the temperature in degree centigrade and the component dependent constants are given in table 2.7. The density of a mixture of the components (biodiesel) can be estimated using a simple linear rule as given as:

\[
\rho_{mix} = x_i (a_i t + b_i) \quad \text{………………………………………………………………………………. (Equation 2.9)}
\]

Where \( x_i \) is component fraction in the mixture.

2.16.10 Acid Number and Iodine Value

Acid Number determines the acidic or basic constituents in petroleum products and lubricants. For biodiesels, the acid number is an indicator of the quality of the product. Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used in processing. This is also an indication of the condition of the stability of the fuel, because the acid number increases as the fuel ages. ASTM D664 is a standard test procedure for determining the acid number in diesel fuels.

Iodine value measures the amount of iodine required to saturate the olefinic bonds. The iodine value is an indicator of the unsaturation of the fuel, which has been linked with formation of engine deposits and problems in storing the fuel. It has been suggested that values over 115 may
be unacceptable; the biodiesels easily meet this requirement. ASTM D675 is a standard test procedure for determining the iodine value in diesel fuels.

2.16.11 Low-temperature flow test (LTFT) and Cold flow properties

Low-temperature flow test reports a temperature under a standard set of conditions, defined in ASTM D4539, at which a fuel filter plugs. LTFT employs slow cooling at one degree centigrade per hour (1ºC/h) and simulates the most severe (and common) fuel system designs in North American heavy-duty trucks from the standpoint of low-temperature operability.

One of the major problems associated with the use of biodiesel is poor low-temperature flow properties, indicated by relatively high cloud points and pour points (PP). The CP, which usually occurs at a higher temperature than the PP, is the temperature at which a liquid fatty material becomes cloudy due to formation of crystals and solidification of saturates. Solids and crystals grow and agglomerate, clogging fuel lines and filters and causing major operability problems. With increasing temperature, more solids form and the approaches the pour point, the lowest temperature at which it will still flow. Saturated fatty compounds have significant higher melting points than unsaturated fatty compounds and in a mixture they crystallize at higher temperature than the unsaturated. Thus biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher CPs and PPs. Besides CP (ASTM D2500) and PP (ASTM D97), two test methods for the low-temperature flow properties of conventional DF exist, namely the low-temperature flow test (LTFT) used in North America (ASTM D4539) and cold filter plugging point (CFPP) used mainly outside North America (European standard EN 116). These methods have also been used to evaluate biodiesel and its blends with Nos. 1 and 2 conventional DF.

2.16.12 Cloud Point and Pour point

Cloud point is the temperature at which crystal growth is large enough (diameter≥ 0.5 µm) to be visible to the naked eye. The temperature at which small solid crystals are first visually observed as the fuel is cooled. At temperature below CP, large crystals fuse together and form agglomerations that eventually become extensive enough to prevent pouring of the fluid.
Below the cloud point, these crystals might plug filters or could drop to the bottom of a storage tank. However, fuels can usually be pumped at temperatures below cloud point. ASTM D2500 is the standard test procedure.

Pour point measures the lowest temperature at which the oil is observed to flow. It is important because this defines the lowest temperature at which the fuel can still be moved, before it has gelled. Fuels with high pour points are more difficult to use in areas with lower temperatures because the fuel must be kept warm by some method, e.g., electric heaters with insulated tanks. Distributors and blenders use pour point as an indicator of whether the fuel can be pumped, even if it would not be suitable for use without heating or taking other steps.

2.16.13 Cold filter plugging point (CFPP)
This is the lowest temperature at which a given volume of biodiesel completely flows under vacuum through a wire mesh filter screen within 60s. The CFPP test employs rapid cooling conditions. The CFPP is generally considered to be a more reliable indicator of low-temperature operability than CP or PP, since the fuels will contain solids of sufficient size to render the engine inoperable due to fuel filter plugging once the CFPP is reached (Dunn and Bagby 1995; Dunn et al., 1996; Park et al., 2008a,b). The test simulates the performance of an average or typical vehicle and is not protective of the most challenging fuel system designs from a low-temperature operability standpoint, which make up roughly one-third of heavy-duty vehicles or one-fifth of light-duty vehicles.

2.16.14 Contaminants
Contaminants in biodiesel may include methanol, water, catalyst, glycerol, FFA, soaps, metals, MAG, DAG, and TAG. Methanol contamination in biodiesel is indirectly measured through flash point determination following ASTM D93. If biodiesel is contaminated with methanol, it fails to meet the minimum flash point specified in relevant fuel standard. Methanol contaminant normally results from insufficient purification following transesterification reaction.

Water is a major source of fuel contamination. While fuel leaving a production facility may be virtually free of water, once it enters the existing distribution and storage network, it will come into contact with as a result of environmental humidity (Knothe et al., 2005). Water in biodiesel
causes serious problems: corrosion of engine fuel system components, promotion of microbial growth, and hydrolysis of FAME. Water may be present in biodiesel as either dissolved or free water. Dissolved water, which is measured by Karl Fisher titration method in EN 14214 according to ISO 12937, is water that is soluble in biodiesel. Free water which is measured by centrifugation method (ASTM D2709) arises after biodiesel becomes saturated with water, resulting in a separate water phase.

Residue homogeneous alkali catalyst may be present in biodiesel through insufficient purification following the transesterification reaction. The catalyst can be detected through combined sodium and potassium determination (EN 14538). Calcium and magnesium, determined according to EN 14538, may also be introduced into biodiesel during purification through washing with hard water or through the use of drying agents such as magnesium sulfate that contain these metals. The primary problem associated with metal contamination is elevated ash production during combustion (Knothe et al., 2005).

Glycerol may be present in insufficient purified biodiesel, which is determined using ASTM D6584 or EN14105. Glycerol is suspected to contributing to engine deposit formation during combustion. Bound glycerol (MAG + DAG + TAG) in biodiesel results from incomplete conversion of TAG into FAAE during the transesterification reaction and may cause carbon deposits on fuel injector tips and piston rings of diesel engines during combustion. The presence of bound glycerol in biodiesel may also influence low-temperature operability, kinematic viscosity, and lubricity.

Free fatty acids may be present in biodiesel that was prepared from feedstock with high FFA content or may be formed during hydrolysis of biodiesel in the presence of water and catalyst. The presence of FFA is determined by AV (Acid Value) according to ASTM D664. The presence of FFA in biodiesel may impact other important fuel properties such as low-temperature performance, oxidative stability, kinematic viscosity, and lubricity. In addition to these issues with soap formation, FFA in biodiesel are known to act as pro-oxidants (Miyashita and Takagi 1986; Frankel 2005), so the presence of FFA in biodiesel may also have negatively impact oxidative stability. FFA also have significantly higher kinematic viscosities and melting point than the corresponding methyl esters, as evidenced by comparison of oleic acid (19.91 mm²/s; 12°C) and methyl oleate (4.51 mm²/s; -20°C) (Knothe and Steidley 2005a)
2.17 Other uses of Biodiesel

Fatty acid alkyl esters have attracted considerable interest as alternative bio-based fuels for combustion in CI engines. However, a number of additional applications have been developed or discovered for these versatile oleochemical materials. For instance, biodiesel may be used as a replacement for petroleum as heating oil (Mushrush et al., 2001). Another combustion-related application of biodiesel is as an aviation fuel, although the relatively poor low-temperature properties of biodiesel restrict its use to low-altitude aircraft (Dunn, 2001).

Additionally, the use of biodiesel in diesel-fueled marine engines to reduce environmental impact is another important application of this biodegradable and non-toxic fuel (Nine et al., 2000). Since there are less harmful exhaust emissions from biodiesel than those from petrodiesel, the use of biodiesel to power underground mining equipment is attractive for such applications. Biodiesel may also be used as a fuel for generators and turbines for the generation of electricity (Hashimoto et al., 2008; Kalbande et al., 2008; Lin et al., 2008) or as substitute for hydrogen in fuel cells (Kram, 2008a,b). Moreover, other niches uses such as in national parks and other environmentally sensitive locations are important combustion-related applications of biodiesel.

An important non-fuel application of FAAE (fatty acid alkyl esters) is as an industrial environmentally friendly solvent, since they are biodegradable, have high flash points, and have very low volatilities (Wildes, 2002). The high solvent strength of biodiesel makes it attractive as a substitute for a number of conventional and harmful organic solvents (Hu et al., 2004) in application such as industrial cleaning, and removal (Wildes, 2002), plasticizers in the production of plastics (Wehlmann, 1999), liquid-liquid extraction (Spear et al., 2007), polymerization solvent (Salehpour and Dube, 2008), and as a medium in site bioremediation of crude petroleum spills (Gloria and Mudge 2004; Fernandezalvarez et al., 2006). The strong solvent properties of biodiesel are particularly noticeable in cases where diesel engines have been operated with petrodiesel for many years or miles, which result in build-up of insoluble deposits in fuel tanks and lines. Upon switching to biodiesel, especially B100, the deposits will get released, which result in vehicle inoperability due to clogging fuel filters with deposits in cases such as these, it is in fact the fault of the petrodiesel from which the deposits originated, since biodiesel is merely acting as a solvent.
Fatty acid alkyl esters can also serve as valuable starting materials or intermediates in the synthesis of fatty alcohols (Peters, 1996), lubricants (Sharma et al., 2007; Dailey et al., 2008; Padua, 2008), cold flow improver additives (Moser and Erhan 2007; Dailey et al., 2008), cetane improving additives (Poireier et al., 1995), and multifunctional lubricity and combustion additives (Suppes et al., 2001; Suppes and Dasari, 2003). Lastly, biodiesel in conjunction with certain surfactants can act as a contact herbicide to kill broadleaf weeds in turf grass (Vaughn and Holser, 2007).

2.18 Glycerol
Glycerol (or glycerine; 1,2,3-propanetriol) is produced in addition to FAAE during transesterification of vegetable oils and animal fats. Prior to the increase in biodiesel production that occurred over the past decade as a result of the continued interest in renewable fuels, the market demand for glycerol was relatively balanced with supply. However, with emergence of the biodiesel industry has generated a surplus of glycerol, which has spawned numerous efforts to find new applications, products, and markets using this versatile chemical. In the recent developments on chemistry the uses and utility of glycerol has been reviewed (Behr et al., 2008). In general, glycerol may be used as a chemical feedstock in the production of polyurethanes, polysters, polyethers, and other materials. Glycerol may also be found in lubricants, wrapping and packaging materials, foods, drugs, cosmetics, and tobacco products. Applications and products that displace existing petroleum–derived materials or feedstock are of particular interest. A recent significant advance is the development of synthetic route to propylene glycerol (1, 2-propanediol) from glycerol, which represents a viable alternative to the classic petrochemical route from propylene (Dasari et al., 2005; Suppes, 2006; Feng et al., 2008). Propylene glycerol represents a replacement for the common toxic antifreeze component ethylene glycerol.

2.19 Analytical Monitoring of Transesterification Reaction
The amount of contaminants (such as glycerol; mono-, di-, and triglycerides; and alcohol) present in the fuel after post-transesterification purification is a major factor in determining fuel quality. The analysis of contaminants in biodiesel fuel is a major issue influencing commercial success because contaminants can lead to severe operational problems such as engine deposits.
Most analytical procedures for determining biodiesel fuel quality utilize gas chromatography (GC). Preseparation of biodiesel and its contaminants by high-performance liquid chromatography (HPLC) prior to GC also has been reported (Lechner et al., 1997). Other analytical methods applied to biodiesel include viscosity (De Filippis et al., 1995) and HPLC with density detection (Trathnigg and Mittelbach, 1990) or pulsed amperometric detection for determining glycerol (Lozano et al., 1996). $^1$H NMR spectroscopy was used for determining the yield of the transesterification reaction of rapeseed oil with methanol (Gelbard et al., 1995). Analyses of fatty materials by near infrared (NIR) spectroscopy have become widespread in recent years (Sedman et al., 2006). Biodiesel was determined in lubricating oil by fiber-optic Fourier transforms infrared spectroscopy (Sadeghi-Jorabchi et al., 1994).

2.19.1 Near-Infrared Spectroscopy
Near-Infrared Spectroscopy (NIRS) is a technology that uses the property of organic materials to absorb near-infrared light. This enables analysis for composition and functional properties. Near-infrared light is light with wavelengths of 700 to 2500 nm, next to and longer than visible light. Specific features of the absorption of the near-infrared light by the organic materials are used in the calibration process. Calibration involves developing a mathematical model between the spectral features of a set of samples and chemical or other conventional analytical data (reference data) on the same samples. Once NIR instruments are calibrated, they accurately predict the quantities of up to 30 constituents or functional properties of new samples simultaneously in seconds. Little or no sample preparation is required. Occasional conventional reference analyses are required for QA/QC in a routine NIRS operation. Analysis by NIRS is rapid, cost-effective, non-destructive, and environmentally-safe.

Near-infrared spectroscopy has been shown to be useful in monitoring the transesterification reaction used to convert vegetable oils, animal fats, or waste oils into biodiesel (Meher et al., 2006). Standards for biodiesel set by the ASTM address the presence of materials such as free and total glycerol, water, free fatty acid, and residual alcohol. These materials need to be limited in biodiesel so that it does not deteriorate during storage and it is safe for use in engines. Knothe (1999) used NIR spectroscopy to monitor the trans-esterification reaction. The basis for quantization of the turn over from triglyceride feedstock to methyl ester product is differences in
the NIR spectra of these classes of compounds. At 6005 cm\(^{-1}\) and 4425 - 4430 cm\(^{-1}\), the methyl esters display peaks, while triglycerides display only shoulders. Ethyl esters could be distinguished in a similar fashion (Knothe, 1999). The absorption at 6005 cm\(^{-1}\) gave better result than the one at 4425 cm\(^{-1}\). The mid-range IR spectra of triglycerides and methyl esters of fatty acids are almost identical and offer no possibility for distinguishing. In the acid catalyzed transesterification reaction, alcohol-to-oil ratio can be as high as 30:1 (Freedman et al., 1986) in order to drive the equilibrium shift toward the product side. Monitoring such a reaction would be difficult due to the broad peaks presented by the alcohol. In a subsequent study, Knothe, (2000) used NIR to quantitatively monitor the transesterification reaction by correlating the NIR data with 1H nuclear magnetic resonance spectroscopy (NMR) results. The study used neat vegetable oil as feedstock, which is relatively free from contaminants.

### 2.19.2 Gas Chromatographic Method (GC)

During the trans-esterification process, intermediate MAG and DAG are formed, small amounts of which can remain in the final biodiesel product. Besides these partial glycerols, unreacted TAG as well as unseparated glycerol, FFA, residual alcohol, and catalyst can contaminate the final product. The contaminants can lead to severe operational problems when using biodiesel, such as engine deposits, filter clogging, or fuel deterioration.

