DEVELOPMENT OF SOLID CATALYST FOR TRANSESTERIFICATION OF CROTON MEGALOCARPUS HUTCH OIL IN BIODIESEL PRODUCTION AND BLENDING WITH KEROSENE

By

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Dedication

To my parents who supported me when I confronted setbacks encouraged me when I felt hesitant and depressed, and guided me when I could not make up my mind. It is their patience; unconditional love and support that helped me go through the difficult periods of my life journey, follow my interests and fulfill my dreams.
Acknowledgement

I would like to express my sincere gratitude to my advisor and my supervisors Dr. Jacob Kithinji and Prof. Geoffrey Kamau for guiding and supervising this research with a lot of dedication and who made me realize the fascination and meaning of chemistry, with their wisdom, intelligence and selflessness.

I would like to extend my gratitude to my friends and colleagues for their help and support, especially technicians Ms. Rose Mutungi and Mr. Kimega of the Physical Chemistry laboratory of University of Nairobi (UoN), Mr. Keter of Government Chemist labs, Mr. Oguna KIRDI research labs and Mr. Cheseto of ICIPE.
ABSTRACT

The accelerating and frequently fluctuating price of conventional diesel, together with growing environmental concerns has sparked renewed attention on the search for alternative fuel. The awareness of the toxic effects related to the tailpipe emissions of vehicle has driven many countries to look for a less-polluted transportation fuel.

In this regard, biodiesel (alkyl esters) from vegetable oils or animal fats via transesterification is a catalyzed process and, traditionally, homogenous catalysts are employed. However, this type of catalyst is not able to be re-used and requires tedious washing and separating steps, hence, stimulating the conception of heterogeneous-catalyzed transesterification.

Despite the success of various heterogeneous catalysts, many are not viable for wide industrial usage as most of the catalysts are expensive and need additional preparation effort. Among them CaO seems to have a promising place and the increasing research on CaO is self-evidence of its capability in catalyzing the reaction.

Therefore, in this research CaO obtained from eggshell is employed as a catalyst in carrying out transesterification of Croton Megalocarpus Hutch oil and methanol. Methyl esters obtained were characterized by FT-IR and GC–MS and further tested for fuel properties with kerosene blend.

The results showed methyl hexadecanoate and methyl octadecanoate were common fatty acids esters both in CaO and KOH catalyzed reactions. Total unsaturation was highest for *Croton* ester with 68.0%. The esters viscosities at 40 °C were in the range of 4.16 - 4.63 mm²/s. Croton Megalocarpus esters were found to be less volatile than kerosene fuel.
The density of the croton methyl ester was found to be higher than that of kerosene and automotive diesel. The heating value of the esters was lower compared to kerosene and diesel.

The esters of Croton Megalocarpus Hutch were further blended with kerosene in ranges of 5-10% on volume to volume ratio. Blend of 10% biodiesel in 90% kerosene demonstrated the most ideal properties with viscosity, density same as that of kerosene. The methyl esters were further tested in a multi-wick stove following standard water boiling test (WBT) and their performance in terms of time to boil, heat transfer efficiency, power output, specific fuel consumption CO, CO_2 and particulate matter emissions.

The esters burnt with odorless and non-pungent smell. Biodiesel blends took more time to boil and consumed more fuel by weight, than kerosene to boil 2.5 liters of water. Heat transfer efficiency for esters was lower than for kerosene during boiling phase while specific consumption for the esters was higher than kerosene. Biodiesel blends produced more particulate matter and CO_2 compared to kerosene, while CO was higher in kerosene than biodiesel blends.
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<tr>
<td>AOCS</td>
<td>American oil chemists’ society</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>AV</td>
<td>Acid value</td>
</tr>
<tr>
<td>B0</td>
<td>Pure kerosene</td>
</tr>
<tr>
<td>B10</td>
<td>Blend of 5% biodiesel in 95% kerosene fuel</td>
</tr>
<tr>
<td>B100</td>
<td>Pure biodiesel fuel</td>
</tr>
<tr>
<td>B5</td>
<td>Blend of 5% biodiesel in 95% kerosene fuel</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acid methyl esters</td>
</tr>
<tr>
<td>GC – MS</td>
<td>Gas chromatography Mass spectroscopy</td>
</tr>
<tr>
<td>IV</td>
<td>Iodine value</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>ME</td>
<td>Methyl ester</td>
</tr>
<tr>
<td>SV</td>
<td>Saponification value</td>
</tr>
<tr>
<td>WBT</td>
<td>Water boiling test</td>
</tr>
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</table>
1.0 Introduction

Globally, estimated 500 million households still use fuels, particularly kerosene, for cooking, lighting, and heating are the main household services provided by kerosene [EAN, 2000], although there are kerosene refrigerators and other appliances in some areas. Kerosene heating is not widespread in temperate or highland areas of developing countries, mainly because of cost. Where heating fuel is needed, biomass or coal is usually used because it is cheaper or readily available.

Portable kerosene room heaters are used primarily in developed countries, and some developing countries, although many countries have either prohibited or discouraged their use, particularly because of the risk of carbon monoxide (CO) poisoning [Long, 1997].

Kerosene cooking is widespread in many developing countries, especially in urban populations, where biomass needs to be purchased, and electricity and LPG are expensive or unreliable [Schweres, 2004]. There are many kerosene stove designs, but they can be broadly categorized into two broad types depending on how the fuel is burned-wick stoves, which rely on capillary transfer of fuel, and the more efficient and hotter burning pressure stoves with vapor-jet nozzles that aerosolize the fuel using manual pumping or heat. In low-income households, wick stoves are more commonly used, because they are cheaper, and easily provide simmer heat for some staple foods, and moreover they have no nozzles that can get clogged by soot.

Use of kerosene as a lighting fuel—either in wick lamps or brighter burning (but less common) pressure lamps—is common in some developing countries, particularly in regions where electricity supply is unaffordable, unreliable, or unavailable. An estimated one-fifth of
the global population (approximately 1.3 billion) in 2009 lacked access to electricity, while an even greater but unknown number had only intermittent access [IEA, 2011].

Detailed data on the source or frequency of lighting in houses are not as commonly collected as cooking fuel data in household surveys; however, fuel-based lighting is widely used in India and much of Africa [DGDA, 2010].

In India, in 2004–2005, an estimated one in three households reported kerosene as their primary source of lighting, 44.4% of rural and 7.1% of urban households [NSSO, 2007]. In the lowest four socioeconomic deciles of India, 60% of households use kerosene for lighting [Parikh, 2010].

In several of the most populated African countries, including Uganda, Ethiopia, and Kenya, more than 60% of the population relies on kerosene as the primary lighting fuel [Apple et al., 2010; IFC/WB, 2008a; Uganda Bureau of Statistics, 2010]. Less is known of the quantity of kerosene used for lighting, since it is often difficult to differentiate kerosene used for lighting from that used for other purposes, particularly cooking.

Based on existing surveys, reports, and local correspondence from 23 countries, monthly consumption has been reported to vary between 1 and 10 L per household [Mills, 2005]. These estimates may include the use of kerosene to illuminate businesses as well as residences, which would imply that the higher end of this scale is an overestimate. Recognition of the potential welfare benefits resulting from cleaner and more effective lighting technology has led to several large-scale government and private sector efforts to develop and disseminate solar lighting appliances in India and Africa [DGDA, 2010; Palit and Singh, 2011].
There is thus a dire need to invest in alternative, renewable and sustainable energy source. Biodiesel represents a viable and available alternative use for internal combustion engines as well as replacement for kerosene for cooking purposes. Kenya has potential for production of oil from local oil crops which are well adapted to the harsh agro-ecological zones which constitute about 80% of the total landmass [Kalua, 2008].

Relative to petroleum emissions, biodiesel emissions have been shown to contain less particulate matter, carbon monoxide, and polycyclic aromatic hydrocarbons (PAH) as shown on table 1.1 [Graboski et al., 2003; McDonald and Spears, 1997; Sharp et al., 2000] furthermore, sulfur-containing compounds appear to be undetectable. However, the combustion of biodiesel in a diesel engine typically does increase the release in nitrogen oxides, which, in addition to inducing potential health effects itself, have been identified as an ozone precursor. Additionally, despite the reduction in a total mass of particulate matter, the soluble organic fraction of the emitted particles is commonly a greater percentage of biodiesel exhaust emissions while a smaller percentage of insoluble mass is present relative to petroleum diesel soot [Durbin et al., 1999]. One researcher has demonstrated a 30% decrease in particulate emissions with use of 100% biodiesel, but the soluble organic fraction increased by roughly 40% [Sharp, 1998]. This smaller production of particles with a greater concentration of soluble organic fraction may impact the biological effects and toxicity of biodiesel exhaust particles. The US EPA has enacted a series of emission standards for various on road and non-road diesel engine types. This emission standards are already in place and are being enforced [US EPA, 2004d]. These standards are intended to reduce specific components of diesel exhaust (i.e., NOx and PM concentrations) through various strategies such as decreased fuel sulfur content and particle traps; however it is unclear how much decrease (if any) will be observed for many gas phase components derived from petroleum and biodiesel combustion.
The US EPA in 2002 released a draft technical report [EPA 420-P-02-001] of a comprehensive analysis of the emission impacts of biodiesel using publicly available data [US EPA, 2002a]. Statistical regression analysis correlated the concentration of biodiesel in mixtures of conventional diesel fuel with changes in regulated and unregulated pollutants emitted from on-road heavy-duty diesel engines. A selection of Mobile Source Air Toxics (MSAT) were included in the analysis of biodiesel’s effects on emission and are referred to as the Aggregated Toxics” (i.e., acetaldehyde, acrolein, benzene, 1, 3-butadiene, ethylbenzene, n-hexane, naphthalene, styrene, toluene, and xylene); most are currently unregulated.

Biodiesel production in USA increased significantly from 1999 to 2005 (Figure 1.1), demonstrating the interest in this renewable energy approved.

The cultivation and eventual processing of biodiesel in Kenya will not only offer the liquid fuel supply security but will also reclaim the already degraded landmass.

![Figure 1.1: Estimated US Biodiesel Production per year.](image)

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; Hess et al., 2005; Hess et al., 2007; Lapuerta et al., 2008; Song et al., 2002]. 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 matters, SOx and HC. 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 NOx emissions increased by 12% because oxygen in the fuel increases the combustion temperature. To overcome the increase of NOx 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 NOx emissions. In addition, they showed that NOx 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
The results of a study conducted by the EPA on the emissions produced by biodiesel show that except for nitrogen oxides (NOx), regulated and non-regulated emissions from both B100 (100% biodiesel) and B20 (20% biodiesel) are significantly lower than for conventional petroleum based diesel (Table 1.1). where the negative (-) indicates how much emissions is saved by using of a biodiesel blend or in pure form, whereas (+) indicates the additional emissions generated as a result of using biodiesel.

**Table 1.1: Average Biodiesel (B100 and B20) Emissions Compared to Conventional Diesel**

<table>
<thead>
<tr>
<th>Emission Type</th>
<th>B100</th>
<th>B20</th>
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<tbody>
<tr>
<td>Total Unburned Hydrocarbons</td>
<td>-67%</td>
<td>-20%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>-48%</td>
<td>-12%</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>-47%</td>
<td>-12%</td>
</tr>
<tr>
<td>NOx</td>
<td>+10%</td>
<td>+2% to -2%</td>
</tr>
<tr>
<td>Sulfates</td>
<td>-100%</td>
<td>-20%a</td>
</tr>
<tr>
<td>PAH (Polycyclic Aromatic Hydrocarbons)b</td>
<td>-80%</td>
<td>-13%</td>
</tr>
<tr>
<td>nPAH (nitrated PAH’s)c</td>
<td>-90%</td>
<td>-50%c</td>
</tr>
<tr>
<td>Ozone potential of speciated HC</td>
<td>-50%</td>
<td>-10%</td>
</tr>
</tbody>
</table>
1.1 Biodiesel Definition

Biodiesel is defined as the mono alkyl esters (such as methyl and ethyl esters) of long chain fatty acids derived from vegetable oils or animal fats, for use in compression-ignition (diesel) engines [Van Gerpen et al., 2002]. Biodiesel is prepared via catalytic reaction between triglycerides and alcohol. The reaction involves the breakage of the glycerol structure and exchanges of alkyl group between the alcohol and ester part of the triglyceride molecule.

\[
\begin{align*}
\text{Triglyceride} & \rightarrow \text{Fatty Esters} + \text{Glycerol} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_1 & \quad \text{CH}_2 - \text{O} - \text{C} - \text{R}_1 \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_2 + 3 \text{CH}_3\text{OH} \quad \overset{\text{Catalyst}}{\rightarrow} \quad \text{CH}_2 - \text{O} - \text{C} - \text{R}_2 + \text{CH}_3\text{OH} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_3 & \quad \text{CH}_2 - \text{OH}
\end{align*}
\]

1.2 Alternative Energy World

The energy sector in Kenya is dominated by biomass fuel with charcoal and wood fuel accounting for more than 68% of the national consumption [Kalua, 2008]. Petroleum, the largest government investment, provides 22% while electric power generated through geothermal and hydro power projects accounts for 10% total energy needs. Hydro power, however, raises worries which stems from the perennial droughts that often lead to power outages. Solar power which could provide another viable source of energy remains way too expensive for ordinary Kenyans, half of whom live on less than a dollar a day. Currently, a PhotoVoltaic (P.V.) solar panel cost US $250. The use of solar energy cannot thus be emphasized at this time. Wind energy in the country remains almost untapped despite Kenya’s land mass being 80% arid and semi-arid with fierce winds blowing [Schweres, 2004]. There is no accurate data as yet on the exact potential and risks if any involved in production of wind energy.
Renewable energy will thus take the agricultural path opting for bio-fuel. The selection of an appropriate crop or mix of crops for the production of feedstock oil and the location of biodiesel production units are critical factors in developing a sustainable production system [Wilson et al., 2005]. Key considerations should ensure that the expansion of the sector does not lead to further deforestation. The crop of choice should not compete for water resources or land used to grow food crops and sustain wildlife resources, otherwise development goals of biodiesel production will be lost. The use of already existing food based products like soya and maize particularly in a continent like Africa where there is a dire need for food is also unreasonable. Assessment of the fuel properties of Croton Megalocarpus Hutch plant oil derivatives has therefore been undertaken to establish their viability as a substitute to kerosene for domestic applications.