Generally, GC has been the most widely used method for the analysis of biodiesel owing to its generally higher accuracy in quantifying minor components (Zagonel et al., 2002). However, accuracy of GC analyses can be influenced by factors such as baseline drift, overlapping signals, and aging of standards and samples. The specifications regarding glycerol esters are analyzed by GC using an FID in both ASTM D 6751 and EN 14214. ASTMD 6751 uses ASTM D 6584, whereas there are several specifications in EN 14214 using GC-based methods. Methyl heptadecanoate is a common standard for FA components, although the stability of standard solutions is an issue (Mittelbach and Gangl, 2006); freshly prepared solutions should be used, and pyridine may be more suitable as solvent than heptane. The standard reference method EN 14103, for determining ester content in EN 14214, is a GC method utilizing a 30-mCARBOWAX (or comparable) column for determining FA profile. However, methyl heptadecanoate used as standard presents a problem when using animal fat-based biodiesel.
because of the latter’s natural content there of (Schober et al., 2006). Both use high-temperature (up to 400°C) capillary columns. ASTM D 6584 specifies (5% phenyl) polydimethylsiloxane columns of 10 or 15 m length with 0.32 mm inner diameter and 0.1 mm film thickness. EN14105 allows for 10m columns of either 100% dimethylpolysiloxane or 5% diphenylpolysiloxane with the same inner diameter and film thickness. Trimethylsilylation of the free hydroxyl groups of glycerol, mono- and di-glycerides, however, ensures excellent peak shapes, good recoveries and low detection limits and enormously improves the ruggedness of the procedure. For complete silylation of glycerol and partial glycerides, the conditions of the derivatization reaction have to be controlled carefully (Meher et al., 2004).

2.19.3 Viscometry
The viscosity difference between component TAG of vegetable oils and their corresponding methyl esters resulting from trans-esterification is approximately one order of magnitude. The viscosity difference forms the basis of an analytical method, viscometry, applied to determining the conversion of vegetable oil to methyl ester (De Filippis et al., 1995). The progress of the trans-esterification can be followed by monitoring the viscosity of the mixture in the reactor based on the compositional change because the reactants and the products have different viscosities (Naoko et al., 2008). The viscosity difference forms the basis of viscometry as an analytical method, applied to determine the conversion of vegetable oil to methyl ester (De Filippis et al., 1995). The progress of the reaction as indicated by the results they got clearly showed decrease in the viscosity of the mixture; the viscosity reached a plateau once the reaction had attained steady state.

2.19.4 Thin-layer chromatography
Thin layer chromatography (TLC) was performed on a sheet of glass, plastic, or aluminum foil, which had been coated with a thin layer of adsorbent material, usually silica gel, aluminium oxide, or cellulose (blotter paper). This layer of adsorbent is known as the stationary phase. TLC is normally used as a qualitative technique for the identification of components within a mixture since it is hard to quantitatively deposit known quantities of the mixture on the plate.
2.19.5 High performance liquid chromatography method

The ‘high performance’ relates to the ability of HPLC for offering very selective and, therefore, high-quality separations in the minimum of time. This separatory capability is achieved by passing a mobile liquid phase through a finely divided stationary support under high pressure.

HPLC with pulsed amperometric detection (the detection limit is usually 10-100 times lower than for amperometric detection and the detection limit is 1 mg/g) was used to determine the amount of free glycerol in vegetable oil esters. The HPLC-DAD method has proved to be simple, rapid and accurate (Lozano et al., 1996). The major advantage of this method is its high sensitivity. The simultaneous detection of residual alcohol is also possible with this technique (Knothe, 2001). Komers et al., (2001) studied HPLC method of quantification of mono-, di-, tri- glycerides and esters using UV detection method at the region of 205 nm for methanolysis of rapeseed oils. Noureddini and Zhu (1997) used a HPLC equipped with a refractive index detector for the analysis of biodiesel produced from soybean oil.

2.20 Effect of biodiesel on engine performance

2.20.1 Thermal efficiency

Thermal efficiency is the true indication of the efficiency with which the chemical energy input in the form of fuel is converted into useful work. Much work has been done at many research institutes to examine the potential of biodiesel engines for achieving high thermal efficiency. Researchers such as Tsolakis (2006), Senatore et al., (2000), Shaheed and Swain (1999), Graboski et al., (1996) and Canakci (2005), reported no improvement in thermal efficiency when using different types of biodiesel fuels. A small number of experiments, however, have reported some improvement in thermal efficiency when using biodiesel fuels. Kaplan et al., (2006) explained their observed increase in efficiency by means of improved combustion, giving no further reasoning. Linseed-oil biodiesel blended with high sulfur diesel fuel was tested in a single cylinder 4 kW portable engine widely used in the agricultural sector and showed increases in thermal efficiency, especially at low loads (Agarwal et al., 2008, Agarwal and Das (2001)).

2.20.2 Fuel consumption

Brake-specific fuel consumption (BSFC) is the ratio between mass of fuel consumption and brake effective power, and for a given fuel, it is inversely proportional to thermal efficiency. If
the latter is unchanged for a fixed engine operation mode, the specific fuel consumption when using a biodiesel fuel is expected to increase by around 14% in relation to the consumption with diesel fuel, corresponding to the increase in heating value in mass basis. In other words, the loss of heating value of biodiesel must be compensated for with higher fuel consumption. Researchers such as Graboski et al., (1996), Hansen and Jensen (1997) and Canakci (2005) have reported increases in BSFC ranging from 2% to 10%. Most of the authors have explained these increases by the loss of heating value, although some others attributed them to the different densities of biodiesel and diesel fuels.

2.20.3 Brake effective power (Brake Horsepower (BHP))
This is measured by a dynamometer and represents the power output of the engine. At full-load conditions, with the accelerator fully pressed down, or at partial load but with equal fuel consumption or equal accelerator position, the power output delivered by biodiesel is reduced with respect to that delivered by diesel fuel. Although due to the loss of heating value in volume basis of biodiesel, reduction of power of about 8% would be expected. However, the reported results show some variations. Many authors found that the loss of power is lower than expected. Researchers such as Kaplan et al. (2006); Cetinkaya et al., (2005) and Lin et al., (2006) have reported loss of torque and power ranged between 5% and 10%. The authors suggest the reduced heating value and difficulties in the fuel atomization as responsible for this reduction. Conversely some authors such as Altiparmak et al., (2007), Usta (2005) have found increase in power output of biodiesel engines. They suggested the increase in density, viscosity and an improved combustion to explain this.
CHAPTER THREE

MATERIALS AND METHODS

3.1 Collection of the Seeds
The candlenut seeds were obtained from Jinja (near source of River Nile), Uganda and city council of Nairobi mainly from Uhuru Park and major streets of Nairobi. The Calodendrum capense seeds were handpicked from Chiromo campus and Main Campus hall of residence compound of the University of Nairobi, City Park of Nairobi as well Arboretum and Kenyatta university main campus compound. Figure 3.1 and 3.2 shows the calodendrum capense and candlenut plants respectively.

Figure 3.1: Calodendrum capense tree, seeds and flowers.

Figure 3.2: Candlenut (Aleurites moluccanus) tree, foliage, flowers and nut.
3.2 Sample Preparation
After collection, the seeds were sun dried for a week to the required dry weight and moisture content and then the hard nuts of the seeds were removed by physically hitting with a hard metal and the kernel obtained. A total of 9.91Kg (Ugandan origin seeds) and 18.46Kg (Kenyan origin seeds) kilograms of dried *candlenut* seeds were obtained respectively. For the *calodendrum capense* 16.48 kilograms of dried seeds were obtained.

3.3 Oil Extraction
The seeds were decorticated to remove the outer shell and dried to minimum moisture. The oil was extracted using different techniques. This included oil pressing machine or mechanical extraction method: Oil was mechanically extracted using the mechanical oil extractor at Kenya Industrial Research and Development Institute (KIRDI). Figure 3.3 below shows the mechanical extractor that was used. The obtained oil was filtered to remove solid impurities and packed in dry clean air tight containers.

![Fig 3.3: The mechanical Extractor.](image)

The oil was also extracted from the seeds using hexane as the solvent using a Soxhlet extractor as shown in figure 3.4 below.
A Soxhlet apparatus consisting of a Soxhlet extraction tube, reflux condenser, 250ml round-bottomed flask, and heating mantel was used to extract the oily dark brown residue (oil cake) from the fuel filter samples. Extraction was performed with 125ml of n-hexane solvent. Approximately 25g of the fuel filter were weighed into a thimble and placed in the Soxhlet extraction apparatus. The contents of the thimble were allowed to extract at 68°C for about 2-4 hours until the extraction solution ran clear into the round-bottom flask. The extract obtained (a mixture of oil and solvent) was then taken to a rotor evaporator to get rid of the solvent.

### 3.4 Base catalyzed transesterification

The transesterification reaction was carried out in a 5 litre reactor (figure 3.5) equipped with a mechanical stirrer and a thermostat which was capable of maintaining the constant reaction temperature. A thermometer and a stop watch were used to monitor the reaction. The following procedure was used in carrying out transesterification process.

The reactor was initially charged with one litre of *candlenut* oil then heated to 50°C. The potassium hydroxide (8.0g) was dissolved in the 200ml methanol and the solution was fed to the reactor. The mixture was then heated to 60°C and the reaction was timed as soon as the potassium hydroxide-methanol solution was fed to the reactor. During the reaction, samples were taken every 15 minutes and placed in clean test tubes. A total of four samples were taken to determine the optimum time for biodiesel to separate from glycerol. The samples were immediately quenched in water to stop the reaction and two phases were formed. The biodiesel layer was carefully separated and washed by the distilled water.
The upper layer consisted of methyl esters and partial triglycerides and the lower phase contained the glycerol, excess methanol and the remaining catalyst together with the soaps formed during the reaction. The procedure was repeated for *calodendrum capense* oil (8.8g of potassium hydroxide was used for this oil).

Some of the *Candlenut* and *Calodendrum capense* oil used as raw material had a high FFA content of 20.9% and 15.3% (v/v) respectively. To avoid formation of soap and difficult of biodiesel-glycerine separation, a two stage process described below was used.

In the first stage the oil was filtered to remove any solid particles and for successful reaction, the oil had to be free of water. The oil was heated to 60°C and maintained for 15 minutes at this temperature and then poured into a settling tank. After settling for at least 12 hours, the tank was emptied to about 95% of its volume.

One litre of the dry oil was transferred into the reactor and heated to 40°C to ensure that all of it had melted. To the heated oil, 80ml of methanol (99% pure) was added and mixed for 5 minutes where the mixture became murky because of solvent change (methanol is a polar compound, oil is strongly non-polar) forming a suspension. Using a graduated pipette, 1 ml of 95% pure sulfuric acid was added to the mixture. While maintaining the temperature at 40°C the mixture was mixed gently at 550 rpm for one hour. After one hour, heating was stopped and the mixture was stirred for another extra hour and then settled for at least 8 hours.

In the second stage, 120ml of methanol was mixed with 5.80 grams of potassium hydroxide (KOH). To the settled unheated mixture half of the prepared potassium methoxide was poured into it and mixed for 5 minutes. This was done to neutralize the sulfuric acid and boost the base catalysis. The mixture was then heated to 60°C and second half of the prepared potassium methoxide was added and stirred at 550rpm. To monitor the reaction, a small sample was withdrawn after every 15 minutes and the straw yellow colour of the ester portion watched. The clear colour was obtained after one and half hours. The reactor was turned off and the ester-glycerine mixture was then settled for one hour. The glycerine was drained off for easy washing of the biodiesel. The same procedure was repeated for *Calodendrum capense* oil.
3.4.1 Optimization of base catalyzed transesterification Process

The factors that affect transesterification were monitored as follows: The preliminary work was done in the research laboratory, Chemistry Department and Science workshop in the School of Physical Science, University of Nairobi. Optimum conditions for transesterification were determined and this included amount of base catalyst per liter of oil, amount of methanol per liter of oil, reaction time and reaction temperature.

One of the important variables affecting the yields of ester is catalyst concentration. It was observed 1% (5.80g) of the potassium hydroxide concentration gave good results in transesterification (two stage processes) for both *Candlenut* and *Calodendrum capense* oil. The addition of more potassium hydroxide gives rise to the formation of an emulsion and leads to the formation of gel. Moreover, it may also hinder glycerin separation and result in dilution of methyl ester and the ester yield tends to decrease.

The amount of base catalyst (KOH) per liter of oil was determined by a titration method. To one liter of distilled water 1g of KOH was dissolved in it to make 0.1% w/v KOH solution. In 100ml conical flask 1ml of the oil was dissolved in 10ml of pure isopropyl alcohol (propan-2-ol). The mixture was gently warmed in a hot plate till all the oil dissolved and after addition of 2 drops of phenolphthalein indicator the mixture was titrated against the 0.1%w/v KOH solution until the resulting solution remained pink for 10 to 15 minutes. The volume of KOH used for complete titration was recorded. For each volume of KOH obtained, 4.9ml was added to account for the
purity of Potassium Hydroxide which was 85%, as proposed by Keith (2007). A total of 8.0g and 8.8g KOH for *Calodendrum Capense* and *Candlenut* oil was used respectively. This was for the oil which had a low acid value.

### 3.4.2 Biodiesel washing and drying

Washing of the obtained biodiesel was done using a 2.5litre separating funnel (figure 3.6). For every one litre of oil 700ml of distilled water was used. The distilled water was heated to 45°C (distilled water was used to avoid affecting the PH of the biodiesel). The warm water was then poured gently into the separating funnel. The separating funnel was shaken vigorous until a uniform mixture was formed. To allow the biodiesel to settle faster, the separating funnel was carefully placed in a water bath and allowed to settle for 2 hours (a water bath was used to enable the tiny bubbles formed by water in the biodiesel to clear faster hence easy separating). Washing was repeated until clear clean water separated out. Water was easily run out as it formed the lower layer and the biodiesel at the top. The washed clean biodiesel was then transferred into a clean 2litre pot and heated to a temperature of 110°C to dry it. A clean golden yellow biodiesel was obtained. The methodology of washing was repeated for all the biodiesel for both *candlenut* and *calodendrum capense* oil.

Fig 3.6: Separating funnel which shows layers of Biodiesel and water during washing.
3.5 Enzyme catalyzed transesterification

Lipase- catalyzed transesterification of *candlenut* oil and *Calodendrum capense* oil and methanol for biodiesel production in tert-amyl alcohol was investigated. The tert-amyl alcohol was used to avoid the effect on lipase enzymes by methanol hence high efficiency in conversion of oil to methyl esters.

3.5.1 Growth Conditions for enzyme extraction

The LB 5A cells were obtained from a stock that had been previously isolated from Lake Bogoria waters. They were grown on LB agar constituting yeast extract (Sigma), tryptone (Oxoid), agar (Oxoid) and NaCl at PH 9.0. The cells were incubated at 37˚C for 48 hours. The cells were then used to inoculate LB broth at PH 9.0 followed by incubation at 37˚C for 48 hours. The broth was centrifuged at 10,000 x g for 5 minutes at 25˚C, the cells were discarded and the supernatant was used as the crude extract containing the enzymes.

3.5.2 Procedure for Enzymatic Transesterification

Transesterification of *candlenut* oil and *calodendrum capense* with methanol was carried out in a 50 ml tight-capped bottle (figure 3.7). The process parameters were 10ml of either *candlenut* oil or *calodendrum capense* oil, 2.4ml of methanol, 6ml tert-amyl alcohol, 2ml of LB 5A lipase enzymes, and 45˚C. The mixture was agitated on a shaker at 150rpm for 24h reaction time. Centrifuging for 10 minutes was done to obtain the methyl esters and byproduct layer (figure 3.7). The upper methyl ester was separated for further analysis using thin layer chromatography.