The production of biodiesel may cut down by a small percentage the ever increasing use of petrol (Figure 1.2).

Figure 1.2: World petroleum consumption between years 1960 to 2007.
1.3 The Process of Making Biodiesel

A number of methods have been considered in biodiesel production from oils of vegetable and animal origin. The essence being to reduce the high viscosity of the oils, among the most practiced methods are: blending with diesel fuel [Schwab et al., 1987], micro emulsions with short chain alcohols, thermal cracking (pyrolysis) and transesterification [Fungrai and Milford, 1999]. Transesterification has been reported as the most practical because the physical characteristics of fatty acid esters (biodiesel) produced are very close to those of diesel fuels. The process is also relatively simple [Fukuda et al., 2001]. The lower alkyl esters can be burned directly in unmodified diesel engines and common wick stove with very low deposit formation [Mittelbach and Tritthart, 1988]. Several types of vegetable oils with diversified composition of fatty acids may be used for preparation of biodiesel. Soya beans, rapeseed, sunflower and palm oil are the most studied. However, there is no technical restriction to the use of other types of vegetable oils. Considering the type of alcohol, methanol is better as it allows the simultaneous separation of glycerol [Demirbas, 2005].

1.4 History of Biodiesel

Industrial use of biofuels started around 1880s. The first public demonstration of operation of a diesel engine was seen in the exhibition of Paris in 1898 using peanut oil as fuel [Shay, 1993]. The inventor, Rudolph Diesel, thought that the future of this engine (in contrast with those of steam at the time) would be connected to use of fuel coming from biomass. This situation changed in the 1920’s, when diesel engine manufacturers altered their engines to utilize the lower viscosity of the fossil fuel (petro diesel) rather than vegetable oil. The petroleum industries were able to advance in fuel markets because their fuel was much cheaper to produce than the biomass alternatives. The result was, for many years, a near elimination of the biomass fuel production infrastructure. The Present environmental impact
concerns and a decreasing oil deposits have made biomass fuels such as biodiesel a growing alternative [Hatcher, 2004].

1.5 Current Situation on Biodiesel in Kenya

Development of biodiesel in Kenya from locally grown plants has received high-level government attention as a result of the continued increases in the cost of fossil fuels and the increased environmental awareness regarding over reliance on wood fuel in Kenyan homes. This attention resulted in the formation of the National Biodiesel Committee under the Ministry of Energy, provided by the Energy Act (2006) [Kalua, 2008].

The committee, which is composed of government officials, stakeholders in research institutions, the private sector and non-government organization, is currently deliberating on the framework of policy issues such as blending mandate, tax mandate, production and subsidies. The committee has put much emphasis on promotion of *Jatropha curcas* oil for sustainable biodiesel production in the country, claiming benefits of energy security, climate change mitigation and rural development [Tomomastu and Swallow, 2007]. While this is going on, researchers in universities and other institutions are engaged in laboratory research on appropriate technical aspects of production and analysis biodiesel fuel. This formed a basis for the choice of this research project.

1.6 Statement of the Problem

Kenya is an energy intensive country, and energy is a key pillar to achieving vision 2030. The high and steadily growing use of conventional fossil fuel energy is less and less compatible with the notion of sustainable development that promotes durable, safe and environmentally friendly sources of energy. A strong rise in the use of renewable energy is thus inevitable. Vegetable oils may provide such an alternative.
1.7 Justification

Kenya, like many other developing countries continues to import petroleum products which accounts for over 40% of foreign exchange. Out of the total petroleum imports, 60% goes to diesel fuel oil [MPND, 2005]. This coupled with diminishing fossil fuel resources, as witnessed by escalating oil prices and environmental problems associated with use of fossil fuel, drives the country to slowly shift from dependence on petrol kerosene fuel to biodiesel alternative [Mittelbach, 2005].

Biodiesel industry will create employment and reduce poverty to the rural poor families which constitute 80% women and youth. In implementing its energy policies, the government also hopes to protect the environment. Biodiesel is a clean burning and biodegradable fuel compared to petroleum kerosene [Bowman et al., 2006]. Use of biodiesel will reduce greenhouse gas emissions, monitor environmental degradation and improve general population health. Extraction of vegetable oils from which biodiesel is processed produces a dry high protein meal by-product which if correctly processed is a most valuable stock feed or organic fertilizer. In addition, glycerin a core product of transesterification has both medicinal and industrial applications [Hori et al., 2005].

An immediate need for any research focused on biodiesel exhaust production and collection of sufficient quantities of exhaust material to be shared by researchers. There are investigators who have isolated various extracts of biodiesel exhaust; these emission extracts have used widely divergent engines, conditions of running, fuels, fuel additives, and after treatments. Frequently, they are generated in quantities of milligrams or less. Under these circumstances, there are limits to both the endpoints that can be examined and the reproducibility of studies. Furthermore, it is unclear how applicable the results of any single study would be to the field.
1.8 Objectives

This study was designed to investigate the performance of eggshell as a source of CaO to be used as a heterogeneous catalyst, in transesterification of Croton Megalocarpus Hutch oil in biodiesel production and investigate its suitability as a substitute for kerosene in domestic stoves under the following objectives:

1. To study the oil properties of the oil extract.

2. To prepare biodiesel by transesterification of the extracted oil catalyzed by a heterogeneous catalyst sourced from egg shells and base catalyst and compare the yields.

3. To determine the physical and chemical properties of Croton megalocarpus methyl esters.

4. To carry out a comparison of the biodiesel parameters with those of conventional kerosene fuel and of the kerosene blends.

5. To test the performance of common kerosene wick stove fuelled by the kerosene blends for cooking applications by water boiling test performance.

6. Determine the emissions produced during water boiling tests test performance.
CHAPTER TWO

2.0 Literature review

This chapter gives the general background of plant studied; the transesterification reaction used in the preparation of the biodiesel, analytical and fuels parameters used in characterization of the fuels.

2.1. Croton Megalocarpus Hutch

Croton Megalocarpus Hutch tree is a member of Euphorbiaceae family. Figure 2.1 below shows a mature Croton Megalocarpus Hutch tree. The tree can be found in natural forests margins or as a canopy tree. *C.megalocarpus* is indigenous to East Africa, and has been widely grown in mountainous regions as ornamental for generations. It’s believed the center of its endemism is the Aberdare Mountains of Kenya. It occurs in tropical East Africa, with an altitude range of 1,400 m to 2,300 m; it is mainly planted as a shade tree in coffee plantations [Chudnoff, 1984]. The fruit of *C.megalocarpus hutch* contains 3 ellipsoid ovaid or oblong ellipsoid seeds 2.2-3.4 cm long and 1.2-1.4 cm wide. The tree produces up to 50kgs of seeds and a hectare produces 5-10 tonnes of seeds per year [Makayoto, 1985]. East African *C. megalocarpus* seed has been reported to yield 49% oil which is hemolytic and purgative, of which 78% is octadeca-9,12-dienocic acid (C18:2) [Munavu, 1983].

Figure 2.2 shows mature fruits of *Croton megalocarpus* plant. The plant simply drops its seed pods when they become ripe, over the course of just a few weeks. These can be caught in inverted “umbrellas,” or more simply raked together and picked up. The highly unsaturated oil can be used as drying oil in paint formulations and as fuel since it is similar to sunflower oil, which has been shown to be suitable diesel substitute [Antolin *et al.*, 2002]. *Croton* seed contains carcinogenic fatty acid esters of phorbol, and poisonous alkaloids.
For this reason, use of oil or cake in diet of animal feed is not healthy. The high nitrogen content of kernel cake indicates it can be useful as organic fertilizer [Munavu, 1983b].

2.2. Transesterification of Vegetable Oil

Transesterification describes important class of organic reactions where an ester is transformed into another through interchange of alkoxy moiety. Triglyceride reacts with an alcohol in presence of a strong acid or base catalyst producing a mixture of fatty acid alkyl esters (Biodiesel) and glycerol, as shown in Equation 2.1 below.

\[
\text{CH}_2 - \text{O} - \text{C} - \text{R}_1 \quad \text{O} \quad \text{CH}_2 - \text{O} - \text{C} - \text{R}_1 \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_2 + 3 \text{CH}_3\text{OH} \quad \rightarrow \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_2 + \text{CH}_2 - \text{OH} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_3 \quad \text{O} \quad \text{CH}_2 - \text{OH}
\]

Equation 2.1: Transesterification reaction

The reaction is typically catalyzed by strong acids or bases and is an important step in the production of biodiesel.
The overall process is a sequence of three consecutive and reversible reactions, in which diglyceride and monoglyceride are formed as intermediate, [Freedman et al., 1986]. The transesterification reaction involves catalytic reaction between triglyceride and alcohol (e.g., methanol, ethanol, propanol and butanol) to form biodiesel (FAMEs) and glycerol. In the reaction, three consecutive reactions are required to complete the transesterification of a triglyceride molecule. In the presence of acid or base, a triglyceride molecule reacts with an alcohol molecule to produce a diglyceride and FAME. Then, a diglyceride reacts with alcohol to form a monoglyceride and FAME. Finally, a monoglyceride reacts with alcohol to form FAME and glycerol. Diglyceride and monoglyceride are the intermediates in this process.

Several aspects, including the type of catalyst, alcohol to vegetable oil molar ratio, temperature, water content and free fatty acids have been singled out to have an influence on the course of transesterification [Meher et al., 2006]. Alkaline catalysis is preferred because of less corrosive nature and the fact that the reaction proceeds much faster than in acid catalyzed reaction [De Oliveira et al., 2005]. Metal hydroxides (KOH and NaOH) are used often because they are cheaper than metal alkoxides [Schuchardt et al., 1997].

2.2.1 Catalysts in transesterification

2.2.1.1 Homogeneous catalyst

Homogenous catalysts are the most preferred choice of producing biodiesel. Hydroxides and methoxide of sodium and potassium are the most common homogenous catalyst. Freedman et al., (1984) found out that 0.5% NaOCH₃ performs much better than 1% NaOH. This is understood since methoxide ions are readily available in the case of the NaOCH₃ catalyst and the latter has to react with methanol first. However, both catalysts are able to transesterify to near completion within one hour of reaction time at 60°C, much longer reaction duration (4 h) is needed for a similar performance at 32°C, as a result of this; the reaction temperature seems to have an implication in the kinetics of transesterification. Freedman et al., (1984) also noted
that acid-catalyzed transesterification is much slower compared to alkali-catalyzed reaction.

Although an acid catalyst is preferred for transesterifying feedstock with higher free fatty acid content. In such a situation, a higher temperature and pressure is often employed to speed up the reaction rate but with implication on the production cost.

2.2.1.2 Heterogeneous catalyst

The utilization of waste heterogeneous catalysts was of recent interest. The calcium carbonate obtained from most animal shells has been found to contain high levels of calcium. This shells when subjected to high temperatures as shown in figure 2.3 have shown high level of dissociation forming calcium oxide. The shells of oysters and chicken eggs shells have been evaluated as effective catalysts in converting soybean oil to methyl esters. [Nakatani et al., 2009] showed that using 25 wt of thermally activated (at 700°C) oyster shell at 6:1 MeOH: oil molar ratio, a biodiesel product with a yield of over 70% and purity of 98.4 wt% was achieved in a 5h reaction time. The conversion at a moderate 6:1 (MeOH: Oil) ratio was achieved at the expense of a higher catalysts and a longer reaction time. With 3 wt % of calcined eggshell (at 1000°C) Wei et al. [2009] transesterified soybean oil to obtain over 95% yield in a 3 hr reaction time with the following conditions; 9:1 MeOH: oil molar ratio and 65°C reaction temperature. The authors found out that the waste catalyst can be re-used up to 13 times without much loss in activity. In addition a similar catalyst potential of mud crab shells in palm olein transesterification [Boey et al., 2009].

The activated (at 900°C) crab shell was able to transesterify palm olein to 98.8 wt% purity at 5 wt% concentration with the following reaction settings; 65°C 0.5:1 MeOH: oil mass ratio and 2.5hr reaction time. The prepared methyl ester exhibited similar properties as biodiesel. Most recently waste mollusk shells (apple snail and meretrixvenus) together with eggshell
were successfully employed as a heterogeneous catalyst in palm olein transesterification [Viriya-Empikul *et al.*, 2010]. They concluded that the catalyst surface area and Ca content were responsible for the catalytical activity, which yielded 90% biodiesel in a 2 h reaction period, with the following conditions: 18:1 MeOH: oil molar ratio, 10 wt% catalyst (calcined at 800°C, 4 h) and at a reaction temperature of 60°C. It was found that eggshells exhibited the best catalytic activity followed by apple snail’s shells. Figure 2.3 illustrates the dissociation pressure and temperature of CaCO₃ as a function of temperature.

![Dissociation pressure and temperature of CaCO₃.](image)

**Figure 2.3:** Dissociation pressure and temperature of CaCO₃.

### 2.2.1.3 Mechanism of CaO in transesterification

The reaction mechanism for CaO-catalyzed transesterification has been studied by many researchers. Granados *et al.*, [2007], described in Figure 2.4, the methoxide ion that is attached to the catalyst surface attacks the carbonyl carbon of the triglyceride molecule (step 1). These results in the formation of a tetrahedral intermediate (step 2). Then the intermediate is rearranged to form a diglyceride anion and a mole of methyl ester (step 3). The charged-
anion is then stabilized by a proton from the catalyst surface to form diglyceride and at the same time regenerates the catalyst. The cycle continues until all three carbonyl centres of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters. Calcium diglyceroxide, a compound formed from the reaction between calcium oxide and glycerol, has also been recognized as a catalyst [Gryglewicz, 1999].

Figure 2.4: Reaction Mechanism of transesterification.

2.2.1.4 Catalyst leaching

As far as solid catalysts are concerned, catalyst active species leaching into the reaction media is always the prime concern. The extent of the catalyst leachability is the yardstick for the solid catalysts practical usage as well as their ability to be reused. For the case of CaO, past results indicate that it has a considerably low leaching property and lower (0.035%) solubility in methanol [Gryglewicz, 1999]. A work by Granados et al. [2007] revealed that the contribution of CaO heterogeneity is more crucial and relevant to obtain a higher yield. For reutilization of the catalyst, the leaching of CaO was not so intense (able to be reused eight times with a yield ranging from 81 to 73%), as long as a sufficient amount of catalyst is
employed in each re-use. Arzamendi et al. [2008] found that for a 7.3 hr reaction period, 25% CaO was dissolved at 50% conversion versus 30% for 100% conversion after a 10 h reaction duration. In another related study [Kouzu et al., 2009], a 10.5% soluble substance was found in 2 h for the first reaction and for subsequent re-uses, the amount reduced drastically to around 4%. It is worth noting here that at a 0.5 h reaction time; only 2.6% catalyst was soluble. However, the authors reported that the soluble substance could be removed completely using cation-exchange resin. Comparing the leaching data in these works, it can be deduced that the intense of active species leaching is proportionate with the reaction time, hence, reaction conditions with a shorter catalyst residing time could be the possible solution, of course, without compensating the purity and yield of the final product. In general, although there is CaO lixiviation into reaction media, the heterogeneity of CaO still plays a dominant role over the homogeneity route and by controlling the reaction duration, the degree of catalyst leaching can be further minimized.

2.3 Fuel combustion

Fuel combustion process occurs when a hydrocarbon fuel, chosen for its ability to auto-ignite, is injected into a volume of air that has been compressed to a high temperature and pressure. An alternative fuel may be judged by the ability to meet the requirements of diesel fuel as far as combustion in the engine is concerned. The fuel should not deviate from the engine design specification. The fuel should ignite in the engine and release energy when it burns as per energy demand of the engine and allow the operability of engine even at low temperatures such as winter [Dunn, 2003]. The fuel should not corrode the engine, plug the orifices or cause wear. Environmentally, the fuel should not cause excessive pollution and should be safe to handle.
2.4 Properties of Biodiesel

The American Society for Testing and Materials (ASTM) has developed specifications for biodiesel fuels [ASTM D6751].

Table 2.1: ASTM biodiesel standards

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash point</td>
<td>D93</td>
<td>130 min</td>
<td>°C</td>
</tr>
<tr>
<td>Water content</td>
<td>D2709</td>
<td>0.050 max</td>
<td>% volume</td>
</tr>
<tr>
<td>Viscosity at 40 °C</td>
<td>D445</td>
<td>1.9-6.0</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Ash content</td>
<td>D874</td>
<td>0.020 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Carbon residue</td>
<td>D4530</td>
<td>0.050 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Acid number</td>
<td>D664</td>
<td>0.800 max</td>
<td>mg KOH/g</td>
</tr>
</tbody>
</table>

2.4.1 Analytical Properties

2.4.1.1 Fourier Transform Infra red Spectrophotometer (FT-IR)

This was done to monitor the transesterification process. Infrared spectrophotometer addresses the presence of such as free and total glycerol, water, free fatty acid and residue alcohol.

2.4.1.2 Gas-chromatography (GC) analysis

The sample mixture is separated mainly by the boiling point and the structure (polarity) opponents of the individual compounds [Mittelbach, 1996]. The structure of the components and their boiling points are the major factors determining the retention time [Van Gerpen et al., 2004]. Usually, larger molecules have longer retention time in GC. When a material eluting from the column at a certain n retention time is detected, this is shown by the peak in
the chromatogram. The integrated value of the peak amplitude over time is proportional to
the amount of material causing those [Lencher et al., 1997]. This constitutes the usefulness of
GC in quantifying the amounts of components in a mixture. Compounds with known
retention times are used as standards to indicate when a compound of a specific nature can be
expected to elute. They are therefore very useful in establishing the nature of the compounds
in a mixture [Mittelbach et al., 1996].

The identity or structure is established through the (GC-MS). The spectra in MS record how a
compound is broken up into fragments by a beam of electrons energy. The way a compound
splits into fragments is characteristic of its structure [Van Gerpen et al., 2004].

2.4.1.3 Iodine value

This is the measure of total unsaturation of the fatty acid mixtures, that is, amounting ms of
iodine which can be absorbed by 100 g of fatty acid mixture taken up by double bond. The
vegetable oil sample is reacted with excess of iodine monochloride solution (Wijis reagent)
under controlled conditions. Iodine adds quantitatively to the double bonds in the unsaturated
fatty acids. Unreacted halogen is determined by titrating with sodium thiosulphate [AOCS,
1997a].

2.4.1.4 Saponification value.

Saponification value measures excess alcoholic alkali by back titration with a strong acid
expressed in mg KOH/g of sample. The saponification value thus determines the fraction of
the mixture with potassium hydroxide to form soap [Van Gerpen et al., 2004].

2.4.1.5 Acid value

Acid value measures the amount of free fatty acid in the oil [AOCS, 1997b]. The carboxyl
group of the fatty acid is reacted with a standard alkali and the results expressed in mg of
KOH necessary to neutralize the acidity of 1 g of sample.
2.4.2 Fuel properties test methods

2.4.2.1 Water content (ASTM-D95)

This test method covers the determination of water content in the range of 0 to 25% volume in petroleum products, tars, and other bituminous materials using the distillation method by dean and stark apparatus. The fuel sample to be tested is heated under reflux with petroleum ether, which co-distills with water in the sample [ASTM, 1999a]

2.4.2.2 Density (ASTM-D1298)

This test method covers the laboratory determination density using glass hydrometer. The hydrometer and its contents are placed in constant temperature bath to avoid excessive temperature variation during the test. Accurate determination of the density is necessary for the conversion of the measured volumes to volumes or masses or both, at the standard reference temperatures during custody transfers [ASTM, 1999b]

2.4.2.3 Flush point (ASTM-D93)

The flush point measures the temperature at which the test specimen forms a flammable mixture with air under controlled laboratory conditions. It is thus one of the properties which must be considered.

2.4.2.4 Color (ASTM-D1500)

This test method covers the visual determination of the color of a wide variety of petroleum products. The property is used mainly for the manufacturing control purposes and is an important quality characteristic since color is readily observed by the user of the product. In some cases the color may serve as an indication of the degree of refinement of the material. When the color range of a particular product is known, a variation outside the established range may indicate possible contamination with other products. The ASTM color standard ranges in value from 0.5 to 8.0 units [ASTM, 1998a].
2.4.2.5 Kinematic viscosity (ASTM-D445)

The viscosity of the petroleum fuels is important for estimation of optimum storage, handling and operational conditions [Knothe and Steidley, 2005]. Thus, the accurate determination of viscosity is essential to many product specifications [ASTM, 1997a]. ASTM D445 specifies the procedure for determination of the kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time for a given liquid to flow under gravity through a calibrated glass capillary viscometer.

2.4.2.6 Calorific Value

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 gross calorific value was determined using a bomb calorimeter.

2.4.2.7 Ash content (ASTM-D482)

Knowledge of the amount of ash-forming material present in a product provides information as to whether or not the product is suitable for use in a given application. Ash can result from oil or water-soluble metallic compounds or from extraneous solids such as dirt and rust [ASTM, 2000a].
The test method covers determination of ash in the range 0.001-0.18% mass from petroleum products, in which any ash-forming materials present are normally considered to be impurities or contaminants. The sample, contained in a suitable vessel is ignited and allowed to burn until only ash and carbon remain. The carbonaceous residue is reduced to an ash by heating in a muffle furnace at 775°C, cooled and weighed.

2.4.2.8 Carbon Monoxide and Carbon dioxide

The exhaust emissions of carbon monoxide (poisonous gas) from biodiesel are on average 48 percent lower than carbon monoxide emissions from diesel and kerosene [Apple et al., 2010]. The exhaust emissions of carbon dioxide affect the lungs and irritate the user.

2.4.2.9 Particulate Matter

Particulate matter (PM) is the name for a wide range of particles that are small enough to be carried by the air and therefore be breathed in by people. They can be solid or liquid, or a mixture of both. The size of particles may range from 0.005 µm to 100 µm in diameter. In comparison, the average size of a human hair is 60 µm. PM_{10} are particles that are 10 µm or less in diameter. PM_{2.5} is particles of 2.5 µm or less in diameter. The finer particles pose the greatest threat to human health because they can travel deepest into the lungs. Breathing particulate has been shown to be health hazard. The exhaust emissions of particulate matter from biodiesel are about 47 percent lower than overall particulate matter emissions from diesel [Apple et al., 2010].

2.5 Biodiesel blends

Blends of biodiesel with conventional kerosene fuel represent a common utilization of biodiesel. In the united states, B20 ( a blend of 5% biodiesel with 20% conventional diesel fuel) is recognized as a n alternative diesel fuel under criteria of The Energy Policy Act (EPACT) In France, biodiesel is utilized as a lower-level blend with conventional diesel fuel
The blends are made in volumetric percentages and designated as BX where X is the percentage of biodiesel in the blend. For example, B10 has 10% biodiesel and 90% conventional diesel. B100 is pure biodiesel.

2.6 Water boiling test (WBT)

One of the most common performance tests is the water-boiling test (WBT) where a specified quantity of water is brought to boil, and then simmered, while total fuel consumption is recorded. Performance measures include time to boil, energy efficiency, and fuel usage; emissions data can be collected concurrently. The WBT results allow for direct comparison of cook stoves.
CHAPTER THREE

3.0 Materials and methods

The following chapter describes material and procedure used in preparation and analysis of the biodiesel fuel. These include oil extraction and analysis, FT-IR and GC-MS analysis of biodiesel prepared, fuel property determination and stove testing procedures. All experiments were done in triplicates and the means and standard deviations determined.

3.1 Collection and preparation of plant and catalyst material

The Croton Megalocarpus hutch oil was purchased from an organization in Naromoru on the slopes of the Aberderes ranges. The oil was obtained from the seeds by pressing method.

3.1.1 Catalyst Preparation

The eggshell was dried at 105°C for 3 hours to remove any moisture that may be present. Then cooled and crushed using a mortar and pestle into small particles. The crushed eggshell was then calcinated at 900°C in the muffle furnace to convert them to calcium oxide, and stored in air tight flask, and then allowed to cool for 4 h [Khemthongv et al., 2012]. The product was obtained as white powder. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide (CO₂) and humidity in air before use.

3.2 Determination of moisture content

The oil sample was weighed and the mass taken as (w1), this was then dried in the oven at a temperature of 100 °C and the weight after drying was taken as (w2). The percentage moisture in the oil was then calculated using the formula % moisture content. Equation 3.1 below

\[
\text{% moisture} = \frac{w_1 - w_2}{w_1} \times 100
\]  

Where \( w_1 \) = weight of oil sample before drying
3.3 Determination of Physical and Chemical parameters of oil

Viscosity was determined using viscometer, density by hydrometer at room temperature and reflective index using a refractometer. Acid values and iodine numbers were analyzed according to standards methods of American oil chemist [AOCS, 1997a; AOCS, 1997b].

3.3.1 Iodine value

The weight of 2 g 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, [AOCS,1997a] 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 0.1 M sodium thiosulphate 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 [AOCS, 1997a]. Using Equation 3.2 below;

\[
Iodine\ value = \frac{Blank\ titre\ (ml) - sample\ titre\ (ml) \times 12.69}{weight\ of\ sample\ (gms)}
\]

Where;

\( IV = \) Iodine value, \( N = \) normality of sodium thiosulphate and 12.69 = number of grams of iodine in 0.1 M ICl (Wijis solution).
3.3.2 Saponification Value (SV)

A mass of 2 grammes of sample was weighed into a conical flask. Exactly 25 ml of potassium hydroxide (0.5 Min 95% ethanol) was added. To the flask, a reflux condenser was attached and the sample heated for one hour on a hot plate magnetic stirrer while stirring gently. Phenolphthalein indicator was added to the sample, while still hot, and then titrated against 0.5 M HCl. Average volume obtained from triplicate of experiments was recorded as Titre = a ml. blanks were run at the same time and average volume obtained recorded as titre= b ml. Saponification value was calculated from Equation 3.3 [Van Gerpen et al., 2004].

\[
SV = \frac{(b-a) \times 28.05}{\text{sample weight in grams}}
\]

Where; \( SV \) = saponification value and 28.05 = grams KOH in 0.5 M KOH solution

\[
SV = \frac{(b-a) \times 28.05}{\text{sample weight in grams}}
\]

Equation 3.3

3.3.3 Acid Value (AV)

The acid value is defined as the amount of milligrams of KOH required to neutralize the free acidity in one gram of the oil sample. A volume of 50 ml diethyl ether was mixed with ethanol (95%) and 1 ml of phenolphthalein solution. Exactly 2 g of oil sample was dissolved in the mixture and titrated with 0.1 M NaOH while shaking constantly until a pink color persisted for at least 15 seconds [AOCS, 1997b]. Acid value was calculated from Equation 3.4.

\[
Av = \frac{\text{titre volume} \times 4.0}{\text{sample weight in grams}}
\]

Where;

\( Av \) = acid value, titre volume = volume of NaOH used to neutralize the oil sample and 4.0 = number of grams NaOH in 0.1 M NaOH solution.
3.3.4 Calorific Value

Approximately 0.8 g of fuel sample was weighed in the bomb crucible. The bomb cup was placed on its stand provided with the outfit. Firing nickel wire piece was stretched between the electrodes of the bomb. A winking cotton tread, 9 cm long tied to the stretched wire and the end dipped inside the sample in the crucible. The crucible was placed in the support ring. 1 ml of distilled water was pippeted out into the body of the bomb and the filled with 3.0×106 N/M$^2$ of oxygen gas. Calorimeter can was filled with distilled water until the bomb was submerged completely. The bomb was placed on the three supports in the calorimeter vessel and checked for leakage. Cooling water was adjusted to flow at slower rate. Cover of the water jacket with thermometer and stirrer were lowered and circuit completed by firing circuit test plug. The temperature of the vessel was allowed to stabilize and the initial temperature taken at 0.001°C, the fire was then pressed for 2 seconds to ignite the sample. Satisfactory firing was confirmed by failure of the test switch [Muthengia et al., 2005], the final temperature of the apparatus was taken after 10 mins. Readings were taken after every 3 mins until the readings were found to be within a range of ±0.002°C. The final temperature was recorded. Rise in temperature was calculated as a difference from initial to final temperature reading. The overall set up of the bomb calorimeter is shown in Figure 3.1. Each sample was tested three times and the average values of weight of the sample and temperature rise taken for the final determination of total hat realized from the sample. The gross heat released was calculated using Equation 3.5.

$$H = \frac{(C_v\Delta T - 0.001260)}{M}$$

where;

$H$ = calorific value, $C_v$ = heat capacity of apparatus (10.38 J/°C) and 0.12600 J = constant heat gain
3.4 Preparation of methyl esters (Biodiesel) from croton oil

3.4.1 Dehydration of Methanol

Methanol was initially dried by Lund and Bjerrum method using magnesium turnings in a reaction catalyzed by iodine [Furniss et al., 1989] as shown in Equations 3.6 and 3.7.