![Methyl esters and byproducts](image)

*Fig.3.7: Separation of methyl ester and byproduct layers after enzymatic transesterification*
3.5.3 Optimization of enzymatic transesterification process

The factors that affect enzymatic transesterification were monitored as follows:- Reaction temperature has a significant influence on the activity and stability of the lipase enzymes. Higher temperature activates the substrate molecules, reduce the viscosity of reaction and lead to higher reaction rate. However, higher temperature will lead to higher lipase deactivation rate and the loss of solvent through evaporation. Therefore an optimal temperature was selected in terms of the overall performance of the reaction. The effect of temperature (30 to 65°C) on the ME yield was investigated.

Various agitation speeds (90-180 rpm) were studied to investigate the effect of agitation speed on the ME yield. In varying the agitation speed the reactor was set at different speeds and at each speed the conversion yield was measured. Excessive methanol inhibit the lipase activity and a low ME is obtained. To reduce this effect, tert-amyl alcohol was added into the reaction medium. The molar ratio of methanol/oil was varied from 3 to 6 in order to evaluate the effect of methanol on lipase activity. Different amount of lipase enzymes were used in order to determine the minimum dosage of lipase required to obtain the maximum conversion.

3.6 Determination of Biodiesel Physicochemical Properties

To ascertain the quality of the biodiesel the following physical properties were performed.

3.6.1 Methanol test

Biodiesel dissolves easily in methanol but vegetable or animal oils and fatty (triglycerides) do not dissolve in methanol. Any unconverted oil left in the biodiesel will settle out at the bottom of the test flask. This means the processing didn’t go far and needs improvement. All the oil should be fully converted to biodiesel. If some unconverted triglycerides remains in the biodiesel, there will also be partly converted to diglycerides and monoglycerides. This may result to poor quality fuel that will not meet the quality specifications and could easily damage the engine. Diglycerides and monoglycerides cause emulsions when washing the biodiesel.

The following procedure was used for both *candlenut* and *calodendrum capense* biodiesel. To 225ml of methanol measured into a clean dry conical flask, 25ml of biodiesel was added to it and carefully dissolved. The biodiesel was fully soluble in the methanol, forming a clear bright phase.
3.6.2 Calorific Value (Heating value)

The procedures for determining the calorific value using a bomb calorimeter shown in figure 3.8 was as follows. The empty capsule was weighed using optical beam balance and its mass recorded. The capsule was filled with oil then reweighed and the mass of the oil determined by subtracting the mass of the empty capsule. Into the cooling jacket of the calorimeter 1.7 litres of water was measured. The capsule with the oil was put on the crucible and placed in the firing apparatus of the calorimeter. The bomb calorimeter was then assembled, charged with oxygen up to 25atms and the stirrer turned on. The temperature readings were taken at intervals of one minute for five minutes to make sure that the temperatures of the bomb were stable and then the bomb was fired. Temperatures were taken at intervals of half a minute for the entire range of the temperature rise and at one minute interval for five minutes after temperatures started to drop.

![Constant –volume bomb calorimeter](image)

**Fig 3.8: Constant –volume bomb calorimeter**

3.6.3 Acid value or free fatty acids (FFA)

A dry conical flask was weighed and 1ml of the oil sample was measured into it. The weight of sample oil and the conical flask was recorded. To the oil in the flask 10ml of isopropyl alcohol was added and the mixture warmed. Using 2 drops of 1% phenolphthalein solution, the mixture was carefully titrated with aqueous 0.1M potassium hydroxide while shaking constantly until a
pink colour which persisted for 15 seconds was obtained. The acid value was calculated using the following equation

$$AN = (V_{eq} - b_{eq}) N \frac{56.1}{W_{oil}}$$  \hspace{1cm} (Equation 3.1)

Where

- $V_{eq}$ = amount of KOH (ml) consumed by the oil sample at the equivalent point
- $b_{eq}$ = amount of KOH consumed by the blank sample
- $N$ = concentration of KOH
- $W_{oil}$ = mass of the oil sample used

The molecular mass of KOH is 56.1

### 3.6.4 Iodine Value

The weight of 0.5 ml of the oil sample was weighed accurately into a 250 ml Erlenmeyer flask and 20 ml of carbon tetrachloride was added into the flask. To the mixture 25 ml of Wijs reagent was pipetted into it. The flask was stoppered, the contents mixed by swirling and stored in a dark place at room temperature for thirty minutes. At the end of 30 minutes, 10 ml of 30% potassium iodide solution was added to the sample solution followed by 100 ml of purified water. The contents were immediately titrated with standard 0.1M sodium thiosulfate solution until the yellow color almost disappeared. To continue the titration 1 ml of 1% starch indicator solution was added and swirling was done until the blue starch-iodine color disappeared. This was repeated for the blank where the flask contained all the chemicals except the oil sample. The Iodine value was calculated using the expression below;

$$\text{Iodine Value} = \left( \frac{\text{Blank Titer (ml)} - \text{Sample Titer (ml)}}{\text{Weight of Sample (g)}} \right) \times 1.269$$  \hspace{1cm} (Equation 3.2)

### 3.6.5 Blend preparation

The obtained biodiesel for both *candlenut* and *calodendrum capense* after transesterification was labeled neat biodiesel (B100). From the neat biodiesel other blends of biodiesel and fossil diesel were prepared. To prepare a 2 litre B5 blend, 100 ml (5%) of either neat *candlenut* or *calodendrum capense* biodiesel was measured and mixed thoroughly with 1900 ml (95%) of fossil diesel. For B10 blend 200 ml (10%) of the neat biodiesel was well mixed with 1800 ml
(90%) of the fossil diesel. The B20 blend also was prepared by mixing 400 ml (20%) of the neat biodiesel of either *candlenut* or *calodendrum capense* with 1600 ml (80%) of fossil diesel.

### 3.6.6 Specific Gravity

A 10ml capacity empty density bottle was cleaned and dried in the oven and weighed using an optical beam balance and its mass recorded. The bottle was filled with distilled water to brim over and corked, the excess water escaped through the hole in the cork and what remained was exactly 10ml. The bottle was immersed in the water bath and remained in the bath for 15-20 minutes to attain uniform temperature. The test temperatures investigated were from 15 to 60°C at an increment of 5°C. It was then removed and dried of any water on its surface and reweighed, from which the mass of water was determined by subtracting the mass of the empty bottle. This process was done for all temperatures. The fuels under study were tested using the same method as the distilled water and their masses at different temperatures were determined and recorded. The relative density was calculated from the relation:

\[
\rho = \frac{M_{\text{oil}}}{M_{\text{water}}} \tag{Equation 3.3}
\]

Where
- \(\rho\) = density
- \(M_{\text{oil}}\) = mass of oil
- \(M_{\text{water}}\) = mass of water

### 3.6.7 Kinematic Viscosity

The Ostwald viscometer size D BS/U 790 (figure 3.9) was used to determine the viscosity. The viscometer was cleaned and rinsed with distilled water and dried in the oven. It was then clamped in a temperature controlled water bath in a vertical position, such that the marks ‘a’ and ‘c’ were below the water level and clearly visible through the water bath. Into the wider arm distilled water was pipetted which was to fill the upper bulb ‘b’ between the two marks and at the same time leaving the lower bulb ‘B’ a least 1/3 full. The temperature of the bath was adjusted to 15°C using ice cold water with the help of a thermostatic thermometer and left for between 15-20 minutes to reach thermal equilibrium. The water was sucked up through tube ‘T’ to a level above mark ‘a’ and allowed to flow down. The time taken for the meniscus to pass from ‘a’ to ‘c’ was determined as shown in the figure below. This was repeated three times and averaged. The procedure was repeated for the temperatures 15°C to 60°C at increment of 5°C.
This procedure was done to all the test fuels and the viscosities of the fuels were determined using the relationship below;

\[ \frac{\nu_f}{\nu_w} = \frac{\rho_f t_f}{\rho_w t_w} \]  
(Equation 3.4)

Where

- \( \nu_f \) – is the viscosity of the fuel sample at a given temperature
- \( \nu_w \) – is the viscosity of water at a given temperature
- \( \rho_f \) – is the density of the fuel sample at a given temperature
- \( \rho_w \) – is the density of water at a given temperature
- \( t_f \) – is the time taken for fuel sample to run between ‘a’ and ‘b’
- \( t_w \) – is the time taken for water to run between ‘a’ and ‘b’

![Fig. 3.9: Ostwald Viscometer](image)

**3.6.8 Flash point**

This was carried out in Kenya Industrial Research Institute. The test cup was thoroughly cleaned and dried to ensure the removal of any solvent which had been used to clean the apparatus. Toluene and acetone were used to clean and dry the test cup and its cover. Taking into consideration the volume capacity of the test cup, the test cup was filled with the test fuel up to
the filling mark in it. Excess test fuel added to the test cup was removed using a syringe. The test cover was placed on the test cup and the apparatus assembled. The locking device was ensured to be properly engaged and when the temperature measuring device was not already in place, the device was inserted into its holder.

The electric igniter was switched on and the intensity adjusted in accordance with the manufacturer's instructions. In case of lighting test flame the diameter had to be adjusted to about 3.2 to 4.8mm. The gas pressure was not allowed to exceed 3 kPa of water pressure. Appropriate safety precautions were exercised during the initial application of the ignition source, since test fuel containing low-flash like biodiesel blends can give an abnormally strong flash when the ignition source is first applied. The temperatures attained during these test method, up to 370°C, were considered to be hazardous and hence precaution was always taken when carrying out the tests method. The heat was applied at such a rate that the temperature, as indicated by the temperature measuring device, was increasing 5 to 6°C per minute. The stirring device was then turned at 90 to 120 rpm, stirring in a downward direction. The fuel to be tested and the tester were brought to a temperature of 15 ± 5°C to ensure that the flash point was accurately determined.

The reading on the temperature measuring device at the time ignition source application caused a distinct flash in the interior of the test cup was record as the observed flash point. The sample was deemed to have flashed when a large flame appeared and instantaneously propagated itself over the entire surface of the test fuel. When a flash point was detected on the first application, the test was discontinued, the result discarded, and the test repeated with a fresh test specimen. The first application of the ignition source with the fresh test specimen shall be 23 ± 5°C below the temperature at which a flash point was detected on the first application.

When a flash point was detected at a temperature greater than 28°C above the temperature of the first application of the ignition source, or when a flash point was detected at a temperature which was less than 18°C or 32°F above the temperature of the first application of the ignition source, the result was be considered approximate, and the test was repeated with a fresh test fuel. The expected flash point for this next test was adjusted to the temperature of the approximate result. The apparatus were allowed cool down to a safe handling temperature, less than 35°C the test
cover and the test cup were removed and apparatus cleaned for another test. This was repeated for all test fuel.

3.7 Engine Tests

The engine used in this study was a Ford 6-six cylinder turbo charged diesel engine rated at 86 BHP, at 2250 RPM. The engine is coupled to a G-type Froude dynamometer for measuring the engine output over the entire range of operation. The loads were applied by regulating the amount of water going into the dynamometer with load increments in steps of 1Lb.

The engine’s fuel system is fitted with two filters; primary and secondary filters to ensure that any suspended particles present in the fuel do not reach the injector pump because they can cause blockage. The fuel flow in the fuel system was facilitated by a fuel pump, to achieve fuel flow under pressure.

The engine was water cooled with water flow assisted by a water pump. The external water circuit was via a header tank fitted with a thermometer. The water temperature in the header tank was kept at a constant temperature of 49°C by supplying cold water from the mains and allowing the same amount of hot water to pass to waste from the system. Thermometers were fitted to measure the inlet and outlet water temperatures at the engine.

The temperature of the exhaust gases was measured using a thermocouple fixed at the exhaust manifold of the engine. The temperature was indicated by a moving coil pyrometer fixed to the thermocouple graduated at 10°C increments with a range of 0 – 1500°C. Temperatures were measured at each load increment and for all fuel blends tested and compared to that of engine operations with DF2.

3.7.1 Engine performance testing

The engine performance testing procedures used in this study are as described by Kimilu (2007) and Wanjala (2009). Preliminary engine familiarization tests were done using DF2 fuel. The results indicated that normal engine runs could be achieved for speeds of up to 2000 RPM. After conducting full load test at varying speeds, 1500 RPM showed good repeatability and hence the study was carried out at this speed.
The engine was warmed up prior to test to the recommended operating temperature of cooling water of 52 to 55°C by running the engine on DF2 fuel at idle speed until the cooling water in the header tank attained the above temperature. The engine was then run at a constant speed of 1500 RPM and load varied in increments of 1 Lb. The increment of the load from an initial of 1 Lb was continued until the running of the engine become erratic and the speed started to fluctuate (maximum load was 7 Lb).

For each load the rate of fuel consumption and temperatures of the exhaust gas were recorded. This procedure was repeated for all the test fuels under study and the results obtained used to calculate the following parameters:

- Brake horse power (BHP)
- Brake specific fuel consumption (BSFC)
- Thermal efficiency (TE)

### 3.7.2 Rotational Speed

The rotational speed of the engine was directly read from a mechanically operated tachometer fixed to the dynamometer shaft. The speed could be adjusted by either varying the load or the fuel rack position. The engine tests were conducted at a speed of 1500 RPM.

### 3.7.3 Measuring of fuel consumption

Fuel consumption was obtained by timing the flow of fuel through a calibrated pipette. Timing of flowing of 100ml of fuel was done. The pipette was supported in a frame at a height above that of the injection pump of the engine. The lower outlet of the pipette, the main fuel supply pipe and the pipe to the pump were all connected to unions of a three way cork. The position of the cork controlled the direction of the flow as indicated below:

- Position 1: Engine runs and pipette fills from main supply
- Position 2: Engine runs on main supply with filled pipette isolated from the system
- Position 3: Engine runs on fuel from pipette and main supply is isolated from system

On testing the cork was turned to position 1 and the pipette filled above the upper calibration mark. Once the required preconditions were attained the cork was turned to position 3, and the time taken for the level to fall from the upper to the lower calibration marks was determined with the aid of a stop watch. This was repeated for at least two runs except when timings differed by
more than a second when more runs were done. The average time was determined for each load
and for all the test fuels.