Equation 3: Dehydration of methanol

\[
\text{Mg} + 2\text{MeOH} \rightarrow \text{H}_2 + \text{Mg(OMe)}_2 \tag{Equation 3.6}
\]

\[
\text{Mg(OMe)}_2 + 2\text{MeOH} \rightarrow \text{Mg(OH)}_2 + 2\text{MeOH} \text{ (anhydrous)} \tag{Equation 3.7}
\]

A dry flat-bottomed flask of 250 ml capacity was fitted with a double surfaced condenser and a calcium chloride guard tube. Exactly 0.6 g of dry magnesium turnings and 0.125 g of iodine was placed in the flask followed by 10 ml of HPLC grade methanol. The mixture was heated gently until all the iodine disappeared. A further 0.06 g of iodine was added to achieve lively evolution of hydrogen. Heating was continued until all the magnesium was converted into magnesium methanoate (the contents of the flask turned milky) (Equation 3.6). A further 120 ml of the commercial methanol was immediately added and the mixture refluxed for 30 minutes. Dry methanol, (Equation 3. 7), was then distilled off directly in a bottle.
3.4.2 Titrimetric Determination of amount of catalyst

One milliliter of fresh oil was dissolved in 10 ml of isopropyl alcohol to make vegetable oil solution which was then titrated with 0.025 M KOH. The pH of oil solution was checked with a litmus paper after every millimeter of KOH solution titrated. Titration was stopped when the pH rose to between 8 and 9. 28.

The volume of KOH solution used for pH to reach 8-9 was recorded and weight of KOH required for neutralizing 1000 ml of oil calculated. This amount plus 3.5 g KOH to catalyze the reaction was the required amount for 1000 ml of oil [Pelletier, 2008].

3.4.3 Synthesis of Methyl Esters (Biodiesel)

For each sample of the oil, 150 ml was reacted with a solution of predetermined amount of CaO in 67 ml methanol (22.5 % by volume of oil) in a 250 ML quick-fit Erlenmeyer flask. A magnet rod was placed inside the flask which was then fitted with a double surfaced reflux condenser. The contents of the flask were heated in a hot plate magnetic stirrer with different fixed temperature and magnetic revolutions at 700 rpm. The mixture was stirred and refluxed for 3 hours. The solution was then left to cool to room temperature and emptied in a 500 ml capacity separating funnel and left to stand for 24 hours [Ma and Hanna, 1999]. The mixture separated into two layers, the bottom glycerol layer was drained and the crude ester layer left in the separating funnel. The ester was purified by washing gently by sprinkling 20% (v/v) warm distilled water, and then draining the water from the bottom of the separating funnel. Rinsing was repeated until the discarded wash water reached pH level of 6-7 and no soap bubbles appeared. The ester was then dried using 10% (w/v) anhydrous Na$_2$SO$_4$ and stored awaiting fuel properties analysis.
3.5 Fuel property measurement

3.5.1 Methanol test

Ester conversion from the oil was tested in methanol; based on the fact that methyl esters are quite soluble in methanol while triglyceride has a very low solubility. Exactly 27 ml of methanol was well shaken with 3 ml of the ester sample at room temperature. Absence of oily material settling at the bottom of a test tube after 20 minutes indicated complete conversion of the oil into methyl esters [Pelletier, 2008].

3.5.2 FT-IR

The FT-IR spectrum was analyzed on Perkin Elmer RXI FT-IR spectrophotometer as a thin film on KBr plate. The IR spectroscopy instrument was warmed for 1 hour. The sample oil analyzed was dried by passing through anhydrous sodium sulphate to remove traces of water so that it does not to affect the potassium bromide (KBr) plates. The plates were thoroughly cleaned using acetone. Using a syringe pipette a drop of the sample oil was placed between the two KBr plates and analyzed between ranges of 600 cm$^{-1}$ to 4000 cm$^{-1}$.

3.5.3 Gas Chromatography mass spectrometry (GC-MS) Analysis

Composition of fatty methyl esters (FAME) was analyzed with a gas chromatography mass spectrometry (GC.MS QP 2010 plus shimadzu corporation Japan equipment with ionization detector (FID) and capillary column 30 max 0.32 mm x 0.25 μm( DB wax carbowax 20 m) HP ULTRA1 (methyl silicone) high performance capillary column. The column was run in splitless mode under the following conditions: The initial temperature was 50 °C, held for 5 minutes to elute the solvent. Temperature was then increased at 3 °C per minute up to 280 °C with 20 minutes final time. Nitrogen was used as carrier gas at flow rate of 0.84 μl/minute. Calibration was performed using fatty acid methyl esters (FAME) mix in methylene chloride. The standard mixture contained FAME from C6-C20, from fully saturated to tri-unsaturated.
For each biodiesel sample, 1 μl aliquot was mixed with 100 μl of HPLC grade dichloromethane (DCM). A 6 μl injection was used for analysis in each sample [Knothe et al., 1998]. Mass spectra peak identification for methyl esters and structural formula deductions were conducted through library search by fitting the library spectrum in to the spectrum of the unknown [Demuth et al., 2003]. Each peak in the sample was compared with 4 highest ranking spectra from NIST libraries appendices in order to determine the correct identity.

3.5.4 Determination of color

ASTM color of the ester was determined following ASTMD150 procedure [ASTM1998a]. Lovibond colorimeter, consisting of light source, glass color standards, sample container housing cover, and placed in the compartment of the colorimeter through the standard glass was observed. The sample in its container was placed in the other compartment. The two containers were then covered to exclude all the exterior light. The light source was switched on and the color of sample compared with that of the standard glass containing deionized water. The test was repeated 3 times for every fuel sample, average was reported as the AST color value.

3.5.5 Kinematic Viscosity at 40°C

ASTMD445 procedure was followed in the determination of viscosity [ASTM, 1997a]. Viscosity is an important quantity in wick stoves and 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. 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 2005 a, b].

Viscosity affects the capillarity of winks and 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 and winks. 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 FAME, such as chain length, degree of unsaturation, double bond orientation, and type of ester head group. The procedure was done using cannon-fenske viscometer as shown in Figure 3. 2.

![Cannon-fenske viscometer tube](image-url)

Figure 3.2: Cannon-fenske viscometer tube.
3.5.6 Ash content

ASTMD 482 procedure was followed in determination of ash content of the methyl esters developed. Platinum crucibles were weight, the sample were mixed thoroughly to create homogeneity. Exactly 50 g of each fuel sample was weighted into a crucible, using a balance. Each sample was carefully heated in a muffle furnace until the contents ignited after achieving higher temperatures. The sample was left to burn leaving only carbonaceous residue when burning stopped. The crucible was then transferred into desiccators for further cooling to room temperature.

The contents were weighed

\[
\% \text{ Ash} = \frac{w}{W} \times 100
\]

Where; 

\( w \) = mass of the ash in grams and \( W \) = mass of the sample in grams.

3.5.7 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 \( \text{SG} = \frac{\rho}{\rho_{ref}} \). 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.

Specific gravity of methyl ester

\[
\text{density of methyl ester} \quad \frac{\text{density of water}}{\text{density of methyl ester}} = \text{Specific Gravity}
\]
3.5.8 Density Measurement

The test method, ASMD1298 was used in determination of densities using density bottle (ASM, 199B). The density bottle is of known volume, the sample of methyl ester were added into it to the mark and the mass of both empty density bottle and that of the bottle with methyl esters also measured and density determined using this formula in Equation 3.10.

\[
\text{Density of methyl esters} = \frac{(\text{mass of bottle + metylesters}) - (\text{mass of empty bottle})}{\text{volume of the density bottle}}
\]

...............Equation 3.10

3.5.9 Determination of Refractive index

Abbe type of refractometer was used with its temperature controlled to within 25±0.1°C through a thermostatically controlled water bath and motor driven water through the instrument (Ufuk et al., 2008) two drops of moisture free sample were transferred onto the prism of the refractometer. The prism was then closed and tightened firmly with the screw head. The sample was allowed to stand for 3 minutes so as the temperature to be able to be the same as that of the instrument. The instrument and the light source were adjusted to avoid parallax interference, the test button was then pressed and scale pointer for refractive index read accurately and recorded. Each sample was tested three times and average reported as the refractive index of the test sample.

3.5.10 Blending of Biodiesel Fuel with Kerosene

Blends of 5% and 10%, biodiesel fuels of croton with kerosene were prepared in 500 ml lots, on a volumetric basis measured by graduated measuring cylinders. The fuels were manually agitated for 10 minutes to obtain a uniform mixture.
As the biodiesel and the stock fuels have different colors, the uniform color of the blended fuel was used as an indication of thorough mixing. Samples of the blends were analyzed for fuel parameters in comparison with pure biodiesel and unblended automotive diesel.

3.5.11 Water Boiling Test (WBT)

Stove performance indicators were tested by determining the quantity of water that was turned to water vapor by a given quantity of fuel within a given duration of time, in a standard water boiling test(WBT) version 3.0 [Baillis, et al., 2007]. The test compared the ester fuel against kerosene fuel. A multi wink (8) kerosene stove was used for each fuel tested.

Aluminum pot of a determined weight was used and capacity of 2.5 liters was used for each fuel. The stove was fitted with new winks of particular length and diameter, the stove weight was determined using electronic balance. The stove tank was filled with 500 ml of test fuel and total weight of stove plus fuel determined to ±1 g, 30 minutes duration was allowed for the new winks to draw fuel.

During high power (cold start), 2.5 liters of cold clean water was weighed and poured into the pot. The ambient air and initial water temperatures were recorded. The water was heated to boiling with temperature changes being recorded after every minute using a thermometer probe positioned in the center of the pot, roughly 2 cm above the pot bottom [Baillis, et al., 2007]. Fire was put off after boiling and the weight of water evaporated and the mass of the fuel consumed determined (a wooden ply wood was used to protect the balance from the heat). For each fuel triplicates of experiments were performed and mean values recorded.

High power (hot start) followed after test while stove was still hot. Time taken and fuel consumed to boil 2.5 liters of cold water was recorded. Low power (simmering) phase followed after the second test while the stove and the water in the pot were still hot. The
boiled water remaining from the second phase was returned to the stove for simmering lasting 45 minutes. The fire was controlled by varying the wink heights to keep the water 2-3 °C below the boiling point. Fire was put out after the 45 minutes and water vaporized and the fuel consumed determined. This test was repeated three times for each fuel sample. The setting was as shown on Figure 3.3 below.

Figure 3.3: Water Boiling Test in progress.

3.5.12 Calculation of stove performance indicators

Calculation was performed on the water boiling revised calculation procedure [Bailis et al., 2007].

3.5.12.1 Thermal Transfer Efficiency

This is the ratio of the work done by heating and evaporating water to the energy consumed by burning the fuel. It is calculated using Equation 3.11 [Bailis et al., 2007].

\[
\eta_c = \frac{(4.186 \times M_1 \times \Delta T) + (2260 \times M_2)}{m \times C_v}
\]

Equation 3.11

where; \( \eta_c \) = thermal transfer efficiency, \( M_1 \) = the mass (g) of water in the pot, 4.186 J/g °C = the specific heat capacity of water, \( \Delta T \) = change in water temperature in °C, \( M_2 \) = mass in (g) of water evaporated from the pot, 2260 J/g = latent heat of evaporation of water, \( m \) = the mass (g) of fuel consumed during test phase of the test, \( C_v \) = the calorific value of the sample (J/g).
3.5.12.2 Burning rate (Rc)

This is the measure of fuel consumption while bringing water to boil. It was calculated by dividing the equivalent fuel consumed by the time of the test in minutes [Bailis et al., 2007]

\[ Rc = \frac{m}{t} \]  

Equation 3.12

Where;

\( m \) = the mass (g) of fuel consumed during test phase of the test and \( t \) = time of test in minutes.

3.5.12.3 Specific Fuel Consumption

Specific fuel consumption is defined for any number of cooking tasks and should be considered “the fuel required to produce a unit output” whether the output is boiled water; cooked food etc [Smith, 1993].

\[ SCc = \frac{m}{M1} \]  

Equation 3.13

Where;

\( m \) = the mass (g) of fuel consumed during test phase of the test, \( M1 \) = the mass (g) of water in the pot.

3.5.12.4 Fire Power (FPc)

This is the ratio of the fuel energy consumed by the stove per unit time. It tells the average power output of the stove (in watts) during the test phase [Bailis et al., 2007]

\[ FPc = \frac{m \times C_v}{60 \times t} \]  

Equation 3.14

Where;

\( M \) = the mass (g) of fuel consumed during test phase of the test, \( t \) = time of the test in minutes.
Cv = the calorific value of the fuel sample (J/g) and 60 = number of seconds in one minute.

3.5.12.5 Evaporation rate ($W_c$)

This is a measure of the rate of water loss through evaporation during the test [Bailis et al., 2007].

$$W_c = \frac{M_2}{t}$$                      \hspace{1cm} \text{Equation 3.15}

Where:

$\ t =$ time of test in minutes, and $M_2 =$ mass (g) of water evaporated from the pot.

3.5.13 Determination of emissions

3.5.13.1 Carbon Monoxide

TSI CO$_2$-CO meter was used to measure the carbon dioxide emissions. Total emissions were calculated using the Equation 3. 16.

Total carbon dioxide = \( \frac{CO_{\text{CO}_2} + CO_{\text{HS}}}{2} \) + CO simmer \hspace{1cm} \text{Equation 3.16}

3.5.13.2 Particulate Matter

UCB particulate 2.5 mg/m$^3$ monitor was used to carry out the analysis.

Total particulate matter = \( \frac{PM_{\text{CS}} + PM_{\text{HS}}}{2} \) + PM simmer \hspace{1cm} \text{Equation 3.17}

3.5.13.3 Carbon dioxide

TSI CO-CO$_2$ meter was also used to carry out the study.

The total carbon monoxide emission was calculated using Equation 3.18.

Total carbon dioxide = \( \frac{CO_{\text{CO}_2} + CO_{\text{HS}}}{2} \) + CO simmer \hspace{1cm} \text{Equation 3.18}
CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Catalyst Preparation

The yields of calcium oxide obtained after calcination of the eggshells are as shown on Table 4.1. The total weight of calcium oxide after calcination was found to be 90.9% compared to 98.9% found by [Buasri et al., 2013]. During calcination, the thermal treatment resulted in a change in the XRD pattern, caused by the removal of CO$_2$ from the starting material. The diffraction patterns of the samples heated at temperatures <800°C have been found to have characteristics of CaCO$_3$, while samples calcined at temperatures >800°C displayed diffraction reflections characteristic of CaO [Buasri et al., 2013]. Samples calcined at 800°C have been found contain to CaCO$_3$ as the major phase and CaO as a minor phase [Wei and Xu, 2009]. Therefore major component of the calcined waste at 900°C for 4 h was CaO species.

Table 4.1: Yield of CaO from CaCO$_3$ by thermal catalytic oxidation of egg shell

<table>
<thead>
<tr>
<th>Weight of crushed eggshells</th>
<th>Weight of CaO generated</th>
<th>Percentage conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>305 g</td>
<td>277.43 g</td>
<td>90.9%</td>
</tr>
</tbody>
</table>

4.2 Oil moisture content

Croton Megalocarpus hutch oil moisture content was found to be 2.8%, with a golden yellow appearance.

4.3 Preparation of methyl esters (biodiesel) from crude oils

The experimental yields of methyl ester from Croton Megalocarpus hutch were determined in a range of 78- 86% by volume of oil. The remaining percentage was lost in form of glycerol
formed during saponification of free fatty acid present in the oil. Figure 4.1 shows the separation process of glycerol and biodiesel, while Figure 4.2 shows pure biodiesel obtained from the process.

Figure 4.1: A mixture of biodiesel and glycerol. Figure 4.2: Pure biodiesel.

4.3.1 Effect of reaction temperature on transesterification of Croton oil

Studies were carried out at different temperatures from 50 – 70°C with 2.5% CaO as catalyst and methanol to oil molar ratio of 12:1. As shown in Figure 4.3.

Figure 4.3: Graph of temperature against % yield verses the temperature.
From Figure 4.3 it was observed that temperature has positive influence on methanolysis of croton oil. The reaction rate was slow at low temperature due to the diffusion resistance, as the heterogeneous catalyst forms a three phase system, oil-methanol-catalyst. The reaction temperature above boiling point of alcohol is avoided since at high temperature it tends to accelerate the saponification of glycerides by the catalyst before completion of the alcoholysis. Hence the optimum temperature is 65°C. Figure 4.3, shows that an increase in reaction temperature led to higher yields. At the beginning of reaction, yield of FAME was increased because reactant contacted fresh catalyst. Then the yields decreased due to slightly deactivated but stabilized catalyst, and the conversions reached steady state at all temperatures. This result compares with that of Buasri et al. [2013] that at 65°C, the reaction yield was highest at 92.92% from duck eggshell waste.

4.3.2 Effect of mass ratio of catalyst to oil on transesterification of croton oil

Transesterification of croton oil was carried out with CaO and KOH as catalysts at a concentration of 1.5-10 % wt. of oil at 65°C with methanol/oil molar ratio of 12:1.

A plot of yield of methyl esters versus different catalytic concentrations give the curve given in Figure 4.4 below.

![Figure 4.4: Graph of catalyst consumed against yield.](image-url)
The lower catalytic concentration was insignificant to catalyze the reaction to completion. However, 5% of both CaO and KOH were optimal in the reaction with a yield of 82% in 180 minutes. With the increase in the concentration of catalyst, there was decrease in the yield of methyl esters.

4.4 Analysis of oils and methyl esters

4.4.1 FT-IR analysis of FAME of biodiesel from Croton Megalocarpus oil

Fatty acids of the biodiesel prepared from Croton Megalocarpus methyl ester was determined by FT-IR analysis and the spectrum peaks interpreted by register on Appendix 1 and results tabulated in Table 4.2.

![FT-IR croton methyl ester spectrum](image)

**Figure 4.5: FT-IR croton methyl ester spectrum.**

Table 4.2 below shows the interpretations of the peaks of the FTIR spectrum obtained.
Table 4.2: FTIR results of Croton Megalocarpus methyl esters

<table>
<thead>
<tr>
<th>Absorption band[cm(^{-1})]</th>
<th>Functional group</th>
<th>Absorption intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3008.7</td>
<td>-CH- stretching vibration</td>
<td>strong</td>
</tr>
<tr>
<td>2854-2927</td>
<td>-CH(_2)- asymmetric and symmetric vibration</td>
<td>strong</td>
</tr>
<tr>
<td>1743.5</td>
<td>-C=O stretching vibration</td>
<td>strong</td>
</tr>
<tr>
<td>1435-1462</td>
<td>-CH(_2)- shear type vibration</td>
<td>moderate</td>
</tr>
<tr>
<td>1361.7</td>
<td>-CH(_3)Bending vibration</td>
<td>moderate</td>
</tr>
<tr>
<td>1169-1195</td>
<td>-C-O-C Anti-symmetric stretching vibration</td>
<td>moderate</td>
</tr>
<tr>
<td>1016</td>
<td>-C-O-C Anti-symmetric stretching vibration</td>
<td>Weak</td>
</tr>
<tr>
<td>852.5</td>
<td>Epoxy ring vibration</td>
<td>Weak</td>
</tr>
<tr>
<td>721.3</td>
<td>-CH(_2)- Plane rocking vibration</td>
<td>Weak</td>
</tr>
</tbody>
</table>

Raw oils and the methyl esters are noted as fairly strong absorbers in the infrared region of the electromagnetic spectrum. From a study of the literature, there are units that use integration of the side (1750-1760 cm\(^{-1}\)) of carbonyl peak (~1744 cm\(^{-1}\)) to monitor the progress of the reaction. Lin-Vien et al. [1991] studied this method to be effective in a known system but noted its limitation because it is not specific for the end product and there could be a number of interferences. This method is however, being used because spectral resolution is not needed for specific analysis. They pointed out that the peak typical of the methyl ester (OCH\(_3\)) at 1436 cm\(^{-1}\) is very narrow and moves along the raw oil bio diesel reaction. However, they observed the peak measurement to give a direct indication of the attachment
of the alkyl group of the alcohol with the fatty acids of triglycerides but the peak is not influenced by the alkyl group (-CH₃) [Lin-Vien, et al., 1991].

Ivaanoiu and others [2011] performed a comparative study on bio diesel synthesis from different vegetable oils and used infrared spectroscopy using KBr plates in the range of 4000-400 cm⁻¹. The ester carbonyl group stretching vibration at 1740 cm⁻¹ is shown by strong bands, esteric –COC vibration at 1171 and 1207 cm⁻¹ reveals medium intensity bands, and the presence of the (CH₂)ₙ group vibration band is seen at 724 cm⁻¹. They observed the absence of a broad band at the 2500-3300 cm⁻¹ region which confirms the low moisture and free fatty acid content of the sample [Ivaanoiu, et al., 2011].
4.4.2 GC-MS Analysis of FAME of biodiesel from *croton megalocarpus* oil

Figure 4.6: GC-MS spectrum of methyl esters catalyzed by CaO catalyst.
Figure 4.7: GC-MS spectrum of methyl esters catalyzed by KOH catalyst.
Table 4.3: Biodiesel produced using CaO catalyst from eggshell

<table>
<thead>
<tr>
<th>Compound name</th>
<th>RT</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-heptene</td>
<td>3.4453</td>
<td>0.070506</td>
</tr>
<tr>
<td>Methyl tetradecanoate</td>
<td>21.251</td>
<td>0.341339</td>
</tr>
<tr>
<td>Hexadecanoic acid, methyl ester</td>
<td>23.3563</td>
<td>10.83133</td>
</tr>
<tr>
<td>Heptadecanoic acid, methyl ester</td>
<td>24.3194</td>
<td>0.19474</td>
</tr>
<tr>
<td>9,12-Octadecadienoic acid (Z,Z)-, methyl ester</td>
<td>25.0585</td>
<td>68.13182</td>
</tr>
<tr>
<td>Octadecanoic acid, methyl ester</td>
<td>25.2825</td>
<td>9.041635</td>
</tr>
<tr>
<td>Methyl 10-trans,12-cis-octadecadienoate</td>
<td>25.4393</td>
<td>5.664826</td>
</tr>
<tr>
<td>Methyl 9-cis,11-trans-octadecadienoate</td>
<td>25.6856</td>
<td>0.864839</td>
</tr>
<tr>
<td>Methyl 9-cis.,11.trans,t,13.trans.-octadecatrienoate</td>
<td>26.6487</td>
<td>0.603529</td>
</tr>
<tr>
<td>Methyl 11-eicosenoate</td>
<td>26.7831</td>
<td>2.988406</td>
</tr>
<tr>
<td>Methyl 18-methylnonadecanoate</td>
<td>26.9847</td>
<td>1.267034</td>
</tr>
</tbody>
</table>

Table 4.4: Biodiesel produced using KOH catalyst

<table>
<thead>
<tr>
<th>Compound name</th>
<th>RT</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Heptene</td>
<td>3.4452</td>
<td>0.38777</td>
</tr>
<tr>
<td>Methyl tetradecanoate</td>
<td>21.251</td>
<td>0.552992</td>
</tr>
<tr>
<td>Methyl hexadec-9-enoate</td>
<td>23.1323</td>
<td>0.404486</td>
</tr>
<tr>
<td>Hexadecanoic acid, methyl ester</td>
<td>23.3563</td>
<td>13.31009</td>
</tr>
<tr>
<td>9,12-Octadecadienoic acid (Z,Z)-</td>
<td>24.0954</td>
<td>0.214238</td>
</tr>
<tr>
<td>Heptadecanoic acid, methyl ester</td>
<td>24.3194</td>
<td>0.331502</td>
</tr>
<tr>
<td>9,12-Octadecadienoic acid (Z,Z)-, methyl ester</td>
<td>25.0585</td>
<td>71.07925</td>
</tr>
<tr>
<td>Methyl 10-trans,12-cis-octadecadienoate</td>
<td>25.5288</td>
<td>4.837891</td>
</tr>
<tr>
<td>Methyl 9-cis,11-trans-octadecadienoate</td>
<td>25.6856</td>
<td>0.698253</td>
</tr>
<tr>
<td>Methyl9,cis.,11.trans,t,13.trans.-ctadecatrienoate</td>
<td>26.3799</td>
<td>1.15922</td>
</tr>
<tr>
<td>cis-11-Eicosenoic acid, methyl ester</td>
<td>26.783</td>
<td>4.84304</td>
</tr>
</tbody>
</table>

From Table 4.3 and Table 4.4, the main fatty esters indentified in croton biodiesel are methyl 9(Z), 12 (Z)-octadecadienoate (C18:2) 71.1% and 68.1%, methyl stearate (C18:0) was only
detected was only detected in traces ester of 18:1 and methyl hexadecanoate (C16:0) 10.8 and 13.3%, were only detected for KOH and CaO catalyst respectively. These components have all been reported [Munavu and Odhiambo, 1984; Wagutu, 2010]. The percent composition obtained from the analysis of the biodiesel fuels are shown in Table 4.5, alongside their literature values from other records. In all the samples the solvent and derivetizing agents used for preparing the sample were the first materials to elute from the GC. These are shown by small low intensity peaks occurring at retention time depending on their structure (polarity) and boiling point [Mittebach, 1996] large molecules took a longer retention time in the G.C. However from the results KOH proved to be a better catalyst than CaO obtained from egg shell, though the eggshell can be used as a substitute.

4.4.3 Physiochemical properties of Croton oil and Croton Methyl Esters

Table 4.5: Physical-chemical properties of Croton Megalocarpus oil and Croton Megalocarpus methyl esters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density at 20°C (g/cm³)</th>
<th>Viscosity at 40°C (mm²/s)</th>
<th>Iodine value (mg/g)</th>
<th>(Acid value (mg/g))</th>
<th>Saponification value (mg/g)</th>
<th>Calorific value (MJ/kg)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Croton oil</td>
<td>0.914±0.001</td>
<td>4.32±0.1</td>
<td>81.6±0.2</td>
<td>1.2±0.2</td>
<td>216.2±0.04</td>
<td>39.7±0.02</td>
<td>1.4728±0.01</td>
</tr>
<tr>
<td>CMME</td>
<td>0.882±0.002</td>
<td>4.21±0.01</td>
<td>137.0±0.04</td>
<td>0.7±0.01</td>
<td>196.4±0.08</td>
<td>36.7±0.01</td>
<td>1.4545±0.02</td>
</tr>
</tbody>
</table>
The Croton Megalocarpus oil viscosity and density results obtained were found to be 27.6 and 0.914 respectively, the same as those obtained Lujaji, Munavu and Wagutu [Lujaji et al., 2010; Munavu, 1983a; Wagutu, 2010].