3.7.4 Determination of brake horse power
Brake power is the measured power of an engine. Thus the prefix "brake" refers to where the
power is measured; at the engine's output shaft, as on an engine dynamometer. The engine is
connected to a brake or dynamometer which can be loaded such that the engine torque can be
measured. A Froude type G hydraulic dynamometer was used in this study and brake horse
power was calculated using the formula below;

\[
\text{B.H.P} = \frac{WN}{K}
\]

Where:
- \( W \) = net weight lifted by the dynamometer in pound (Lb)
- \( N \) = dynamometer shaft speed in RPM
- \( K \) = dynamometer constant
- Dynamometer constant, \( K = 200 \)

3.7.5 Determination of Brake Specific Fuel Consumption
Brake Specific Fuel Consumption (BSFC) is the ratio of the engine fuel consumption to the
engine power output as measured at the flywheel. Brake Specific Fuel Consumption has units of
grams of fuel per kilowatt-hour (g/kWh) or (Kg/kWh). BSFC is also a measure of engine
efficiency and is calculated using the formula below;

\[
\text{BSFC} = \frac{M \times 3600}{T \times \text{BHP}}
\]

Where:
- \( M \) = mass of fuel
- \( T \) = time in seconds used to consume mass of fuel \( M \)

3.7.6 Determination of thermal efficiency
Thermal efficiency is the relationship between actual heat energy stored within the fuel and
power produced in the engine (indicated horsepower). The thermal efficiency figure indicates the
amount of potential energy contained in the fuel that is actually used by the engine to produce
power and what amount of energy is actually lost through heat. It therefore expresses power
output of the engine as a percentage of the power obtained from chemical energy supplied of the
fuel supplied.
It is calculated using the formula below;

\[ TE = \frac{(BHP \times 100)}{P_{in}} \] .......................... (Equation 3.7)

Where:
- \( TE \) = Thermal efficiency, 
- \( P_{in} \) = Power input
- Power input = (Energy input) / (Time, t)
- Energy input = Mass \times \text{Calorific value of fuel}

3.8 Methyl Esters Determination in B100 Biodiesel

3.8.1 Thin-layer chromatography

The methyl esters obtained for both \textit{Candlenut} and \textit{Calodendrum capense} were analyzed using TLC. This was done to ascertain the transesterification process and to determine the above mentioned optimum conditions. The methyl esters, Triacylglycerol (TAG), Diacylglycerol (DAGs), monoacylglycerol (MAGs) and Free Fatty Acids (FFA) were separated on silica gel 60 TLC plates using mobile phase n-hexane/ diethyl ether/ acetic acid (50:50:1). In order to visualize the methyl esters, lipids and fatty acids, the TLC plates were exposed to iodine vapour.

3.8.2 Infrared spectroscopy

This was done to monitor the transesterification process. IR addresses the presence of such as free and total glycerol, water, free fatty acid and residue alcohol. The IR spectroscopy machine was warmed for 1 hour.

The sample oil to be analyzed was dried of water so that it does not to affect the potassium chloride (KCL) plates. The plates were thoroughly cleaned using acetone. Using a syringe pipette a drop of the sample oil was placed between the two KCL plates and analyzed between a range of 600cm\(^{-1}\) to 4000cm\(^{-1}\).
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Oil obtained
From the dried seeds a total of 3.2, 6.6, 5.8 liters for Ugandan, Kenyan origin candlenut oil and *calodendrum capense* oil respectively were obtained after mechanical extraction. This translated to 32.3%, 35.4% and 35.2% (v/w) oil yield per total weight of the seeds respectively. More oil was obtained from the seed cake after mechanical extraction by use of n-hexane solvent extraction and this gave 0.78 litres of *candlenut* Kenyan origin and 0.50 litres of *calodenrum capense* which was a total of 1.28 litres.

4.2 Optimization of transesterification process
4.2.1 Pretreatment process
Some of the *Candlenut* and *Calodendrum capense* oil used as raw material had a high FFA content of 20.87% and 15.3% (v/v) respectively. The high FFA had to be reduced using 0.80 v/v methanol to oil ratio, 1% sulfuric acid as catalyst, reaction temperature of 55°C for 1hr 15mins reaction time. It was found out that the FFA reduced to 2.8% and 1.70% respectively. This was done using the two stage process described above. During the first stage, free fatty acids esterified and some triglycerides were transesterified. In the base-catalyzed stage, complete trans-esterification took place.

4.2.2 Effect of temperature
One of the variables affecting the yields of ester is the reaction temperature. Catalytic methanolysis of vegetable oil is normally investigated close to the boiling point of the methanol. Nevertheless, the reaction may be carried out at room temperature which could be very interesting for industrial scale production. It would be very interesting for industrial scale production due to the energy savings that it would imply. For this work, a temperature of 50°C, 55°C, 60°C, 65°C and 70°C were investigated for the transesterification of both *Candlenut* oil and *Calodendrum capense* oil. It was observed a good conversion occurred at 60°C.
4.2.3 Effect of methanol to oil molar ratio

The methanol to oil molar ratio is one of most important variable affecting the ester yields. It was observed that, the triglycerides increase as the molar ratio rises. The best result was found on 6:1 molar ratio. The result was similar to those found in the literature (Meher et al., 2004, Anh and Tan, 2008, Wanjala, 2009). At higher molar ratio, more triglyceride will be reacted. However an excess of methanol, will interfere with the separation of glycerin because there is an increase in solubility with part of the glycerin present in the biodiesel phase. This was observed when a 9:1 methanol to oil ratio was used. In addition, the glycerin that remained in the ester phase may drive the equilibrium back to the reverse reaction. When excess of methanol was used, it was observed that separation takes time and is also not complete. Therefore the molar ratio of 6:1 seems to be the most appropriate.

4.2.4 Enzymatic transesterification

Under the optimum conditions identified (6ml tert-amyl alcohol, 3:1 molar ratio of methanol to oil, 2mL of 5A lipase enzyme, temperature 45 °C, 150 rpm and 24 h), the highest biodiesel conversion yield of 92% was obtained. As the temperature was at first varied from 30 to 45 °C, the ME yield increased from 75% to 92% with increasing temperature. When the temperature was increased from 45 to 65 °C, the ME yield held steady at 92%. Therefore, 45 °C was selected as the optimum reaction temperature. The difference in the yield could be due to the reduced viscosity of the reaction with increasing temperature. In addition, the limitation on the mass transfer of the substrate and the product on the surface of, or within the lipase were reduced in this process.

The methyl esters yield increased from 60 to 92% when the agitation speed was increased from 90 to 150 rpm. This is probably due to the reduction in the mass transfer resistances between the substrates, lipase and tert-amyl alcohol with increasing agitation speed. However, as the speed was increased to 180 rpm, the ME yield sharply decreased to 72%. It was observed that substantial catalyst particles were thrown outside the liquid phase, sticking on the wall of the reactor, which reduces the effective catalyst loading. Thus an optimum speed of 150 rpm was selected for the reaction and used in all further studies.
When the amount of tert-amyl alcohol was increased to 6 ml, the highest ME yield of 92% was obtained. This indicates that 6 mL tert-amyl alcohol is the suitable amount for the reaction due to improved solubility of methanol and glycerol in the reaction medium, so lipase can maintain high catalytic activity. The ME yield decreased gradually by further increasing the amount of tert-amyl alcohol. This might be caused by dilution of reactants due to tert-amyl alcohol present in the reaction system. With tert-amyl alcohol present in the reaction medium, the negative effects caused by excessive molar ratio of methanol to oil and the byproduct glycerol was reduced. When the molar ratio of methanol/oil was increased from 3 to 6, similar ME yields of around 92% were obtained, indicating that lipase was tolerant to methanol presence within this range and maintained its activity. However, when the molar ratio of methanol/oil was increased to 6, significant reduction in conversion was observed. This is probably attributable to the inactivation of lipase caused by the high methanol concentration. Considering the operational stability of lipase for long times, running and production cost, the molar ratio of 3 was considered as the optimum condition. As the lipase dosage was increased, the conversion of ME yield also increased. When the lipase dosage 2 ml (based on oil weight), the ME yield of 92% was obtained at 24 h. However, further increase in the lipase dosage above 2ml did not increase the ME yield. Therefore, 2 ml lipase of oil weight was used for further study.

4.3 Physicochemical Properties of Fuel

The following abbreviations are used

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B5</td>
<td>A blend of 5% Biodiesel +95% Diesel fuel</td>
</tr>
<tr>
<td>B10</td>
<td>A blend of 10% Biodiesel +90% Diesel fuel</td>
</tr>
<tr>
<td>B20</td>
<td>A blend of 20% Biodiesel +80% Diesel fuel</td>
</tr>
<tr>
<td>B100</td>
<td>Neat biodiesel</td>
</tr>
<tr>
<td>CL</td>
<td><em>Calodendrum capense</em> oil</td>
</tr>
<tr>
<td>CLME</td>
<td><em>Calodendrum capense</em> Methyl Esters</td>
</tr>
<tr>
<td>CDN</td>
<td><em>Candlenut</em> oil</td>
</tr>
<tr>
<td>DF2</td>
<td>Grade two diesel fuel</td>
</tr>
<tr>
<td>CDNME</td>
<td><em>Candlenut</em> Methyl Ester</td>
</tr>
<tr>
<td>KCDN</td>
<td>Kenyan origin <em>Candlenut</em> oil</td>
</tr>
<tr>
<td>KCDNME</td>
<td>Kenyan origin <em>Candlenut</em> Methyl Esters</td>
</tr>
</tbody>
</table>

90
UCDN  Ugandan origin  *Candlenut* oil

UCDNME  Ugandan origin Methyl Esters

### 4.3.1 Specific Gravity

The specific gravity of the test fuels at each temperature was determined as the ratio of the mass to that of water at the same temperature. The results are presented in table 4.1 below.

**Table 4.1: Specific gravity for Neat oils and their resultant biodiesel**

<table>
<thead>
<tr>
<th>TEMP. °C</th>
<th>B100-KCDNME</th>
<th>B100-UCDNME</th>
<th>KCDN OIL</th>
<th>UCDN OIL</th>
<th>CLME B100</th>
<th>CL OIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.8771</td>
<td>0.8792</td>
<td>0.923</td>
<td>0.9248</td>
<td>0.871</td>
<td>0.9115</td>
</tr>
<tr>
<td>20</td>
<td>0.8742</td>
<td>0.878</td>
<td>0.9219</td>
<td>0.9228</td>
<td>0.8707</td>
<td>0.9107</td>
</tr>
<tr>
<td>25</td>
<td>0.8713</td>
<td>0.8747</td>
<td>0.9208</td>
<td>0.9213</td>
<td>0.8696</td>
<td>0.9102</td>
</tr>
<tr>
<td>30</td>
<td>0.8699</td>
<td>0.8716</td>
<td>0.9195</td>
<td>0.9201</td>
<td>0.8689</td>
<td>0.9086</td>
</tr>
<tr>
<td>35</td>
<td>0.8664</td>
<td>0.8693</td>
<td>0.9162</td>
<td>0.9177</td>
<td>0.8672</td>
<td>0.9081</td>
</tr>
<tr>
<td>40</td>
<td>0.8628</td>
<td>0.8673</td>
<td>0.9155</td>
<td>0.9161</td>
<td>0.8641</td>
<td>0.9063</td>
</tr>
<tr>
<td>45</td>
<td>0.8589</td>
<td>0.8633</td>
<td>0.9133</td>
<td>0.9143</td>
<td>0.863</td>
<td>0.905</td>
</tr>
<tr>
<td>50</td>
<td>0.8557</td>
<td>0.8605</td>
<td>0.9112</td>
<td>0.913</td>
<td>0.8614</td>
<td>0.9025</td>
</tr>
<tr>
<td>55</td>
<td>0.8536</td>
<td>0.8589</td>
<td>0.9103</td>
<td>0.9117</td>
<td>0.8595</td>
<td>0.9013</td>
</tr>
<tr>
<td>60</td>
<td>0.8526</td>
<td>0.8572</td>
<td>0.9085</td>
<td>0.9109</td>
<td>0.8587</td>
<td>0.9006</td>
</tr>
</tbody>
</table>

From the results in table 4.1 above graph of specific gravity against temperature for neat oils and neat biodiesel for both *candlenut* and *calodendrum capense*, figure 4.1 was obtained.

**Fig. 4.1: Variation of specific gravity with temperature of Neat oils and their resultant temperature.**
From figure 4.1 above, it can be observed that specific gravity is a temperature dependent property. As the temperature increased from 15 to 60 °C the specific gravity decreased. The *candlenut* oil from both the Uganda and Kenyan seeds had the highest specific gravity at all test temperatures as compared to *calodendrum capense* oil. Also the biodiesel of *candlenut* had a higher specific gravity as compared to that of *calodendrum capense* biodiesels. This shows that the physical property of biodiesel depends on the properties of neat oil used. After transesterification the specific gravity at 15 °C for biodiesel decreased by 5.23%, 4.93% and 4.44% for Kenyan *candlenut*, Uganda *candlenut* and *calodendrum capense* respectively. At 60 °C the specific gravity decreased by 6.15%, 5.90% and 4.65% for Kenyan *candlenut*, Uganda *candlenut* and *calodendrum capense* respectively. After blending the biodiesel with fossil diesel oil (DF2), there was a significant decrease in specific gravity at all test temperatures as shown in the table 4.2 and 4.3 below.

**Table 4.2: Specific gravity for Candlenut neat biodiesel and their blends with DF2**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>KCDNME Blends</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DF2</td>
<td>B5</td>
<td>B10</td>
<td>B20</td>
<td>B100</td>
<td>B5</td>
<td>B10</td>
<td>B20</td>
<td>B100</td>
</tr>
<tr>
<td>15</td>
<td>0.8367</td>
<td>0.8429</td>
<td>0.8467</td>
<td>0.8508</td>
<td>0.8771</td>
<td>0.8439</td>
<td>0.8482</td>
<td>0.8529</td>
<td>0.8792</td>
</tr>
<tr>
<td>20</td>
<td>0.8359</td>
<td>0.8408</td>
<td>0.8456</td>
<td>0.8496</td>
<td>0.8742</td>
<td>0.8424</td>
<td>0.8464</td>
<td>0.8515</td>
<td>0.878</td>
</tr>
<tr>
<td>25</td>
<td>0.8356</td>
<td>0.8387</td>
<td>0.8445</td>
<td>0.8479</td>
<td>0.8713</td>
<td>0.8395</td>
<td>0.845</td>
<td>0.8496</td>
<td>0.8747</td>
</tr>
<tr>
<td>30</td>
<td>0.8341</td>
<td>0.8366</td>
<td>0.8423</td>
<td>0.8466</td>
<td>0.8699</td>
<td>0.8372</td>
<td>0.8433</td>
<td>0.8475</td>
<td>0.8716</td>
</tr>
<tr>
<td>35</td>
<td>0.8319</td>
<td>0.8352</td>
<td>0.8407</td>
<td>0.8447</td>
<td>0.8664</td>
<td>0.8356</td>
<td>0.8419</td>
<td>0.8463</td>
<td>0.8693</td>
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<tr>
<td>40</td>
<td>0.8301</td>
<td>0.833</td>
<td>0.8388</td>
<td>0.8431</td>
<td>0.8628</td>
<td>0.8338</td>
<td>0.8394</td>
<td>0.8451</td>
<td>0.8673</td>
</tr>
<tr>
<td>45</td>
<td>0.8289</td>
<td>0.8316</td>
<td>0.8373</td>
<td>0.8408</td>
<td>0.8589</td>
<td>0.8328</td>
<td>0.8376</td>
<td>0.8441</td>
<td>0.8633</td>
</tr>
<tr>
<td>50</td>
<td>0.8270</td>
<td>0.8308</td>
<td>0.8351</td>
<td>0.839</td>
<td>0.8557</td>
<td>0.8316</td>
<td>0.8354</td>
<td>0.8392</td>
<td>0.8605</td>
</tr>
<tr>
<td>55</td>
<td>0.8263</td>
<td>0.8299</td>
<td>0.8345</td>
<td>0.8373</td>
<td>0.8536</td>
<td>0.8312</td>
<td>0.8348</td>
<td>0.8382</td>
<td>0.8589</td>
</tr>
<tr>
<td>60</td>
<td>0.8255</td>
<td>0.8284</td>
<td>0.8339</td>
<td>0.8353</td>
<td>0.8526</td>
<td>0.8304</td>
<td>0.834</td>
<td>0.8365</td>
<td>0.8572</td>
</tr>
</tbody>
</table>
Table 4.3: Specific gravity for *Calodendrum capense* neat biodiesel and their blends

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>CL-B5</th>
<th>CL-B10</th>
<th>CL-B20</th>
<th>CL-B100</th>
<th>Temp °C</th>
<th>CL-B5</th>
<th>CL-B10</th>
<th>CL-B20</th>
<th>CL-B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.8379</td>
<td>0.8407</td>
<td>0.8447</td>
<td>0.871</td>
<td>40</td>
<td>0.8326</td>
<td>0.8351</td>
<td>0.8371</td>
<td>0.8641</td>
</tr>
<tr>
<td>20</td>
<td>0.837</td>
<td>0.8397</td>
<td>0.8438</td>
<td>0.8707</td>
<td>45</td>
<td>0.8306</td>
<td>0.8334</td>
<td>0.8356</td>
<td>0.863</td>
</tr>
<tr>
<td>25</td>
<td>0.8365</td>
<td>0.8388</td>
<td>0.8434</td>
<td>0.8696</td>
<td>50</td>
<td>0.8291</td>
<td>0.8316</td>
<td>0.8334</td>
<td>0.8614</td>
</tr>
<tr>
<td>30</td>
<td>0.8359</td>
<td>0.8385</td>
<td>0.8411</td>
<td>0.8689</td>
<td>55</td>
<td>0.8284</td>
<td>0.8307</td>
<td>0.8321</td>
<td>0.8595</td>
</tr>
<tr>
<td>35</td>
<td>0.8341</td>
<td>0.8367</td>
<td>0.8397</td>
<td>0.8672</td>
<td>60</td>
<td>0.8269</td>
<td>0.8304</td>
<td>0.8317</td>
<td>0.8587</td>
</tr>
</tbody>
</table>

The following figures 4.2 below show the relationship of specific gravity against temperature for UCDNME biodiesel, blends and fossil diesel (DF2).