Saponification value for crude croton oil was found to be 127.0 compared with 126.2 obtained by Wagutu [2010]. The iodine value of croton oil was found to be 81.6±0.002, while that of the croton methyl ester rose to 137.0. The refractive index seemed to rise with increase in the iodine value of the oil. This could suggest a relationship between the degree of unsaturation and the optical characteristics of the oil. Viscosity of the croton Megalocarpus oil improved from 4.32 to 4.21 after transesterification. CMME showed higher iodine value (137) than ≤120 recommended in European biodiesel standard [EN, 14214].

The use of IV is rendered redundant when oxidative stability is described by indices of allylic positions and bis-allylic equivalents. The positions of allylic to double bonds are especially susceptible to oxidation. For instance, the bis-allylic positions in (9Z, 12Z)-octade-9,12-dionoic acid (linoleic acid) which was identified as the main unsaturated fatty acids in the biodiesel is prone to auto-oxidation than the allylic positions. The relative rates of oxidation given in the literatures are one for oleates (methyl, ethyl esters), 41 for linoleates, and 98 for linoleates [Lencher et al., 1997]. A major drawback for the IV is it does not distinguish these differences. Other factors such as storage conditions should be considered while defining the susceptibility of unsaturated fuel to oxidation [Leung et al., 2006].

The saponification value (SV) is an indicator of molecular weight of the biodiesel and increases with decreasing molecular weight [Knothe, 2002]. Croton Megalocarpus constitute of C18 fatty acid therefore having a higher saponification value due to the presence of linoleic acid, on transesterification, the saponification value of esters increased slightly compared to that of the parent oil. The increase in SV may be explained by the fact that the
process removes the heavier glycerol molecules from the oil thus reducing the average molecular weight of the resulting esters.

The limitation on acid value for biodiesel by ASTM standard is a maximum of 0.8 mg KOH/g and CCME passed this requirement.

4.5 Fuel Properties

The fuel properties of the CMME were compared with that of kerosene and automotive diesel fuels are shown in Table 4.6. Kinematic viscosity of biodiesel samples was determined at 40 °C [ASTM D445]. The data obtained was used to define the influence of compound structure on its flow ability. The viscosity of biodiesel was found to be greater than that of kerosene and diesel fuels but much lower than that of Croton Megalocarpus oil (Table 4. 6). Viscosity difference of parent oil and biodiesel could thus form a basis for an analytical procedure applied to determining the conversion of vegetable oil to methyl ester [De Filippis et al., 1995].

On the basis of the data obtained in table 4.6, the ester viscosity has a direct relationship with some chemical characteristics of the lipids, such as the degree of unsaturation, the position of the double bond and the chain length of the fatty acids that constitute the triacylglycerides from which the esters are derived [Knothe, 2005]. From Table 4.6, the double bond reduces the kinematic viscosity of the corresponding methyl ester. The viscosity reduces even more with increase in the number of the double bonds in the chain. This is seen with Croton methyl ester which has the highest degree of unsaturation (68%) of C18:2.
4.6. Fuel properties of methyl esters and kerosene fuel and different biodiesel blends

properties

Table 4.6 below describes the comparison of fuel properties obtained for CMME, kerosene and diesel.

**Table 4.6: Fuel properties of CMME, diesel and kerosene**

<table>
<thead>
<tr>
<th>Test</th>
<th>Kerosene</th>
<th>diesel</th>
<th>B5</th>
<th>B10</th>
<th>B100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear</td>
<td>clear</td>
<td>Clear</td>
<td>Clear</td>
<td>Clear</td>
</tr>
<tr>
<td>Water content</td>
<td>0.004±0.1</td>
<td>0.005±0.2</td>
<td>0.006±0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>1.4</td>
<td>0.4</td>
<td>0.39</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Ash content</td>
<td>0.002±0.001</td>
<td>0.028±0.1</td>
<td>0.048±0.12</td>
<td>0.7±0.01</td>
<td></td>
</tr>
<tr>
<td>Calorific value</td>
<td>43.0±0.01</td>
<td>40.7±0.1</td>
<td>42.1±0.01</td>
<td>36.7±0.2</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.482±0.1</td>
<td>1.468±0.2</td>
<td>1.4678±0.01</td>
<td>1.45±0.001</td>
<td></td>
</tr>
<tr>
<td>Density at 20°C</td>
<td>0.7884±0.2</td>
<td>0.8244±0.2</td>
<td>0.814±0.1</td>
<td>0.8270±0.01</td>
<td>0.88±0.02</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>2.29±0.1</td>
<td>2.29±0.02</td>
<td>4.17±0.02</td>
<td>4.16±0.04</td>
<td>4.2±0.06</td>
</tr>
</tbody>
</table>

**Table 4.7: Viscosities of saturated and unsaturated compounds at 40°C**

<table>
<thead>
<tr>
<th></th>
<th>C10:0</th>
<th>C12:0</th>
<th>C14:0</th>
<th>C16:0</th>
<th>C18:0</th>
<th>C16:1</th>
<th>C18:1</th>
<th>C18:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acid</td>
<td>5.63</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19.91</td>
<td>13.46</td>
</tr>
<tr>
<td>Methyl ester</td>
<td>1.72</td>
<td>2.43</td>
<td>3.30</td>
<td>4.38</td>
<td>5.85</td>
<td>3.67</td>
<td>4.51</td>
<td>3.65</td>
</tr>
</tbody>
</table>
The main factor that influences the viscosity of the investigated biodiesel is the chain lengths of the constituent esters. This explains why CCME which constitute mostly C16-C18 esters gives viscosity of 4.2 mm²/s.

CMME fuel recorded higher density than kerosene and automotive diesel (Table 4.7) the high density could enhance the fuel to air mixture resulting into the greater power output. This would compensate the fuel to air mixture resulting into greater power output. This will compensate for the lower heating value of the biodiesel fuels as compared to diesel fuels. This gives to the two fuels of different origins equal or very close power output, qualifying biodiesel as a viable substitute for both kerosene and diesel fuel. The densities at 40 °C of the analyzed was found to have a significant range, kerosene having recorded the lowest density of 0.787, diesel 0.824 and CMM recording 0.884.

4.7 Biodiesel blends with kerosene fuel

Pure biodiesel (B100) is highly unsaturated; this affects the fuel stability under poor storage conditions. As a result of this B100 fuel could not perform the water boiling test to completion, hence need for blending.

Blending of the biodiesel with kerosene fuels improve these condition. Comparison of fuels properties of kerosene blends in ranges of 5% to 10% biodiesel in the mixture.

Pure biodiesel showed higher viscosity compared to pure kerosene and biodiesel blends of B5 and B10. Blend in this range also seemed ideal for improvement of heating value of the fuel from 36.7 MJ/Kg to 40.7 and 42.1 MJ/kg for B5 and B10 respectively as shown in Table 4.6.

4.8 Water Boiling Test (WBT)

Water Boiling Tests (WBT) [Vita, 1985] was conducted to demonstrate suitability of the CMM esters as a substitute to kerosene in domestic cooking applications. All the biodiesel blends (B5, B10 and B100) were tested using a common capillary-fed wink stove. The fuel
burnt with a transparent blue flame producing no smell apart from sweet smell esters, no matter was deposited at the bottom of the cooking pot. Kerosene (B0) on the other hand produced the normal strong smell and an agglomeration of elemental carbon was deposited at the bottom of the cooking pot.

4.8.1 Time to boil

Time to boil was measured beginning when the oil and the oil blends were considered lit and ending when the water started boiling (at local atmospheric pressure). The oil was qualitatively determined to be lit when all the winks were up burning to keep the fire dying out.

The pure kerosene lit stove brought water to a boil more quickly than the other two stoves with biodiesel blends as shown on the tabulated results on table 4.8 below. In the cold start phase, water heated on pure kerosene stove took 21 minutes to boil compared to 25.5 minutes spent by a 5% biodiesel -kerosene blend fuel lit stove and 27 minutes spent by 10% biodiesel-kerosene blend oil. Although the performance of the Croton Megalocarpus hutch biodiesel blends were slower compared to pure kerosene, they performed similarly to each other with averages ranging from 25.5 to 27, a difference of 1.5 minutes.
Table 4.8: Mean stove performance indicators high power (cold start analysis) test

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>Units</th>
<th>BO</th>
<th>B5</th>
<th>B10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to boil</td>
<td>Min</td>
<td>21±0.1</td>
<td>25.5±0.02</td>
<td>27±0.01</td>
</tr>
<tr>
<td>Burning rate</td>
<td>g/min</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>%</td>
<td>43±0.45%</td>
<td>43±0.24%</td>
<td>45±0.2%</td>
</tr>
<tr>
<td>Specific fuel consumption</td>
<td>g/liter</td>
<td>25±0.1</td>
<td>28±0.4</td>
<td>31±0.01</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>G</td>
<td>54±0.1</td>
<td>67±0.2</td>
<td>64±0.8</td>
</tr>
<tr>
<td>Firepower</td>
<td>Watts</td>
<td>1859±0.2</td>
<td>1761±0.4</td>
<td>1715±0.4</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>ppm</td>
<td>7±0.01</td>
<td>5±0.2</td>
<td>3±0.2</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>ppm</td>
<td>539±0.1</td>
<td>544±0.02</td>
<td>555±0.1</td>
</tr>
<tr>
<td>Particulate emissions</td>
<td>µg/m³</td>
<td>64±0.2</td>
<td>55±0.01</td>
<td>49±0.04</td>
</tr>
</tbody>
</table>

Various properties were found to affect the stove performance in different ways: the viscosity of the fuel affected its availability to combustion chambers. The capillary action which draws the fuel up through the wink fibers was faster for the less viscous fuels like kerosene which achieved the boiling point after 21 minutes compared to 25.5 and 27 minutes for B5 and B10 respectively. The specific fuel consumption and fire power seemed to be affected by fuel’s heating value and the viscosity; kerosene produced the highest power output while B10 produced the lowest. Low viscosity and high energy content for kerosene fuel resulted in less fuel consumption and a short time to boil. The thermal efficiency was found to be 43% for kerosene while biodiesel blend had 43 and 45% for B5 and B10 respectively. Kerosene took the least time to boil water 21 minutes, while B10 to longest time to boil taking 27 minutes consuming 25 g/l mass of fuel, 28 g/l and 31 g/l of the B5 and B10 esters blends were consumed respectively to bring equal volume of water to boil.
4.8.2 Thermal Efficiency

Thermal efficiency is the ratio of the heat content of increasing the water temperature and evaporating the mass of water released as steam, to the energy consumed by burning the fuel. Calculation for determining thermal efficiency can be found in the WBT protocol.

Table 4.10 below shows the thermal efficiency for the thermal efficiency for simmering phase as well as average efficiency of all the three phases of WBT. Average thermal efficiency results for the kerosene lit stove was equal to that of B10 blend while that of B5 blend was slightly lower. All the stoves showed higher efficiency during the simmer phase than the hot or cold start phases. The average thermal efficiency of all the three phases, B10 was found to be the most efficient compared to the other two.

In the hot start phase, in which room temperature water was placed on already heated stoves, the results are similar. Once again, the pure kerosene lit stove was faster than any improved stove, and the 55 and 10% croton Megalocarpus biodiesel blends performed similarly to one another. The results obtained were recorded in Table 4.9.
Table 4.9: Mean stove performance indicators high power (hot start) phase

<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>Units</th>
<th>BO</th>
<th>B5</th>
<th>B10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to boil</td>
<td>Min</td>
<td>14±0.1</td>
<td>24±0.02</td>
<td>24±0.01</td>
</tr>
<tr>
<td>Burning rate</td>
<td>g/min</td>
<td>3±0.01</td>
<td>3±0.01</td>
<td>2±0.02</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>%</td>
<td>48±0.1</td>
<td>44±0.2</td>
<td>51±0.1</td>
</tr>
<tr>
<td>Specific fuel consumption</td>
<td>g/liter</td>
<td>20±0.5</td>
<td>29±0.01</td>
<td>24±0.02</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>g</td>
<td>42±0.2</td>
<td>51±0.01</td>
<td>49±0.08</td>
</tr>
<tr>
<td>Firepower</td>
<td>Watts</td>
<td>2269±</td>
<td>1864±</td>
<td>1871±</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>ppm</td>
<td>5±0.01</td>
<td>4±0.02</td>
<td>3±0.01</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>ppm</td>
<td>516±0.01</td>
<td>519±0.02</td>
<td>528±0.01</td>
</tr>
<tr>
<td>Particulate emissions</td>
<td>µg/m³</td>
<td>45±0.01</td>
<td>41±0.2</td>
<td>37±0.04</td>
</tr>
</tbody>
</table>

4.8.3 Specific Fuel Consumption.

Specific fuel consumption is defined in 2007 WBT as “the fuel required to produce a unit output" whether the output is boiled water or cooked food. In the case of cold start phase, high power WBT, it is a measure of "the amount of fuel producing one kilo of boiling water starting with cold stove."

The result in Tables 4.8, 4.9 and 4.10 shows the temperature- correlated specific fuel consumption, which adjusts for differences in initial water temperature. As seen in Table 4.10, the simmering phase accounted for large portion of the fuel consumed by each blend of fuel. More biodiesel was consumed compared to pure kerosene, on average B10 and B5 were consumed more than B0 in the three phases.
Slightly lesser time (0.5-7 minutes) was required to boil the water than in cold start for each fuel. This gave a small increase in the power output (5-18%) during this phase. This would be explained by the fact that the fuel in the stove tank would be in a slightly higher temperature than room temperature.

This increases the flash point and lowers the viscosity, thus increasing the fuel mobility by capillarity and increasing the ease of burning. Heat transfer efficiency increased by (1-6%) due to the elevated temperatures at the hot start phase, possibly because the metallic stove body conducts heat fast such that within five minutes the body would be at room temperature.

**Table 4.10: Mean stove performance indicators low power hot start (simmering) phase**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>BO</th>
<th>B5</th>
<th>B10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to boil</td>
<td>Min</td>
<td>45±0.2</td>
<td>45±1.2</td>
<td>45±0.8</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>%</td>
<td>45±0.01</td>
<td>41±2.5</td>
<td>45±2.1</td>
</tr>
<tr>
<td>Specific fuel consumption</td>
<td>g/liter</td>
<td>40±0.1</td>
<td>44±0.02</td>
<td>44±0.01</td>
</tr>
<tr>
<td>Burning rate</td>
<td>Min</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Fire power</td>
<td>Watts</td>
<td>1073±0.4</td>
<td>1132±2.1</td>
<td>1117±0.4</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>G</td>
<td>73±0.2</td>
<td>77±0.4</td>
<td>76±0.6</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>ppm</td>
<td>6±0.1</td>
<td>3±0.01</td>
<td>2±0.1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>ppm</td>
<td>524±0.01</td>
<td>538±0.01</td>
<td>548±0.1</td>
</tr>
<tr>
<td>Particulate emissions</td>
<td>µg/m³</td>
<td>50±0.2</td>
<td>42±0.2</td>
<td>29±1.4</td>
</tr>
</tbody>
</table>

The goal of this phase is to maintain water at a high temperature with minimal power output from the stove. The power required to keep the water at simmering (3-4 °C) below the boiling temperature seemed the same for all the fuel (1073-1132 W). The efficiency for all the fuels
remained relatively the same (41-45%). Simmering the results indicate that the power output and efficiency for all the fuels remains the same. Esters, however, consumed more fuel compared to kerosene to simmer for an equal amount of time at almost the same temperature.

The rate of burning was 1% lower than in high power phases but remained within the same range for all the fuels (2.0 g/min). Specific consumption during this phase seemed to be only a factor calorific value of the fuel, kerosene. Thus kerosene consumed the least mass of fuel 70 g to maintain the water at simmer for 45 minutes while B5 and B10 with lower heating value consumed 77 g and 76 g mass of fuel respectively to simmer.

4.8.4 Fuel emissions

4.8.4.1 Total Carbon Dioxide (CO₂)

In each WBT conducted, CO₂ emissions were monitored, recorded and summed for each phase of WBT. Those sums were averaged across multiple tests to calculate the total CO₂ released per phase. Total CO₂ emission for the entire WBT, combining all phases, was calculated by summing these averaged phase totals. Carbon dioxide emitted from BO, B5 and B10 increased in that order as shown in Figure 4.15 below. A significant portion of carbon in the biodiesel is based upon biomass from croton oil, which in turn is based upon CO₂, taken by croton plant from the atmosphere. Therefore, the life cycle of biodiesel was considered, net CO₂ emission released from the biodiesel fuel would be curtailed significantly. These results are consistent with the observations in the literature [El-kasaby and Nemit-allah, 2013]. Biodiesel is an oxygenated fuel that contains 11–12% more oxygen in its molecular structure. This causes higher adiabatic flame temperatures and helps to achieve more complete combustion and therefore higher CO₂ emissions for biodiesel blend. Biodiesel naturally contains more double-bonded molecules than diesel. These double-
bonded molecules have slightly higher adiabatic flame temperatures, which cause the increase in \( \text{CO}_2 \) emissions for biodiesel blends.

### 4.8.4.2 Total Carbon Monoxide (CO)

In each WBT conducted, CO emissions were monitored, recorded, and summed for each phase of the WBT in Tables 4.8, 4.9 and 4.10 above. The sums were then averaged in the three phases. Kerosene lit stove produced the highest amount of CO in the three phases.

It is known that the CO from kerosene stoves is released due to the incomplete combustion of fuel containing carbon. The reduction of CO was linear to the base fuel, the reason for CO reduction in the biodiesel blends could be credited to the additional oxygen content in the fuel and increased centane number. The higher the centane number, the lower the probability of fuel-rich zones formation, usually related to CO emissions. These results are supported by literature [Lapuerta and Fernandez, 2008]. This is due to the higher oxygen content of biodiesel (10–12% higher oxygen that kerosene fuel) which results in a complete combustion. Therefore, as the percentage of biodiesel increased in the blend, the higher oxygen content of biodiesel allowed more carbon molecules to burn and the combustion became more complete. Moreover, low aromatics in the blends may be an additional reason for reduction in CO emissions.

The maximum instantaneous CO concentration and average CO concentration of all the samples was below the maximum acceptable value of 15 ppm per 15 minutes from the national institute of occupational safety and health [World Health Organization].

### 4.8.4.2 Total Carbon Monoxide

Table 4.8 showed that blending biodiesel with kerosene at various ratios, leads to a decrease in the amount of particulate matter being emitted as the amount of biodiesel is increased in the blend from B5 to B10. From B5 to B10 there is a significant decrease in the amount of
particulate matter emitted. This is as a result of increase of oxygen with the addition of more biodiesel hence complete combustion. This is supported by the work of Rashid [2011]. He reported that in an assessment of the environmental hazards caused by the use of fossil fuels, biodiesel is being considered to be the best fuel for diesel engines since burning biodiesel and its blends has the lowest Green House gas Emissions on a life cycle basis. His review paper also showed that particulate soot emissions which have adverse health effect in terms of respiratory impairment and related illness on human beings is significantly reduced with the use of biodiesel or its blends [Rashid, 2011].

The overall variation of the CO and CO$_2$ emissions of kerosene (B0), 5% biodiesel blend (B5), and 10% biodiesel blends (B10) are shown in Figure 4.8.

![Biodiesel Emission Trends](image)

**Figure 4.8:** Average emission from WBT test.
CHAPTER FIVE

5.0 Conclusion and recommendations

5.1 Conclusions

The results reported in the present work were aimed at production of fatty acid methyl esters (biodiesel fuel) from Croton Megalocarpus hutch using eggshells as a catalyst source which would be cost-effective and environment-friendly catalyst. The eggshells were successfully converted to CaO after calcination at temperatures of 900°C for 3 h. Catalyst conversion from eggshell to CaO was found to be 90.8% while the yield of refined methyl esters ranged from 68.0 to 72%. CaO-catalyzed transesterification sourced from eggshell was found to have a potential of being used as a heterogeneous catalyst in biodiesel production in the near future due to the high yield of methyl esters 68.1% and 13.3%, compared to 71.1% and 10.8% achieved by use of KOH for the main fatty esters indentified. The optimum conditions, which yielded a conversion of croton oil of nearly 92 and 94% were reaction time of 4h, reaction temperature 65°C, methanol/oil molar ratio 1:12. The experimental results showed that CaO catalyst sourced from egg shell had excellent activity and stability during transesterification. The fuel properties of the biodiesel obtained met all biodiesel standards. This research work demonstrates that CaO sourced from eggshell can be used as a solid catalyst, can decrease the cost of biodiesel and the steps of purification. It has potential for industrial application in the transesterification of oils to FAME.

GC analysis identified and quantified various types of fatty acids in the vegetable oil esters obtained by CaO and KOH catalysis, three main fatty acid compounds were dominant after transesterification namely; methyl octadecanoate, methyl 9(Z)-octadecanoate and methyl 9(Z), 12(Z)-octadecadienoate esters.
Fuel parameters analysis showed that the heat of combustion of the vegetable oil esters was on average 38 MJ/kg which measured 12% (on average) less than that of kerosene fuels. Analysis of volatility characteristics and viscosity showed esters of *Croton* to have higher viscosity compared to kerosene fuel. The work also evaluated the fuel parameters of the ester in comparison to kerosene fuel in domestic stoves; in order to demonstrate suitability of the esters as substitutes or supplements for fossil kerosene fuel. Analysis of the results of WBT for the pure methyl esters indicated that fuel is able to burn effectively in common wick stove but could not achieve boiling water to the required temperature of 94ºc since it was more viscous hence slow in moving up the capillaries of the winks however, it showed compatible properties to those of kerosene thus can be used as neat or blended fuels in domestic stoves when proper thinners are found to lower viscosity and anti-gelling additives to improve the cold flow property during cold seasons.

Utilization of the Croton *Megalocarpus* oil ester as a substitute to kerosene in cooking stoves as a source of fuel has varied ecological, economical, and sociological benefits to the general population; this was seen from the CO, CO₂ and particulate emissions measured. Blends of 5 and 10% passed the WBT, demonstrating a reduced amount of CO emission between 33% and 55% for 5% and 10% blends and particulate matter emission of 13.2% and 27.7% and a slight increment of carbon dioxide emission by 1.39% and 3.12% for 5% and 10% blends of biodiesel respectively. Croton crop plantations would utilize marginal land in Kenya and control environmental degradation. Esters production industry would create jobs for many youths and women raising their standard of living.

Blends of 10% biodiesel in 90% kerosene gave the best fuel properties, giving high energy content, wide volatility range and low viscosity, low density similar to that of kerosene. Blending could also reduce other problems associated with pure biodiesel such as oxidative
instability (due to unsaturated components) and emissions of nitrogen oxides and affinity to water. The emission concentration of cold-start was higher than hot start because of initial warm-up phase of stove, irrespective of biodiesel blend level. Absence of strong smell and matter deposited at the bottom of the pot, low CO and particulate emissions accrues the fuel better health benefits as compared to the smoke, particulate matter and complex mix of organic compounds produced by the burning of biomass fuels and kerosene. The properties of Croton Megalocarpus biodiesel fuel and its blends agree with ASTM D6751. Finally it can be concluded that CMME biodiesel blend has the potential of replacing kerosene in the future in cooking stoves and lighting either pure or in blends with kerosene for purposes of improving performance and reduce toxic exhaust emissions, in terms of environmental assessment and renewability.

5.2 Recommendations

Many areas need to be explored to further enhance the performance of CaO from eggshell and production and use of CMME in cooking stoves, which includes:

- Consideration of a simpler and cost-effective ways to transform CaCO₃ from eggshell to CaO. At present, almost all are using the calcination method at high temperatures, which translates into higher catalyst preparation costs in terms of furnace energy.
- Pelleting CaO, with sufficient pores.
- New methods to reduce viscosity of the biodiesel.

Notwithstanding the many areas to be explored further, the outlook of progressing intense and diverse research on CaO sourced from locally available eggshell is evident of its potential as a heterogeneous catalyst in producing biodiesel at the industrial level.


Appendix 1

Library Search Report - ChemStation Integrator

Unknown Spectrum based on Apex minus start of peak
Scan 16 (3.445 min) B.D Data ms (-3) (-)

Data File: C:\msdchem1\DATAi2014\B.D
Sample: B
Peak Number: 1 at 3.445 min Area: -53979276 Area % -0.38

The 3 best hits from each library.

<table>
<thead>
<tr>
<th>Ref#</th>
<th>CAS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:\Database\NIST08.L 1 1-Heptene</td>
<td>3268 000592-76-7 94</td>
</tr>
<tr>
<td>2 Isopropylpentane</td>
<td>3308 000872-56-0 91</td>
</tr>
<tr>
<td>3 1-Heptene</td>
<td>3272 000592-76-7 90</td>
</tr>
<tr>
<td>C:\Database\chemecol.L 1 1-Decene</td>
<td>527 000872-56-0 72</td>
</tr>
<tr>
<td>2 Hexanol</td>
<td>467 000111-70-8 50</td>
</tr>
<tr>
<td>3 Nonanol</td>
<td>465 028473-21-4 33</td>
</tr>
<tr>
<td>C:\Database\NIST08.L 1 1-Heptene</td>
<td>3268 000592-76-7 94</td>
</tr>
<tr>
<td>2 Isopropylpentane</td>
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<tr>
<td>3 1-Heptene</td>
<td>3272 000592-76-7 90</td>
</tr>
</tbody>
</table>
Data File: C:\msdchem\1\DATA\2014B.D
Sample : B
Peak Number: 2 at 21.251 min Area: 7697805 Area % 0.54

The 3 best hits from each library.

<table>
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<th>Library</th>
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<th>Ref#</th>
<th>CAS#</th>
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<tr>
<td>C:\Database\NIST08.L</td>
<td>1 Methyl tetradecanoate</td>
<td>91835</td>
<td>000124-10-7</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>2 Methyl tetradecanoate</td>
<td>91838</td>
<td>000124-10-7</td>
<td>96</td>
</tr>
<tr>
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<td>3 Methyl tetradecanoate</td>
<td>91836</td>
<td>000124-10-7</td>
<td>93</td>
</tr>
<tr>
<td>C:\Database\chemecol.L</td>
<td>1 Methyl palmitate (Methyl hexadec..</td>
<td>154 000112-39-0</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 Methyl octanoate</td>
<td>337</td>
<td>000111-11-5</td>
<td>8</td>
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<tr>
<td></td>
<td>3 2-Methylbutanoic acid</td>
<td>299</td>
<td>000116-53-0</td>
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</tr>
</tbody>
</table>

C:\Database\NIST08.L
1 Methyl tetradecanoate 91835 000124-10-7 97
2 Methyl tetradecanoate 91838 000124-10-7 96
3 Methyl tetradecanoate 91836 000124-10-7 93
Unknown Spectrum based on Apex minus start of peak

Scan 895 (23.132 min)

111879: Methyl hexadec-9-enoate

111919: 9-Hexadecenoic acid, methyl ester, (Z)-

111916: 7-Hexadecenoic acid, methyl ester, (E)-

m/z 55.05 100.00%

m/z 69.10 78.08%

m/z 74.00 76.64%

Data File: C:\msdsc\1DATA\2014\B.D
Sample : B

Peak Number: 3 at 23.132 min Area: 56306154 Area % 0.40

The 3 best hits from each library.