**Fig. 4.2: Variation of specific gravity with temperature of UCDNME (Uganda *Candlenut Methyl Esters*)**
From the above results it is evident that the specific gravity of the blends increased with percentage of biodiesel in a given blend. As compared to B10, B20 and B100, the B5 blend had the lowest specific gravity in all test temperatures. From the table 4.2 at 15 °C B5 KCDME had a specific density of 0.8429 which was a decrease of 4.0% as compared to B100 KCDNME. At the same temperature there was a decrease of specific density of 3.5 and 3.0% for B10 and B20 KCDNME respectively as compared to B100 KCDME. As the temperature increased there was a significant decrease in the specific gravity as shown in figure 4.2 and 4.3 respectively.

Fig. 4.3: Variation of specific gravity with temperature of KCDNME (Kenya Candlenut Methyl Esters)

The specified range of specific gravity of DF2 by Kenya Bureau of Standards (KEBS) standard KS1309-1(Appendix I) is 0.820 and 0.870 at 20 °C. As shown in figures 4.2 to 4.4, all the biodiesel blends investigated are within this specified range at all test temperatures. However neat UCDNME (B100) could only attain the highest range after it was heated to over 35 °C; neat KCDNME attained the range after the temperature exceeded 30 °C while neat CLME (B100) attained this highest range after the temperature exceeded 25 °C. Further, the neat Kenyan Candlenut, Uganda Candlenut and Calodendrum capense oils gave values that were far above the specified upper limit range of 0.870 at all test temperatures. Kimilu et al., (2011) noted that the specific gravities of the blends increased with percentage of Jatropha methyl esters
(biodiesel) in the blend at all temperatures and decreased with increase in temperature for all the tested fuels.

![Specific gravity for CLME, its blends and DF2 Vs Temperature](image)

**Fig. 4.4: Variation of specific gravity with temperature of CLME (Calodendrum Capense Methyl Esters)**

Figures 4.2, 4.3 and 4.4 shows that blends of both the candlenut and calodendrum capense biodiesel had a close specific gravity to that of DF2 in almost all the temperatures. At 20 ºC there was a difference of 0.59, 0.78% and 0.13% for KCDNME, UCDNME and CLME B5 blends respectively from that of DF2. For B20 blends from DF2 there was a difference of 1.64%, 1.87% and 0.94% for KCDNME, UCDNME and CLME respectively. For a temperature of 40 ºC the B5 blend for both candlenut and calodendrum capense biodiesel showed specific gravity values almost similar to that of fossil diesel.

### 4.3.2 Kinematic Viscosity

Viscosity is a very important property since it directly affects combustion of the fuel in the engine. For complete combustion to take place, proper air and fuel mixing is necessary. The quality of spray on injection is attributed to the viscosity of the fuel. Apart from the effects on combustion, viscosity is associated with lubrication and durability of fuel system parts (Maube et al., 2011).

The measured kinematic viscosities are presented in tables 4.4, 4.5 4.6 and 4.7 below. The results indicate that the neat oils and biodiesel of 100% KCDNME, UCDNME and CLME and their
blends at different ratios (B5, B10 and B20) have high kinematic viscosity compared to diesel. However, blending with diesel up to B20 reduced the viscosity comparable to that of diesel and made it suitable to be used in diesel engines.

Table 4.4: Relationship between kinematic viscosity of different oils and their corresponding methyl esters (B100).

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>CLME B100</th>
<th>KCDNME B100</th>
<th>UCDNME B100</th>
<th>CL OIL</th>
<th>UCDN OIL</th>
<th>KCDN OIL</th>
<th>DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>9.5111</td>
<td>8.7109</td>
<td>9.7608</td>
<td>65.7824</td>
<td>70.4320</td>
<td>67.8003</td>
<td>5.6103</td>
</tr>
<tr>
<td>20</td>
<td>8.1058</td>
<td>7.5779</td>
<td>8.1621</td>
<td>51.4076</td>
<td>57.2255</td>
<td>54.3054</td>
<td>4.8141</td>
</tr>
<tr>
<td>25</td>
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<td>6.1085</td>
<td>6.6189</td>
<td>38.9413</td>
<td>44.0275</td>
<td>39.3096</td>
<td>4.0485</td>
</tr>
<tr>
<td>30</td>
<td>5.7273</td>
<td>5.6871</td>
<td>5.7006</td>
<td>30.0174</td>
<td>34.9027</td>
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<td>3.4255</td>
</tr>
<tr>
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<td>5.0048</td>
<td>4.9047</td>
<td>4.9291</td>
<td>25.5966</td>
<td>27.8424</td>
<td>26.1867</td>
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</tr>
<tr>
<td>45</td>
<td>3.8266</td>
<td>3.9579</td>
<td>3.5297</td>
<td>17.1073</td>
<td>19.7247</td>
<td>17.4285</td>
<td>2.3203</td>
</tr>
<tr>
<td>55</td>
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<td>2.7774</td>
<td>9.5786</td>
<td>11.9372</td>
<td>10.6485</td>
<td>1.7924</td>
</tr>
<tr>
<td>60</td>
<td>2.6094</td>
<td>2.2863</td>
<td>2.5561</td>
<td>8.3983</td>
<td>10.1339</td>
<td>9.3119</td>
<td>1.6747</td>
</tr>
</tbody>
</table>

The kinematic viscosity for both neat oils and neat methyl esters (B100) decreased as the temperatures increased from 15 to 60 °C (Figure 4.5 and 4.6). After transesterification of the oils to their corresponding methyl esters, the kinematic viscosity decreased by 87.2%, 86.1% and 85.5% at 15 °C for Kenya Candlenut, Uganda Candlenut and Calodendrum Capense respectively. American Society for Testing and Material specifies the standard kinematic viscosity of biodiesel at 40 °C as 1.9 – 6.0 cSt (ASTM D6751) at 40 °C. The kinematic viscosity at 40 °C were 23.95, 21.19, 20.45 cSt for Uganda, Kenya candlenut and calodendrum capense oil respectively. However, for the biodiesel at 40 °C the kinematic viscosity decreased significantly to 4.571, 4.148 and 4.235 cSt for Kenya, Uganda candlenut methyl esters and calodendrum capense methyl esters respectively. The values show good comparison to those reported by Maube et al., (2011), Kimilu et al., (2011) and Wanjala (2009). The biodiesel obtained for both
the oils had kinematic viscosity which was within the ASTM range. Figures 4.5 to 4.9 below show the variation of kinematic viscosity with temperature for all the fuels investigated:

**Fig 4.5:** Variation of kinematic viscosity with temperature of Kenya *Candlenut*, Uganda *Candlenut* oil and their resultant biodiesel

**Fig 4.6:** Variation of kinematic viscosity with temperature of *Calodendrum capense* oil and its resultant biodiesel

As shown in figure 4.6 above the kinematic viscosity for *calodendrum capense* oil decreased significantly after transesterification. As the temperature increased further decrease in the viscosity was observed.
When the biodiesel of *Calodendrum capense*, Kenya, Uganda *Candlenut* and were blended with fossil diesel (DF2), the kinematic viscosity decreased even more as shown in the tables 4.5, 4.6 and 4.7 respectively. From table 4.5 above the kinematic viscosity at 40 °C was 3.56, 3.00, 2.60 and 4.24 cSt for CLME B20, CLME B10, CLME B5 and CLME B100 respectively. The CLME B5 was having similar kinematic viscosity as that of DF2 which was 2.559 cSt at 40 °C.

Figure 4.7 below it shows that at all measured temperatures the kinematic viscosities for the blends of *calodendrum capense* biodiesel were close to that of fossil diesel. At 60 °C the B5, B10 and B20 CLME were having 1.675, 2.065 and 2.465 cSt respectively and this was close to that of DF2 of 1.647 cSt.

In Table 4.6 below, at 40 °C the kinematic viscosities for B5, B10, B20 and B100 KCDNME were 2.606, 2.935, 3.636 and 4.571 cSt respectively. The neat biodiesel B100 and all the blends were within the range of ASTM D6751 (1.9 – 6.0 cSt) and that of KEBS (1.6 – 5.5 cSt) given in appendix I. As shown in figure 4.8 below the kinematic viscosity of B5 at all measured temperatures were similar to those of DF2. At 20 °C the B100, B20, B10 and B5 were 57.41%, 36.52%, 15.89% and 3.33% different from that of DF2.

### Table 4.5: Kinematic Viscosities of Calodendrum capense biodiesel blends with Diesel Fuel

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>CLME B20</th>
<th>CLME B10</th>
<th>CLME B5</th>
<th>CLME B100</th>
<th>DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>7.5685</td>
<td>6.5500</td>
<td>5.6016</td>
<td>9.5111</td>
<td>5.6103</td>
</tr>
<tr>
<td>20</td>
<td>6.4862</td>
<td>5.4560</td>
<td>4.8839</td>
<td>8.1058</td>
<td>4.8141</td>
</tr>
<tr>
<td>25</td>
<td>5.3709</td>
<td>4.6181</td>
<td>4.0794</td>
<td>6.5912</td>
<td>4.0485</td>
</tr>
<tr>
<td>30</td>
<td>4.6057</td>
<td>3.9281</td>
<td>3.4755</td>
<td>5.7273</td>
<td>3.4255</td>
</tr>
<tr>
<td>35</td>
<td>4.1918</td>
<td>3.4508</td>
<td>3.0888</td>
<td>5.0048</td>
<td>3.1291</td>
</tr>
<tr>
<td>40</td>
<td>3.5574</td>
<td>3.0004</td>
<td>2.6106</td>
<td>4.2351</td>
<td>2.5591</td>
</tr>
<tr>
<td>45</td>
<td>3.2410</td>
<td>2.6714</td>
<td>2.3572</td>
<td>3.8266</td>
<td>2.3203</td>
</tr>
<tr>
<td>50</td>
<td>2.8215</td>
<td>2.3503</td>
<td>1.9709</td>
<td>3.2907</td>
<td>1.9660</td>
</tr>
<tr>
<td>55</td>
<td>2.5843</td>
<td>2.1927</td>
<td>1.8028</td>
<td>2.8942</td>
<td>1.7924</td>
</tr>
<tr>
<td>60</td>
<td>2.4651</td>
<td>2.0653</td>
<td>1.6752</td>
<td>2.6094</td>
<td>1.6747</td>
</tr>
</tbody>
</table>
Fig 4.7: Variation of kinematic viscosity with temperature of *Calodendrum capense* biodiesel, its blends and fossil diesel (DF2).

Table 4.6: Kinematic Viscosities Kenyan *Candlenut* biodiesel blends with Diesel Fuel.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>KCDNME B20</th>
<th>KCDNME B10</th>
<th>KCDNME B5</th>
<th>KCDNME B100</th>
<th>DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>7.4500</td>
<td>6.7428</td>
<td>6.0921</td>
<td>8.7109</td>
<td>5.6103</td>
</tr>
<tr>
<td>20</td>
<td>6.5724</td>
<td>5.5792</td>
<td>4.9746</td>
<td>7.5779</td>
<td>4.8141</td>
</tr>
<tr>
<td>25</td>
<td>5.3154</td>
<td>4.7368</td>
<td>4.1157</td>
<td>6.1085</td>
<td>4.0485</td>
</tr>
<tr>
<td>30</td>
<td>4.8629</td>
<td>3.8534</td>
<td>3.4671</td>
<td>5.6871</td>
<td>3.4255</td>
</tr>
<tr>
<td>35</td>
<td>4.2483</td>
<td>3.2086</td>
<td>3.1266</td>
<td>4.9047</td>
<td>3.1291</td>
</tr>
<tr>
<td>40</td>
<td>3.6358</td>
<td>2.9347</td>
<td>2.6060</td>
<td>4.5711</td>
<td>2.5591</td>
</tr>
<tr>
<td>45</td>
<td>2.8896</td>
<td>2.5641</td>
<td>2.3403</td>
<td>3.9579</td>
<td>2.3203</td>
</tr>
<tr>
<td>50</td>
<td>2.6963</td>
<td>2.3823</td>
<td>1.9695</td>
<td>2.8544</td>
<td>1.9660</td>
</tr>
<tr>
<td>55</td>
<td>2.3508</td>
<td>2.1070</td>
<td>1.7985</td>
<td>2.5921</td>
<td>1.7924</td>
</tr>
<tr>
<td>60</td>
<td>2.0558</td>
<td>1.8774</td>
<td>1.6824</td>
<td>2.2863</td>
<td>1.6747</td>
</tr>
</tbody>
</table>

When the temperature was increased from 15 °C to 60 °C the difference in the kinematic viscosity of the blends of KCDNME and that of DF2 reduced greatly. At 45 °C the percentage difference from that of DF2 was 0.86%, 10.50% and 24.53 for B5, B10 and B20 KCDNME blends respectively. The closeness of the kinematic viscosities of the blends for KCDNME to that of DF2 at all the measured temperatures shows that they can result to complete combustion when they burn.
Table 4.7 below shows that at 40 °C the kinematic viscosity for the neat biodiesel and the blends for UCDNME were within the specified limits by ASTM D6751 and KEBS (appendix I). The B5, B10, B20 and B100 showed kinematic viscosity of 2.79, 2.94, 3.69 and 4.15 cSt at 40 °C respectively.