<table>
<thead>
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<td>NIST08.L</td>
<td>1 Methyl hexadec-9-enoate</td>
<td>111879 010030-74-7</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>2 9-Hexadecenoic acid, methyl ester...</td>
<td>111920 001120-25-8</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>3 7-Hexadecenoic acid, methyl ester...</td>
<td>111919 056875-67-3</td>
<td>99</td>
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<tr>
<td>chemcol.L</td>
<td>1 C14-ol Tetradeanol</td>
<td>22 000000-00-0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2 Methyl octanoate</td>
<td>337 000111-11-5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3 Methyl hexanoate</td>
<td>338 000106-70-7</td>
<td>9</td>
</tr>
<tr>
<td>NIST08.L</td>
<td>1 Methyl hexadec-9-enoate</td>
<td>111879 010030-74-7</td>
<td>99</td>
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</tr>
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</table>

DEFAULT-USER1.M Mon May 26 07:54:58 2014
Library Search Report - ChemStation Integrator

Unknown Spectrum based on Apex minus start of peak

Scan 905 (23.356 min): B:Didata.ms (-901) (-)

#113682: Hexadecanoic acid, methyl ester

#113705: Pentadecanoic acid, 14-methyl, methyl ester

#113582: Hexadecanoic acid, methyl ester

Data File: C:\msdchem\11DATA2014\B.D
Sample : B

Peak Number: 4 at 23.356 min Area: 1852821412 Area % 13.01

The 3 best hits from each library. Ref# CAS# Qual

C:\Database\NIST08.L
1 Hexadecanoic acid, methyl ester 113682 000112-39-0 99
2 Pentadecanoic acid, 14-methyl- ... 113705 005129-60-2 99
3 Hexadecanoic acid, methyl ester 113690 000112-39-0 98

C:\Database\chemeco.L
1 Methyl palmitate (Methyl hexadecanoate) 154 000112-39-0 93
2 Methyl octanoate 337 000111-11-5 17
3 Methyl hexanoate 338 000106-70-7 2

C:\Database\NIST08.L
1 Hexadecanoic acid, methyl ester 113682 000112-39-0 99
2 Pentadecanoic acid, 14-methyl- ... 113705 005129-60-2 99
3 Hexadecanoic acid, methyl ester 113690 000112-39-0 98

The 3 best hits from each library:

C:\Database\NIST08.L
1 9,12-Octadecadienoic acid (Z,Z)- 121228 000060-33-3 98
2 cis-10-Heptadecenoic acid, methy... 122826 1000333-62-1 93
3 9,12-Octadecadienoic acid (Z,Z)- 121227 000060-33-3 93

C:\Database\chemecol.L
1 Z7-C16-enol 449 000000-00-0 43
2 E13-C18-enol 453 000000-00-0 36
3 Z9-C18-enol 451 000000-00-0 38

C:\Database\NIST08.L
1 9,12-Octadecadienoic acid (Z,Z)- 121228 000060-33-3 98
2 cis-10-Heptadecenoic acid, methy... 122826 1000333-62-1 93
3 9,12-Octadecadienoic acid (Z,Z)- 121227 000060-33-3 93

DEFAULT-USER1.M Mon May 26 07:54:59 2014
Unknown Spectrum based on Apex minus start of peak
Scan 948 (24 319 min): B.Dialdata.ms (.944 .)

#124602: Heptadecanoic acid, methyl ester

Data File: C:\msdchem\1DfDAT\2014\B.D
Sample : B
Peak Number: 6 at 24.319 min Area: 46146525 Area % 0.32

The 3 best hits from each library. Ref# CAS# Qual
-----------------------------------------------------------------
C:\Database\NIST08.L
1 Heptadecanoic acid, methyl ester 124602 001731-92-6 99
2 Heptadecanoic acid, methyl ester 124601 001731-92-6 98
3 Heptadecanoic acid, methyl ester 124600 001731-92-6 98

C:\Database\chemcoc.L
1 Methyl palmitate (Methyl hexadec. 154 000112-39-0 42
2 Methyl octanoate 337 000111-11-5 20
3 Methyl hexanoate 338 000106-79-7 4

C:\Database\NIST08.L
1 Heptadecanoic acid, methyl ester 124602 001731-92-6 99
2 Heptadecanoic acid, methyl ester 124601 001731-92-6 98
3 Heptadecanoic acid, methyl ester 124600 001731-92-6 98

DEFAULT-USER1.M Mon May 26 207:55:00 2014
Unknown Spectrum based on Apex minus start of peak

Data File: C:\msdchem\1\DATA\2014\B.D
Sample: B
Peak Number: 7 at 25.058 min Area: 9894534935 Area % 69.47

The 3 best hits from each library.

<table>
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<th>CAS#</th>
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<td>C:\Database\NIST08.L</td>
<td>1 9,12-Octadecadienoic acid (Z,Z)-... 132273 000112-63-0 99</td>
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<tr>
<td></td>
<td>2 8,11-Octadecadienoic acid, methy... 132258 056599-58-7 99</td>
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<tr>
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<td>3 Methyl 10-trans,12-cis-octadeca... 132261 1000336-44-2 99</td>
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</tr>
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<td>C:\Database\chemecol L</td>
<td>1 Z,Z-3,13-C18-dienol 443 000000-00-0 35</td>
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<td>2 E13-C18-enol 453 000000-00-0 27</td>
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<td></td>
<td>3 Z11-C18-enol 452 000000-00-0 22</td>
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<td>1 9,12-Octadecadienoic acid (Z,Z)-... 132273 000112-63-0 99</td>
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<tr>
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<td>2 8,11-Octadecadienoic acid, methy... 132258 056599-58-7 99</td>
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</tbody>
</table>
Unknown Spectrum based on Apex minus start of peak

Scan 1002 (25.529 min): B.data.ms (-498) (-)

m/z→
Abundance
5000
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
41 55 67 81 95 109 123 136 150 164 178 192 206 220 234 248 262 276 290 304
#132261: Methyl 10-trans,12-cis-octadecadienoate

m/z→
Abundance
5000
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
55 67 81 95 109 123 136 150 164 178 192 206 220 234 248 262 276 290 304
#132260: Methyl 9-cis,11-trans-octadecadienoate

m/z→
Abundance
5000
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360
67 81 95 109 123 136 150 164 178 192 206 220 234 248 262 276 290 304
#132201: Methyl 10-trans,12-cis-octadecadienoate

Data File: C:\msdchem\1\DATA\2014\B.D
Sample : B
Peak Number: 8 at 25.529 min Area: 673455132 Area % 4.73
The 3 best hits from each library.

<table>
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<th>Ref#</th>
<th>CAS#</th>
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<tr>
<td>C:\Database\NIST08.L</td>
<td>1 Methyl 10-trans,12-cis-octadecadienoate...</td>
<td>132261 1000336-44-2</td>
</tr>
<tr>
<td>2 Methyl 9-cis,11-trans-octadecadienoate</td>
<td>132260 1000336-44-0</td>
<td>99</td>
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<tr>
<td>3 9,11-Octadecadienoic acid, methyl...</td>
<td>132284 013038-47-8</td>
<td>95</td>
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<tr>
<td>C:\Database\chemecol.L</td>
<td>1 Bornyl acetate</td>
<td>35000076-49-3</td>
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<tr>
<td>2 Neotuerciol</td>
<td>48000000-00-0</td>
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<tr>
<td>3 cis-3-Hexenyl hexanoate</td>
<td>407031501-11-8</td>
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<tr>
<td>C:\Database\NIST08.L</td>
<td>1 Methyl 10-trans,12-cis-octadecadienoate...</td>
<td>132261 1000336-44-2</td>
</tr>
<tr>
<td>2 Methyl 9-cis,11-trans-octadecadienoate</td>
<td>132260 1000336-44-0</td>
<td>99</td>
</tr>
<tr>
<td>3 9,11-Octadecadienoic acid, methyl...</td>
<td>132284 013038-47-6</td>
<td>95</td>
</tr>
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</table>

DEFAULT-USER1.M Mon May 26 07:55:00 2014
Unknown Spectrum based on Apex minus start of peak
Scan 1009 (25.686 min): B.D:Data.ms (-1007) (-)

Data File: C:\msdchem\11DATA\2014\B.D
Sample : B
Peak Number: 9 at 25.686 min Area: 97199843 Area % 0.68

The 3 best hits from each library.

C:\Database\NIST08.L
1 Methyl 9-cis,11-trans-octadecadienoate... 132260 1000336-44-0 99
2 Methyl 10-trans,12-cis-octadecadienoate... 132261 1000336-44-2 99
3 9,11-Octadecadienoic acid, methyl... 132284 013038-47-6 95

C:\Database\chemecol.L
1 Neothujol 480 000000-00-0 9
2 (Z)-3-hexenyl propanoate 273 033467-74-2 4
3 cis-3-hexen-1-ol 56 000928-96-1 4

C:\Database\NIST08.L
1 Methyl 9-cis,11-trans-octadecadienoate... 132260 1000336-44-0 99
2 Methyl 10-trans,12-cis-octadecadienoate... 132261 1000336-44-2 99
3 9,11-Octadecadienoic acid, methyl... 132284 013038-47-6 95

DEFAULT-USER1.M Mon May 26 07:55:01 2014
The 3 best hits from each library.

<table>
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<tr>
<th>Ref#</th>
<th>CAS#</th>
<th>Qual</th>
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<tbody>
<tr>
<td>C:\Database\NIST08.L</td>
<td>1 Methyl 10-trans,12-cis-octadecadienoic acid</td>
<td>132261 1000336-44-2</td>
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<tr>
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<td>2 Methyl 9-cis,11-trans-octadecadienoic acid</td>
<td>132260 1000336-44-0</td>
</tr>
<tr>
<td></td>
<td>3 9,12-Octadecadienoic acid, methyl ester</td>
<td>132278 002566-97-4</td>
</tr>
</tbody>
</table>

C:\Database\chemecol.L
1 cis-3-hexen-1-ol | 56 000928-96-1 | 9 |
2 (Z)-3-hexenyl propanoate | 273 003467-74-2 | 2 |
3 E,E-2,4-Heptadienal | 87 004313-03-5 | 2 |

C:\Database\NIST08.L
1 Methyl 10-trans,12-cis-octadecadienoic acid | 132261 1000336-44-2 | 99 |
2 Methyl 9-cis,11-trans-octadecadienoic acid | 132260 1000336-44-0 | 99 |
3 9,12-Octadecadienoic acid, methyl ester | 132278 002566-97-4 | 98 |
Unknown Spectrum based on Apex minus start of peak

Data File: C:\msdchem\1DATA\2014\B.D
Sample : B

Peak Number: 11 at 26.380 min Area: 161368435 Area % 1.13

The 3 best hits from each library.

C:\Database\NIST08.L
2 Methyl 6,9,12-octadecatrienoate 130765 1000336-38-9 72
3 9,12,15-Octadecatrienoic acid, m... 130797 000301-00-8 72

C:\Database\chemecol.L
1 Linacetyl acetate 200 000115-95-7 27
2 (E,E)-a-Farnesene; ( (E,E)-a-? 51 000502-61-4 16
3 Camphene 117 000079-92-5 11

C:\Database\NIST08.L
2 Methyl 6,9,12-octadecatrienoate 130765 1000336-38-9 72
3 9,12,15-Octadecatrienoic acid, m... 130797 000301-00-8 72

DEFAULT-USER1.M Mon May 26 07:55:01 2014
Data File: C:\msdchem\1\DATA\2014\B.D
Sample : B
Peak Number: 12 at 26.649 min Area: 98474558 Area % 0.69

The 3 best hits from each library.

C:\Database\NIST08.L
1 Methyl 9-cis,11,trans,t,13.trans-octa decanoate... 130795 1000336-42-6  95
2 Methyl 6-cis,9-cis,11-trans-octa decanoate... 130780 1000336-37-7  90
3 Bicyclo[2.2.1]heptane, 7,7-dimethyl... 15693 000471-84-1  64

C:\Database\chemecol.L
1 Camphene 117 000079-92-5  38
2 g- Terpinene 108 000099-85-4  18
3 Linalyl acetate 200 000115-95-7  16

C:\Database\NIST08.L
1 Methyl 9-cis,11,trans,t,13.trans-octa decanoate... 130795 1000336-42-6  95
2 Methyl 6-cis,9-cis,11-trans-octa decanoate... 130780 1000336-37-7  90
3 Bicyclo[2.2.1]heptane, 7,7-dimethyl... 15693 000471-84-1  64

DEFAULT-USER1.M Mon May 26 07:55:02 2014
Unknown Spectrum based on Apex minus start of peak

Abundance

Scan 1067 (26.985 min): B.data.ms (-1964) (-)

Data File: C:\msdchem1\DATA\2014\B.D
Sample : B

Peak Number: 14 at 26.985 min Area: 303642051 Area % 2.13

The 3 best hits from each library.

<table>
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<th>Ref#</th>
<th>CAS#</th>
<th>Qual</th>
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<tbody>
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<td>C:\Database\NIST08.L</td>
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</tr>
<tr>
<td>1 Eicosanic acid, methyl ester</td>
<td>156023 001120-28-1</td>
<td>99</td>
</tr>
<tr>
<td>2 Methyl 18-methylnonadecanoate</td>
<td>156020 1000352-20-6</td>
<td>99</td>
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<tr>
<td>3 Eicosanic acid, methyl ester</td>
<td>156024 001120-28-1</td>
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<td>C:\Database\chemolc.L</td>
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<tr>
<td>1 Methyl palmitate (Methyl hexadecanoate)</td>
<td>154 000112-39-0</td>
<td>64</td>
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<tr>
<td>2 Methyl octanoate</td>
<td>337 000111-11-5</td>
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<td>3 Methyl hexanoate</td>
<td>338 000106-70-7</td>
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<td>1 Eicosanic acid, methyl ester</td>
<td>158023 001120-28-1</td>
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<td>2 Methyl 18-methylnonadecanoate</td>
<td>156020 1000352-20-6</td>
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<tr>
<td>3 Eicosanic acid, methyl ester</td>
<td>156024 001120-28-1</td>
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