**Table 4.7: Kinematic Viscosities Uganda *Candlenut* biodiesel blends with Diesel Fuel.**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>UCDNME B20</th>
<th>UCDNME B10</th>
<th>UCDNME B5</th>
<th>UCDNME B100</th>
<th>DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>7.6292</td>
<td>6.8248</td>
<td>6.3326</td>
<td>9.7608</td>
<td>5.6103</td>
</tr>
<tr>
<td>20</td>
<td>6.7200</td>
<td>5.9846</td>
<td>5.0137</td>
<td>8.1621</td>
<td>4.8141</td>
</tr>
<tr>
<td>25</td>
<td>5.5280</td>
<td>4.8737</td>
<td>4.4779</td>
<td>6.6189</td>
<td>4.0485</td>
</tr>
<tr>
<td>30</td>
<td>5.0052</td>
<td>3.9508</td>
<td>3.7524</td>
<td>5.7006</td>
<td>3.4255</td>
</tr>
<tr>
<td>35</td>
<td>4.3377</td>
<td>3.3217</td>
<td>3.2923</td>
<td>4.9291</td>
<td>3.1291</td>
</tr>
<tr>
<td>40</td>
<td>3.6887</td>
<td>2.9392</td>
<td>2.7895</td>
<td>4.1475</td>
<td>2.5591</td>
</tr>
<tr>
<td>45</td>
<td>3.0755</td>
<td>2.6195</td>
<td>2.4282</td>
<td>3.5297</td>
<td>2.3203</td>
</tr>
<tr>
<td>50</td>
<td>2.7510</td>
<td>2.3924</td>
<td>2.1722</td>
<td>3.2248</td>
<td>1.9660</td>
</tr>
<tr>
<td>55</td>
<td>2.4161</td>
<td>2.1115</td>
<td>1.9750</td>
<td>2.7774</td>
<td>1.7924</td>
</tr>
<tr>
<td>60</td>
<td>2.0893</td>
<td>1.9021</td>
<td>1.7609</td>
<td>2.5561</td>
<td>1.6747</td>
</tr>
</tbody>
</table>

Fig 4.8: Variation of kinematic viscosity with temperature of Kenya *Candlenut* biodiesel, its blends and fossil diesel (DF2)
Fig 4.9: Variation of kinematic viscosity with temperature of Uganda *Candlenut* biodiesel, its blends and fossil diesel (DF2).

The measured viscosities increased as percentage of biodiesel in the blends increased as shown in Figure 4.7 to 4.9. Further, the viscosities decreased with increase in temperature. Kimilu et al (2011) measured viscosities of DF2, *Jatropha* methyl esters (JME) and its blends with DF2 at ten different temperatures found out that the viscosities increased as the percentage of biodiesel in the blends increased and decreased with increase of temperature. The water viscosity and density values at the required temperatures were obtained from the Handbook of Chemistry by Lange (1941) (presented in Appendix IV).

### 4.3.3 Acid Value

The acid values for both neat oils and blends were determined and the results obtained as indicated in Table 4.8. Neat *candlenut* and *calodendrum capense* oils had values of 8.670 and 6.220 mgKOH/g respectively. These values were high according to ASTM D975 (maximum limit is 0.8mgKOH/g). However, the B100 for both *Candlenut* and *Calodendrum capense* were within this limit. The difference of the acid value of oil could be attributed to difference in the fatty acid in the oil. The blends had an acid values that were within the total acid number of DF2 (0.5mgKOH/g) set by KEBS (Appendix I). The acid values for the oils were lower than that reported by Wanjala (2009) who reported a value of 9.685mg KOH/g for *Jatropha curcas* oil. The acid values of B100 for both the *candlenut* and *calodendrum capense* were higher than those.
reported by Wanjala (2009) who had values 0.333 mgKOH/g and 0.348 mg KOH/g for JME and CME respectively.

Table 4.8: The refractive index, the acid value, calorific value, iodine value and flash point values for the neat Candlenut oil, Calodendrum capense oil, B100, their blends DF2.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Refractive index</th>
<th>Acid value (mgKOH/g)</th>
<th>Calorific value (MJ/Kg)</th>
<th>Iodine value (mg I₂/g oil)</th>
<th>Flash point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candlenut oil</td>
<td>1.4748</td>
<td>8.6695</td>
<td>37.0880</td>
<td>136.498</td>
<td>194</td>
</tr>
<tr>
<td>B100</td>
<td>1.4707</td>
<td>0.4051</td>
<td>35.8505</td>
<td>98.670</td>
<td>148</td>
</tr>
<tr>
<td>B20</td>
<td>1.4693</td>
<td>0.2052</td>
<td>40.0085</td>
<td>21.495</td>
<td>82.5</td>
</tr>
<tr>
<td>B10</td>
<td>1.4690</td>
<td>0.2025</td>
<td>41.4516</td>
<td>18.034</td>
<td>79.8</td>
</tr>
<tr>
<td>B5</td>
<td>1.4685</td>
<td>0.1039</td>
<td>41.4750</td>
<td>14.648</td>
<td>75</td>
</tr>
<tr>
<td>Calodendrum capense oil</td>
<td>1.4723</td>
<td>6.2204</td>
<td>35.6393</td>
<td>103.490</td>
<td>160</td>
</tr>
<tr>
<td>B100</td>
<td>1.4702</td>
<td>0.5063</td>
<td>36.6670</td>
<td>82.546</td>
<td>136.5</td>
</tr>
<tr>
<td>B20</td>
<td>1.4687</td>
<td>0.1559</td>
<td>40.6257</td>
<td>20.657</td>
<td>78</td>
</tr>
<tr>
<td>B10</td>
<td>1.4684</td>
<td>0.1539</td>
<td>40.9970</td>
<td>15.930</td>
<td>76</td>
</tr>
<tr>
<td>B5</td>
<td>1.4682</td>
<td>0.1046</td>
<td>42.2375</td>
<td>8.469</td>
<td>75</td>
</tr>
<tr>
<td>Diesel fuel</td>
<td>1.4680</td>
<td>0</td>
<td>43.3791</td>
<td>0</td>
<td>&gt;70</td>
</tr>
</tbody>
</table>

4.3.4 Refractive Index

The measured refractive indices are as indicated in Table 4.8 above. The *candlenut* oil and *calodendrum capense* oils had the highest values (1.4748 and 1.4723 respectively). From the values obtained it showed that the refractive index decreased as the percentage of methyl esters decreased in a blend. The B5 for both the sample fuels had the lowest value of 1.4685 and 1.4682 for *Candlenut* and *Calodendrum capense* respectively. These values were very close to that of conventional diesel (1.4680). The difference in the values could be attributed to the type of oil extraction method used, the transesterification process and biodiesel washing method.
4.3.5 Heating value (Calorific value)

The calorific value of *calodendrum capense* was 35.639MJ/kg while that of *candlenut* oil was 37.088MJ/kg. The values of B100 for both *calodendrum capense* and *candlenut* were 36.667 and 35.851MJ/kg respectively. On blending, the calorific values increased significantly where the B5 for *calodendrum capense* had a value of 42.238MJ/kg. This value was close to that of fossil diesel which had a measured value of 43.379MJ/kg. The heating value obtained for *calodendrum capense* was below that reported (40.80MJ/kg) by Munavu and Odhiambo (1984) (Appendix II). However, the measured heating value compared well with that reported by Maube et al., (2011) where the fossil diesel had a value of 43.38 MJ/kg while that of biodiesel (from edible vegetable oil) was found to be 38.52 MJ/kg. The heating values obtained for the oils were also close to that reported by Wanjala (2009) who found *Croton* oil and *Jatropha* oil to have values 36.410 MJ/kg and 35.777 MJ/kg respectively. The value of B5 for *calodendrum capense* was slightly higher to that reported by Wanjala (2009) who reported corresponding values of 40.698 MJ/kg and 40.333 MJ/kg for B5 for *Jatropha* Methyl esters and *Croton* methyl esters respectively. An increase in the percentage of methyl ester in a blend led to a decrease in the heating value. The difference in the heating value could be attributed to the source of oil seeds, the fatty acid and the analytical method used. The measured heating values are presented in Table 4.8.

4.3.6 Iodine Value

The iodine values measured for the sample fuel are given in Table 4.8. The Iodine values for the blends were within the allowed maximum limits of 115g I₂/100g oil and 120g I₂/100g oil as per ASTM D6751 and EN 14214 respectively. The neat oils had the highest values of 136.498 and 103.490gI₂/100g for *candlenut* and *calodendrum capense* respectively. The value for *calodendrum capense* was slightly higher than that reported (102 g I₂/100g) by Munavu and Odhiambo (1984). The degree of saturation and unsaturation of different fatty acids may have resulted to difference in the iodine values obtained. The values for the neat oils were close to those obtained by Wanjala (2009) who reported 133.849 g I₂/100g and 102.426 g I₂/100g for *Croton Megalocarpus* oil *Jatropha* oil respectively.
4.3.7 Flash point
The flash points for *Candlenut* and *Calodendrum capense* oils were 194 °C and 160 °C respectively. The B100 for both *Candlenut* and *Calodendrum capense* had a flash point of 148 °C and 136.5 °C respectively. The flash points obtained for the biodiesel and fossil diesel blends decreased significantly as shown in Table 4.8. The B5 had a flash point close to that of DF2 due a low percentage of methyl esters in it. The flash point values obtained for B100 for both sample fuels were above the minimum standard temperature of 60 °C for DF2 and 96 °C for *Jatropha* methyl esters (B100 JME) reported by Kimilu (2007).

4.4 Thin Layer Chromatography (TLC)
For the case of enzymatic transesterification, TLC was used to monitor the process. From the results obtained there were no glycerides detected and by using free fatty acids as standard, it was also determined that free fatty acids were also absent after transesterification. This is as shown in the figures 4.10 and 4.11 below.

![Thin layer chromatography for candlenut and methyl esters](image)

**Fig. 4.10: Thin layer chromatography for candlenut and methyl esters**
Fig. 4.11: Thin layer chromatography for calodendrum capense and methyl esters

Figures 4.10 and 4.11 show the separation of methyl esters from the *candlenut* and *calodendrum capense* oils after transesterification. From the spots of the oil it showed that it contains MAG, DAG, TAG and FFA, these were converted to methyl esters after transesterification. The absence of the spots of MAG, DAG, TAG and FFA it showed that the lipase catalyzed them to the respective methyl esters. The spots for the methyl esters moved the furthest due to their high solubility and low kinematic viscosity as compared to neat oils.
4.5 Infrared Analysis

Infrared (IR) is one of the numerous spectrophotometric techniques for analyzing the chemistry of materials. In all cases, spectrophotometric analysis implies a measurement of a very specific wavelength of light energy, either in terms of amount absorbed by the sample in question, or the amount emitted from the sample when suitably energized.

IR is concerned with specific groupings of atoms in specific combinations to form what is called “functional groups.” These various functional groups such as alcohol, amine, amide, ester, alkene etc determine the properties or expected behavior of a given sample.

By knowing which wavelengths are absorbed by each functional group of interest one can cause the appropriate wavelength to be directed at the sample being analyzed, and then measure the amount of energy absorbed by the sample. The more energy absorbed the more of that particular functional group exists in the sample. The unit of measurement is usually *Absorbance Units*.

Using IR Spectroscopy, the functional groups found in the oil and the biodiesel samples were determined and the results are summarized in Table 4.9. The Infra-Red analysis shows that the functional groups present in the fuel sample are: ester stretch, C-H aliphatic, both functional groups present in *Calodendrum capense* oil and methyl esters.

**Table 4.9: Infra-Red values of *Calodendrum capense* and *Candlenut* biodiesel samples**

<table>
<thead>
<tr>
<th>Peak (1/cm)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500</td>
<td>Presence of –OH</td>
</tr>
<tr>
<td>2900</td>
<td>C-H aliphatic stretch</td>
</tr>
<tr>
<td>1720</td>
<td>C=O ester group</td>
</tr>
<tr>
<td>1400-1500</td>
<td>C-H bending</td>
</tr>
<tr>
<td>1140</td>
<td>C-O presence</td>
</tr>
<tr>
<td>700</td>
<td>C-H out of plane</td>
</tr>
</tbody>
</table>
Fig 4.12: IR spectrum for *Calodendrum capense* oil

The Infra-Red analysis of all the samples (shown in the figures 4.13 and 4.14 below) obtained indicates the presence of: ester stretch and C-H aliphatic, both which are the expected functional groups thus confirming the presence of methyl esters. The peak at 2400 cm\(^{-1}\) is from instrumental noise and should be subtracted from IR spectra recorded. Figure 4.13 shows strong peaks at 1710 and 2900 which were due to C=O ester group and C-H aliphatic stretch. The absence of a peak at 1720 cm\(^{-1}\) in figure 4.12 and its presence in figure 4.13 it shows that the oil was converted to methyl esters to methyl esters. The peak at 1436 cm\(^{-1}\) is considered to be the \(-\text{CH}_3\) asymmetric bending vibrations (Al-Alawi, 2006). In the mid-IR spectra region the conversion of TAGs to FAMEs involves the loss of glycerol resulting in decrease in peak height at 1378 cm\(^{-1}\). The peak at 1378 cm\(^{-1}\), which is attributed to the terminal CH\(_3\) group in TAG, DAG, MAG, FFA and FAME and to the OCH\(_2\) group in the glycerol of TG, DG and MG has also been monitored using IR (Zheng et al., 2004).
Figure 4.13 shows a strong peak at 1720 cm\(^{-1}\) and indicates the presence of an ester hence the conversion of fatty acid to methyl esters. The peak from 2785 cm\(^{-1}\) to 2850 cm\(^{-1}\) shows the presence of \(-\text{CH}_2\) asymmetric stretch. The absence of the peak at 3500 cm\(^{-1}\) for OH shows that the methanol that was used was completely converted to \(-\text{CH}_3\) and the peak at 1484 cm\(^{-1}\) shows the \(-\text{CH}_2\) scissor stretch. Figure 4.14 below show that the fossil diesel has a peak at 1720 and 2850 for ester carbonyl group and \(-\text{CH}_2\) respectively. This peaks are comparable to that obtained on the methyl ester of both candlenut and calodendrum capense. Transesterification process can be monitored by comparing the peaks of the methyl esters and that of the oil. The IR spectrum for candlenut oil (figure 4.16) and calodendrum capense oil (figure 4.12) shows a shoulder at 1720 and 2850 cm\(^{-1}\).
Fig. 4.14: IR spectrum for Diesel Fuel

Fig. 4.15: IR spectrum for *Calodendrum Capense* Glycerine.
Figure 4.16: IR spectrum for Candlenut oil.

Figure 4.16 shows negative absorbance at 1500 to 2000 cm\(^{-1}\) due to the difference in the amount of light being absorbed by a functional group in a compound that particular wavelength. The peak at 700 cm\(^{-1}\) it shows the -CH group out of plane. The peak at 1400 to 1500 cm\(^{-1}\) shows the -CH bending. The IR spectrum for the candlenut oil (figure 4.16) at 2850 to 3000 cm\(^{-1}\) it shows a shoulder as compared to that of the methyl ester which showed peaks. This enables one to monitor the transesterification process.
Fig. 4.17: IR spectrum for B100 Candlenut Methyl ester.

Fig. 4.18: IR spectrum for Candlenut Glycerine.
For the case of the glycerine (figure 4.18) there was no ester group at 1720 cm\(^{-1}\) which showed the absence of the methyl esters. In the figure 4.18 it shows a shoulder at 1720 and 2850 which shows that the transesterification process was efficient. In figure 4.19 below it shows a peak at 1720 cm\(^{-1}\) hence the presence of an ester and another at 700 cm\(^{-1}\) which is a \(-\text{CH}\) out of plane peak.

![IR spectrum for Candlenut Lipase catalyzed methyl esters.](image)

**Fig. 4.19:** IR spectrum for Candlenut Lipase catalyzed methyl esters.

### 4.6 Results for Engine Tests.

#### 4.6.1 Brake Specific Fuel Consumption.

The measured Brake specific fuel consumption is presented in tables 4.20 and 4.21. Figures 4.20, to 4.23 gives a comparison of the brake specific fuel consumption of diesel and various blends of isolated CDNME and CLME, at varying brake load in the range of 5.593 to 39.149 KW. It was observed that the specific fuel consumptions of the biodiesel blends as well as diesel oil decreased with increasing load from 5.593 to 33.570 KW and tended to increase with further increase in brake horse power. BSFC represents a more reliable factor for comparing different fuels with different heating values and different values of density.
Table 4.10: Brake specific fuel consumption for B5 and B20 Blends of Candlenut Biodiesel with diesel fuel.

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CDNME B5</th>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CDNME B20</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.593</td>
<td>0.6145</td>
<td>0.6865</td>
<td>5.593</td>
<td>0.6638</td>
<td>0.6647</td>
</tr>
<tr>
<td>11.186</td>
<td>0.4274</td>
<td>0.4179</td>
<td>11.186</td>
<td>0.3853</td>
<td>0.4113</td>
</tr>
<tr>
<td>16.778</td>
<td>0.3460</td>
<td>0.3201</td>
<td>16.778</td>
<td>0.3012</td>
<td>0.3207</td>
</tr>
<tr>
<td>22.371</td>
<td>0.3047</td>
<td>0.3042</td>
<td>22.371</td>
<td>0.2829</td>
<td>0.3003</td>
</tr>
<tr>
<td>27.964</td>
<td>0.2674</td>
<td>0.2688</td>
<td>27.964</td>
<td>0.2699</td>
<td>0.2675</td>
</tr>
<tr>
<td>33.557</td>
<td>0.2685</td>
<td>0.2738</td>
<td>33.557</td>
<td>0.2600</td>
<td>0.2669</td>
</tr>
<tr>
<td>39.149</td>
<td>0.2881</td>
<td>0.2690</td>
<td>39.149</td>
<td>0.2623</td>
<td>0.2686</td>
</tr>
</tbody>
</table>

Frank et al. (2010) also observed that BSFC decreased as the load increased and attributed this decrease to the amount of fuel required for operating engine per unit energy output at higher loads decreases.

**CDNME B5 Blend**

![Graph showing BSFC against BHP for CDNME B5 Blend and Diesel](image)

**Fig. 4.20: Effect of brake horse power (BHP) on brake specific fuel consumption (BSFC) for CDNME B5 blend and diesel.**

The BSFC for CDNME B5 (figure 4.20) decreased as the brake horse power increased up to 27.96 kW and then started decreasing. At a load of 5.59 kW the CDNME B5 blend had a higher BSFC as compared to DF2 of 11.71% and at 33.56 kW the blend had 1.98% BSFC than DF2.
Fig. 4.21: Effect of brake horse power (BHP) on brake specific fuel consumption (BSFC) for CLME B5 blend and diesel.

The same trend as that of B5 CDNME was observed on all the other blends, where at brake horse power of 39.15 kW, B5 CLME had a BSFC of 8.7% lower than DF2 and for B20 CDNME and B20 CLME a BSFC of 2.4% and 7.5% lower than DF2 respectively was observed.

Table 4.11: Brake specific fuel consumption for B5 and B20 Blends of *Calodendrum capense* biodiesel with diesel fuel.

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CLME B5</th>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CLME B20</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.593</td>
<td>0.6638</td>
<td>0.6053</td>
<td>5.593</td>
<td>0.5640</td>
<td>0.5810</td>
</tr>
<tr>
<td>11.186</td>
<td>0.3853</td>
<td>0.4004</td>
<td>11.186</td>
<td>0.3669</td>
<td>0.3919</td>
</tr>
<tr>
<td>16.778</td>
<td>0.3012</td>
<td>0.3394</td>
<td>16.778</td>
<td>0.3117</td>
<td>0.3124</td>
</tr>
<tr>
<td>22.371</td>
<td>0.2829</td>
<td>0.2819</td>
<td>22.371</td>
<td>0.2750</td>
<td>0.2909</td>
</tr>
<tr>
<td>27.964</td>
<td>0.2699</td>
<td>0.2654</td>
<td>27.964</td>
<td>0.2385</td>
<td>0.2667</td>
</tr>
<tr>
<td>33.557</td>
<td>0.2600</td>
<td>0.2517</td>
<td>33.557</td>
<td>0.2247</td>
<td>0.2539</td>
</tr>
<tr>
<td>39.149</td>
<td>0.2623</td>
<td>0.2395</td>
<td>39.149</td>
<td>0.2253</td>
<td>0.2421</td>
</tr>
</tbody>
</table>
Fig 4.22: Effect of brake horse power (BHP) on brake specific fuel consumption (BSFC) for CDNME B20 blend and diesel

Kimilu (2007) noted that the BSFC for all the tested fuels decreased with increasing BHP up to about 40 kW and subsequently started to increase with BHP. He also observed that the BSFC increased with increase in the percentage of *Jatropha* methyl esters in the fuel blends. The same trend was noted by Wanjala (2009) where in his study of *Jatropha* methyl esters and Croton methyl esters, the specific fuel consumption of the blends as well as diesel oil decreased with increasing load from 5.595 kW to 33.57 kW and tended to increase with further increase in brake horse power. Qi et al., (2010), Godiganur et al., (2010) and Reheman et al., (2007) also observed that increase in load led to a decrease of BSFC of biodiesel. Gumus and Kasifoglu (2010) showed that the BSFC initially decreased with increasing engine load until it reached a minimum value and then increased slightly with further increasing engine load for all kind of fuels. The higher BSFC for biodiesel and its blends with diesel oil was attributed to the difference in calorific value and viscosity Maube et al. (2011). The lower calorific value of biodiesel and blends prompts the injection of more fuel to sustain the same power output while the high viscosity of biodiesel would tend to constrain the rate of flow.
The results obtained can be attributed mainly due to the combined effects of reduced fuel density, reduced viscosity and increased calorific (heating) value of the blends up to 20% biodiesel and 80% diesel oil (figure 4.23).

**B20 CLME Blends**

![BSFC against BHP for CLME B20 Blend and Diesel](image)

**Fig 4.23: Effect of brake horse power (BHP) on brake specific fuel consumption (BSFC) for CLME B20 blend and diesel**

Tests have shown that the actual efficiency at which the energy in the fuel is converted to power is the same for biodiesel and petroleum-based diesel fuel reference. Therefore, the brake specific fuel consumption (BSFC), the parameter most often used by engine manufacturers to characterize fuel economy will be at least 12.5% higher for biodiesel (Garpen et al., 2004). Since BSFC measures how much fuel may be required to do a certain quantity of work it automatically implies that the smaller the BSFC, the more efficient the engine. Thus from this study it can be observed that operating the engine on diesel and blends of diesel with biodiesel up to 20% (B20) can be efficient.
4.6.2 Brake Thermal Efficiency

The measured thermal efficiencies are as presented in tables 4.12 and 4.13. The variation of brake thermal efficiency of the engine at different loads for various biodiesel blends of isolated, are shown in Figures 4.24 to 4.27 below compared with the brake thermal efficiency obtained with diesel.

Table 4.12: Thermal efficiency for B5 and B20 blends of Candlenut biodiesel with diesel fuel.

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CDNME B5</th>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CDNME B20</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5928</td>
<td>13.5050</td>
<td>12.6369</td>
<td>5.5928</td>
<td>12.5021</td>
<td>13.7370</td>
</tr>
<tr>
<td>16.7783</td>
<td>23.9866</td>
<td>27.0967</td>
<td>16.7783</td>
<td>27.5504</td>
<td>28.4754</td>
</tr>
<tr>
<td>22.3710</td>
<td>27.2397</td>
<td>28.5166</td>
<td>22.3710</td>
<td>29.3396</td>
<td>30.4045</td>
</tr>
<tr>
<td>27.9638</td>
<td>31.0317</td>
<td>32.2706</td>
<td>27.9638</td>
<td>30.7503</td>
<td>34.1357</td>
</tr>
<tr>
<td>33.5565</td>
<td>30.9060</td>
<td>31.6790</td>
<td>33.5565</td>
<td>31.9143</td>
<td>34.2126</td>
</tr>
<tr>
<td>39.1493</td>
<td>28.8046</td>
<td>32.2449</td>
<td>39.1493</td>
<td>31.6376</td>
<td>33.9936</td>
</tr>
</tbody>
</table>

The thermal efficiency for B5 CDNME blend increased from 12.64% (at BHP 5.59 kW) to a maximum 32.27% (BHP 27.96 kW) and then started decreasing. The same was noted for B20 CDNME where it varied from 13.74% (at BHP 5.59 kW) to a maximum 34.21% (BHP 33.56). For DF2 the thermal efficiency varied from 13.74% (at BHP 5.59 kW) to a maximum 34.21% (at BHP 33.56).
B5 CDNME Blends

Fig 4.24: Effect of brake horse power (BHP) on Thermal Efficiency (TE) for CDNME B5 blends and diesel.

B 20 CDNME Blends

Fig 4.25: Effect of brake horse power (BHP) on Thermal Efficiency (TE) for CDNME B20 blends and diesel.
Table 4.13: Thermal Efficiency for B5 and B20 Blends of *calodendrum capense* with Diesel Fuel

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>CLME B5</th>
<th>BHP (kW)</th>
<th>CLME B20</th>
<th>DF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.3710</td>
<td>29.3396</td>
<td>30.2355</td>
<td>22.3710</td>
<td>30.4582</td>
<td>30.1721</td>
</tr>
<tr>
<td>27.9638</td>
<td>30.7503</td>
<td>32.1207</td>
<td>27.9638</td>
<td>33.2217</td>
<td>34.8013</td>
</tr>
<tr>
<td>33.5565</td>
<td>31.9143</td>
<td>33.8582</td>
<td>33.5565</td>
<td>34.8990</td>
<td>36.9281</td>
</tr>
<tr>
<td>39.1493</td>
<td>31.6376</td>
<td>35.5846</td>
<td>39.1493</td>
<td>36.6046</td>
<td>36.8341</td>
</tr>
</tbody>
</table>

There was an increase in the thermal efficiency for both the B5 and B20 CLME blends. Maximum thermal efficiencies of 35.58% and 36.60% were observed at brake horse power of 39.15 kW for B5 and B20 CLME respectively.

![Thermal Efficiency against BHP for CLME B5 Blend and Diesel](image)

Fig 4.26: Effect of brake horse power (BHP) on Thermal Efficiency (TE) for CLME B5 blends and diesel.
The results as shown in figures 4.24 to 4.27 compare well with other studies done (Kimilu, 2007; Wanjala 2009). Kimilu (2007) noted that the thermal efficiency of B20 of *Jatropha* methyl esters increased from 21.41% (at BHP 11.19 kW) to a maximum 33.07% (BHP 39.15 kW) while that of DF2 increased from 22.64% (at BHP 11.19 kW) to a maximum 33.76% (at BHP 39.15 kW). Wanjala (2009) also observed that the thermal efficiency varied from 13.25%, 13.56% and 14.42% (BHP 5.59 kW) to a maximum 34.49%, 34.74% and 35.62% (at BHP 33.57 kW) for DF2, CME and JME respectively. In addition, maximum thermal efficiencies of 32.41%, 35.15% and 35.27% (at BHP 39.16 kW) were obtained for B20 blends of DF2, CME and JME respectively (Wanjala; 2009). Lujaji et al. (2010) also noted that the brake thermal efficiency increased as the load increased for all the test fuels.

**B20 CLME Blend**

![Thermal Efficiency against BHP for CLME B20 Blend and Diesel](image)

**Fig 4.27: Effect of brake horse power (BHP) on Thermal Efficiency (TE) for CLME B20 blends and diesel.**

The drop in thermal efficiency with increase in proportion of vegetable oil or neat alkyl ester is always attributed to the poor combustion characteristics due to their high viscosity and poor volatility (Pramanik, 2003). Overall, this implies poor quality of biodiesel. Brake thermal
efficiency refers to the relationship between actual heat energy stored within the fuel and power produced in the engine (indicated horsepower). The thermal efficiency figure indicates the amount of potential energy contained in the fuel that is actually used by the engine to produce power and what amount of energy is actually lost through heat. Hence, in this study the increase in brake thermal efficiency for biodiesel blends with diesel up to 20% biodiesel as compared to diesel fuel can be attributed to the high degree of combustion the blends in the engine. The increase can also be due to increased fuel flow by reducing internal pump leakage because of high density and viscosity of biodiesel. The lower mass-based heating values indicate that the blends required larger mass fuel flow to maintain constant energy input to the engine. High thermal efficiency implies more of the energy input in the blends with diesel was converted to work by the engine, thereby decreasing unburned fuel emissions as compared to commercial diesel.

4.6.3 Exhaust gas temperature

The measured exhaust gas temperature as a function of brake horse power is presented in table 4.14 and 4.15. The exhaust gas temperatures are affected by changes in ignition delay. Higher ignition delays result in a delayed combustion and higher exhaust gas temperatures. Mevlüt et al., (2007) observed that the exhaust gas temperature for Canola oil methyl esters were 6.4% lower at all engine speeds than diesel fuel and attributed this to lower heating values and higher Cetane number than the other fuel.

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>B5 CDNME</th>
<th>B5 CLME</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5928</td>
<td>215.0</td>
<td>210.0</td>
<td>187.5</td>
</tr>
<tr>
<td>11.1855</td>
<td>272.5</td>
<td>252.5</td>
<td>237.5</td>
</tr>
<tr>
<td>16.7783</td>
<td>332.5</td>
<td>297.5</td>
<td>300.0</td>
</tr>
<tr>
<td>22.3710</td>
<td>387.5</td>
<td>375.0</td>
<td>325.0</td>
</tr>
<tr>
<td>27.9638</td>
<td>432.5</td>
<td>430.0</td>
<td>410.0</td>
</tr>
<tr>
<td>33.5565</td>
<td>510.0</td>
<td>505.0</td>
<td>475.0</td>
</tr>
<tr>
<td>39.1493</td>
<td>550.0</td>
<td>572.5</td>
<td>540.0</td>
</tr>
</tbody>
</table>
Figures 4.28 and 4.29 show the variation of exhaust gas temperature with load in the range of 5.593 to 39.149 brake horse powers for diesel, CDNME and CLME with DF2. The results show that the exhaust gas temperature increased with increase in brake horse power in all cases.

**B5 CDNME BLENDS**

![Exhaust Temperature against BHP for B5 CDNME blends](image)

**Fig 4.28: Effect of brake horse power on exhaust temperatures for B5 blends and diesel**

The highest value of exhaust gas temperature of 572.5°C for B5 CDNME and 540 °C for B5 CLME was observed with the biodiesel blends, whereas the corresponding value with diesel was found to be 550 °C only. For the B5 blends at the maximum load the exhaust temperature for CDNME was slightly higher than that of DF2 and this could be attributed to the difference in viscosities. The biodiesel blends having slightly higher viscosities than the DF2 resulted to the difference in the exhaust temperature. For both the B5 and B20 CDNME and CLME the exhaust temperature increased with B.H.P.
Table 4.15: Exhaust temperatures for B20 Blends for both *candlenut* and *calodendrum capense* biodiesel with Diesel Fuel

<table>
<thead>
<tr>
<th>BHP (kW)</th>
<th>DF2</th>
<th>B20 CDNME</th>
<th>B20 CLME</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5928</td>
<td>215.0</td>
<td>205.0</td>
<td>202.5</td>
</tr>
<tr>
<td>11.1855</td>
<td>272.5</td>
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<td>245.0</td>
</tr>
<tr>
<td>16.7783</td>
<td>332.5</td>
<td>282.5</td>
<td>287.5</td>
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<tr>
<td>22.3710</td>
<td>387.5</td>
<td>347.5</td>
<td>350.0</td>
</tr>
<tr>
<td>27.9638</td>
<td>432.5</td>
<td>380.0</td>
<td>407.5</td>
</tr>
<tr>
<td>33.5565</td>
<td>510.0</td>
<td>475.0</td>
<td>460.0</td>
</tr>
<tr>
<td>39.1493</td>
<td>550.0</td>
<td>540.0</td>
<td>512.5</td>
</tr>
</tbody>
</table>

The exhaust temperatures for the B20 blends for all the loads were lower than those of the DF2 as shown in figure 4.29. Pramanik (2002) noted that high exhaust temperatures are usually associated with biodiesel fuels due to their high viscosities. They usually have low thermal efficiencies with most energy dissipated as heat, hence high exhaust temperature. Kimilu (2007) and Wanjala (2009) noted that the difference between the exhaust temperature for DF2 and the blended fuels was minimal.

**B20 Blends**

Fig 4.29: Effect of brake horse power on exhaust temperatures for B20 blends and diesel.
CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

The primary objective of this research project was to extract biodiesel from Calodendrum capense and candlenut as alternative fuel to fossil diesel. The vegetable oils were converted to biodiesel through transesterification using base catalyst (potassium hydroxide). Biodiesel blends containing 20% CDNME and 80% DF2, 10% CDNME and 90% DF2 and 5% CDNME and 95% DF2 was prepared, the same was done for the case of CLME. The physicochemical properties of these biodiesel mixtures plus the isolated methyl esters from calodendrum capense and candlenut were characterized by specific gravity, kinematic viscosity, acid value, calorific value and iodine value and compared to those of diesel fuel.

Neat candlenut oil had a high acid value of 8.7 mgKOH/g oil as compared to calodendrum capense oil of 6.2 mgKOH/g oil. Calodendrum capense oil had a low iodine value of 103.5 mg I₂/g oil compared to that of candlenut of 136.5 mg I₂/g oil. These values however dropped after transesterification and decreased even further upon blending of biodiesel with commercial diesel fuel to fall within the allowed limits. The B100 of candlenut had an iodine value of 98.7 mg I₂/g oil , 82.6 mg I₂/g oil for B100 calodendrum capense, 14.7 mg I₂/g oil for B5 candlenut and 8.5 mg I₂/g oil for B5 calodendrum capense. The flash point of candlenut oil was with a value of 194 °C as compared to that of calodendrum capense with a value of 160 °C. After transesterification the flash point decreased significantly for both candlenut (148 °C) and calodendrum capense (136.5 °C) neat biodiesel respectively. This even decreased after blending the biodiesel with the fossil diesel and the values obtained for both the neat biodiesel and the blends were within the required limits.

Higher specific gravity values as well as kinematic viscosity values were observed in the case of neat biodiesel as compared to diesel. Specific gravity was in the range of 3.4 to 5.0% high at 15 °C and kinematic viscosity was in the range of 62.1 to 65.5% high at 40 °C than diesel oil. Blending the biodiesel with diesel up to B20 reduced both specific gravity and kinematic viscosity significantly to compare to those of diesel at all test temperatures from 15 to 60 °C. Neat biodiesel gave low calorific values, about 15.5% to 17.4% lower than that of commercial
diesel. These property (calorific value) however improved upon blending the biodiesel with commercial diesel and increase depended on the amount of biodiesel in a given blend mixture. The engine tests investigated included; brake specific fuel consumption and brake thermal efficiency. There was no significant difference observed on the brake specific fuel consumption between the biodiesel blends up to B20 from those of commercial diesel. All values obtained were comparable and almost similar in the entire load range. On the other hand there was a considerable increase in thermal efficiencies of the biodiesel blends up to B20 compared to the thermal efficiency of diesel oil. This was attributed to high degree of combustion of the biodiesel blends in the engine and increased fuel flow as a result of reduced internal pump leakage because of high density and viscosity of the blends.

Based on the findings of this study the following conclusion can be made:

1. It was found that the feed stocks with high FFA could not directly be transesterified with KOH catalyst. The reason for this is because KOH catalyst reacts with the FFA to form soap that prevents the separation of the glycerine and ester. The high FFA level of crude *candlenut* and *calodendrum capense* can be reduced to less than 2% in pretreatment process of esterification using acid catalyst at 65 °C temperature and 1 hour reaction time.

2. The biodiesel production by methanolysis of *Candlenut* and *Calodendrum capense* oil can be undertaken at ambient conditions. This is interesting due to the energy savings and reduction of the operating cost of production.

3. In lipase catalyzed transesterification of methanol and both *Candlenut* and *Calodendrum capense* oil, tert-amyl alcohol was used as the reaction medium for the preparation of biodiesel. Under optimum operating conditions described in this study, a maximum biodiesel yield of 92% was obtained. Thus, it may be concluded that lipase-catalyzed promises future large scale production of biodiesel and thus promoting green chemistry.

4. The biodiesel products had comparable fuel properties with that of diesel fuel. The viscosity of biodiesel was nearer to that of diesel oil. The flash point of biodiesel slightly greater than that of standard biodiesel.

5. Blends of biodiesel with diesel up 20% for both *candlenut* and *calodendrum capense* biodiesel gave both high brake thermal efficiency and brake specific fuel consumption than commercial DF2.
6. Biodiesel blends with commercial DF2 can be used in diesel engine without major modification of the engine because most of the physicochemical properties were comparable.

7. The present analysis and engine test reveals that biodiesel from crude candlenut oil and calodendrum capense is quite suitable as an alternative to diesel oil.

8. The biodiesel will in the medium term find use as alternative fuel and diversification of the energy supply in countries with agricultural over production or with sufficient resources of land.

The following work is recommended for further study:

1. Engine performance testing using neat candlenut and calodendrum capense biodiesel (B100).

2. The long term (3 to 6 months) durability of the engine performance using biodiesel as fuel.

3. Quantification of fatty acid methyl esters using the GC and HPLC in candlenut and calodendrum capense biodiesel.
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## APPENDICES

### APPENDIX I: Kenya Bureau of Standards (KEBS) DF2 Requirements

<table>
<thead>
<tr>
<th>Serial No. Characteristics</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity @40 °C (cSt)</td>
<td>Min - 1.6</td>
</tr>
<tr>
<td></td>
<td>Max - 5.5</td>
</tr>
<tr>
<td>Copper strip corrosion, 3 h at 100 °C, max</td>
<td>1</td>
</tr>
<tr>
<td>Distillation recovery at 365 0°C, % (v/v)</td>
<td>Min - 90 End point 0°C max, 400</td>
</tr>
<tr>
<td>Density @ 20 °C, g/ml</td>
<td>Min - 0.820</td>
</tr>
<tr>
<td></td>
<td>Max - 0.870</td>
</tr>
<tr>
<td>Flash point, Pensky Martens closed cup, °C min.</td>
<td>60</td>
</tr>
<tr>
<td>ASTM, color max.</td>
<td>3.5</td>
</tr>
<tr>
<td>Cetane index (calculated) min</td>
<td>48</td>
</tr>
<tr>
<td>Cloud point, 0°C</td>
<td>Report</td>
</tr>
<tr>
<td>Cold Filter Plugging Point, CFPP, 0°C max</td>
<td>6</td>
</tr>
<tr>
<td>Cloud point - CFPP 0°C</td>
<td>12</td>
</tr>
<tr>
<td>Sediment % (m/m) max</td>
<td>0.01</td>
</tr>
<tr>
<td>Water, (v/v) max</td>
<td>0.05</td>
</tr>
<tr>
<td>Ash, % (m/m) max</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulfur content % (m/m)</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon residue conradson 10% residue, % (m/m) max</td>
<td>0.15</td>
</tr>
<tr>
<td>Neutralization value, strong acid no.; mg KOH/g</td>
<td>Nil</td>
</tr>
<tr>
<td>Total acid no.; mg KOH/g</td>
<td>0.5</td>
</tr>
</tbody>
</table>
APPENDIX II: Oil content for non-conventional oil seeds and their heating values
(Calorific values)

<table>
<thead>
<tr>
<th>oil seed</th>
<th>Heating Value (Kj/g)</th>
<th>Ratio (Relative to Diesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Afzelia cuanzensis</td>
<td>42.10</td>
<td>93.70</td>
</tr>
<tr>
<td>Annona squamosal</td>
<td>40.80</td>
<td>90.80</td>
</tr>
<tr>
<td>Areesstrum romanzofianum</td>
<td>39.60</td>
<td>88.10</td>
</tr>
<tr>
<td>Azadirachta indica</td>
<td>40.10</td>
<td>89.20</td>
</tr>
<tr>
<td>Balnnites aegyiaca</td>
<td>40.80</td>
<td>90.70</td>
</tr>
<tr>
<td>Bauhinia purpulea</td>
<td>39.90</td>
<td>88.70</td>
</tr>
<tr>
<td>Caesalpenia decapetala</td>
<td>41.50</td>
<td>92.40</td>
</tr>
<tr>
<td><strong>Calodendrum capense</strong></td>
<td>40.80</td>
<td>90.80</td>
</tr>
<tr>
<td>Citrullus vulgaris</td>
<td>39.40</td>
<td>87.50</td>
</tr>
<tr>
<td>Craibbia ellioti</td>
<td>39.60</td>
<td>88.10</td>
</tr>
<tr>
<td>Croton megalocarpus</td>
<td>37.60</td>
<td>83.60</td>
</tr>
<tr>
<td>Cucumis spp</td>
<td>40.30</td>
<td>89.70</td>
</tr>
<tr>
<td>Cupresssus lusitanica</td>
<td>39.30</td>
<td>88.80</td>
</tr>
<tr>
<td>Erythrina abysinnica</td>
<td>39.20</td>
<td>87.30</td>
</tr>
<tr>
<td>Passiflora edulis</td>
<td>40.70</td>
<td>90.60</td>
</tr>
<tr>
<td>Sesamum indica</td>
<td>40.80</td>
<td>90.70</td>
</tr>
<tr>
<td>Sterulia Africana</td>
<td>40.00</td>
<td>88.90</td>
</tr>
<tr>
<td>Jatropha curcas</td>
<td>31.50</td>
<td>91.35</td>
</tr>
</tbody>
</table>

Source: Munavu and Odhiambo 1984
### Appendix III: Density, Viscosity and Iodine values of some non-conventional oil seeds

<table>
<thead>
<tr>
<th>Oil seed</th>
<th>Density, g/ml (25 °C)</th>
<th>Kinematic viscosity (cSt)</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia podalynifolia</td>
<td>0.9250</td>
<td>54.3</td>
<td>116</td>
</tr>
<tr>
<td>Afzelia cuanzensis</td>
<td>0.9175</td>
<td>40.5</td>
<td>101</td>
</tr>
<tr>
<td>Annona squamosal</td>
<td>0.9190</td>
<td>55.4</td>
<td>84</td>
</tr>
<tr>
<td>Arecastrum romanzofianum</td>
<td>0.8715</td>
<td>22.2</td>
<td>35</td>
</tr>
<tr>
<td>Azadirachta indica</td>
<td>0.8890</td>
<td>20.6</td>
<td>61</td>
</tr>
<tr>
<td>Balanites aegyptica</td>
<td>0.9050</td>
<td>43.6</td>
<td>79</td>
</tr>
<tr>
<td>Bauhinia purpurea</td>
<td>0.9495</td>
<td>24.6</td>
<td>105</td>
</tr>
<tr>
<td>Caesalpenia decacetala</td>
<td>0.9825</td>
<td>55.1</td>
<td>108</td>
</tr>
<tr>
<td><strong>Calodendrum capense</strong></td>
<td>0.8764</td>
<td>28.1</td>
<td>102</td>
</tr>
<tr>
<td>Craibbia ellioti</td>
<td>0.8900</td>
<td>29.6</td>
<td>148</td>
</tr>
<tr>
<td>Citrus sinsensis</td>
<td>0.9100</td>
<td>29.4</td>
<td>38</td>
</tr>
<tr>
<td>Croton megalocarpus</td>
<td>0.8756</td>
<td>29.7</td>
<td>133</td>
</tr>
<tr>
<td>Erythrina abyssinica</td>
<td>0.8565</td>
<td>23.6</td>
<td>66</td>
</tr>
<tr>
<td>Erythrina lystemon</td>
<td>0.9470</td>
<td>46.6</td>
<td>85</td>
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<tr>
<td>Jatropha curcas</td>
<td>0.9135</td>
<td>31.5</td>
<td>92</td>
</tr>
<tr>
<td>Macadamia ternifolia</td>
<td>0.9170</td>
<td>20.6</td>
<td>81</td>
</tr>
<tr>
<td>Passiflora edulis</td>
<td>0.9165</td>
<td>18.8</td>
<td>127</td>
</tr>
<tr>
<td>Sterculia Africana</td>
<td>0.9210</td>
<td>18.8</td>
<td>118</td>
</tr>
</tbody>
</table>

Source: Munavu and Odhiambo 1984
Appendix IV: Water viscosity and density

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density (g/ml)</th>
<th>Viscosity (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.99919</td>
<td>1.1390</td>
</tr>
<tr>
<td>20</td>
<td>0.99823</td>
<td>1.0087</td>
</tr>
<tr>
<td>25</td>
<td>0.99713</td>
<td>0.8910</td>
</tr>
<tr>
<td>30</td>
<td>0.99567</td>
<td>0.8004</td>
</tr>
<tr>
<td>35</td>
<td>0.99408</td>
<td>0.7200</td>
</tr>
<tr>
<td>40</td>
<td>0.99224</td>
<td>0.6536</td>
</tr>
<tr>
<td>45</td>
<td>0.99022</td>
<td>0.5960</td>
</tr>
<tr>
<td>50</td>
<td>0.98807</td>
<td>0.5492</td>
</tr>
<tr>
<td>55</td>
<td>0.98565</td>
<td>0.5040</td>
</tr>
<tr>
<td>60</td>
<td>0.98324</td>
<td>0.4699</td>
</tr>
</tbody>
</table>